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Physical metallurgy of Ti–Ni-based shape memory alloys

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Abstract

Ti–Ni-based alloys are quite attractive functional materials not only as practical shape memory alloys with high strength and ductility but also as those exhibiting unique physical properties such as pre-transformation behaviors, which are enriched by various martensitic transformations. The paper starts from phase diagram, structures of martensites, mechanisms of martensitic transformations, premartensitic behavior, mechanism of shape memory and superelastic effects etc., and covers most of the *fundamental issues* related with the alloys, which include not only martensitic transformations but also diffusional transformations, since the latter greatly affect the former, and are useful to improve shape memory characteristics. Thus the alloy system will serve as an excellent case study of physical metallurgy, as is the case for steels where all kinds of phase transformations are utilized to improve the physical properties. In short this review is intended to give a self-consistent and logical account of key issues on Ti–Ni based alloys from physical metallurgy viewpoint on an up-to-date basis. © 2004 Elsevier Ltd. All rights reserved.

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Nomen	clature
A	elastic anisotropy = c_{AA}/c'
$A_{\rm f}$	reverse transformation finish temperature
$A_{\rm s}$	reverse transformation start temperature
$A_{\rm s}^{\rm d}$	reverse transformation start temperature after deformation
AO_f	reverse transformation finish temperature for B2-B19 transformation
AO_s	reverse transformation start temperature for B2-B19 transformation
AR_{f}	reverse transformation finish temperature for B2-R transformation
AR_s	reverse transformation start temperature for B2–R transformation
$\frac{B}{D}$	lattice deformation matrix with respect to the parent axis system
В	martensite
B2	CsCl type ordered structure; the structure of the parent phase in Ti-Ni-
	based alloys
B19	orthorhombic martensite structure
B19′	monoclinic martensite structure
с′	elastic constant in a cubic crystal, which represents resistance for $\{110\}\langle 1\bar{1}0\rangle$ shear. $c' = 1/2(c_{11} - c_{12})$
<i>c</i> ₄₄	elastic constant in a cubic crystal, which represents resistance for
	$\{001\}\langle 100\rangle$ shear
c_{11}	one of the three independent elastic constants in cubic crystal
c_{12}	one of the three independent elastic constants in cubic crystal
c.v.(s)	correspondence variant(s)
d_1	shape strain direction (unit vector) (see Fig. 17)
$\boldsymbol{d}_1^{\mathrm{P}}$	component of d_1 parallel to the invariant plane (unit vector) (see Fig.
E	
r F	calculated structure factor
F	observed structure factor
F_1	diagonal matrix
\mathbf{F}_{a}	symmetric matrix
h.p.v.(s	s) habit plane variant(s)
I	nucleation rate. It is the number of stable nuclei formed in the assembly
	in unit time
$I_{\rm GB}$	nucleation rate at grain boundaries
$I_{\rm GI}$	nucleation rate at grain interior
k	Boltzmann constant
K_1	twinning plane (undistorted and un-rotated: see Fig. 18)
K_2	another undistorted plane in mechanical twinning (see Fig. 18)
$M_{\rm f}$	martensitic transformation finish temperature
$M_{\rm s}$	martensitic transformation start temperature
m_1	magnitude of snape strain (see Fig. 1/)

m_1^n m_1^p P_1	component of m_1d_1 normal to the invariant plane = $\Delta V/V$ (see Fig. 17) component of m_1d_1 parallel to the invariant plane (see Fig. 17) shape strain matrix, which represents the total deformation upon mar-
	tensitic transformation
p ₁	unit vector representing the habit plane normal
P_2	matrix representing the lattice invariant shear
p_2 P (fact	vector representing the plane normal of the fattice invariant shear (a) reliability factor (see Eq. (1) for definition)
R(-Iact	\mathbf{R}_{-} nhase transformation finish temperature
$R_{\rm m}$	R-factor used in the Rietveld method (for powder diffraction analysis)
$R_{\rm s}$	R-phase transformation start temperature
R(-pha	se) trigonal martensite phase
S	entropy
S	twinning shear
Т	temperature
T^*	definition in Landau theory: temperature at which harmonic instability
	occurs (i.e. phonon energy becomes zero). Actually martensitic trans-
T	formation occurs above this temperature
I_0	a temperature at which the parent phase and martensite have equal free
TA.	transverse phonon branch for phonons traveling along [001]* with
171	polarization vector along $[1\bar{1}0]$ direction
TA_2	transverse phonon branch for phonons traveling along [110] [*] with
2	polarization vector along $[1\bar{1}0]$ direction
U	internal energy
wR	weighted reliability factor (see Eq. (2) for definition)
$wR_{\rm p}$	wR-factor used in the Rietveld method (for powder diffraction analysis)
α-angle	an angle characterizing a rhombohedral crystal, especially for R-phase (see Fig. 13)
β -angle	an angle characterizing monoclinic crystal in second setting, especially
	for B19' martensite (see Fig. 37)
$\Delta G_{\rm c}$	critical free energy to form a nucleus
$\Delta G_{ m v}$	chemical free energy change associated with the precipitation reaction
$\Delta g_{ m ch}$	chemical free energy change per unit volume between parent and mar- tensite in thermoelastic transformation
$\Delta g_{ m el}$	elastic strain energy per unit volume stored around martensite plate
ΔH^*	enthalpy change upon transformation
ΔS	entropy change upon transformation
$\Delta V / V$	strain
С С	suam nermanent strain
ср Ег	residual strain
es Es	superelastic strain
5	1

ε _t	total strain
$\varepsilon_{\rm tw}$	two-way memory strain
η	Landau order parameter of a martensitic system
η_1	twinning shear direction (see Fig. 18)
η_2	the intersection of the plane of shear and the K_2 plane (see Fig. 18)
η_{M}	Landau order parameter of martensite
λ	an angle between the shear component of the shape strain and the ten-
	sile axis
λ_i	eigenvalue of matrix $F_{\rm d}$
σ	σ is used in two different meanings: (1) stress, (2) interfacial energy (in
	Section 9.2)
$\sigma_{ m M}$	critical stress to induce B19' martensite
$\sigma_{\rm R}$	critical stress for reverse transformation from B19' to B2
χ	an angle between the habit plane and the tensile axis

1. Introduction

The motivation to write the present review article is twofold. Firstly, the Ti–Nibased alloys are the most important practical shape memory alloys (SMA) with excellent mechanical properties. Although there had been many controversial problems in the past as described below, most of them have been solved by now. Thus it will be useful to review them in a unified manner on an up-to-date basis. Secondly, there are many phase transformations in Ti–Ni-based alloys system, which include not only diffusionless/martensitic transformations, from which shape memory and superelastic effects arise, but also diffusional transformations. Thus even the latter transformations have been used effectively to improve shape memory characteristics. Thus the alloy system will serve as an excellent case study of physical metallurgy, as is the case for steels where all kinds of phase transformations are utilized to improve the physical properties.

The unique shape memory effect in an equiatomic Ti–Ni alloy was first found by Buehler et al. [1] in 1963. Although the same effect was found in Au–47.5at.%Cd¹ [2] and In–Tl [3,4] alloys earlier, it had not attracted much attention of researchers. In contrast, the Ti–Ni alloy became quite popular soon after the discovery, partly by the world-wide publicity by the people in Naval Ordinance Laboratory who found it, and partly by the good mechanical properties of the alloy, which were suitable for applications. Despite the fact, the understanding of the phenomena and the martensitic transformation, from which the phenomena originate, did not develop rapidly. This is because the Ti–Ni alloy system is quite a complicated system, as it turned

 $^{^{1}}$ All compositions are expressed by "at.%" in this paper, and thus "at.%" is omitted hereafter as "Au–47.5Cd".

out later. The phase diagram of the system had been controversial until the end of 1980s. Various precipitates, which appear under certain heat-treatments, had not been understood well from the proposed phase diagram until then. Furthermore, the R-phase transformation which were thought to be a pre-martensitic phenomenon at one time, and is characterized by the 1/3 reflections along $\langle 110 \rangle^{*2}$ direction in the reciprocal space, appears under certain conditions prior to the martensitic transformation. These complexities may often appear all at once, which make them difficult to understand. Thus, it took a long time to separate each factor and to make them understandable. In fact, it took much longer time for the understanding of the martensitic transformation and the shape memory effect in the present alloy compared to those in other shape memory alloys. However, most of the difficulties including the structure determination of martensites are cleared by now by many systematic and extensive researches in 1970s, 1980s and thereafter after the incubation period in 1960s.

Although Ti–Ni-based alloys have many common characters with other shape memory alloys by exhibiting shape memory effect, superelasticity, two-way shape memory effect (known as the all round shape memory effect) etc., they also exhibit many other characteristics, which are quite unique compared to other shape memory alloys such as shown below. They exhibit quite a low elastic anisotropy (defined as $A = c_{44}/c'$) as low as nearly 2, although most of other shape memory alloys exhibit the value of about 10 or more. Here c' represents resistance for $\{110\}\langle 1\overline{1}0\rangle$ shear, and c_{44} resistance for $\{001\}\langle 100\rangle$ shear. The elastic constant c_{44} decreases with decreasing temperature, which is just the opposite behavior in most of other shape memory and normal alloys. Besides, the structure of martensite B19'(monoclinic) appears only in TiNi-based alloys, and the structure of R-phase has similarity only with ζ'_2 martensite in Au–Cd alloys. Amorphisation of the alloys by sputtering is another advantage for the applications of thin films, since the process of amorphisation leads to small grain sizes, which are useful for mechanical properties. In addition to the above, Ti–Ni-based alloys have other good properties. Although it is a kind of intermetallic compound, it is quite ductile, under certain conditions 60% cold working being possible. One of the reasons for such an incredible high ductility probably lies in its low elastic anisotropy described above. Corrosion resistance and abrasion resistance are also superb. Because of these excellent properties, most of the commercial applications have been done for Ti–Ni alloys among many shape memory alloys, such as a flap in air-conditioner, coffee maker, brassiere, antenna for mobile phones, medical applications such as orthodontic wire, guide wire and stent etc.

The purpose of the present review is to provide a detailed account of the major aspects of Ti–Ni-based shape memory alloys from physical metallurgy point of view in a most updated manner. To the authors' knowledge, there is no comprehensive reviews nor books in English on Ti–Ni-based shape memory alloys, except for some rather short chapters on shape memory alloys such as Refs. [5,6]. However, this overview is not intended to be exhaustive, because there are so many papers on this

² The symbol * associated with $\langle uvw \rangle$ represents that it is the direction in the reciprocal space.

subject and quite active researches are still going on, which will make it difficult to do so. Instead the paper is intended to give a self-consistent and logical account of key issues about Ti–Ni-based alloys. From this spirit the descriptions and discussions will be limited to fundamentals, but they are aimed to provide sound basis to applications (in the framework of materials science) as well.

Since the present review concerns solely those in Ti–Ni-based alloys, readers may refer to Refs. [7–14] for the mechanism of martensitic transformation, from which shape memory and superelastic effects are originated, and Refs. [15–17] for the mechanisms of shape memory and superelastic effects in general. NASA report published in 1972 [18] also provide extensive experimental results in early days, although the mechanisms were not well understood at that time. Many conference proceedings on martensitic transformations/shape memory alloys [19–43] are also useful. Since applications of shape memory alloys themselves are not treated in the present review, readers are referred to the related sections in Refs. [16,17], and the papers cited there-in. More specific reference will be made in the following sections when we discuss each problem.

2. Phase diagram

The phase diagram of Ti-Ni alloy system is important for heat-treatments of the alloys and improvement of the shape memory characteristics. Thus it is first discussed here in this section. The phase diagram had been controversial for more than 30 years before it was established. To make the following discussion easily understandable, we refer to the phase diagram of Hansen's "Constitution of Binary Alloys" (Fig. 575 and 575a in Ref. [44]), which was not established. Our interests are restricted in the central region bounded by Ti₂Ni and TiNi₃ phases (as may be seen in Fig. 2 to be described later). The presence of a single phase "TiNi" near the equiatomic composition was first recognized by Laves and Wallbaum [45] at higher temperatures. Duwez and Taylor [46] first reported the decomposition of TiNi into Ti₂Ni and TiNi₃ at 800 °C (and at 650 °C). ³ However, Margolin et al. [47], who used higher purity alloys, did not find any evidence of such decomposition. In 1955, Poole and Hume-Rothery [48] made a thorough examination of the phase diagram. They determined the solubility limit of the "TiNi" phase above 900 °C metallographically. According to their examination, the boundary on Ti-rich side is close to 50Ni, and is very steep, while on Ni-rich side the solubility decreases greatly with lowering temperature. Furthermore, they confirmed the conclusion of Duwez and Taylor that the TiNi eutectoidally decomposes into Ti₂Ni and TiNi₃, by stating "(in X-ray diffraction of filings), four diffuse lines could be attributed to Ti₂Ni and five extremely faint lines were identified with those of TiNi3". Fig. 575 and 575a in Hansen's book are

³ Unit of temperature, K vs. $^{\circ}$ C: In the present review we use mostly K systematically, but $^{\circ}$ C may also be used, especially with respect to phase diagrams, which are usually represented by $^{\circ}$ C and in the parts, which are application-oriented to some extent.

essentially based on the above works by Margolin et al. and Poole and Hume-Rothery, respectively.

In 1961, Purdy and Parr [49] studied the phase diagram by employing high temperature X-ray diffraction and metallographic techniques. The diagram proposed by them was similar to Margolin et al.'s in that the "TiNi" phase extends to lower temperatures, but it differs from the latter in that the solubility range decreases rapidly with lowering temperature on Ni-rich side. It was also similar to Hume-Rothery's in the reduced solubility on the Ni-rich side at temperatures above 900 °C, but it differs from the latter in the absence of eutectic decomposition. Furthermore, they found that the "TiNi" phase transforms to a phase called " π phase", tentatively indexed hexagonal at 36 °C, and that the transformation is reversible. They noticed that the transformation occurs at a temperature low enough to prohibit diffusion-controlled process. Although they did not use the term "martensitic", this is the first observation of martensitic transformation in the Ti–Ni alloy.

After the discovery of the shape memory effect in 1963, the phase diagram was reexamined by Wasilewski et al. [50] in 1971, by utilizing metallography, X-ray diffraction and EPMA (X-ray probe microanalyzer). As a result, they found a new phase Ti_2Ni_3 (the result of the analysis was closer to $Ti_{42}Ni_{58}$, but they suggested the former composition in view of the uncertainty involved in EPMA analysis), and proposed a phase diagram, which involves a peritectoid reaction at 625 °C. They also noticed that the solubility range of the "TiNi" phase is very narrow at 500 °C or below. The phase diagram is characteristic in the vertical boundary on Ti-rich side and the large solubility limit on Ni-rich side, which reduces greatly to negligible down to 500 °C. These characteristics were supported by other workers later (see Ref. [51] by Bastin and Rieck), but the peritectoid reaction has never been confirmed by other workers. Meanwhile, the same problem was studied by Koskimaki et al. [52] by electron microscopy in nearly the same period. They found plate-shaped precipitates in specimens which were aged at temperatures below 625 °C, and indexed it with FCC with $a_0 = 1.52$ nm. This is the precipitate, which was called "X-phase" later, and the indexing was proved to be incorrect later. Upon prolonged aging (e.g., 600 °C for 1 month), they claimed that "TiNi" eutectoidally decomposes into Ti₂Ni and TiNi₃ and X-phase is an intermediate phase, but the direct evidence was not shown.

So far, we have seen many phase diagrams as if there are as many as the number of investigators. However, the followings seem to be established by this stage. (1) The boundary of "TiNi" on Ti-rich side is nearly vertical. (2) The boundary on Ni-rich side decreases with decreasing temperature greatly, and the solubility becomes negligible at about 500 °C. (3) The possibility of eutectoid decomposition at 630 °C seems unrealistic, since no direct evidence had been obtained. Very diffuse and faint lines in Debye-Scherrer patterns indexed to Ti₂Ni and TiNi₃ by Duwez and Taylor, and Poole and Hume-Rothery, could be indexed to other structures, since X-phase and Ti₂Ni₃ phase were not known by that time. On the other hand, there were difficulties on how to understand the presence of the "X-phase" and "Ti₂Ni₃" phase. However, these difficulties were straightened out by the works by Nishida et al. [53] thereafter, as described below. They extensively studied diffusion-controlled transformations at higher temperatures for a Ti–52Ni alloy, by utilizing metallography, electron microscopy and EDS (energy dispersive X-ray spectroscopy). As a result, they found that three phases Ti₃Ni₄, Ti₂Ni₃ and TiNi₃, each composition of which was confirmed by EDS, appear depending upon aging temperature and time. That is, at lower aging temperature and shorter aging time, Ti₃Ni₄ phase appears, while at higher aging temperature and longer aging time TiNi₃ phase appears and at intermediate temperature and time Ti₂Ni₃ phase appears. They also observed that by prolonged aging the preexisted Ti₃Ni₄ phase is absorbed in the matrix, and the number and size of Ti₂Ni₃ phase increase. In the same way, by prolonged aging the preexisted Ti₂Ni₃ phase was observed to be absorbed in the matrix, and the number and size of TiNi₃ phase increase. That is, they confirmed that both Ti₃Ni₄ and Ti₂Ni₃ phases are intermediate phases, and the diffusional transformations occur in the following order with increasing aging temperature and time, TiNi₃ being the equilibrium phase:

$$Ti_3Ni_4 \rightarrow Ti_2Ni_3 \rightarrow TiNi_3$$
.

In fact these transformations are summarized by TTT (time-temperature-transformation) diagram as shown in Fig. 1. The TTT diagram also shows the upper temperature limit for each precipitate, e.g. the upper limit for the Ti_3Ni_4 phase is 680 °C. Kainuma et al. [54] carried out a similar work for the Ti–54Ni and Ti–56Ni alloys in addition to the Ti–52Ni alloy, and determined the TTT diagrams for these alloys. They also determined the solubility limit of the TiNi phase on Ni-rich side, and confirmed that the solubility limit by Wasilewski et al. was correct.

By considering the above extensive works, it is now possible to summarize. i.e. The most reliable phase diagram in the central portion of the Ti–Ni system is as



Fig. 1. TTT diagram describing aging behavior for Ti–52Ni alloy (after Nishida et al. [53] reproduced by permission of ASM International).

shown in Fig. 2, which is essentially the same as that published by Massalski et al. [55], although a possible eutectoid reaction in the latter (indicated by a dotted line at 630 °C) is deleted, and the order–disorder transition from B2 to BCC at 1090 °C is added based on the work of Ref. [57], but this has not been confirmed by independent works. Fig. 2 also shows a metastable phase equilibrium between TiNi phase and Ti₃Ni₄ phase determined recently, which is very useful in adjusting transformation temperatures and in designing heat-treatments for improving shape memory characteristics, but that will be discussed in Sections 8 and 9. We now briefly describe the structures of various phases in the phase diagram including intermediate precipitates.

The TiNi phase has a B2 (CsCl) type ordered structure with a lattice constant of 0.3015 nm at room temperature [58]. There is an order–disorder transition from B2 to BCC at 1090 °C, as described above. The B2 phase retains upon quenching or slow cooling to room temperature. This is the phase which plays an essential role in the martensitic transformation and the associated shape memory effects, which are described in later sections.

The Ti_2Ni phase is cubic with space group Fd3m. The lattice constant is 1.132 nm and the unit cell contains 96 atoms. Oxides appearing in the present alloy are mostly the Ti_4Ni_2O phase, which has nearly the same structure with Ti_2Ni [59].



Fig. 2. Phase diagram of a Ti–Ni alloy by Massalski [55], to which the phase equilibrium between the B2 and Ti_3Ni_4 phases are added [56] (reproduced with the permission of ASM International and Materials Research Society).

The TiNi₃ phase has the hexagonal DO₂₄ type ordered structure. The lattice constants are a = 0.51010 nm, c = 0.83067 nm and c/a = 1.6284 [60].

After a few prior works, the structure of Ti₂Ni₃ precipitate was studied in detail by Hara et al. [61] along with that of Ti₂(Ni,Cu)₃, in which a single phase is obtained by the addition of Cu with the similar structure, by utilizing various diffraction techniques. Surprisingly the precipitate has two phases as a function of temperature, and one phase transforms to the other martensitically by changing temperature. The higher temperature phase has a tetragonal structure with space group I4/mmm, the lattice parameters being a = 0.3095 nm and c = 1.3585 nm (at 373 K), while the low temperature phase has an orthorhombic structure with space group Bbmm, the lattice parameters being a = 0.4398 nm, b = 0.4370 nm and c = 1.3544nm (at 298 K). See Ref. [61] for more details.

The Ti₃Ni₄ phase is a very important phase, with respect to shape memory characteristics, as will be discussed in later sections. The structure was established after investigations for a long time by many researchers following electron microscopy observation by Koskimaki et al. [52] in 1969. The shape is lenticular as typically shown in Fig. 3. The composition of the precipitate was first determined by EDS to be $Ti_{11}Ni_{14}$ by Nishida and Honma [63], and later it was taken to be Ti_3Ni_4 by taking account the accuracy of EDS. The first clue to understand this structure was the observation of reflections from the precipitate, which are located at 1/7 positions along $(123)^*$ reciprocal vectors of the B2 type matrix phase. The series of such electron diffraction patterns are shown in Fig. 4. After a long investigations on these electron diffraction patterns, Nishida et al. [64] and Saburi et al. [65] arrived at essentially the same lattice parameters for a rhombohedral until cell, a = 0.670 nm and $\alpha = 113.8^{\circ}$. Finally, the crystal structure was determined by Tadaki et al. [62] and Saburi et al. [65], identically but independently. The space group thus determined is R3. The structure may be easily explained by taking hexagonal axes rather than rhombohedral ones, following Saburi et al. [65]. In the B2 type matrix phase, (111) planes consist of alternate Ti hexagonal layers and Ni hexagonal layers, and six such suc-



Fig. 3. Typical electron micrograph of Ti₃Ni₄ precipitates in Ti-51Ni alloy aged at 773 K for 540 ks [62].



Fig. 4. Various electron diffraction patterns of Ti_3Ni_4 precipitates. The indices without suffixes are represented in rhombohedral lattice, while those with suffix "B2" means that they nearly coincide with those of matrix indicated: (a) [111] zone, (b) [323] zone, (c) [212] zone, (d) [010] zone, (e) [121] zone, (f) [232] zone. All patterns are related by the rotation around $[2\overline{1}\overline{3}]_{B2}^*$ axis in the reciprocal space [62].

cessive layers make one period. In the present Ti_3Ni_4 phase, the basal planes take the similar stacking, but excess Ni atoms are distributed in each original Ti layers as shown in Fig. 5. Thus, the final structure is represented by Fig. 5, where the basal planes are stacked in the sequence ABCDEFA... Fig. 5 also explains how "1/7" reflections appear by such distribution of excess Ni atoms. That is, the new period of 7 layers is created by such distribution of excess Ni atoms.

According to this structure, the habit plane of the precipitate is expected to be $\{111\}_{B2}$, and the orientation relationship between the matrix and the precipitate is expected to be $(001)_h || (111)_{B2}$, $[010]_h || [\overline{2} \overline{1} 3]_{B2}$. This is confirmed by electron microscopy [65]. Inside the precipitate, $\{\overline{1}54\}_R$ twins are sometimes observed [62]. By using the above lattice parameters and that of matrix, we can calculate the lattice strain upon transformation from matrix to the precipitate. The strain is -2.3% in the direction of the habit plane normal, and -0.5% in the habit plane [62]. This situation is schematically shown in Fig. 6, which is important when we consider all round shape memory effect in later sections.

3. Crystal structures of martensites and their lattice defects

3.1. Brief description of martensitic transformations in Ti–Ni-based alloys

Although we are solely concerned with the crystal structures of martensites in this section, we briefly describe the martensitic transformations themselves to make them



Fig. 5. The arrangements of Ti and Ni atoms for Ti_3Ni_4 precipitate: (a) atom arrangement in the six layers composing the unit cell of Ti_3Ni_4 precipitate; (b) stacking of the six layers along $\langle 111 \rangle_{B2}$ axis in (a). See text for details (after Saburi et al. [65] reproduced with permission of Elsevier).

more familiar with. To give the perspective first, there are three distinct types of martensitic transformations in Ti–Ni-based alloys, as typically shown in each electrical resistivity vs. temperature curve in Fig. 7. ⁴ Fig. 7(a) is obtained when binary Ti– Ni alloys are quenched from high temperature B2 parent phase. The martensite in

⁴ Notation for transformation temperatures: When there is only one martensitic transformation exists in the attainable temperature range, as shown in Fig. 7(a), we use the usual notation: M_s (martensitic transformation start temperature), M_f (martensitic transformation finish temperature), A_s (reverse transformation start temperature), and A_f (reverse transformation finish temperature). When successive transformations exist such as in Fig. 7(b) and (c), many notations have been used (especially for R-phase transformation), which is quite confusing. In this case we use the following notation for unification. However, we left the previous notation (especially in figures) as well in order not to confuse readers. Instead we write both when necessary. For B2–R transformation, we use: R_s (R-phase transformation start temperature), R_f (R-phase transformation finish temperature). For B2–B19 transformation start temperature), and AR_f (its reverse transformation finish temperature). For B2–B19 transformation, we use: O_s (B19 transformation start temperature), O_f (B19 transformation finish temperature). AO_s (its reverse transformation start temperature), and AO_f (its reverse transformation finish temperature). Thus, e.g. $T'_R = R_s$ in Fig. 7(b), and $M'_s = O_s$ and $A'_s = AO_s$ in Fig. 7(c). The above notation is analogous to "the notation for suffix to indices" to be described in Section 4.1.1, which reflects the symmetry of the martensite concerned (see footnote 7).



Fig. 6. Schematic illustration of the lattice distortion of the matrix surrounding Ti₃Ni₄ precipitate [62].



Fig. 7. Electrical resistance vs. temperature curves for three typical transformations in Ti–Ni-based alloys: (a) B2–B19' transformation; (b) B2–R–B19' transformation; (c) B2–B19–B19' transformation. $T'_{\rm R} = R_{\rm s}$, $M'_{\rm s} = O_{\rm s}$, $A'_{\rm s} = AO_{\rm s}$. See text for details (after (a) [66], (b) [67], and (c) Nam et al. [68] reproduced by permission of Japan Institute of Metals).

this case is called B19' (monoclinic), and its structure will be discussed later. The evidence of surface relief, i.e. the evidence of martensitic transformation, was obtained by Otsuka et al. [69] and Sandrock and Hehemann [70] independently. They further confirmed that the transformation is thermoelastic by observing the gradual growth and shrinkage of martensites upon cooling and heating, respectively. By considering the presence of the transformation hysteresis further, we can conclude that the transformation is the first order thermoelastic one. Next the second type of transformation is represented in Fig. 7(b). In this case the resistivity vs. temperature curve is characterized by a sharp increase in resistivity upon cooling, and then decrease upon further cooling. The first transformation upon cooling characterized by the sharp increase in resistivity and extremely small temperature hysteresis (1-2 K) is called "Rphase transformation", since the product phase was considered to be rhombohedral at one time, although it turned out to be trigonal later, as will be discussed in detail later. Furthermore this R-phase transformation was considered to be a premartensitic behavior (precursor effect) prior to the subsequent martensitic transformation, but it is now established that it is a martensitic transformation itself, which competes with the subsequent martensitic transformation, as will be discussed in Sections 5 and 6. The second transformation characterized by a large temperature hysteresis in Fig. 7(b) represents the subsequent transformation from R-phase to B19' phase. Although the present data are shown for Ti-47Ni-3Fe alloy, the similar transformations are obtained even for Ni-rich Ti-Ni alloys, if they are heat-treated at proper temperatures so as to produce Ti₃Ni₄ precipitates. The R-phase transformation is also available in binary Ti-Ni alloys, if they are cold-worked followed by annealing at proper temperatures (say, 673 K), so that high density of rearranged dislocations are left in specimens. The conditions, under which the R-phase transformation occurs, are to suppress B19' transformation relative to R-phase transformation by introducing precipitates or dislocations, as will be discussed in detail in Section 8. The third type of transformation is obtained when Ni is substituted by Cu in a binary Ti-Ni alloy, as shown for Ti-40Ni-10Cu in Fig. 7(c). In this case the transformation occurs in two steps, as indicated by M'_{s} and M_{s} , respectively, upon cooling. The martensite upon the first transformation is called B19 (orthorhombic), and the second transformation represents the one from B19 to B19'. The martensitic transformations in $Ti_{50}Ni_{50-x}Cu_x$ alloys have composition dependence, as shown in Fig. 8. When $x \ge 7.5$, B2–B19–B19' two stage transformations occurs as described above. However, it is an open question whether the B19–B19' second transformation actually occurs or not, when x > 16. Furthermore, when $5 \le x \ge 7.5$, the two stage transformations actually occur, but the second transformation soon occurs, and the B19 phase does not exist in a large amount [71]. Thus it is difficult to observe the B19 phase during the transformation by X-ray diffraction.

Thus we may classify the three types of transformations as shown in Fig. 9. In this scheme we notice that all alloys have a tendency to transform from B2 to B19' martensite in Ti–Ni-based alloys, and in fact for the solution-treated binary Ti–Ni alloys the transformation occurs from B2 to B19' directly, while for the upper and lower cases two successive transformations occur upon continuous cooling. However, depending upon the composition and heat-treatment only the first transformation



Fig. 8. Cu-content dependence of transformation temperatures for $Ti_{50}Ni_{50-x}Cu_x$ alloys. $M'_s = O_s$ (after Nam et al. [68] reproduced by permission of Japan Institute of Metals).



Fig. 9. Three transformation paths in Ti-Ni-based alloys.

may occur, and the second one may be lost, because the possible transformation temperatures for the second one to B19' becomes too low (i.e. below 0 K) in that case. These will be discussed in later sections with respect to the stability of various martensites.

3.2. Crystal structure of the B19' martensite

First we discuss the crystal structure of the martensite, which is obtained when binary Ti–Ni alloys are quenched from high temperature after solution-treatment. The crystal structure of such martensite had been an unsolved problem for many years after the first report as hexagonal by Purdy and Parr [49] in 1961. Dautovich and Purdy [73], who studied it by electron diffraction and X-ray powder diffraction method, reported it to be triclinic with lattice parameters a = 0.460 nm, b = 0.286 nm, c = 0.411 nm, $\alpha = 90.1^{\circ}$, $\beta = 90.9^{\circ}$, $\gamma = 96.7^{\circ}$. Wang et al. [74] claimed that the martensite is formed by the shear in $\langle 111 \rangle$ direction, but the structure is non-defined, since the amount of displacement of atoms is a function of specimen temperature. Marcinkowski et al. [75] reported two distinct monoclinic martensites, whose lattice parameters are: $a_{\rm M} = 0.519$ nm, $b_{\rm M} = 0.496$ nm, $c_{\rm M} = 0.425$ nm, $\gamma_{\rm M} = 99^{\circ}$ and $a'_{\rm M} = 0.519$ nm, $b'_{\rm M} = 0.552$ nm, $c'_{\rm M} = 0.425$ nm, $\gamma'_{\rm M} = 116^{\circ}$. On the other hand, Nagasawa [76] reported it to be a long period stacking order structure, consisting of 4H and 12R types in Ramsdel notation. Thus, the above reported structures were all different.

In 1971, however, Otsuka et al. [77] and Hehemann and Sandrock ⁵ [78] arrived at the same monoclinic lattice with essentially the same lattice parameters. However, the two structures were different in the direction and the plane of shufflings relative to the monoclinic angle. Neither structure could explain the observed extinction rule completely. Thereafter, Michal and Sinclair [79] arrived at space group $P2_1/m$, by the consideration of systematic forbidden reflections. They also analyzed atomic positions by taking into account the atomic radius ratio and bond length, but the result was not good enough. More recently, Bührer et al. [80] carried out more thorough structural analysis by utilizing powder neutron diffraction technique and Rietveld analysis. They determined the atomic parameters for space group $P2_1/m$ under the assumption of preferred orientation correction with R-factors ($R_{wp} = 11.6\%$, $R_1 = 4.1\%$), which are pretty good. (R- and wR-factors for single crystal X-ray diffraction method will be defined in detail soon below in Eqs. (1) and (2). $R_{\rm I}$ and $R_{\rm wp}$ here are those for Rietveld method using powder samples, and the structure factor Fis replaced by intensity I in the definition of R-factor for $R_{\rm I}$.) The reason why it took such a long time in the structure analysis of the martensite lied in the lack of a martensite single crystal. If it is available, the structure analysis can be done in a more straightforward manner by utilizing the single crystal X-ray diffraction method, which is much better in resolution than neutron diffraction. Such a complete analysis without any assumption was actually carried out by Kudoh et al. [81] in 1985, by utilizing X-ray 4-circle diffractometer and precession camera for a Ti-49.2Ni martensite single crystal. Single crystals in the parent phase were grown by the strain anneal method, and martensite single crystals were made by the stress-induced transformation technique. The results are introduced in some detail in the following. Fig. 10(a), (b) and (c) represent zero layer precession photographs in [100], [010] and [001] zone axes, respectively. Since no monochromater was used, two kinds of reflections due to K_{α} and K_{β} radiations are present, along with radiant streaks due to white rays. It is apparent: $b^* \perp c^*$, $a^* \perp b^*$, $\beta = \pi - \beta^* = 97.8^\circ$ and the lattice is primitive one. The diffraction patterns in Fig. 10(a) and (c), both of which include b^* -axis, have the sym-

⁵ There are two ways in the choice of axes in a monoclinic cell. Otsuka et al. used the second setting, in which the monoclinic angle is β , while Hehemann and Sandrock, and Michal and Sinclair [79] to be described soon below used the first setting, the monoclinic angle being γ . The present review use the second setting throughout, after the recommendation by International Union of Crystallography. The first setting may be converted to the second setting by interchanging *b* and *c* axes.



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Fig. 10. Zero layer X-ray precession photographs in [100], [010] and [001] zone axes for B19' martensite (monoclinic), showing (a) 0kl, (b) h0l and (c) hk0 reciprocal net, respectively. The two types of symbols in the key diagrams, large and small circles, indicate strong and weak reflections, respectively. Ti–49.2Ni [81].

metry of two dimensional point group 2mm, and that in Fig. 10(b) the symmetry of point group 2. Thus, the crystal belongs to Laue symmetry 2/m. Next we pay attention to 0k0 reflections in Fig. 10(a) and (c). The reflections with odd k are

systematically absent. It is thus deduced that the crystal has twofold screw axis 2_1 . The space group with 2_1 axis must be either $P2_1$, $P2_1/m$ or $P2_1/c$. Next we pay attention to *h*0*l* reflections in Fig. 10(b). We note that the reflections are present, irrespective of whether *l* is even or odd. This excludes the possibility of the presence of *c*-glide plane, i.e., space group $P2_1/c$ is excluded. The distinction between $P2_1/m$ and $P2_1$ lies in whether the center of symmetry is present or not. Here it is assumed that the crystal has center of symmetry, and the structure analysis was carried out. As will be described later, the result was quite consistent. Thus, the space group was concluded to be $P2_1/m$, in a quite straightforward manner.

The lattice parameters were determined by the method of least squares using 15 reflections obtained by the 4-circle diffractometer. The result is shown in Table 1, along with those determined by other researchers. The small difference between the present result and that by Otsuka et al. is due to the small difference in alloy composition (the composition of the alloy Otsuka et al. used was Ti-49.75Ni).

The structure analysis was carried out following the standard method of leastsquares for 307 independent observed reflections. The final *R* factors for anisotropic temperature factors were R = 4.5% (wR = 5.7%), which are very good. Here *R* is defined by

$$R = \frac{\sum ||F_{\rm o}| - |F_{\rm c}||}{\sum |F_{\rm o}|},\tag{1}$$

and wR (weighted R) by

wR =
$$\frac{\sum (|F_o| - |F_c|)^2 / \sigma^2}{\sum |F_o|^2 / \sigma^2}$$
, (2)

where F_o and F_c are observed and calculated structure factors, respectively, and σ is a standard deviation. The atomic parameters thus determined are shown in Table 2. It is to be added that the recent first principle calculations [83,84] confirmed that the above atomic parameters gives the lowest ground state energy and is most stable

comparison of crystanographic data for The matchistic [61]							
	OSS ^a	HS ^b	MS ^c	KTSO ^d			
<i>a</i> (nm)	0.2889	0.2883	0.2885 (4)	0.2898 (1)			
b (nm)	0.4120	0.4117	0.4120 (5)	0.4108 (2)			
<i>c</i> (nm)	0.4622	0.4623	0.4622 (5)	0.4646 (3)			
β (°)	96.8	96.8	96.8 (1.0)	97.78 (4)			
$V (nm^3)$	0.05463	0.05449	0.05455	0.05479 (4)			
Atoms per unit cell	4	4	4	4			
Space group	P2/c	P21/m	$P2_1/m$	$P2_1/m$			

Table 1 Comparison of crystallographic data for TiNi martensite [81]

^a Otsuka et al. [77].

^b Hehmann and Sandrock [78].

^c Michal and Sinclair [79].

^d Kudoh et al. [81].

Table 2

(a) Atomic paramete	ers	
Ti	x	0.4176(5)
	Ζ	0.2164(3)
Ni	x	0.0372(4)
	Z	0.6752(2)
Conventional coordin	ates	
Ti		0, 0, 0
		0.1648, 1/2, 0.5672
Ni		0.6196, 0, 0.4588
		0 5452 1/2 0 1084

(a) Atomic parameters for TiNi martensite x1/4z, $\overline{x}3/4\overline{z}$ and (b) anisotropic temperature factors (×10⁴) for TiNi martensite [81]

(b) Anisotropic temperature factors

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$B(Å^2)$
Ti	226	90	131		-12		0.84
Ni	391	47	144		-66		0.99

The anisotropic temperature factors are expressed in the form

 $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$

The B's are equivalent isotropic values [82].

compared to those reported by other researchers such as Michal and Sinclair [79], and Bührer et al. [80]. Thus the structure of B19' martensite is established.

This result is also shown graphically in Figs. 11 (and the projected figure to b-plane is shown in Fig. 3 of Ref. [81]). It is interesting to note that the structure is



Fig. 11. Illustrate the structure of B19' martensite (after Ohba [85]).

not stacking order structure of two-dimensional close-packed planes, which is usually the case for β -phase alloys such as Cu–Al, Cu–Zn, Cu–Sn and Au–Cd etc. Instead, it is a three-dimensionally close-packed structure [81]. In this respect, the structure is quite different from those in other β -phase alloys, although the Ti–Ni alloy near equiatomic composition is often classified into a β -phase alloy. This is not appropriate. In the β -phase alloy, *ela* (electron–atom ratio) is nearly 1.5, for which BCC structure is stabilized by the nesting of the Fermi surface at the Brillouin zone. In the case of the Ti–Ni alloy, the value of *ela* depends on how it is counted. According to the Hume-Rothery rule, *e* of transition metals is counted as zero [86], thus *ela* resulting in 0. If both *s* and *d* electrons are counted, *ela* of the Ti–Ni alloy results in 7. In either ease, *ela* is far from 1.5. Thus, the Ti–Ni alloy should not be classified into the β -phase alloy. If the alloy is classified in the different category, it is not surprising that the martensite has a structure different from those in β -phase alloys.

After Kudoh et al.'s work, another work by utilizing time-of-flight neutron diffraction technique for Ti–50.43Ni polycrystals was reported by Golestaneh and Carpenter [87], without referring to Kudoh et al.'s work. They proposed a model for the martensite structure, which consists of two cells M and M' with space group of P112₁/m and P12/c₁, respectively. However, there is no direct evidence to prove the model, which is quite unlikely.

3.3. Crystal structure of the B19 martensite

The structure of the martensite in the first stage of $Ti_{50}Ni_{50-x}Cu_x^{6}$ (x = 10-30) alloys were first reported by Shugo et al. [88] as orthorhombic (B19), and then confirmed by Tadaki et al. [89]. The structure is simple and is essentially the same as those of γ'_2 martensite in Au–47.5Cd and γ'_1 martensite in Cu–Al–Ni alloy etc. (i.e. 2H structure in Ramsdel notation). The lattice parameters of the parent phase and the martensite in $Ti_{49.5}Ni_{40.5}Cu_{10}$ alloy reported by Saburi et al. [90] are:

 $a_{\rm c} = 0.3030$ nm (for parent phase), $a_{\rm o} = 0.2881$ nm, $b_{\rm o} = 0.4279$ nm, $c_{\rm o} = 0.4514$ nm.

The lattice parameters as a function of composition are also reported in Refs. [88,91].

Recently Potapov et al. [92] carried out more detailed structure analysis for meltspun Ti₅₀Ni₂₅Cu₂₅ ribbon, which was crystallization-treated at 500 °C for 5 min, by using Rietveld refinement and electron diffraction. Space group was found to be Pmmb, which is essentially the same as that of γ'_2 martensite in Au–47.5Cd (In the

⁶ Notations for representing composition: In order to represent composition of ternary alloys, two notations are possible; e.g. Ti-(50 - x)Ni-xCu vs. $Ti_{50}Ni_{50-x}Cu_x$. Both have advantage and disadvantage. The former is better to show that the material is not a compound but an alloy, but the latter is more convenient to see the composition quickly. Besides both are used in literature, especially in figures and tables, which are referred in the present review. Thus we retain both notations in the present review.

latter it is reported to be Pcmm due to the different choice of axes [93]). In this analysis they report the displacement of Ni atom along *c*-axis in the close-packed plane, which they term *v*. Such displacement was also found in γ'_2 martensite in Au–47.5Cd, and it was ascribed due to the atomic size effect. However, Potapov et al. suggest that it is a displacement toward the monoclinic distortion in the next stage.

3.4. Crystal structure of the R-phase

As shown in Fig. 9, the so-called R-phase appears under certain conditions prior to the transformation to B19' phase. This transformation is characterized by a sharp increase of electrical resistivity with extremely small temperature hysteresis (1-2 K)as shown in Fig. 7(b) and the appearance of sharp superlattice reflections in diffraction patterns at 1/3 positions along $(110)^*$ and $(111)^*$ directions of the parent phase in reciprocal space, as shown in the series of diffraction patterns in Fig. 12. In fact the understanding of this phenomenon was controversial for many years including the nature of the phenomenon itself. The appearance of such superlattice reflections was first found by Wang et al. [95] by X-ray precession camera, and was then observed by electron diffraction as well later [77]. This phenomenon was interpreted in various ways such as order-disorder transition [95], phonon softening [96] etc., and after the extensive work by Sandrock et al. [97], it was considered to be a precursor/premartensitic phenomena due to displacement waves, which is necessary to create the subsequent B19' martensite structure. However, it is now established from the following reasons that this phenomenon is a martensitic transformation from B2 parent phase to R-phase, which has a distinct crystal structure. Firstly R-phase martensite plates are clearly observed by electron microscopy [98]. Secondly the direct transformation from B2 to B19' without precursory effect occurs depending upon conditions, as shown in Fig. 9. Thirdly the shape memory and superelasticity effects [67,99–102], which are characteristic of thermoelastic martensitic transformation, are also observed associated with this phenomenon. This simply means that B2-R transformation is a martensitic transformation, which competes with B2–B19' transformation. If R-phase appears first, the successive transformation occurs such as B2-R-B19'. However, if B19' transformation occurs first, R-phase transformation is suppressed. There are three cases [66], in which the R-phase transformation occurs: (1) a few % of Ni in Ti–50Ni alloy is substituted by Fe or Al; (2) Ni-rich Ti–Ni alloys are aged at proper temperatures (say 400 °C) to cause the precipitation of Ti_3Ni_4 phase; (3) heat-treatment of Ti-Ni alloys after cold-working to create rearranged dislocation structures. In these cases, both R-phase and B19' phase are affected by (1) the third element (Fe or Al), (2) stress field of precipitates (recently it turned out that the effect of precipitates is more complex, and this will be discussed in detail in Section 9.2), and (3) stress field of dislocations, respectively. However, the effect for B19'phase is larger than that for R-phase, and thus make the transformation temperatures of both phases separable.

We first discuss the lattice of the R-phase. Although the R-phase was reported to be tetragonal [103] at one time, people later recognized rhombohedral distortion upon the transformation from X-ray powder diffraction patterns, since {110} and



Fig. 12. Electron diffraction patterns of R-phase. Indexes are written with respect to hexagonal lattice. (a) [001] zone, (b) [100] zone, (c) [101] zone, (d) $[\bar{2}01]$ zone (e) $[\bar{1}\bar{1}\bar{1}]$ zone and (f) $[1\bar{1}0]$ zone. Ti_{50.75}Ni_{47.5}Fe_{1.50} (after Hara [94]).

{112} reflections split with decreasing temperature, although {200} reflections do not [100,101,104]. This means that the lattice can be described by stretching the cubic parent lattice along the $\langle 111 \rangle$ diagonal direction. That is, if we define the corner angle α , which is 90° in B2 parent phase, as shown in Fig. 13, it deviates from 90° with



Fig. 13. Lattice change from B2 to R-phase. The axes a', b' and c' represent the principal axes in that lattice deformation [105].

decreasing temperature. The α -angle as a function of temperature is shown for Ti₅₀-Ni_{46.8}Fe_{3.2} in Fig. 14, which was measured by Salamon et al. [104]. The characteristic of this data is that the α -angle is acute one, which changes discontinuously at the R-phase transformation temperature, and changes further rather rapidly with decreasing temperature, the other lattice constant *a* being constant. Similar α -angle dependence of temperature was measured by Lin and Kaprov [101] for Ti–Ni alloy, but their α -angle is obtuse. Similarly the α -angle reported by Dautovich and Purdy [73] for their rhombohedral phase is 90.7°, which is obtuse (and a = 0.602 nm, twice



Fig. 14. The change of α -angle as a function of temperature for Ti₅₀Ni_{46.8}Fe_{3.2} alloy upon B2–R transformation (after Salamon et al. [104] reproduced with permission of American Physical Society).

larger than the correct one). Since the differentiation of acute angle and obtuse one by powder diffraction method is difficult, which the latter two reporters employed, the earlier acute angle is probably correct, since Salamon et al. used the single crystal X-ray diffraction method, by which the differentiation is easy. By the way, recently a similar α -angle dependence on temperature was measured for the similar B2– ζ_2' transformation in a Au–49.5Cd alloy [106]. It is interesting to compare Fig. 14 with that result. Although the α -angle dependence is similar with acute angle in general, the discontinuous change at the transformation temperature is larger and the further change with decreasing temperature is much smaller in the latter case.

Since the lattice has been determined in the above, we now discuss the atomic parameters/positions for the R-phase. In the early stage Vatanayon and Hehemann [107] pointed out the similarity of diffraction patterns of the R-phase and those of ζ'_2 martensite in Au–50Cd, suggesting the space group of the latter to be P31m. Then Goo and Sinclair [108] studied the structure of R-phase by convergent beam electron diffraction (CBED) method, and reported the space group to be $P\overline{3}1m$. However, the atomic parameters were not determined. Then Ohba et al. [109] determined the crystal structure of ζ'_2 martensite in Au–49.5Cd by the single crystal X-ray diffraction method with space group P3, which does not have a center of symmetry. Considering this situation, Hara et al. [110] studied the structure of R-phase by utilizing various techniques such as CBED, electron diffraction taking into account dynamical effect, X-ray powder diffractions by Pauly method and Rietveld method, and final refinement was carried out by the Rietveld method. As a result they reported the atomic parameters in Table 3 with space group P3 (R-factors were: $R_p = 6.10\%$, $R_{wp} = 8.19\%$). This result is graphically shown in Fig. 15(a), along with the comparison with the case of space group P31m (Fig. 15(b)), in which c-axis is taken along $\langle 111 \rangle_{B2}$ axis. Roughly speaking, the characteristic of the structure may be described in the following way. In the B2 parent phase {111} planes are stacked with period of 6, with alternate Ti and Ni layers. On the contrary, in the P3 structure one atom on every third $\{111\}$ plane is pushed out of the plane in one direction, and because of this the atoms in the adjacent planes move in each {111} plane. Thus this structure looses the center of symmetry. On the other hand, in the $P\bar{3}1m$ structure {111} is a mirror plane, and thus the atoms

Atom	g	x	у	Z
Ti(la)	1/3	0	0	0
Ti(lb)	1/3	1/3	2/3	0.083(27)
Ti(lc)	1/3	2/3	1/3	0.009(25)
Ti(3d)	1.0	0.335(11)	-0.004(7)	0.361(12)
Ti(3d)	1.0	0.677(9)	0.010(6)	0.684(18)
Ni(la)	1/3	0	0	0.457(18)
Ni(lb)	1/3	1/3	2/3	0.541(14)
Ni(lc)	1/3	2/3	1/3	0.396(25)
Ni(3d)	1.0	0.318(8)	-0.022(6)	0.854(16)
Ni(3d)	1.0	0.688(6)	0.021(5)	0.160(15)

All atomic temperature factors, B, are fixed to be 0.8 [110].

Table 3



Fig. 15. Schematic illustration of the structures of the P3 model (a) and the $P\bar{3}1m(1)$ model (b) for R-phase [110].

are in the plane. If we compare P3 structure in the present case with that in ζ'_2 Au–Cd martensite, the above characteristic of P3 structure is more distinct in the latter, while the present case is more close to P $\bar{3}1m$, although it belongs to P3.

More recently Schryvers and Potapov [111] reexamined the structure of the R-phase by utilizing nanoprobe electron diffraction patterns from single crystalline areas in the R-phase. Generally speaking, the accuracy of electron diffraction is of

course worse compared with that of X-ray diffraction. Despite the fact, they tried to overcome the difficulty by using the least-squares minimization approach developed by Jansen et al., which is available as a software package MSLS [112]. As a result, they obtained the best fit for space group P3 with the total R-factor of 4.7, which is consistent with the result of Hara et al. They also obtained the total R-factor of 5.5 for space group $P\bar{3}$. The difference between space group P3 and $P\bar{3}$ is that the former does not have a center of symmetry, while the latter does. Clearly the R-factor for the former is much better than the latter, but they claim that $P\bar{3}$ is more reasonable than P3, by considering the interatomic distances of constituent atoms. i.e. They claim that the variation in the interatomic distances become smaller by choosing P3 rather than P3. Sitepu [113] also carried out synchrotron radiation experiments of powder sample, and obtained the results indicating that $R_{\rm p}$ $R_{\rm wp}$, and χ^2 (goodness of fit indices), except for $R(F^2)$, which is R-factor with respect to F^2 , are better for P3 than for $P\overline{3}$, but he claims to support $P\overline{3}$, as Schryvers and Potapov suggested. Since the difference between the two is very subtle, we may need to wait a little more time until to arrive at the final determination.

4. Mechanism of martensitic transformations in Ti-Ni-based alloys

In this section we discuss the mechanism of the above three martensitic transformations in Ti–Ni-based alloys from crystallographic point of view, which is one of the important characteristic of martensitic transformations. From such viewpoint there is a well-established theory called "phenomenological crystallographic theory of martensitic transformation" developed by Wechsler, Lieberman and Read (WLR theory) [114,115], and Bowles and Mackenzie (BM theory) [116–119] independently. Although formulations are different in the two theories, both are shown to be equivalent [120]. In both theories deformation and rotation of a parent lattice is represented by matrices as operators, which act on arbitrary vector, and the habit plane between parent and martensite is considered to be an invariant plane, which is undistorted and un-rotated, since the invariant plane gives the lowest strain energy. Before we go into detail in the following sections, we give basic ideas of the crystallographic theory briefly following WLR theory, since it is easier to follow from physical point of view.

According to WLR theory, the total deformation matrix P_1 (called shape strain) is represented as follows:

$$\boldsymbol{P}_1 = \boldsymbol{\phi}_1 \boldsymbol{P}_2 \boldsymbol{B},\tag{3}$$

where matrix **B** represents lattice deformation from parent lattice to martensite lattice, P_2 lattice invariant shear, which is an inhomogeneous shear occurring without changing the martensite structure such as twinning or slip, ϕ_1 lattice rotation. The matrices P_2 and ϕ_1 are necessary, because **B** alone usually cannot create an invariant plane. This situation is shown schematically in Fig. 16 for the case where the lattice invariant shear is twinning. The left -hand side represents the parent phase, while the right-hand side a martensite plate. This martensite plate, which consists of martensi-



Fig. 16. Schematic illustration of parent and martensite with invariant plane as a habit plane.

ite matrix and its twin, is called the habit plane variant (h.p.v.). On the other hand, the martensite matrix and the twin, which are the smallest scale martensite variants, also have specific lattice correspondence with the parent phase. These are called correspondence variants (c.v.) respectively. Thus habit plane variant and correspondence variant are differentiated in the later discussions. Now if we solve Eq. (3) under the invariant plane strain condition, we can obtain all the crystallographic parameters such as habit plane (p_1), orientation relationship between parent and martensite, the magnitude (m_1) and direction (d_1) of shape strain etc. from only the following three input parameters:

- (i) The lattice parameters of parent and martensite.
- (ii) The lattice correspondence between parent and martensite.
- (iii) The plane and direction of the lattice invariant shear.

Eq. (3) may be changed into the following form by diagonalization of matrix etc., as will be explained more in detail later:

$$\boldsymbol{P}_{1} = \boldsymbol{\phi}_{1} \boldsymbol{\Psi} \boldsymbol{\Gamma} \boldsymbol{F}_{\mathrm{d}} \boldsymbol{\Gamma}^{\mathrm{T}}. \tag{4}$$

Here F_d represents a diagonal matrix as shown below, and all other matrices represent rotation matrices:

$$\boldsymbol{F}_{\rm d} = \begin{pmatrix} \lambda_1 & 0 & 0\\ 0 & \lambda_2 & 0\\ 0 & 0 & \lambda_3 \end{pmatrix}.$$
 (5)

Thus only F_d carries the strain among the matrices in Eq. (4). It is proved that an invariant plane exists, if and only if the following conditions are satisfied [7,114]:

- (i) One λ_i is equal to 1, another is larger than 1, and the rest is smaller than 1 (e.g. $\lambda_1 < 1, \lambda_2 > 1, \lambda_3 = 1$).
- (ii) Two λ_i 's are equal to 1.

In fact in the former case (i), which are the usual case, there are two invariant planes, and they will be described as solution (+) and solution (-) in later sections. Although the shape strain P_1 in Eq. (3) is represented by the product of the three matrices, the end result of the invariant plane strain is graphically represented as shown in Fig. 17. This is the most general deformation with an invariant plane. Obviously the invariant plane is a habit plane, and the volume change is taken over by the longitudinal change normal to the invariant plane. Since the volume change in thermoelastic alloys are usually small (~0.3% or less), the shape strain is very close to a shear along the invariant plane. This shape strain is represented in the following form:

$$\boldsymbol{P}_1 = \boldsymbol{I} + m_1 \boldsymbol{d}_1 \boldsymbol{p}_1^{\mathrm{T}},\tag{6}$$

where *I* represents the identity matrix, m_1 magnitude of the shape strain, d_1 direction of the shape strain (unit vector), p_1 habit plane normal (unit vector), and p_1^T is a transpose to p_1 (i.e. row matrix). The above shape strain in Eq. (6) may be resolved into two components parallel to and normal to the habit plane, respectively, as follows:

$$m_1 d_1 = m_1^{\rm p} d_1^{\rm p} + m_1^{\rm n} p_1, \tag{7}$$

where m_1^p and d_1^p (unit vector) represent the magnitude and direction of the component of m_1d_1 parallel to the habit plane, and m_1^n and p_1 (unit vector) the magnitude and direction of the component normal to the habit plane. Obviously m_1^n is equal to $\Delta V/V$, the volume change upon transformation. All these parameters such as m_1 , d_1 , d_1^p etc. are calculated from the phenomenological crystallographic theory. See Ref. [8] for more details on the phenomenological crystallographic theory.



Fig. 17. Illustration of invariant plane strain, $P_1 = I + m_1 d_1 p'_1$, and the resolution into two components, $m_1^p d_1^p$ and $m_1^n p_1$, d_1 , p_1 and d_1^p being unit vectors [15].

Similarly, with respect to the lattice invariant shear described above, we give a brief description on twinning, since those twins as a result of lattice invariant shear are introduced without diffusion. When we discuss twinning by shear (i.e. deformation twinning), we encounter five important twinning elements as shown in Fig. 18. Here the sphere represents a half unit sphere, which is deformed, and the half ellipsold the shape of the sphere after the deformation. K_1 represents the shearing plane, which is undistorted and un-rotated, and η_1 the shearing direction. The plane, which contains the η_1 direction and K_1 plane normal, (i.e. the plane of this paper), is called the plane of shear. The K_2 is the second undistorted plane, the first being K_1 plane. The intersection of K_2 plane and the plane of shear is called η_2 . s represents the twinning shear, which is necessary to create twinned lattice. K_1, K_2, η_1, η_2 and s are called twinning elements. If two elements such as K_1 and η_2 or K_2 and η_1 are given, other elements can be calculated by Bilby–Crocker theory [121] using tensors. In general there are two types of twins, Type I and Type II. Type I twins are characterized by rational indices of K_1 plane and η_2 direction, K_2 and η_1 being irrational, and the two twin crystals are related by mirror symmetry with respect to K_1 plane. On the other hand, Type II twins are characterized by rational indices of K_2 plane and η_1 direction, K_1 and η_2 being irrational, and the two twin crystals are related by rotation of 180° around the η_1 axis. Although both type of twinning are possible geometrically, Type II twinning are rather rare compared with Type I twinning. According to the Bilby–Crocker theory, for a Type I twinning mode, Type II twinning mode which is conjugate to the Type I twinning (in which K_1 and K_2 , and η_1 and η_2 are simultaneously interchanged) is always geometrically possible with the same twinning shear. It is also possible in some cases, especially in high symmetry crystals, that K_1, K_2, η_1, η_2 are all represented by rational indices. In such a case the twinning mode is called compound twinning, and the two twin crystals have the symmetry properties of both Type I and Type II. See Refs. [13,122,123] for more details on the geometry of twinning, which occurs without diffusion.

With respect to twins in martensite, there was a belief from early investigations of martensitic transformations that two twin components (i.e. martensite matrix and its twin) are crystallographically equivalent correspondence variants of martensite [114,117]. Then it is proved that for Type I twinning the K_1 plane must originate



Fig. 18. Deformation of a unit sphere into an ellipsoid by shear, and the definition of K_1 , K_2 , η_1 , η_2 and s. See text for details.

from a mirror plane in parent [117], while that for Type II twinning the η_1 direction must originate from a twofold axis in parent [124]. Furthermore, by considering Type I and Type II twins, which are conjugate to each other, it follows that the η_2 direction for a Type I twin originates from the twofold axis normal to the mirror plane which becomes the K_1 plane. Similarly, for Type II twin the K_2 plane originates from the mirror plane normal to the twofold axis which becomes the η_1 direction [124].

4.1. $B2 \rightarrow B19'$ transformation

4.1.1. Twins in B19' martensite

As discussed in the above, the lattice invariant shear (i.e. twinning modes) is an important input parameter for the phenomenological theoretical calculations, thus we discuss here the twinning modes in B19' martensite first. They were investigated extensively by using electron microscopy by many workers as follows. Otsuka et al. [77] found $\{\overline{1}\,\overline{1}\,1\}_m^{-7}$ Type I twins and stacking faults on the basal plane. Gupta and Johnson [125] found $(001)_m$ compound twins and $\{011\}_m$ Type I twins, in addition to the reconfirmation of $\{\overline{1}\,\overline{1}\,1\}_m$ twins. Knowles and Smith [126] found important $\langle 011\rangle_m$ Type II twins, as we discuss in detail below. In addition, Onda et al. [127] found $(100)_m$ compound twins, which are conjugate to $(001)_m$ twins. Furthermore, Nishida et al. [128] found $\{20\bar{1}\}_m$ twins under heavy deformation, although they cannot be a lattice invariant strain, as will be discussed below.

These results are summarized in Table 4, which is the expanded version of the previous table by Onda et al. [127] (Madangopal and Banerjee [129] also gave a similar table as that of Onda et al.). In this table we notice that $\{011\}_m$ Type I twinning and $\langle 011 \rangle_m$ Type II twinning are conjugate to each other, since the latter twinning elements are obtained by interchanging K_1 and K_2 , and η_1 and η_2 simultaneously with the same twinning shear. Similarly, $(001)_m$ compound twinning and $(100)_m$ compound twinning are conjugate to each other. In this respect we may expect the conjugate twinning mode of $\{\overline{111}\}_m$ Type I twinning, i.e. $\langle \overline{211} \rangle_m$ Type II twinning mode, but they have not been experimentally observed. Since B19' structure is low symmetry monoclinic, many twinning modes were found as expected. However, there is a consensus among researchers now such that $\langle 011 \rangle_m$ Type II twinning mode is dominant among the observed twinning modes, after Knowles and Smith [126] first found it. The table shows all the twinning elements calculated by the Bilby– Crocker theory. The column next to the last described as "Sol." indicates whether

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⁷ Notation for suffix to indices: For brevity we use the following notation for suffix to indices hereafter. For parent phase (B2) we use "p". Since there are three types of martensite structures in Ti–Ni-based alloys, as shown in Fig. 9, we use the following suffix according to their symmetry: "m" for monoclinic (B19'), "o" for orthorhombic (B19), and "R" for rhombohedral (R-phase). Strictly speaking, "R" should be "t", since the true symmetry of R-phase is trigonal, as discussed already in Section 3.4. However, "R" was retained in order to avoid confusion, since the term "R" has been used so widely. Although the above is a principle in the choice of suffix, the structure notation such as B19′ and B19 may also be used in order to make clear or emphasize the structures cited in some special cases.

Table 4 Twinning modes of B19' martensite

Twinning mode	K_1		η_1		K_2	η_2	S	Sol.	Ref.
{111} Type I	$(\bar{1} \ \bar{1} \ 1)$ $(\bar{1} \ 1 \ 1)$	$(\bar{1}\bar{1}0)_{p}$ $(\bar{1}01)_{p}$	[0.540430.459571] [0.540430.459571]		$(0.24695 \underbrace{0.506111}_{(0.24695 \overline{0.50611}1)})$	$[\bar{2} \ \bar{1} \ 1]$ $[\bar{2} \ 1 \ 1]$	0.30961 0.30961	Yes Yes	[126] [126]
{111} Type I	$(1\ 1\ 1)$ $(1\ \overline{1}\ 1)$	$(101)_{p}$ $(1\bar{1}0)_{p}$	$[\overline{1.51172}0.511721] \\ [\overline{1.51172}0.511721]$		$(\overline{0.66875} \underbrace{0.337501}_{(\overline{0.66875}} \underbrace{0.337501}_{0.33750}))$	$[2\ 1\ 1]$ $[2\ \overline{1}\ 1]$	0.14222 0.14222	No No	[131] [131]
{011} Type I	(011) $(01\overline{1})$	(001) _p (010) _p	$\frac{[1.572711\overline{1}]}{[\overline{1.5727111}]}$		$(\underbrace{0.720531\bar{1}}_{(\overline{0.72053}11)} $	$[0\ 1\ 1]$ $[0\ 1\ \overline{1}]$	$0.28040 \\ 0.28040$	Yes Yes	[126] [126]
(011) Type II	$\begin{array}{c} (0.720531\bar{1})\\ (\overline{0.72053}11) \end{array}$		$[0\ 1\ 1]\\[0\ 1\ \overline{1}]$	[001] _p [010] _p	(011) $(01\bar{1})$	$[\frac{1.57271}{[1.57271}1\overline{1}]$	$0.28040 \\ 0.28040$	Yes Yes	[126] [126]
Compound	(001) (100)	$(0\bar{1}1)_{p}$ $(100)_{p}$	[100] [001]	[100] _p [011] _p	(100) (001)	[001] [100]	$0.23848 \\ 0.23848$	No No	[126] [127]
$\{20\bar{1}\}$	(201)	$(41\bar{1})_p$	$[\bar{1}0\bar{2}]$	$[\bar{1}2\bar{2}]_p$	(001)	[100]	0.4250	No	_

(1) All indices without suffix represent those in B19' martensite, while those with suffix "p" represent those in the parent phase, which is related to the preceding indices in the martensite by lattice correspondence.

(2) The column indicated by "Sol." represent whether a solution for the phenomenological crystallographic theory exists or not.

(3) $\{20\bar{1}\}\$ twinning in the last row is a deformation twinning mode, which appears under heavy deformation. See text for details.

the phenomenological theory gives a solution or not, when the twinning mode is used as a lattice invariant shear, and the last column denoted as "Ref." is a reference for that calculation. Thus, if it does not give a solution, it means that the particular twinning mode cannot be a lattice invariant shear. Thus the presence of the solution indicates that $\langle 011 \rangle_m$ Type II twinning will be a strong candidate as a lattice invariant shear for B2 \rightarrow B19' transformation, although this will be discussed in detail in the following section. Similarly the presence of the solution such as $\{\bar{1}\ \bar{1}\ 1\}_m$ Type I twinning may indicate that this mode may also act as a lattice invariant shear under certain conditions. We also note that $(\bar{1}\ \bar{1}\ 1)_m$ twinning mode and $(1\ 1\ 1)_m$ twinning mode are not equivalent, as is clear from the different values of the twinning shear, because the crystal is monoclinic.

From this table we see some interesting point as follows, if we compare the twinning shear of each twinning mode. Since the twinning mode with the twinning shear smaller than that of $\langle 011 \rangle_m$ Type II twinning, such as $(111)_m$ and $(001)_m$ twinning, does not give a solution for phenomenological theory, it seems natural that $\langle 011 \rangle_m$ Type II twinning becomes a lattice invariant shear. Similarly $\{011\}_m$ Type I twinning, which is conjugate to $\langle 011 \rangle_m$ Type II twinning, could be a lattice invariant shear, since it is associated with the same twinning shear. However, the observation of the former is very rare. A similar situation is also observed in Cu–Al–Ni alloy, where both $\langle 111 \rangle$ Type II twinning and $\{121\}$ Type I twinning, which is the conjugate twinning mode for the former, have the same twinning shear of 0.261, only the former becomes a lattice invariant shear, and the reason for it is not understood as yet [130]. In the same table $\{20\overline{1}\}_m$ twinning is also added as an observed twinning mode. However, this twinning mode appears only under heavy deformation, and this cannot be a candidate for a lattice invariant shear, because $\{20\overline{1}\}_m$ planes originates from $\{4\bar{1}\bar{1}\}_{p}$ planes of the parent phase, which is not a mirror plane. This point will be discussed in detail in Section 6.3.

An example of electron micrograph of twins in B19' martensite is shown in Fig. 19, along with diffraction patterns described below. Fig. 19(a) shows a TEM micrograph, which covers two habit plane variants (h.p.v.'s) designated as "B" and "C" regions, which are bounded by a horizontal interface designated as "D". Parallel bands in each of the two h.p.v.'s are twins as a result of lattice invariant shear in each h.p.v. Fig. 19(b) is the diffraction pattern taken from the region "B", which covers two bands from a unique axis of $[011]_m$, which is the η_1 axis of $[011]_m$ Type II twinning (see Table 4). Thus, the fact that the diffraction pattern is a single pattern is a direct proof showing that the two bands are [011]_m Type II twins, as indicated as "Type II" in the figure, because the diffractions from the two bands coincide to each other by the rotation of 180° around the η_1 axis in this case. Similarly the diffraction pattern in Fig. 19(c) is a proof that the parallel bands in region "C" are [011]_m Type II twins as shown in Fig. 19(a). Now the diffraction pattern of Fig. 19(d) was taken from the region, which covers two c.v.'s (c.variants) above and below the interface "D". This diffraction pattern clearly shows that the two crystals are related by mirror symmetry with respect to $(11\overline{1})_m$ plane, which is parallel to the interface "D". Thus we see that the two h.p.v.'s "B" and "C" are related by $(111)_m$ Type I twinning (see Table 4).



Fig. 19. TEM image (a) of two h.p.v.'s (upper part and lower part) of B19' martensite, and associated selected area diffraction patterns (b–d). B, C, D in (a) and (b), (c), (d) correspond to each other, respectively. E.g. diffraction pattern of (b) was taken from the region B in (a) etc. Ti–50.0Ni (after Nishida et al. [132] reproduced with permission of Elsevier).

High resolution TEM (HRTEM) micrographs corresponding to these are shown in Fig. 20. Fig. 20(b) shows a HRTEM image of $(11\bar{1})_m$ Type I twin plane, which was observed from the direction parallel to the K_1 plane and normal to the η_1 direction. We see that the interface is straight and the atom columns have mirror symmetry with respect to the $(11\bar{1})_m$ twin plane, as expected. Fig. 20(a) is an important case for $\langle 011 \rangle_m$ Type II twins, which were observed from the unique direction, which is



Fig. 20. High resolution TEM images of $\langle 011 \rangle_m$ Type II twin boundary and, (b) $(11\bar{1})_m$ Type I twin boundary in B19' martensite. Ti–50.0Ni. See text for details (after Nishida et al. [135] reproduced with permission of Elsevier).

parallel to the η_1 direction as well as the K_1 plane. In this case the two twin crystals are related by the rotation of 180° around the η_1 axis, and thus the orientations of the atom columns of the two twin crystals (i.e. upper part and lower one) are the same, which is consistent with the inserted single diffraction pattern. Since the K_1 plane of Type II twinning is irrational, Knowles [133] argued that the K_1 plane consists of the $(11\bar{1})_m$ ledge and $(01\bar{1})_m$ step. However, they made the argument based on HRTEM micrographs in the orientations, which are not in the unique orientation along the η_1 axis. Recently Liu and Xie [134] also made HRTEM observations of Type II twinning and discussed from the same view as Knowles, but they did not make observations along the unique η_1 direction either. However, the critical observations made by Nishida et al. [132,135] in Fig. 20(a) does not show any ledge nor step. This is a clear evidence to show that there is no ledge nor step in Type II twin boundaries. Thus it is most probable that the K_1 plane is irrational even on an atomic scale, and the strains at the Type II twin boundary are accommodated elastically along some distance (i.e. broad twin boundary). Similarly Type II twin boundaries were ob-
served by HRTEM for a γ'_1 martensite in a Cu–Al–Ni alloy from the unique η_1 axis by Hara et al. [136,137]. The result in that case is the same as the present one, and some strain contrast was observed at the Type II twin boundary, which reflects the elastic strain at the twin boundary. More details on the role of various twins will be discussed in the later section associated with self-accommodation of martensites.

4.1.2. Crystallography of $B2 \rightarrow B19'$ transformation

We now discuss the crystallography of $B2 \rightarrow B19'$ martensitic transformation. First such calculation was made by Knowles and Smith [126] for $\{11\bar{1}\}_m$ Type I twinning and $\langle 011 \rangle_m$ Type II twinning as a lattice invariant shear by using WLR theory. However, they did not have experimental data to critically compare with, because Ti–Ni single crystals were not available by that time. The first report on the habit plane measured by two-surface analysis on Ti–Ni single crystals was made by Saburi et al. [138] and Miyazaki et al. [139]. More complete work on the crystallography of the transformation in a Ti–Ni alloy was done by Matsumoto et al. [131], who measured habit plane, orientation relationship and shape strain simultaneously on single crystals and made critical comparison with the theory. The results of their calculations are essentially the same as those by Knowles and Smith. In the following, we will discuss the crystallography of the transformation in some detail, mostly following Matsumoto et al.'s work, which was done for solution-treated Ti–49.8Ni single crystals.

We begin with the description of three input parameters. First the lattice parameters we used for the parent phase and martensite are the following: $a_0 = 0.3015$ nm, and a = 0.2889 nm, b = 0.4120 nm, c = 0.4622 nm, and $\beta = 96.8^{\circ}$. Secondly we describe the lattice change as shown in Fig. 21. Fig. 21(a) shows the B2 parent structure 4 times in volume, and a tetragonal cell is delineated by bold lines. The cell delineated by dotted lines in Fig. 21(b) is the same one as that delineated in Fig. 21(a). Upon transformation, $[\bar{1}00]_p$ vector shrinks to become a, $[01\bar{1}]_p$ vector shrinks to become b axis of the martensite, and $[0\bar{1}\bar{1}]_p$ vector expands to become c axis of the martensite. Then a shear is introduced to make the β angle from 90° to 96.8° on $(011)_p$ plane in $[100]_p$ direction, and thus the final monoclinic lattice is created as drawn in bold lines in Fig. 21(b). Thus, the monoclinic lattice is created. In practice, the above process occurs in one step, but the process was described in two steps for mathematical clarity. To arrive at the final martensite structure discussed in Fig. 11, further atom shuffles are necessary, but those shuffles are ignored in the phenomenological crystallographic theory.

As is clear from the above description, the lattice deformation matrix \overline{B} with respect to i', j' and k' axis system in Fig. 21 is written as follows:

$$\overline{B} = \begin{pmatrix} 1 & 0 & \cot \beta \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} a/a_0 & 0 & 0 \\ 0 & b/\sqrt{2}a_0 & 0 \\ 0 & 0 & c\sin\beta/\sqrt{2}a_0 \end{pmatrix}.$$
(8)

Then, the lattice deformation matrix B with respect to the parent axis i, j, k system in Fig. 21 is given by the similarity transformation as



Fig. 21. The lattice change from B2 parent (a) to B19' martensite (b). i, j, and k refer to parent lattice, and i', j' and k' refer to the martensite lattice. See text for details.

$$\boldsymbol{B} = \boldsymbol{R}\overline{\boldsymbol{B}}\boldsymbol{R}^{\mathrm{T}},\tag{9}$$

where \boldsymbol{R} is a rotation matrix given by

$$\boldsymbol{R} = \begin{pmatrix} -1 & 0 & 0\\ 0 & 1/\sqrt{2} & -1/\sqrt{2}\\ 0 & -1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}$$
(10)

and \mathbf{R}^{T} is a transpose to \mathbf{R} .

From the above argument referring to Fig. 21, the lattice corresponding matrix between parent and the martensite variant is given by

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & -1 & -1 \end{pmatrix} \begin{pmatrix} U \\ V \\ W \end{pmatrix},$$
(11)

where [uvw] is an arbitrary vector in the parent phase and [UVW] is a corresponding vector in the martensitic phase. From the similar argument, we derive 12 lattice correspondences for the present transformations, as listed in Table 5. In the table, the correspondence variants (c.v.'s) with and without prime for the same number refer to the ones with opposite shears. The correspondence variant described above is for c.v. 2'. If we choose c.v. 1, the relation between i, j, k and i', j', k' axis systems may become simpler, but in order to keep consistency to the following, we chose c.v. 2' in the above.

As a lattice invariant shear, all the twinning modes except for $\{201\}_m$ mode in Table 4 are possible candidates. In fact, we made calculations for all cases, but $(111)_m$ and $(1\bar{1}1)_m$ Type I twinning and $(001)_m$ and $(100)_m$ compound twinning did not give rise to solutions. Thus, they cannot be lattice invariant shears. Only possible lattice invariant shears are either $\langle 011 \rangle_m$ Type II twinning or $\{\bar{1}\bar{1}1\}_m$ and $\{011\}_m$ Type I twinning. The lattice invariant shear matrix P_2 is given by the following expression:

$$\boldsymbol{P}_2 = \boldsymbol{I} + m_2 \boldsymbol{d}_2 \boldsymbol{p}_2^{\mathrm{T}},\tag{12}$$

where I is the 3×3 identity matrix, d_2 a twinning shear direction (a column matrix), p_2^T a twinning plane (a row matrix), m_2 the magnitude of the lattice invariant shear, which is an unknown parameter until Eq. (3) is solved. The rotation matrix Φ_1 is another unknown parameter, which is to be determined by the invariant plane strain condition. Once **B** and P_2 are known in Eq. (3), it is possible to solve Eq. (3) so as to have an invariant plane, by using the standard technique in the theory. In general, four solutions are obtained, depending upon the value of m_2 (m_2 takes two values), and two solutions are obtained for a particular value of m_2 . m_2 is related with the relative twin width x, where (1 - x) represents the width ratio of the martensite matrix, and x that of the martensite twin. The two solutions are distinguished by (+) and (-) signs. The computer output for the phenomenological theoretical calculations for $[01\bar{1}]_m$ Type II twinning is shown in Table 6. It is clear from the table that

Variants	[100]	[010]	[0.0.1]
varialits	[100Jm	[010]m	[001]m
1	[100] _p	[011] _p	[0 1 1] _p
1'	$[\bar{1}00]_{p}$	$[0\bar{1}\bar{1}]_{p}$	$[0\bar{1}1]_{p}$
2	[100] _p	$[0\bar{1}1]_{p}$	$[0\overline{1}\overline{1}]_{p}$
2'	$[\bar{1}00]_{p}$	$[01\bar{1}]_{p}$	$[0\overline{1}\overline{1}]_{p}$
3	[010] _p	[101] _p	$[10\overline{1}]_{p}$
3'	$[0\bar{1}0]_{p}$	$[\overline{1} 0 \overline{1}]_{p}$	$[10\overline{1}]_{p}$
4	[010]p	$[10\bar{1}]_{p}$	$[\bar{1} 0 \bar{1}]_{p}$
4'	$[0\bar{1}0]_{p}$	$[\bar{1}01]_{p}$	$[\bar{1} 0 \bar{1}]_{p}$
5	[001]p	[110]p	[110]p
5'	$[00\bar{1}]_{p}$	[1 1 0]p	[1 1 0]p
6	[001]p	[110]p	[1 1 0]p
6'	[001] _p	[1 1 0] _p	$[\bar{1}\ \bar{1}\ 0]_p$

Lattice correspondences between parent and B19' martensite [131]

Table 5

Γ	Ψ	
$(-0.35561 \ 0.91265 \ 0.20150)$	(0.80966 0.06986 0.35581)	
0.63674 0.07875 0.76704	0.11592 0.01000 0.05094	
(0.68418 0.40107 -0.60913)	(0.40490 0.03494 0.17794)	
d_1	m_1	P_1
(0.43449)		(0.94949 0.02298 0.01223)
0.48739	0.13079	-0.05667 1.02578 0.01372
(0.75741)		(-0.08806 0.04006 1.02132)
Θ	Ω	
(-0.98983 0.10700 0.09377)	(0.99379 0.06960 -0.08686)	
0.00683 0.69404 -0.71990	0.02296 0.63542 0.77182	
(-0.02407 -0.72470 -0.69889)	(-0.00959 -0.77732 0.64023 /	
d_1	m_1	P_1
(-0.91387)		(0.95503 - 0.06139 - 0.09217)
0.37101	0.13079	0.01825 1.02492 0.03742
0.16490		(0.00525 0.01135 1.01688)
Θ	Ω	
(-0.99955 0.02877 -0.00795)	(0.98899 0.14767 0.00986)	
0.02532 0.67611 -0.73637	$\left(-0.10487 0.65224 0.75072\right)$	
	F $\begin{pmatrix} -0.35561 & 0.91265 & 0.20150 \\ 0.63674 & 0.07875 & 0.76704 \\ 0.68418 & 0.40107 & -0.60913 \end{pmatrix}$ $\begin{pmatrix} d_1 \\ \begin{pmatrix} 0.43449 \\ 0.48739 \\ 0.75741 \end{pmatrix}$ Θ $\begin{pmatrix} -0.98983 & 0.10700 & 0.09377 \\ 0.00683 & 0.69404 & -0.71990 \\ -0.02407 & -0.72470 & -0.69889 \end{pmatrix}$ $\begin{pmatrix} d_1 \\ \begin{pmatrix} -0.91387 \\ 0.37101 \\ 0.16490 \end{pmatrix}$ Θ $\begin{pmatrix} -0.99955 & 0.02877 & -0.00795 \\ 0.02532 & 0.67611 & -0.73637 \end{pmatrix}$	$\begin{array}{ccccccc} & \mathbf{\Gamma} & \mathbf{\Psi} \\ \begin{pmatrix} -0.35561 & 0.91265 & 0.20150 \\ 0.63674 & 0.07875 & 0.76704 \\ 0.68418 & 0.40107 & -0.60913 \end{pmatrix} & \begin{pmatrix} 0.80966 & 0.06986 & 0.35581 \\ 0.11592 & 0.01000 & 0.05094 \\ 0.40490 & 0.03494 & 0.17794 \end{pmatrix} \\ \\ & \mathbf{d}_1 & \mathbf{m}_1 \\ \begin{pmatrix} 0.43449 \\ 0.48739 \\ 0.75741 \end{pmatrix} & 0.13079 \\ 0.13079 \\ \begin{pmatrix} -0.98983 & 0.10700 & 0.09377 \\ 0.00683 & 0.69404 & -0.71990 \\ -0.02407 & -0.72470 & -0.69889 \end{pmatrix} & \begin{pmatrix} 0.99379 & 0.06960 & -0.08686 \\ 0.02296 & 0.63542 & 0.77182 \\ -0.00959 & -0.77732 & 0.64023 \end{pmatrix} \\ \\ & \mathbf{d}_1 & \mathbf{m}_1 \\ \begin{pmatrix} -0.91387 \\ 0.37101 \\ 0.16490 \end{pmatrix} & 0.13079 \\ \hline & 0 \\ \begin{pmatrix} -0.99955 & 0.02877 & -0.00795 \\ 0.02532 & 0.67611 & -0.73637 \end{pmatrix} & \begin{pmatrix} 0.98899 & 0.14767 & 0.00986 \\ -0.10487 & 0.65224 & 0.75072 \end{pmatrix} \end{array}$

Table 6 Output for phenomenological theoretical calculations for $[01\bar{1}]$ Type II twinning [140]

the two solutions are not equivalent. To explain the meanings of the symbols in Table 6, some descriptions follow.

Starting from Eq. (3), we define and diagonalize the matrix F as follows:

$$\boldsymbol{F} = \boldsymbol{P}_2 \boldsymbol{B} = \boldsymbol{\Psi} \boldsymbol{F}_{\mathrm{s}} = \boldsymbol{\Psi} \boldsymbol{\Gamma} \boldsymbol{F}_{\mathrm{d}} \boldsymbol{F}^{\mathrm{T}},\tag{13}$$

where Ψ is a rotation matrix, F_s a symmetric matrix representing a pure distortion. This second equation comes from a mathematical theorem such that any matrix (i.e. P_2B in this case) can be represented as the product of a symmetric matrix (F_s) and a rotation matrix (Ψ). Since F_s is symmetric, it can be diagonalized into F_d by rotation matrix Γ , and Γ^T a transpose of Γ . When Eq. (3) is solved for an invariant plane strain, we have shown earlier that P_1 is represented as Eq. (6), which graphically corresponds to Fig. 17.

Now, from Table 6, it is seen that (+) solution and (-) solution are not equivalent. Since there are 12 lattice correspondences and two lattice invariant shears ($[011]_m$ and $[01\overline{1}]_m$ Type II twinning), there are 24 (+) habit plane variants (h.p.v.'s) and 24 (-) h.p.v.'s, as shown in Fig. 22 by the stereographic projection. A particular h.p.v. is represented such as 2'-1' (+), following Saburi and Nenno [141]. Here c.v. 2' represents a martensite matrix, which is larger in volume, and c.v. 1' a martensite twin, which is related to c.v. 2' by $[01\overline{1}]_m$ Type II twinning, and the symbol (+) the (+) solution. In the following, we use the notation.



Fig. 22. Stereographic projection of 24 habit plane variants for (+) solution of phenomenological crystallographic calculation for $\langle 011 \rangle_m$ Type II twinning. B2–B19' transformation (after Matsumoto [140]).

We now make a critical comparison of the theory with experimental observations made on single crystals. Fig. 23 shows the habit planes of stress-induced martensites observed in solution-treated specimens (we do not include those in aged specimens, since they may be affected by the preceding R-phase transformation) by two-surface analysis, along with those by other investigators and theoretical predictions. Although there are substantial scattering in the data, they are gathered in a certain orientations, except for Mohamed's data [142], which were measured on polycrystals previously. It is to be noted that the habit planes in Ti-Ni alloys are quite different from those in β -phase alloys, which are located fairly close to $\{011\}_p$ such as $\{155\}_{p}$, since the structure of the martensite and the lattice invariant shear of the former alloys are quite different from those of the latter. It is clear that the theoretical predictions for Type II (-) and Type I (-) solutions do not fit with the experimental observations. Thus, Type II (+) and Type I (+) solutions are left as possible candidates. However, the Schmid factor calculations showed too small values for the latter solution. Thus, Type I twinning is excluded as a lattice invariant shear, and Type II twinning is left as a possible candidate for the lattice invariant shear. As will be shown below, Type II (+) solution is consistent with observed orientation relationship and the shape strain as well.



Fig. 23. Comparison of observed habit planes with theoretical ones for B2-B19' transformation [131].

The orientation relationship between parent and martensite measured by microbeam X-ray diffraction technique, and the shape strain measured by scratch displacement technique are compared with theoretical predictions in Fig. 24 for two single crystals, along with their habit planes. We see a good agreement between theory and experiment. The same result is shown numerically in Table 7. Furthermore, twin width ratio (1 - x):x measured by TEM by Knowles and Smith [126] is 2.45:1, which is comparable to the theoretical prediction of 2.69:1. Thus, although the agreement is not as good as those in Cu-Al-Ni [143] and Au-47.5Cd [144] alloys, the result is consistent in *all* respects. One of the reasons why the agreement is not so good possibly lies in the shape of the martensites. Although plate martensites are formed under stress, the shape is often quite irregular as shown in Fig. 25, and even two martensites with close habit planes are often nucleated as shown in the figure. This is probably because various twinning modes may activate during the transformation associated with the main lattice invariant shear. Besides slip may be easily introduced during the transformation, since the critical stress for slip in solution-treated sample may be as low as 150 MPa [145]. Despite the above complexities, the above



Fig. 24. Comparison between theory (closed symbols) and experiment (open symbols) for shape strain direction (d_1) and orientation relationship ($a_{2'}$, $b_{2'}$ and $c_{2'}$) for B2–B19' transformation. Two specimens were used for the two experiments and different h.p.v.'s were stress-induced. Habit planes were simultaneously measured for both specimens. Ti–49.8Ni single crystals. Specimens are solution-treated [131].

somparison between theory and experiment for B2 (B1) transformation [151]					
	Theoretical	Experimental	Deviation		
Habit plane (p_1)	(-0.88888, 0.21523, 0.40443)	$(-0.8684, 0.26878, 0.4138)^{a}$	3.3°		
Direction of shape strain (d_1)	[0.43448, 0.75743, 0.48737]	[0.4580, 0.7706, 0.4432] ^a	3.0°		
Magnitude of shape strain (m_1)	0.13078	0.140 ^a	0.009		
Orientation relationship	$(100)_{\rm m} \sim (\bar{1}00)_{\rm B2} \ 1.42^{\circ}$				
	$(010)_{\rm m} \sim (01\overline{1})_{\rm B2} \ 1.12^{\circ}$	See Table 4	≤1.2°		
Variant 2'	$(010)_{\rm m} \sim (0\bar{1}\bar{1})_{\rm B2} 8.23^{\circ}$				

Table 7

Comparison between theory and experiment for $B2 \rightarrow B19'$ transformation [131]

^a These values are mean ones.



Fig. 25. Optical micrographs of stress-induced B19' martensites. Two arrows indicate two h.p.v.'s Ti-49.8Ni single crystals, which are solution-treated [131].

experiments clearly showed that the phenomenological crystallographic theory applies to the B2 \rightarrow B19' transformation in Ti–Ni alloys with the lattice invariant shear of $\langle 011 \rangle$ Type II twinning. However, this statement does not exclude the possibility of other twinning modes such as $\{\overline{1}11\}_m$ and $\{011\}_m$ Type I twinning as a lattice invariant shear under certain conditions, since they also have solutions, as was mentioned previously. This may be especially true in polycrystals, since transformations are especially complex in polycrystals, as will be discussed in the following section.

4.1.3. Self-accommodation of B19' martensite

In the previous section we have seen that the elastic strains associated with martensitic transformations are relieved by the invariant plain strain condition, and this

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condition determines the crystallography of martensitic transformation such as habit plane, orientation relationship etc. However, this condition cannot eliminate the transformation strains completely, because the shear component is not eliminated under this condition, as clearly seen in Fig. 17. If, however, two h.p.v.'s with opposite shears are formed side by side, the shear strains are eliminated macroscopically. That is, there is a hierarchy in reducing elastic strain energy upon transformation [130], and the process such that elastic strain energy is further reduced by the combination of multiple variants is called self-accommodation of martensite. The mechanism of self-accommodation in most of the β -phase alloys such as Cu–Zn–Ga, Cu–Al–Ni, Ag–Cd, Ni–Al etc. were successfully analyzed by Saburi–Wayman–Nenno [141,146,147] by the averaging out of the shape strain matrices determined by the phenomenological crystallographic theory. According to the mechanism, four or two clusters of h.p.v.'s around $\langle 011 \rangle_p$ poles self-accommodate, and the averaged shape strain matrix becomes close to the identity matrix, which represents the strain free state.

On the contrary, the self-accommodation in B19' martensite in Ti–Ni is very complex, because the structure is monoclinic, and many twinning modes are available in the martensitic state. Generally the triangular morphology is believed for this selfaccommodation. Furthermore, Madangopal [148] claims that there are two scales in the morphology; the one in a larger scale (primary plates) is triangular hollow cones, which form rather accidentally, and the other in smaller scale (secondary plates) represents real self-accommodation in a triangular solid arrangement of three plates, as shown in Fig. 26.

The first analysis of self-accommodation of B19' martensite was done by Miyazaki et al. [149], who studied it by one surface trace analysis of surface reliefs observed in Ti–50.5Ni single crystals, which were solution-treated at 1173 K for 3.6 ks followed by aging at 673 K for 3.6 ks. They analyzed it in detail from both



Fig. 26. TEM observation of B19' martensites in annealed and quenched Ti–Ni alloy. "Primary" or first formed martensites (larger ones) and "secondary" martensite clusters (smaller ones) are observed (after Madangopal [148] reproduced with permission of Elsevier).

macroscopic factor (with respect to shape strain matrix) and microscopic factor (with respect to twinning relationship of junction plain between two h.p.v.'s), considering the clustering of habit planes around $\{111\}_p$, $\{011\}_p$ and $\{001\}_p$ poles, and they concluded that the triangular self-accommodation for this transformation consists of three h.p.v.'s out of four h.p.v.'s around $\{001\}_p$ poles, instead of clustering of habit plane poles around $\{111\}_p$. However, this conclusion seems unlikely from the following two reasons. Firstly, the self-accommodation model depicted in Fig. 4(b) of Ref. [149], is quite unlikely, because the junction plane, $(001)_m$ in the model has not been observed by TEM observations. Instead $\{\overline{1}\,\overline{1}\,1\}_m$ Type I twin boundaries were observed as junction planes between h.p.v.'s by Madangopal [148] and Nishida et al. [132] (e.g. see Fig. 19 in this review). Secondly, the cancellation of strain for three h.p.v.'s around $\{001\}_{n}$ (see Table 5 of Ref. [149]) is not so good, especially in diagonal strain elements. The above inappropriate result probably originates from the lack of TEM observations, since one-surface analysis alone may introduce some ambiguity. Furthermore, more importantly the use of aged Ni-rich specimens may be inappropriate, because the introduced R-phase transformation may affect the morphology, as is discussed in Section 4.3.4. Thus, we will introduce the mechanism by Madangopal [148] in the following, who carried out detailed TEM observations, in addition to detailed calculations. This is for the triangular solid self-accommodating morphology formed by the secondary plates. Although the composition of the specimens are not specified strangely in this paper, probably it is close to Ti-50Ni, since no precipitates are observed.

Madangopal first took electron diffraction patterns from various regions in Fig. 27 systematically, such as, regions A, B, C, A + B, A + C and B + C etc. In identifying crystallographic relation between plates such as two plates in region A etc., he writes down correspondence variant relation between parent and martensite in matrix form for all possible lattice correspondences in Table 5. Then he takes the two planes/directions of parent and martensite, which are in lattice correspondence relation, to be parallel to each other. Strictly speaking, the lattice correspondence relation does not guarantee that the two planes/directions of parent and martensite in the relation are parallel to each other, because lattice rotation and lattice deformation are associated with the transformation. However, he ignores the effects, and proceeds further to detailed analysis. Thus he confirmed the crystallographic relations as schematically shown in the schematic diagram in the upper right corner of Fig. 27. That is, the lattice invariant shears in each h.p.v. A, B, and C are $(011)_m$ Type II twinning, and h.p.v. A, B, and C consist of c.v. 1-2', 5'-6' and 4-3, respectively, where former variant represents major variant following Saburi-Nenno notation [141]. He further determined the junction planes between h.p.v.'s by trace analysis and orientation relationships, as indicated in the figure. That is, the junction plane A-B is $(11\overline{1})_{m,1}$ Type I twinning plane, and the major and minor twins are Type I twin related with the twinning plane simultaneously. Similarly, the junction plane A–C is $(1\overline{1}\overline{1})_{m1}$ Type I twinning plane, but only the major twin is twin related with this plane, and the minor twin is tapered, so that two major twins attached to each other, as indicated. The junction plane B–C is $(11\bar{1})_{m,4}$, Type I twinning plane, and only major twins are twin related to each other, the minor twins being tapered. Thus



Fig. 27. TEM observation of typical triangular morphology of B19' martensites (a), selected area diffraction pattern (b) and the results of analysis (right-hand side). See text for details (after Madangopal [148] reproduced with permission of Elsevier).

this self-accommodating morphology seems microscopically reasonable. If we identify the locations of 1–2', 5'–6' and 4–3 habit planes in the standard projection of Fig. 22, we notice that the three habit planes are not symmetrically located around $(1\,1\,1)_p$ pole. In this respect the result is different from other β -phase alloys mentioned earlier. Concerning the macroscopic self-accommodation, instead of using the shape strain averaging method, they [150,151] introduced the parameter called "degree of self-accommodation (DSA)" by using the Eshelby solution for displacement at a point remote from a coherent ellipsoid inclusion [152], as follows:

$$DSA = (r^{1} - r^{n}) \cdot 100/r^{1}, \tag{14}$$

where r^1 = partial term for the strain energy density due to an isolated plate and, r^n = partial term for the strain energy density due to a cluster of "*n*" plates. By taking suitable values for constants in *r*, which is not explicitly shown here, he calculates DSA for 3-variant plates of 1–2′, 5′–6′ and 4–3, as DSA = 89.4%. He also claims that this is the highest DSA obtained among various clustering around {111}_p, {011}_p and {001}_p. Furthermore, by discussing from the viewpoint of autocatalysis, he concluded that the above self-accommodating plates group of 1–2′, 5′–6′ and 4–3 are autocatalytically nucleated by compressive strain along the $\langle 111 \rangle_p$ direction. Readers are referred to Ref. [148] for more details, since the analysis is quite complicated. (Readers should be careful in reading it, since there are several misprints including some miscalculations in the tables of the paper.)

4.2. $B2 \rightarrow B19$ transformation

In this section we discuss $B2 \rightarrow B19$ (orthorhombic) transformation, which appears in $Ti_{50}Ni_{50-x}Cu_x$ ($x \ge 7.5$) alloys. Strictly speaking, even for the alloy with $x = 5.0, B2 \rightarrow B19$ transformation occurs as will be discussed later, but it is soon followed by $B19 \rightarrow B19'$ transformation, and thus it is difficult to observe the $B2 \rightarrow B19$ transformation separately. In the following we mostly describe the results obtained by Saburi et al. for $Ti_{49.5}Ni_{40.5}Cu_{10}$ alloy, which has M_s point slightly above room temperature, since the reverse transformation by beam heating is easily observed by TEM for this M_s .

4.2.1. Twins in B19 martensite

The twinning modes in B19 martensite were studied by electron microscopy [153], and the result is shown in Table 8. As seen from the table, there are two twinning modes; $\{111\}_{o}$ Type I and $\{011\}_{o}$ compound ones, and both are associated with small twinning shears. The $\{111\}_{o}$ and $\{011\}_{o}$ planes are originated from $\{011\}_{p}$ and $\{001\}_{p}$ planes of the parent phase, respectively.

4.2.2. Crystallography of $B2 \rightarrow B19$ transformation

The phenomenological theoretical calculation was made by Saburi et al. [90] for this transformation, and the habit plane was reported to be $\{\bar{3}34\}_p$ as a result of comparison with one surface analysis of TEM observations. However, critical comparison with experiments has not been done yet for other crystallographic parameters, since single crystals of Ti–Ni–Cu alloys are not easily available. One of the important characteristics of this transformation is that there is no lattice invariant shear in this transformation. This occurs because one of the element of the lattice deformation matrix from B2 to B19 in the diagonalized form, i.e. $b/(\sqrt{2}a_0) = 0.999$, is very close to unity without introducing a lattice invariant shear [89,90]. Here *b* represents the lattice parameter of *b*-axis of B19 martensite, and a_0 the lattice parameter of the parent phase. Thus the lattice invariant shear is not needed for this transformation. Therefore, the twins described with respect to Table 8 are all introduced as a result of self-accommodation, as will be described in the following section.

4.2.3. Self-accommodation of B19 martensite

The morphology of B19 martensite is undoubtedly triangular, as typically shown in an optical micrograph of Fig. 28. The morphology was analyzed in detail by

Type of twinning	Twinning element					
	K_1	η_1	K_2	η	S	
Type I	{111}	$\langle 5.88 \overline{1} \overline{4.88} \rangle$	$\{4.06\overline{1}\overline{7.11}\}$	(211)	0.17	
Compound	{011}	$\langle 0 1 \overline{1} \rangle$	$\{01\overline{1}\}$	$\langle 011 \rangle$	0.11	

Table 8 Twinning elements of B19 martensite [153]



Fig. 28. Optical micrograph of surface relief due to B2–B19 transformation in $Ti_{49.5}Ni_{40.5}Cu_{10}$ alloy, which was taken at room temperature ($O_s = 35$ °C) (after Saburi et al. [90] reproduced with permission of The Iron & Steel Inst. Japan).

Watanabe et al. by using the result of phenomenological theoretical calculation and one surface analysis of TEM observations. Table 9 shows six lattice correspondences for this transformation. Fig. 29 represents the result of plotting habit plane variants by stereographic projection. We immediately notice that there are three h.p.v. poles around each $\{111\}_p$ pole, which are very close to $\{111\}_p$ poles. This observation indicates that the combination of three poles may make self-accommodation with triangular morphology. In fact the average of the shape strain of the three h.p.v.'s results in the matrix, which is very close to identity matrix, although there are offdiagonal elements with small numbers. This result leads to the self-accommodating scheme of the above three h.p.v.'s, which is consistent with experimental observations. Furthermore they arrived at the scheme shown in Fig. 30 as a more general self-accommodation. Here the numbers represent the number of variants in Table 9, and each variant has a shape of quadrangular pyramid. Each pyramidal plane is $\{111\}_{o}$ Type I twinning plane, which originates from $\{011\}_{p}$ plane of the parent phase, and the basal plane of each pyramid is {011}_o compound twinning plane, which originates from $\{001\}_p$ plane of the parent phase. If we look at this morphology from [111]_p orientation, it reduces to the morphology shown in Fig. 28, and it

Table 9 Lattice correspondences between parent and B19 martensite [153]

-	•			
Variant	[100] _o	[010] _o	[001] _o	
1	[100]p	[011] _p	$[0\bar{1}1]_{p}$	
2	[100] _p	$[0\bar{1}1]_{p}$	$[0\bar{1}\bar{1}]_{p}$	
3	$[010]_{p}$	$[101]_{p}$	$\begin{bmatrix} 1 & \overline{1} \end{bmatrix}_{n}$	
4	[010]p	$[10\overline{1}]_{p}$	$[\overline{1} 0 \overline{1}]_{p}$	
5	[001] _p	[110] _p	$[\bar{1} \ 1 \ 0]_{p}$	
6	$[00\bar{1}]_{p}$	$[1\overline{1}0]_p$	$[\bar{1}\bar{1}0]_{\rm p}$	



Fig. 29. Habit plane normals calculated by phenomenological crystallographic theory for B2–B19 transformation. Note the triangular clusters of habit planes around $\{111\}_p$ (after Saburi et al. [90] reproduced with permission of The Iron & Steel Inst. Japan).



Fig. 30. Schematic representation of the self-accommodation of B19 martensites in 3-dimensions. The axes are shown with respect to the parent lattice (after Watanabe et al. [153] reproduced with permission of Japan Institute of Metals).

shows that the latter is a special case of self-accommodation in Fig. 30. Since the self-accommodation morphology in Fig. 30 consists of 6 variants, if we take the average of the shape strains of the 6 variants, we obtain the following:

$$\overline{\boldsymbol{P}_{1}} = 1/6(\boldsymbol{P}_{1} + \boldsymbol{P}_{2} + \ldots + \boldsymbol{P}_{6}) = \begin{pmatrix} 1.001 & 0 & 0\\ 0 & 1.001 & 0\\ 0 & 0 & 1.001 \end{pmatrix}.$$
 (15)

The slight deviation of the diagonal elements from unity is due to volume change upon transformation, and thus the self-accommodation is perfect. The above analysis shows that the self-accommodation scheme for this transformation is straightforward.

4.2.4. $B2 \rightarrow B19 \rightarrow B19'$ successive transformation

Fukuda et al. [71] studied the $B2 \rightarrow B19 \rightarrow B19'$ successive transformation by using in situ TEM observations and X-ray diffraction for $Ti_{49.5}Ni_{45.5}Cu_{5.0}$ and $Ti_{50}Ni_{44}Cu_5Al_1$ alloys, which exhibit M'_s and M_s of both successive transformations slightly above room temperature. Here M'_{s} represents M_{s} temperature of the first transformation (i.e. O_s), and M_s that of the second transformation. As a result they observed that there is no fixed habit plane between B19 martensite and B19' martensite, and that B19' martensite is formed by [100]_o shear on (001)_o plane, leaving (001)_m compound twins in B19' martensitic phase. This investigation also clarified the following. The martensitic transformation in the above alloys with 5Cu were believed to be B2–B19' direct transformation in the past, although electrical resistivity increases with decreasing temperature, which contradicts with the behavior of B2–B19' direct transformation. However, the actual transformation was found out to be not direct but $B2 \rightarrow B19 \rightarrow B19'$ successive one, and the two successive transformations occurs in the similar temperature range with overlapping, and the effect of the former transformation reflects strongly on electrical resistivity, leading to resistivity increase with lowering temperature. Thus the above contradiction was resolved.

4.3. $B2 \rightarrow R$ transformation

The structure of R-phase is trigonal, as described in Section 3.4, and thus it is convenient to describe it with hexagonal indices. The lattice correspondence for this transformation is listed in Table 10. Since the *c*-axis of the R-phase corresponds to $\langle 111 \rangle_p$ of the parent phase, there are four lattice correspondences as shown in the table, where the directions with respect to R-phase such as $[100]_R$ etc., is represented by three indices notation (Miller notation), while $(0001)_R$ plane is represented by four indices notations (Miller–Bravais notation) of hexagonal indices.

4.3.1. Twins in R-phase

Twinning in R-phase were studied by Miyazaki and Wayman [155], and Fukuda et al. [154], as listed in Table 11. There are two types of twins: $\{11\overline{2}1\}_R$ and $\{11\overline{2}\overline{2}\}_R$, which corresponds to $\{100\}_p$ and $\{011\}_p$, respectively. They are associated with the same value of twinning shear *s*, since they are conjugate twins to each other.

Lattice correspondences between parent and K-phase [154]						
Variant	[100] _R	[010] _R	[001] _R	(0001) _R		
1	[121] _p	$[1 1 \overline{2}]_{p}$	[111] _p	$(111)_{p}$		
2	[211] _p	[112] _p		$(111)_{p}$		
3	[121] _p	[112] _p	$[1 \underline{1} 1]_{p}$	$(1 \ \underline{1} \ 1)_{p}$		
4	[211] _p	[112] _p	[111] _p	(111) _p		

Table 10 Lattice correspondences between parent and R-phase [154]

		K_1	η_1	K_2	η_2	s ^a
Mode 1	R-phase indices	(1121)	[112]	$(11\bar{2}\bar{2})$	[111]	0.0265
	Parent indices	(100)	[011]	(011)	[100]	0.0265
Mode 2	R-phase indices Parent indices	$(1 \ 1 \ \overline{2} \ \overline{2})$ $(0 \ 1 \ 1)$	[1 1 1] [1 0 0]	$(11\bar{2}1)$ $(\bar{1}00)$	$[1 \ 1 \ \overline{2}]$ $[0 \ 1 \ 1]$	0.0265 0.0265

Table 11 Twinning elements of the R-phase [154]

^a The value of *s* was taken from Ref. [155]. Since *s* is a function of temperature, this corresponds to $\alpha = 89.46^{\circ}$ at $T = (T_R - 35)$ K.

4.3.2. Crystallography of $B2 \rightarrow R$ transformation

A typical morphology of R-phase transformation is "herring-bone" type as shown in Fig. 31, which is not associated with a lattice invariant shear. This is in sharp contrast with the B2 $\rightarrow \zeta'_2$ (trigonal) transformation in Au–49.5Cd, which has the same martensite structure as the R-phase. In that case, both transformations with and without lattice invariant shear are possible, and the phenomenological theoretical calculation was made for the former [156]. However, no lattice invariant shear is found for the present case up to now, and thus we will not discuss the transformation from the phenomenological theoretical point of view for a single R-phase martensite plate. Instead we will proceed to the self-accommodation mechanism in the following section.

4.3.3. Self-accommodation of R-phase

The study of self-accommodation mechanism of R-phase was first made by Miyazaki and Wayman [155] in detail by using single crystals of Ti–50.5Ni, which were aged at 400 °C for 1 h. They used two-surface analysis coupled with optical microscopy, but did not make TEM observations. However, the model of the self-accommodation morphology described in Fig. 5 of Ref. [155] is not consistent with the ordinarily observed "herring-bone" type morphology as shown in Fig. 31. Thus we will follow Fukuda et al.'s report [154] in the following, who used both TEM



Fig. 31. Optical microscope observation of B2–R transformation for $Ti_{50.3}Ni_{48.2}Fe_{1.5}$ alloy. Typical herring-bone type morphology is noted. P: parent phase. R: R-phase (after Fukuda et al. [154] reproduced with permission of Japan Institute of Metals).

observations and two-surface analysis of large grains of $Ti_{50.3}Ni_{48.2}Fe_{1.5}$ and $Ti_{50-1}Ni_{48}Al_2$ alloys.

As a result of two-surface analysis of optical micrographs in Fig. 32, and TEM micrographs associated with electron diffraction patterns, Fukuda et al. deduced the self-accommodating morphology shown in Fig. 33. It is clear from the figure that if you observe the morphology from $[001]_p$ direction you will observe the "herringbone" morphology, whereas if you observe along $[010]_p$ direction, you will observe the parallel banded morphology as shown in Fig. 32. The lattice deformation calculation was carried out as follows. (Here lattice deformation is calculated instead of shape strain, since lattice invariant shear is absent in the present case.) The lattice deformation matrix in principal axis \overline{B} is written as the following:

$$\overline{B} = \begin{pmatrix} a_{\rm H}/\sqrt{6}a_{\rm p} & 0 & 0\\ 0 & a_{\rm H}/\sqrt{6}a_{\rm p} & 0\\ 0 & 0 & c_{\rm H}/\sqrt{3}a_{\rm p} \end{pmatrix},\tag{16}$$



Fig. 32. Optical micrographs of R-phase used for two-surface analysis for $Ti_{50.3}Ni_{48.2}Fe_{1.5}$ alloy: (a) topsurface of the grain; (b) side-surface of the grain (after Fukuda et al. [154] reproduced with permission of Japan Institute of Metals).



Fig. 33. Schematic representation of the self-accommodation of R-phase in 3-dimensions. The axes refer to the parent lattice (after Fukuda et al. [154] reproduced with permission of Japan Institute of Metals).

$$\boldsymbol{B} = \boldsymbol{R}_1 \overline{\boldsymbol{B}} \boldsymbol{R}_1^{\mathrm{T}},\tag{9}$$

where \mathbf{R}_1 for c.v. 1 is given as follows: (The readers should note that the matrix given in the original paper is incorrect, because \mathbf{R}_1 must be orthonormal. In the following, the expressions (17)–(19) were corrected by the authors of Ref. [154].)

$$\boldsymbol{R}_{1} = \begin{pmatrix} 1/\sqrt{6} & 1/\sqrt{2} & 1/\sqrt{3} \\ -2/\sqrt{6} & 0 & 1/\sqrt{3} \\ 1/\sqrt{6} & -1/\sqrt{2} & 1/\sqrt{3} \end{pmatrix}.$$
 (17)

Thus by using the values: $a_p = 0.3019$ nm, $a_H = 0.7355$ nm and $c_H = 0.5283$ nm, the lattice deformation matrix is obtained for c.v. 1 as follows:

$$\boldsymbol{B}_{1} = \begin{pmatrix} 1.0007 & 0.0062 & 0.0062 \\ 0.0062 & 1.0007 & 0.0062 \\ 0.0062 & 0.0062 & 1.0007 \end{pmatrix}.$$
 (18)

Similarly by carrying out calculations for c.v. 2–4, we obtain the average lattice deformation matrix \overline{B} (average) as follows: (The readers should not confuse it with \overline{B} in Eqs. (16) and (9). In order to avoid the confusion, the term "average" is added in Eq. (19).)

$$\overline{\boldsymbol{B}} \text{ (average)} = 1/4(\boldsymbol{B}_1 + \boldsymbol{B}_2 + \boldsymbol{B}_3 + \boldsymbol{B}_4) = \begin{pmatrix} 1.0007 & 0 & 0\\ 0 & 1.0007 & 0\\ 0 & 0 & 1.0007 \end{pmatrix}.$$
(19)

In this expression the diagonal elements (i.e. 1.0007) is slightly away from unity. This is due to the volume change upon transformation. Thus we see the self-accommodation is perfect.

4.3.4. $B2 \rightarrow R \rightarrow B19'$ transformation

So far we have discussed the crystallography of $B2 \rightarrow R$ transformation, which was clear and straightforward. On the contrary, the investigation on the crystallography of the second $R \rightarrow B19'$ transformation is not many. Hwang et al. [157] made in situ observations of $R \rightarrow B19'$ transformation in a Ti₅₀Ni₄₇Fe₃ alloy, and reported that the lattice defects in B19' martensite are $(11\overline{1})_m$ twins and stacking faults on the $(001)_{\rm m}$ basal plane. This seems to indicate that the lattice invariant shear in the $R \rightarrow B19'$ transformation is $(11\bar{1})_m$ twinning. Meanwhile, Nishida et al. [158] observed dominant (001)_m twinning in aged Ti-51Ni alloy, which exhibits $B2 \rightarrow R \rightarrow B19'$ transformation, as shown in Fig. 34. They also observed dominant $(001)_{\rm m}$ twinning even in Ti–50Ni alloy, which usually exhibit $\langle 011 \rangle_{\rm m}$ Type II twinning as a lattice invariant shear, when grain size is reduced to less than 4 μ m [159]. Obviously (001)_m twinning is not allowed as the lattice invariant shear for $B2 \rightarrow B19'$ transformation, as shown in Table 4. Nishida et al. [158] considered the reason for the appearance of (001)_m twins in the aged Ti-51Ni as due to the interaction of precipitates and the parent phase, and those in Ti-50Ni alloy as due to the constraint of grain boundaries.

More extensive work on the $R \rightarrow B19'$ transformation has recently been done by Madangopal and Singh [160] by using TEM and electron diffraction technique for a Ti-50Ni alloy. Since Ti-50Ni alloy usually does not exhibit R-phase transformation, they used specimens, which were thermally cycled between the parent phase and martensite. As a result, they observed the parent phase and B19' martensite in the electron micrographs, which contains abundant fine $(001)_m$ twins instead of $(011)_m$ Type II twins, which are characteristic lattice invariant shear for the direct $B2 \rightarrow B19'$ transformation. Obviously this $(001)_m$ twinning is not allowed as the lattice invariant shear for the direct $B2 \rightarrow B19'$ transformation, as mentioned above. Thus they consider that the cycled specimens experience the two-stage



Fig. 34. Electron micrograph and associated diffraction pattern of Ti–51Ni alloy, which was aged at 500 °C for 1 h. Abundant $(001)_m$ twins are observed (after Nishida et al. [158] reproduced with permission of Elsevier).

 $B2 \to R \to B19'$ transformation, although they did not show any evidence for that, such as DSC curves or resistivity vs.temperature curves, except for a very faint super-lattice reflections of the R-phase, which were observed only infrequently. Then they claim that the above $(001)_m$ twinning is the lattice invariant shear for the $R \to B19'$ transformation, and carried out detailed analysis using the phenomenological crystallographic theory of Wechsler–Lieberman–Read, as follows. Mathematically, starting from the R-phase they considered the transformation as follows; $R \to B2 \to B19'$. Then the lattice deformation matrix from R-phase to B19' is written as follows:

$$F = 1/2(BR^{-1} + \phi_1\{\phi_2 BR^{-1}\phi_2^{-1}\}),$$
(20)

where **B** is the lattice deformation of the B2 \rightarrow B19' transformation, **R** is the lattice deformation of the B2 \rightarrow R transformation (here do not confuse **R** with the lattice rotation matrix in earlier sections), ϕ_1 is the rigid body rotation by which the $(001)_m$ plane rotated to different positions by the two lattice deformation strains are brought into coincidence, and ϕ_2 is the rotation matrix which transforms the correspondence variant of one twin fraction into the other. In the above, it is to be noted that the above expression is not a general expression, but it is assumed that the twin width ratio of $(001)_m$ twins is 1:1, which was the observed ratio by TEM observations. Then the invariant plane strain condition is achieved when

$$\det |\boldsymbol{F}\boldsymbol{F}^{\mathrm{T}} - \boldsymbol{I}| = 0, \tag{21}$$

where \mathbf{F}^{T} is the transpose of \mathbf{F} , and \mathbf{I} the identity matrix. By solving the above equation, it turned out that the solution exist only when the rhombohedral angle α takes a critical value less than 86.2°. Under the condition they obtained the results, which are in fair agreement with the observed habit plane and orientation relationship. Although the above result is interesting, and the observations by Nishida et al. described in the above may also be explained in the same framework, if that is correct. There are some controversial problems as well, as described in the following: (1) In Ti–50Ni alloy, it is known that M_s decreases and resistivity increases with cycling [161], but it is not known whether or not the two-stage B2 \rightarrow R \rightarrow B19' transformation is really realized in cycled specimens. (2) The α -angle observed to date is higher than 89° [101,104]. Is such a low value (86.2°) of α -angle really possible? Considering these, new experiments are waited for in the specimens, which exhibit clear two-stage transformation.

5. Precursor effects to martensitic transformations

In this section our discussion will mainly focus on Ti–Ni-based alloys, but at the beginning we will put our discussion to a broader prospect and discuss some general aspects of the precursor effect, because precursor effect is quite general and it is easier to understand a particular case when one has the whole picture.

5.1. What is precursor effect and its importance

Before explaining what precursor effect of martensitic transformation is and why it happens, it is instructive to consider a parallel social phenomenon. ⁸ In the history of any country, there have been many social revolutions that transformed an old empire into a new one. Although such "transition" seems abrupt (i.e., happened in a clearly defined year), one can easily identify from history book that long before the "transition" there had been numerous "battles" or "conflicts" in the old regime that ultimately caused the destruction of the old empire and the birth of a new one. These "battles" gradually intensifies with approaching the "transition point" where the new empire is established. Clearly these "battles" are closely linked to the coming new empire and actually determine the features of the new empire.

These "battles" or "conflicts" within the old empire can be considered as a "precursor" of the eventual social revolution and they are closely linked to the new empire. It is hard to consider that a social revolution could happen without such precursor phenomena. By comparison, martensitic transformation can be considered as a "crystal structure revolution" that changes an "old" structure (parent phase) into a "new" structure (martensite). Anomalies in the parent phase, which are linked to the martensite phase, are called precursor phenomena of martensitic transformation.

In the history of martensite research, there had been much debate about whether or not precursor effect exists. During 1960s through 1980s, there had been a large number of reports on "precursor phenomena" in martensitic alloys, but many without a clear understanding; there were even some "precursor" reports that later turned out to be due to artifacts. Such chaotic situation caused disbelief in the effect among many people, in particular among many metallurgists. Some metallurgists tended to be against the existence of such effect, because they considered that a phase transformation occurs when the free energy of the martensite is lower than that of the parent phase and there is no need to resort to any additional effect. On the other hand, physicists, whose idea is Landau theory, consider precursor effect is inevitable. Nowadays, as more and more reliable and reproducible evidence are accumulated, it is now widely accepted that precursor effects are real and they have strong link to the upcoming new phase.

The importance of precursor effects lies in that it provides important clue for understanding the origin of the transformation and structure of transformation product(s), similar to the case of social revolution. This will be seen in the following.

5.2. Basic microscopic picture of precursor phenomena

In order to understand why precursor phenomena exist, it is helpful to envision martensitic transformation as a distortion of the parent phase structure (mostly

⁸ Y. Yamada also talked at a meeting in 1980s about the analogy between precursor effect and the eve before a revolution with respect to fluctuations, but probably it is not written in his published papers.



Fig. 35. Generic Landau potential of martensitic alloy as a function of temperature for a first order martensitic transformation. "M" represents martensite and "P" represents parent phase. Order parameter η is taken as the shear strain and indicates the shear distortion of the lattice relative to the parent phase.

cubic) into martensite structure. Then one can construct a free energy of the system as a function of such lattice distortion. This free energy function (called Landau free energy) describes both parent phase (no distortion) and martensite (with finite distortion). The specific lattice distortion characteristic of martensite structure is called "order parameter" of the martensitic transformation, or ferroelastic transition (the latter term is used when considering parallelism to ferromagnetic transition and ferroelectric transition). A generic form of Landau free energy that can reproduce first order martensitic transformation is a polynomial of the form [162] 9

$$F = a(T - T^*)\eta^2 - b\eta^4 + c\eta^6,$$
(22)

where η is the characteristic lattice distortion, i.e., the order parameter; *a* (positive), *b* (positive) and *c* (positive) are coefficients. *T* is temperature and T^* is a hypothetical temperature at which the specific phonon of the parent phase related to the transformation reaches zero (note it is not the temperature at which the parent phase and martensite have the same free energy).

Fig. 35 shows the free energy as a function of order parameter and temperature. A prominent feature of this free energy form is the existence of three energy minima. The minimum at $\eta = 0$ corresponds to undistorted lattice, i.e., the parent phase, whereas the two minima at $\eta = +\eta_M$ and $\eta = -\eta_M$ correspond to two different but equivalent martensite variants. Below $T = T_0$ (T_0 is a temperature at which the parent phase and martensite have equal free energy) martensite has lower free energy

⁹ More realistic Landau potential that considers coupling between shuffle (primary order parameter) and shear (secondary order parameter) has been proposed [163]. However, there also exist transformations where shear is the primary order parameter (for example, InTl), such potential is not generally applicable. Therefore, here we use this generic, although primitive, form of Landau potential.

and thus the parent phase transforms into multi-domain martensite (at $T < M_s$). This is a simple but phenomenological explanation of martensitic transformations by Landau theory.

Above $T = T_0$ the parent phase has lower free energy and thus is more stable than martensite, thus transformation does not occur in such temperature range. However, by fluctuation there is still a probability of going from undistorted phase to distorted $\eta = +\eta_M$ and $\eta = -\eta_M$ state. Apparently such a probability decreases when the energy barrier (the barrier between $\eta = 0$ and $\eta = \pm \eta_M$) becomes high. Therefore, above the transformation temperature there is a dynamic structure fluctuation, the extent of which is related to the energy barrier shown in Fig. 35.

Now it is able to give a microscopic picture of the precursor phenomena prior to martensitic transformation. With approaching transformation temperature the energy barrier between two energy minima decreases; as the result structure fluctuation intensifies. This causes two consequences. Firstly, the curvature at $\eta = 0$ becomes smaller as shown in Fig. 35. This curvature corresponds to the "spring constant" (or "harmonic" energy) of interatomic interaction of the parent phase ($\eta = 0$). This decrease in the spring constant is manifested by a softening of related phonon energy and shear elastic constant c'. Secondly, the fluctuation between state $\eta = 0$ and $\eta = \pm \eta_{\rm M}$ becomes intensified. This is manifested by an increase in the diffuse scattering intensity at "martensite position" in reciprocal space, although martensite has not yet been formed.

There is a third effect, which is not predicted by the above ideal picture, in which chemical disorder (composition inhomogeneity at atomic level) is not considered. When disorder is considered, it is possible that the $\eta = \pm \eta_M$ minima may be stabilized by the defects, either through their stress field [164] or composition effect [165]. This causes a "static" spatial modulation of the order parameter η , contrasting the abovementioned dynamic picture. This static effect manifests itself as a "tweed" microstructure observable with TEM and a "central peak" in phonon spectrum. Under cyclic stress the system may locally switches between $\eta = 0$ (undistorted state) and $\eta = \pm \eta_M$ (distorted state) and causes energy dissipation due to the repeated climbing the energy barrier between them. With lowering temperature towards T_0 , the energy barrier becomes lower and the probability of the switching increases. This suggests that internal friction or mechanical attenuation increases with approaching transformation temperature. This will be discussed more in detail in Section 5.7.

All the above three kinds of effect have been observed experimentally in Ti–Nibased alloys and in many shape memory alloys. Elastic constant measurements [166–172,72] always show a softening of elastic constant c' prior to martensitic transformations; Neutron scattering experiment in most cases [173–178] confirm a low-lying TA₂ acoustic phonon which further softens with approaching transformation temperature. Elastic neutron scattering in most cases reveals a central peak [174,175], and X-ray diffraction reveals diffuse scattering and extra diffuse spots [179,104,97,107]. These suggest the existence of static martensite-like structure above the transformation temperature. Many TEM observations have reported diffuse streaks along $\langle 110 \rangle^*$ directions and in some cases discrete diffuse spots were observed [180–184,98,154]. In Ti–Ni–Fe alloys, the diffuse scattering was found to correspond to tiny "domains" [183–185], rather than the tweed structure as observed in Ni–Al alloys [186,187]. Furthermore, ultrasonic attenuation experiment on Ti–Nibased alloys confirmed the existence of premartensitic attenuation [188–190].

There have been a number of review articles on martensitic transformation and precursor phenomena in shape memory alloys [191–198], noticeably a recent comprehensive review by Planes and Manosa on precursor effects [194]. But mostly they are not focused on Ti–Ni. In the following, we will focus on the precursor effect in Ti–Ni and Ti–Ni-based alloys. Emphasis will be put on recent understanding on the origin of the B19' martensite and R phase and the $1/3\langle 110\rangle^*$ diffuse scattering prior to R-phase formation.

5.3. Transformation routes of Ti–Ni-based alloys and structure relationship

The purpose of studying precursor effects is to understand the origin of the martensitic transformation and to answer the question about why certain martensite structure is favored over another. For this purpose, first we need to identify the structure relationship between parent phase and different martensite candidates. Section 3 has given a detailed description of the structures of various martensites in Ti–Ni-based alloys. Here we emphasize the relationship between them and the microscopic transformation mechanism (i.e., how the structure of the parent phase is changed into the structure of martensite by specific shear/shuffle, which is related to the specific premartensitic lattice softening phenomena).

The parent phase of all Ti–Ni and Ti–Ni-based alloys has a cubic B2 (ordered BCC) structure. Depending on composition, thermomechanical treatment, the B2 phase may take one of three transformation paths shown in Fig. 36 [199], which is the same as Fig. 9 but with indication of the exact symmetry relationship among different phases. B2–B19' transformation occurs in quenched Ti–Ni alloys; B2–R–B19' transformation occurs in aged Ti–Ni (with Ti₃Ni₄ precipitation) or cold-worked Ti–Ni, and in ternary Ti–Ni–Fe(Al) alloys; B2–B19–B19' transformation occurs in Ti–Ni–Cu alloys [68]. As mentioned in Section 3.1 and clearly shown in Fig. 36, we notice an important fact: the end product of all martensitic transformations in Ti–Ni-based alloys is B19' martensite. Therefore, B19' martensite can be considered as the ground state of all Ti–Ni and Ti–Ni-based alloys.

Symmetry analysis of various phases by Barsch [199] shows interesting symmetry relationship between B2 and three different martensites, as summarized in Fig. 36. He showed that except R–B19' transformation, all other transformations, B2–B19', B2–R, B2–B19, B19–B19' follow a group–subgroup relation (i.e., the symmetry group of low-temperature phase is a subgroup of that of the high-temperature phase), as the usual case for shape memory alloys. The R–B19' transformation does not follow a group–subgroup relation. B19' martensite has a space group of P2₁/m; it is not a subgroup of R, which has a space group of P3. This situation is rare in shape memory alloy systems.

A detailed crystallographic description of the structures of these martensites has been given in Sections 3 and 4. Here we discuss the relationship between these structures. The structure of B19' martensite [195,81] is rather strange compared with that



Fig. 36. Three possible transformation paths for Ti–Ni-based alloys. The associated phonon mode and symmetry relationship among different phases are also shown. POP: primary order parameter; SOP: secondary order parameter (after Barsch [199] reproduced with permission of Trans Tech Publications).

in other well-known β -phase alloys. It is schematically shown in Fig. 37 [169], which shows the structure relationship among B2 (Fig. 37(a)), B19 (Fig. 37(b)), and B19' (Fig. 37(c)). Usually, most martensite structures are derived from different stacking of the basal plane, the {110} plane of the parent phase. B19 (2H), 3R, 7R, 9R, 18R, etc. can all be understood from this scheme [10]. These structures can be considered as due to the intrinsic instability (Zener instability) of the open BCC structure with respect to {110} $\langle 1\bar{1}0 \rangle$ shear [200], which leads to more close-packed structures. The period of the stacking often relates to the softening of a specific phonon mode [201,202]. However, the B19' martensite can be viewed as a "normal" martensite B19 (2H), but being distorted by a monoclinic shear {001} $\langle 1\bar{1}0 \rangle$; ¹⁰ the resulting

¹⁰ This shear can also be written as $(100)[00\bar{1}]_{B19}$ shear in B19 index, which is also equivalent to $(001)[\bar{1}00]_{B19}$ shear. The latter shear is consistent with Fukuda et al.'s argument mentioned in Section 4.2.4. that B19' is formed by a $(001)[100]_{B19}$ shear to the B19 structure.



Fig. 37. Structure relationship among B2 parent phase and two kinds of martensite, B19, and B19': (a) the parent phase B2 structure with a FCT cell delineated; (b) orthorhombic martensite B19, formed by shear/ shuffle of the basal plane $(110)_{B2}$ along $[1\bar{1}0]$ direction; (c) monoclinic martensite B19', which is viewed as a B19 structure sheared by a non-basal shear $(001)[1\bar{1}0]_{B2}$, the modulus of which corresponds to c_{44} [169].

structure is a monoclinic structure (Fig. 37(c)). For a long time there had been no explanation for the origin of the non-basal shear in forming the B19' structure, but very recently important results from elastic constant measurement enabled a simple understanding of the monoclinicity of the B19' martensite [169–172,72]. The details will be given in the following section.

As shown in Fig. 37(b), B19 (ordered HCP) is a normal close-packed martensite, as encountered in various β -phase alloys, being isostructure with the γ'_2 martensite of Au–Cd alloy [93]. This structure can be understood in terms of the conventional shear/shuffle of the basal plane.

R-phase has a complicated trigonal structure [110]. The main feature of the structure can be schematically illustrated in Fig. 13. As discussed in Section 3.4, R-phase can be roughly viewed as a cubic B2 phase being elongated along one of the body diagonal $\langle 111 \rangle$. This produces a rhombohedral lattice, but the true symmetry is trigonal if considering the actual atom positions. Among all known martensitic alloys, there is only one alloy, except Ti–Ni-base alloys, possessing this structure; it is the near-equiatomic Au–Cd alloy [109]. Therefore, it is often thought that these two alloys might have something in common [107]. The trigonal R-phase is not a closed-packed structure like B19 or 9R, and it cannot be considered as due to the Zener instability, a geometric tendency to form more close-packed structures. Instead, it can be considered as a superposition of three degenerate transverse displacement waves $1/3\langle 110\rangle^*\langle 1\bar{1}0\rangle$ [179]. However, it is unclear what causes the alloy to adopt this complicated, open structure instead of intuitively low-energy, closed-packed structures. First principle calculations [203] suggest the related 1/3 soft phonon mode in TA₂ branch is due to the nesting in the Fermi-surface. However, there are at least two possible candidates corresponding to the 1/3 phonon softening, R-phase and 9R martensite. It is unclear why R-phase is favored over 9R martensite. Besides, the structure relationship between R-phase and B19' martensite is unclear.

5.4. Elastic softening and its correlation with the structure of B19' martensite

The origin of the unique B19' martensite discussed in the previous section can be traced from a remarkable difference in the precursory elastic softening between Ti–Ni alloy and common β -phase alloys, as shown in Table 12. Common β -phase alloys are known to show softening only in elastic constant c' [204–209], with other elastic constants behaving normal. This yields an anisotropy factor A (= c_{44}/c') as large as 10–20, which further increases with lowering temperature. In sharp contrast, Ti–Ni alloy shows softening in both c' and c_{44} (Table 12); this leads to a very low anisotropy ($A \sim 2$), which further decreases with lowering temperature. This difference has been noticed by previous studies [166–168]; but the underlying meaning has not been figured out until very recently [169].

By definition, c' corresponds to the $\{110\}\langle 1\bar{1}0\rangle$ shear modulus, which is naturally related to the Zener instability and to the formation of basal-plane-based martensites. On the other hand, c_{44} is the $\{001\}\langle 100\rangle$ shear modulus, which seems at first sight to have nothing to do with the B19' martensite. However, for cubic crystals, c_{44} also equals to the $\{001\}\langle 1\bar{1}0\rangle$ shear modulus. This $\{001\}\langle 1\bar{1}0\rangle$ shear is just

Table 12

Comparison of elastic properties of Ti–Ni alloy with those of other β -phase alloys in the vicinity of martensitic transformation temperature. c' is the modulus of basal plane shear $\{110\}\langle 1\bar{1}0\rangle$, c_{44} is the modulus of non-basal plane shear $\{001\}\langle \bar{1}\bar{1}0\rangle$, and anisotropy factor $A = c_{44}/c'$ [169]

	I) (),		15	- 44 · L · · J		
Elastic properties around $M_{\rm s}$	Ti–Ni	Cu–Al–Ni	Cu–Zn	Cu–Zn–Al	Au–Zn–Cu	Au–Cd	Ni–Al
c' (GPa)	17–19	~ 7	8	5.8	3–5	3-3.8	14.6
Softening of c'	Yes	Yes	Yes	Yes	Yes	Yes	Yes
<i>c</i> ⁴⁴ (GPa)	35–39	95	90	86	~ 60	42	132
Softening of c_{44}	Yes	No	No	No	No	No	No
$A = c_{44}/c'$	2	13	11	15	20-12	14-11	9
Softening of A	Yes	No	No	No	No	No	No
Feature of martensite structure	BPS+ $\{001\}$ $\langle 110 \rangle$ shear	BPS	BPS	BPS	BPS	BPS	BPS

Note: 1. Here "softening" means a partial softening. 2. BPS: basal plane stacking.

what is required for the monoclinic distortion to make the B19' structure, as shown in Fig. 37(c). Therefore, the unique monoclinic structure B19' of Ti–Ni originates from the additional softening in c_{44} besides softening in c'. For many years, martensitic transformation has been regarded as solely due to the softening in basal shear/ shuffle mode; the discovery of the non-basal mode for B19' martensite strongly suggests that in some cases non-basal mode may also play an important role in martensitic transformations. Recent first-principle calculation by Bihlmayer et al. [210] and Ye et al. [83] were able to reproduce the low c_{44} of TiNi; this may provide some insight into the microscopic reason for the low c_{44} value for TiNi.

Extensive elastic constant measurements have been performed on various Ti–Ni and Ti–Ni-based alloys in order to verify the above view. Three kinds of Ti–Ni-based alloys were tested, corresponding to three transformation-paths, B2–B19', B2–B19–B19', and B2–R–B19'. The results are shown in Fig. 38 [170–172,72]. We can see a common feature among all Ti–Ni-based alloys: for all the tested alloys, c_{44} exhibits significant softening besides a softening in c'. The softening in c_{44} just corresponds to the fact that all these alloys ultimately transform into B19' martensite, as emphasized in the previous section. Therefore, the soft c_{44} is a signature for the ultimate transformation to B19', although other transformations (R, B19) may intervene before the formation of this final product. The softer the c_{44} the higher is the transformation temperature to B19'.

From Fig. 38, we can also see another interesting fact. The temperature dependence of anisotropy factor A (= c_{44}/c') of the B2 phase behaves differently depending on the transformation path. Prior to B2–B19' transformation, anisotropy decreases with approaching transformation temperature (Fig. 38(a)); prior to B2–B19 transformation, anisotropy shows an opposite tendency, i.e., increases with decreasing temperature (Fig. 5(c)). For B2–R transformation, anisotropy becomes unchanged near the transformation temperature (Fig. 38(b)). The different behavior of anisotropy may reflect the different coupling between basal shear/shuffle mode (TA₂) and the non-basal mode (TA₁) [169], and it can be regarded as the signature of different transformations. Elastic constant c_{11} , c_{12} do not show abnormal behavior in all the alloys as shown in Fig. 38(a)–(c).

5.5. Phonon softening and the effect of alloying on transformation product

Phonon dispersion relation provides the most important and comprehensive information concerning the lattice dynamics of the parent phase. Such information is indispensable for a microscopic understanding of the instability of the parent phase, and for the identification of the order parameters of the martensitic transformation [199]. Due to the difficulty of preparing single crystals of Ti–Ni-based alloys, so far there has been only a limited number of reports on the phonon dispersion relation of Ti–Ni binary alloys [175–177] and ternary alloys Ti–Ni–Fe [173,174] and Ti–Ni–Cu [178,211]; some of them are incomplete. Fig. 39 shows an interesting comparison of the TA₂ phonon branch and TA₁ branch between a Ti–46.7Ni–3.2Fe alloy [174] and a Ti–30Ni–20Cu [178,211]. The former alloy undergoes a B2–R–B19' transformation whereas the latter undergoes a B2–B19 transformation. TA₂ pho-



Fig. 38. Single crystal elastic constants of Ti–Ni binary and Ti–Ni–X (X = Fe, Cu) as a function of temperature in B2 phase prior to (a) B2-B19' transformation, (b) B2-R (-B19') transformation, and (c) B2-B19 (-B19') transformation. It is noted that solution-treated and directly quenched binary Ti–Ni undergoes a direct B2-B19' transformation, but after aging it undergoes a B2-R-B19' transformation [72].



Fig. 39. Comparison of TA_2 and TA_1 phonon branch between Ti–Ni–Fe and Ti–30Ni–20Cu alloys (after [178]; TA₂ branch data of (b) are from Moine et al. [174] with permission of Institute of Physics).

nons represent the $\langle 1 1 0 \rangle \{ 1 \overline{1} 0 \}$ "shuffle" and *c'* shear (with $\zeta \to 0$) of the basal plane of the B2 parent phase. TA₁ phonon is related to the "shuffle" and shear (with $\zeta \to 0$) of $\langle 001 \rangle \{ 110 \}$ mode; the shear mode corresponds to c_{44} shear mode.

The whole branch of TA₂ phonons for both Ti–46.7Ni–3.2Fe and Ti–30Ni–20Cu show softening with approaching transformation temperature. But the softening is not complete (not going to zero) at transformation temperature. This partial softening of TA₂ has been seen in many other β -phase alloys with BCC or B2 structure, suggesting an inherent instability of such structure against basal shear or shuffle $\langle 110 \rangle \{1\bar{1}0\}$. This instability was first pointed out by Zener [200], who considered that in the open BCC or B2 structure the stacking of atoms is in a metastable state and has a low resistance against $\langle 110 \rangle \{1\bar{1}0\}$ shear. It is equally true that BCC/B2 structure also has weak resistance against $\langle 110 \rangle \{1\bar{1}0\}$ shuffle, which can be viewed as the same $\langle 110 \rangle \{1\bar{1}0\}$ shear with a periodic reversal in shear direction.

There were no complete data on TA₁ branch of Ti-46.7Ni-3.2Fe and Ti-30Ni-20Cu. The beginning portion of the TA₁ branch shown in Fig. 39 is calculated from elastic constant c_{44} [178]. This indicates that there is some softening of this branch in

both alloys. As discussed in Section 5.4, this mode softening corresponds to the nonbasal shear $\langle 001 \rangle \{110\}$ required by the formation of B19' martensite, suggesting a potential instability toward B19', although the product of first stage transformation is not B19'. This implies that the phonon softening in the parent phase contains information not only about the incipient transformation, but also the potential subsequent transformation(s).

Having discussed the commonalities in phonon dispersion curves of both alloys, now we see their differences, in particular the underlying meaning of such differences. The most obvious difference is in TA₂ phonon branch. Ti–30Ni–20Cu shows a prominent dip around Brillouin Zone (BZ) boundary ($\zeta = 1/2$). By contrast, Ti–46.7Ni–3.2Fe shows two dips; one is at $\zeta = 1/2$ and another is at $\zeta = 1/3$, the latter has lower energy and stronger temperature dependence. From the structure analysis it is known that the softening of 1/3 TA₂ mode is responsible for the incipient R-phase transformation and the softening of 1/3 TA₂ soft mode in Ti–30Ni–20Cu well coincides with the absence of B2–R transformation in this alloy.

As discussed in Section 5.3, formation of B19' martensite requires the coupling of TA₁ mode (c_{44} mode) and TA₂ mode (basal shuffle/shear mode). The strength of the coupling is manifested by anisotropy factor c_{44}/c' . As shown in Fig. 38(c), Ti–30Ni–20Cu has higher and increasing anisotropy toward the transformation temperature, suggesting the coupling between TA₂ and TA₁ mode is weak. This results in a B2–B19 transformation without incorporating TA₁ mode. This uncondensated TA₁ mode is expected to keep on softening in B19 state and will eventually create a transformation. Similarly, the uncondensated TA₁ mode and 1/2 TA₂ mode of Ti–Ni–Fe alloy will keep on softening in R phase and eventually causes a R–B19' transformation.

From the above, we can clearly see that phonon dispersion curves, together with elastic constant information, contain information closely related to the possible martensite phases and transformation. This is indispensable in understanding the microscopic mechanism of martensitic transformation.

The TA₂ branch of a binary Ti–Ni alloy determined by Tietze et al. [175] suggests that the 1/3 TA₂ phonon reaches zero energy (i.e., complete softening) at transformation temperature. However, this seems to be inconsistent with the fact that R-phase transformation or B19' transformation is of first order [181], for which complete mode-softening cannot be expected. As noticed by many researchers, phonon peaks, if being of very low-energy, tend to be smeared by the nearby strong elastic peaks (central peaks); thus it is not easy to tell a zero-energy phonon from a phonon with very low energy.

The incomplete phonon softening suggests that the "spring constant" of the parent lattice is still positive even down to the transformation temperature. Therefore, lattice distortion or displacement waves, if any, should not be static. However, there have been quite a number of reports [173,174] that there exists a "central-mode", or elastic peak near $1/3(110)^*$ in a wide temperature range above the M_s or R_s (an example is shown in Fig. 40); this wave vector corresponds to the 1/3 soft



Fig. 40. Intensity of "central peak" (superlattice peak (5/3, 4/3, 0)) when approaching martensitic transformation temperature for TiNiFe system. The inset shows the shaded region on an expanded scale (after Moine et al. [174] reproduced with permission of Institute of Physics).

TA₂ phonon. X-ray diffraction [179,104,97,107] and electron diffraction [180– 183,98,154] have also found diffuse scattering near $1/3(110)^*$. The elastic peak clearly indicates the existence of static displacement waves in the parent phase. The central-mode has also been known to exist in other martensitic alloys, like Ni-Al [187,201], Cu-Zn-Al [212], Cu-Al-Ni [213], Au-Cu-Zn [214], Au-Cd [202]. Therefore, the existence of static displacement waves, or martensite embryos in classical term, seems to be quite a general feature of the parent phase prior to the transformation. But this feature is difficult to understand in view of the positive "spring constant" of the parent phase. So far, most explanations invoke point defects to stabilize the static embryos [165,192], which are sometimes considered as the "tweed" in real space. Kartha et al. [165] showed that the tweed can be considered as a "glassy phase" due to the coupling between point defects (they called composition disorder) and order parameter (strain/shuffle) of the martensitic transformation, in analogy to the spin-glass transition of some magnetic materials. This coupling leads to a "second order transition" from an undistorted parent phase to the "tweed" (with static lattice distortion). However, so far there has been no evidence for the existence of new anomalies above martensitic transformation temperature, as expected for such "glass transition".

In view of the importance of point defects in understanding the static embryos, it becomes imperative to quantitatively evaluate the type and concentration of point defects in the B2 parent phase as a function of composition and temperature. Unlike pure metals in which vacancy is the only point defect, B2 intermetallic compound has four possible kinds of point defect, two kinds of vacancy on two sublattices and two kinds of anti-site defect (ASD). It is much more complicated to consider the point defect formation in these compounds than in pure metals. Ren and Otsuka [215,216] have recently proposed a unified theory for point defect formation in B2 compounds, which is able to quantitatively account for all possible defect configurations in B2 compounds and in good agreement with available experimental data. The quantitative evaluation of point defects in B2 compounds may provide a basis for a better understanding to the correlation between point defects and martensitic transformation.

5.6. Incommensurate $1/3\langle 110\rangle^*$ diffuse scattering prior to B2–R transformation

In 1970s and early 1980s, it was widely believed that B2–R transformation is a precursor of the subsequent transformation to B19' martensite. However, no close structure relation between R and B19' was found. Now it is accepted that R-phase transformation is nothing but a different martensitic transformation preceding the B19' martensitic transformation, and sometimes B19' martensite forms directly from B2 phase without forming R-phase (e.g., in quenched Ti–Ni alloys). On the other hand, there are many examples of multi-stage martensitic transformation in β -phase alloys [217].

The precursory $1/3\langle 110\rangle^*$ diffuse scattering prior to R-phase transformation has been a controversial issue for a long time. Early study on Ti–Ni–Fe alloy by Salamon–Wayman group [104,180,98] suggested a complicated sequence of changes as shown below:

	2nd order		1st order	
normal parent phase	\Rightarrow	incommensurate $phase(CDW)$	\Rightarrow	commensurate phase (R-phase)
(no 1/3 diffuse spots)		(incommensurate 1/3 diffuse spots)		(commensurate 1/3 spots)
$T>T_{\rm I}$		$T_{ m r} < T < T_{ m I}$		$T < T_{\rm r}$

According to this proposition, there exists a normal parent phase (without the $1/3\langle 110 \rangle^*$ diffuse spots) above a critical temperature $T_{\rm I}$, which corresponds to the onset of a sharp increase of electrical resistivity; between $T_{\rm I}$ and another critical temperature $T_{\rm r}$, the latter being the onset of the R-phase (the temperature interval between $T_{\rm I}$ and $T_{\rm r}$ is about 12 K), there exists an incommensurate phase, which produces diffuse scattering at not exactly $1/3\langle 110 \rangle^*$ positions. This incommensurate phase was thought to be due to "charge density wave (CDW)". The change from normal parent phase to incommensurate phase was assumed to be a "second order transition". The "incommensurate phase" finally changes into the commensurate R-phase by a first order transformation.

However, over the past years there has been some strong evidence against many aspects of this scenario. Firstly, CDW can be denied in view of recent evidence that 1/3 diffuse scattering turned out to represent a transverse displacement wave [183], not the longitudinal wave required by the CDW. Secondly, no evidence was found for the proposed "second order transition" from normal parent phase to the incommensurate phase. Tamiya et al. [181] studied R-phase transformation with in situ TEM technique. They found that there is only a first order transformation from

the parent phase to the commensurate R-phase, without any other transition in-between, and the presence of temperature hysteresis in the resistivity curve clearly manifests the first order nature of the transformation. Since TEM images and diffraction are extremely sensitive to structure change (transformation), this result should be considered as a strong evidence for the non-existence of the second order "normal-to-incommensurate" transition above the R-phase transformation temperature.

Murakami et al. [183] used energy-filter in electron diffraction to eliminate the inelastic scattering, and this made the 1/3 diffuse scattering clearly visible (Fig. 41). They showed that the incommensurability increases with increasing temperature. They further showed that the incommensurate diffuse reflections represent transverse static waves. Cai et al. [182] found that there is a gradual decrease in the intensity of the incommensurate $1/3\langle 110\rangle^*$ peak with increasing temperature; this peak exists over a temperature range as wide as over 60 K, not just a few Kelvin, and no sudden disappearance of the 1/3 peak was found, as expected by a "transition". Therefore, it is hard to say that there exists a well-defined starting temperature ("transition temperature") for the 1/3 diffuse scattering.

There is also another indirect but important evidence for the non-existence of the proposed "normal-to-incommensurate transition". If this displacive transition exists, we can expect that it will create some "new" anomaly in elastic constants or phonon mode prior to the proposed transition temperature ($R_s + 12$ K), like any other displacive transformation. However, as shown in Fig. 38(b), no "new anomaly" in elastic constants prior to B2–R transformation exists, except for the monotonous softening in c' and c_{44} , which is related to R-phase and B19′ transformation [172].



Fig. 41. The change of $1/3(110)^*$ spot in Ti–Ni–2Fe alloy before and after B2–R transformation. It is shown that the filtered diffraction pattern gives better S/N ratio in the diffraction pattern. Weak incommensurate diffuse spots are found above the R_s temperature. After the transformation these spots become sharp and commensurate. Resistance change during the transformation is also shown in the figure (after Murakami and Shindo [183] reproduced with permission of Taylor and Francis Ltd.).

Therefore, there is no doubt that the normal-to-incommensurate transition is non-existent, and the parent phase is incommensurate up to very high temperature; but the amplitude of the static distortion corresponding to $1/3\langle 110\rangle^*$ diffuse peak decreases with increasing temperature until ultimately disappears. Based on this picture, the R-phase transformation path becomes very simple and can be represented as follows:

	1st order	
parent phase	\Rightarrow	R -phase
containing incommensurate		commensurate
static displacement wave		
$(T > R_{\rm s})$		$(T < R_{\rm s})$

in which both the amplitude and incommensurability of the incommensurate displacement waves in the parent phase above R_s is a continuous function of temperature (no abrupt transition). At high temperature the incommensurability is large but the amplitude is small, leading to a very weak but highly incommensurate $1/3\langle 110\rangle^*$ diffuse scattering; at low temperature (near R_s) the incommensurability is small but wave amplitude is large, leading to a strong but nearly commensurate $1/3\langle 110\rangle^*$ diffuse scattering. This is similar to the gradual disappearance of short-range order above the formation temperature T_c of a long-range ordered phase. At the R_s temperature, the incommensurate static displacement waves, the static embryos, transform into the commensurate R-phase.

A direct observation of the evolution of the precursory state into R-phase for a Ti–48Ni–2Fe alloy was made by Murakami et al. [183–185] by using in situ TEM technique, as shown in Fig. 42. They found that prior to the first order R-phase transformation the parent phase shows many nano-sized tiny "domains" (Fig. 42(b)). These domains increase in density with lowering temperature and ultimately form R-phase out of them. These "domains" in parent phase were interpreted as one of the three $\langle 110 \rangle \{1\bar{1}0\}$ transverse shear waves making up the R-phase. It is noted that *the "domains" are granular*, not "tweed-like" as observed in other β-phase alloys. Such a feature was ascribed to the low elastic anisotropy of Ti–Ni-based alloys by them [185].

After the R-phase transformation, a peculiar contrast in electron micrograph as shown in Fig. 42(a) is often observed [98]. This contrast was interpreted as "discommensuration" in the early study of R-phase transformation in terms of charge density waves by Salamon et al. [104]. However, this interpretation was soon denied by Hwang et al. [180,98], because the contrast did not disappear even after locking into commensurate state (i.e. after complete transformation to R-phase) by cooling. So, they called this contrast as "antiphase-like (APB-like) contrast". However, the meaning of "antiphase" was not understood at all thereafter. Recently, Murakami et al. [183–185] gave a new reasonable interpretation for this contrast, as explained in the schematic figure in the lower part of Fig. 42(a). That is, the R-phase has a 8-layered structure, as shown in Fig. 15. Thus if two neighboring domains have different origin, actually an antiphase boundary is created between the two domains, as indicated in the figure. Thus the peculiar APB-like contrast in the R-phase was clarified.



Fig. 42. Evolution of nano-sized premartensitic "domains" in the parent phase (b) into the antiphase-like domains (a) after the R-phase transformation in a Ti-48Ni-2Fe alloy. The schematic below each micrograph is the corresponding explanation for the effect (after Murakami and Shindo [184]).

5.7. Premartensitic attenuation and heterophase fluctuation

Premartensitic attenuation in the parent phase has not received much attention until very recently [188–190,219], mostly because such effect is not expected and hard to explain when considering the parent phase is a homogeneous phase that lacks an apparent mechanism for damping or attenuation. However, if considering there is heterophase fluctuation in the parent phase, it is natural to expect that such fluctuation should interact with alternating stress and cause energy dissipation, as explained in Section 5.2.

Fig. 43(a) shows the premartensitic mechanical attenuation prior to B2–B19 transformation in a single crystal of Ti–30Ni–20Cu [190]. Temperature dependence of the elastic peak or central peak of the elastic phonon scattering (an indicator of static strain modulation) and the 1/2 TA₂ phonon energy of the same sample are also shown. It is clear that there is clear premartensitic attenuation and it strongly correlates with the increase of elastic peak and phonon softening.

The temperature dependence of the Landau potential shown in Section 5.1. gives important information for explaining Fig. 43. At high temperatures well above M_s $(T \gg M_s)$, the harmonic term is dominant because the coefficient $a(T - T^*)$ is large at high temperatures. The parent phase appears nearly harmonic, i.e., it behaves like a linear elastic spring. Then there should be no energy loss during vibration and hence little attenuation exists at such temperatures.


Fig. 43. Different aspects of premartensitic transformation phenomena as a function of temperature: (a) Premartensitic attenuation, (b) Neutron elastic scattering intensity at Brillouin zone boundary (1.5, 0.5, 0) (where martensite peak comes after the transformation), and (c) TA₂ [110][1 $\overline{1}$ 0] phonon energy at Brillouin zone boundary [190].

With lowering of temperature towards M_s the harmonic term decreases as a result of decreasing the harmonic coefficient $a(T - T^*)$. The first consequence of such a decrease is the softening of related phonon, as shown in Fig. 43(c). The second consequence, which is related to the first one, is the increase of anharmonicity and the appearance of metastable energy wells above M_s . This results in two important effects. The first one is that once a certain portion of the parent phase is somehow distorted into the energy well (possibly by point defects or by dislocations etc.), this portion will remain distorted and this is actually a kind of static martensite embryo. Such static embryos can give rise to elastic scattering very similar to that of martensite except for a much lower intensity. This explains the elastic scattering in Fig. 43(b). These static low symmetry embryos together with some dynamic ones (heterophase fluctuations) can switch among degenerate energy wells and parent state following external stress. Such a process involves climbing up energy barriers and thus causes energy dissipation or damping. This explains the existence of attenuation or damping in the parent phase. Obviously the above processes are enhanced with lowering temperature due to the lowering of energy barrier between undistorted state and distorted state. This explains why attenuation and elastic peak increase with approaching M_s Therefore, the heterophase fluctuation, as consequence of anharmonic Landau potential is central for understanding various premartensitic phenomena.

5.8. Microscopic understanding of the lattice instability of the parent phase

A number of first-principles calculations or electronic calculations [203, 210,83,218,220] are devoted to explain the parent phase instability in terms of certain electronic effect. The 1/3 phonon dip and its temperature dependence for Ti-Ni was reproduced by Zhao and Harmon [203] by considering the electron-phonon coupling of nested electronic states on the Fermi surface. This is related to the origin of the R-phase. Nevertheless, the calculated phonon anomaly is confined to near $1/3(110)^*$ in the TA₂ phonon branch; phonons of other wave vectors and in other branches are shown to behave mostly normal and have almost no temperature dependence. However, as can be seen from the phonon dispersion curve shown in Fig. 39, there are two phonon anomalies in TA_2 branch, corresponding, respectively, to $1/3(110)^*$ dip and $1/2(110)^*$ dip, the entire TA₂ branch is lowered with decreasing temperature. The TA1 branch is also likely to become lowered with temperature decrease because c_{44} (the TA₁ zone-center mode) shows an appreciable softening (Fig. 39). These anomalies are related to three possible martensites, R (1/3 TA₂ mode), B19 (1/2 TA₂ mode) and B19' (1/2 TA₂ + TA₁ zone-center mode), as discussed previously. It seems that these important features have not found an explanation by first principle calculations to date, and it may be an interesting problem challenging the power of computational approach.

On the other hand, first-principle total energy calculations by Ye et al. [83], reproduced an important fact: B19' is more stable than B19 and B2 for TiNi, as shown in Fig. 44. But they did not calculate the stability of another important competing phase, the R-phase. It would be interesting to know the relative stability of three competing martensites, R-phase, B19, and B19' as a function of composition and alloying addition. First principle calculation on TiNi by Fukuda et al. [220] showed that the relative stability of the three competing martensites (R, B19, and B19') with respect to the parent phase seems to be related to the total electronic density of state (DOS) at the Fermi energy. According to this criterion, they concluded that the sta-



Fig. 44. Energy changes when deforming TiNi from the B2 structure to B19' and from the B19 structure to B19' (after Ye et al. [83] reproduced with permission of American Physical Society).

bility sequence for TiNi is B19, B2, R, and B19'; this result is different from Ye et al.'s result [83] that B19 is more stable than B2, as shown in Fig. 44. Recently, Santi et al. [84] made a first principles calculation for B19' martensite structure of TiNi and found that the structure determined by Kudoh et al. [81] gives the lowest total energy and they concluded that the structure by Kudoh et al. is the correct martensite structure.

Despite the progress of first-principles calculations, some important experimental facts are yet to be tackled by this approach. One familiar but important example is the effect of composition, alloying and point defects, which have long been known to strongly modify both transformation temperature and transformation path. For example, 1 at.% increase in Ni concentration can lower the M_s temperature (B2– B19') of Ti-Ni alloy by more than 100 K, and 2 at.% addition of Fe into Ti-Ni can change the transformation path from B2-B19' to B2-R-B19'. It is not easy to understand such a high sensitivity of the transformation to composition/alloving from first-principle calculations, although a preliminary explanation based on the effect of point defects/composition on lattice dynamics has been made [221]. Another problem with first principle calculations is its difficulty in dealing with temperature effect. Most calculations are made by assuming that temperature is 0 K, i.e., only internal energy is considered. However, the stability sequence of competing phases may be altered at finite temperature due to the entropy contribution. Therefore, the stability sequence calculated for 0 K does not necessarily represent that at finite temperature. Besides, first principle calculations are yet to be able to reproduce all the observed phonon anomalies observed in Ti-Ni alloys (not only 1/3 TA2 mode but also 1/2 TA₁ mode and TA₁ zone-center mode). Effort toward this direction may bridge electronic structure and phonon anomalies, and may provide a microscopic understanding to the mechanism of the martensitic transformation. We hope more effort will be made in these directions.

Although a comprehensive, microscopic understanding to all martensitic transformations is still lacking, semi-microscopic Landau theory based on lattice dynamics and symmetry [163,164,199,222–225] may provide a fairly general understanding to various martensitic transformations in diverse alloy systems. Krumhansl [223] showed how the incomplete mode-softening, a general feature of first order martenstic transformations, can be explained by considering the coupling between a phonon mode and strain. Barsch [199] provided a rigorous Landau theory for B2–R, B2– B19, and B19–B19' transformations; the 12 structural parameters of the complicated R phase can be fairly accounted for by just two fitting parameters. Ren and Otsuka [169] proposed a Landau model to account for the B2–B19' transformation by considering the coupling between TA₁ zone-center mode (i.e., soft c_{44} mode, which creates the monoclinic shear of the B19') and TA₂ mode.

5.9. Unsolved issues

As described above, there has been significant progress in recent years in understanding the complicated, multi-path martensitic transformations in Ti–Ni and Ti– Ni-based alloys. Despite the progress, several central and general problems (some are not confined to Ti–Ni) still remain to be solved or clarified. They may provide both challenges and opportunities in the 21th century.

- 1. Is there a common microscopic origin for all martensitic transformations? Compared with diffusional or replacive transformations where the transformation can be considered as being driven by certain chemical factors, martensitic transformation involves just a spontaneous lattice distortion and it is not straightforward what causes such a sudden distortion. Zener's explanation for the instability of BCC/B2 structure relative to the more close-packed FCC/HCP based structures is intuitively plausible for the martensitic transformation of most BCC/B2 structures. However, this scenario is obviously inapplicable to martensitic transformation in close-packed structures, such as In–Tl (FCC–FCT) and A15 compounds. Also martensitic transformation of magnetic alloys seem to be strongly affected by magnetism. Therefore, it seems hard to find a common microscopic origin for all different martensitic transformations.
- 2. Relationship among electronic structure, phonon anomalies, and the competing martensite structures.

So far researches on martensitic transformation have been performed mainly independently on three different levels, mesoscopic/crystallographic level, phonon/lattice-dynamics level and electronic level. It would be very informative to combine these three different approaches and to give an overall picture about the transformation mechanism.

- 3. Origin of the static displacement waves (tweed) above transformation temperature, and its possible link to point defects. These static precursors have been ascribed to point defects or chemical disorder, but there have been no direct evidence.
- 4. Is heterophase fluctuation possible despite the large barrier? The explanation of most of precursor effects is based on the existence of heterophase fluctuation in the parent phase. However, such fluctuation requires that the system climb over large energy barrier. It has been questioned whether such fluctuation is really possible [226].
- 5. Abnormal resistivity increase prior to B2–B19' transformation in quenched Ti–Ni alloys. Is it a precursor or not? Numerous experiments have shown that prior to B2–B19' transformation in quenched Ti–Ni binary alloys resistivity shows anomalous increase with lowering temperature, contrasting the behavior of a metal. There have been many studies on this behavior [227] but without a clear understanding. It is noted that such a behavior is absent in any other martensitic systems, and it is unclear whether it is linked to the incipient B19' martensite.
- 6. The nature of the incommensurability of the static displacement waves. The physical or microscopic picture of an incommensurate structure is unclear. There exists a possibility that the incommensurate diffuse spots may be diffraction effect of a mixture of normal parent phase and commensurate martensite embryos. This situation is similar to the "incommensurate" superlattice spots of or-

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dered Au–Cu alloys, which is actually due to a mixing of several ordered phases of different commensurate stacking period.

6. Shape memory and superelasticity effects

6.1. What are the shape memory and superelasticity effects?

The shape memory effect in Ti–Ni alloys was first found by Buehler et al. in 1963, as was described in earlier section, and many investigations have been done including those in other shape memory alloys. We first describe here what shape memory and superelasticity effects are mainly from experimental point of view in this preliminary section, before we discuss them in detail in later sections. Fig. 45 shows a series of stress–strain (S–S) curves of a Ti–50.6Ni alloy as a function of temperature (from low temperature to higher temperature), which was solution-treated at 1273 K for 3.6 ks followed by quenching into water. Thus the specimen is in a homogeneous so-



Fig. 45. Stress-strain curves as a function of temperature of Ti-50.6Ni alloy, which was solution-treated at 1273 K for 1 h. The critical stress for inducing martensites and that for reverse transformation are indicated by an arrow (\rightarrow) and by a double arrow (\rightarrow) in (j) respectively [228].

lid solution state in the parent phase. If we plot the critical stress in each S–S curve as a function of temperature, we obtain Fig. 46, where open circles represent the critical stresses upon loading, and closed ones those upon unloading. We note that M_s determined by electrical resistivity measurement roughly corresponds to the minimum of the critical stress curve upon loading. Thus roughly speaking, the mechanical behavior at temperatures above the minimum point corresponds to the stress-induced martensitic transformation, while that below the minimum point to the deformation of martensite, although the stress-induced transformation is also partly included in the S-S curves near the minimum in this temperature regime, as we will discuss it in detail later. It is clear from the figure that at temperatures a little above A_f (=221 K) the S-S curves are pseudoelastic (i.e. the apparent plastic strain recovers during unloading, and thus the curve shows a closed loop), while that at temperatures below $A_{\rm f}$ the strain remains upon unloading. However, this residual strain recovers by the reverse transformation from martensite to the parent phase upon heating to temperatures above $A_{\rm f}$. The former pseudoelastic behavior is called superelasticity, while the latter behavior, i.e. the phenomena that the apparent plastic strain recovers by the reverse transformation upon heating is called the shape memory effect. Superelasticity occurs by the stress-induced transformation upon loading, and the subsequent reverse transformation upon unloading, as will be discussed in detail in Section 6.2. This essential feature of superelasticity is most clearly shown for $\beta_1 - \beta'_1$ transformation in a Cu-Al-Ni single crystal [232]. When we discuss shape memory effect, there are two cases depending upon the test temperature. When the temperature is below or equal to $M_{\rm f}$ the specimen is in complete martensitic state. Thus the deformation in this case is the deformation of martensite. On the other hand, when the temperature is above $M_{\rm f}$ especially above $M_{\rm s}$ a part or the whole of the deformation occurs by the stress-induced martensitic transformation, and the mechanism is similar to the case



Fig. 46. Critical stress as a function of temperature for inducing martensites $(T > M_s)$ and for yielding $(T < M_s)$ (open circles) and for reverse transformation (solid circles), which were plotted from the data in Fig. 45 [228].

of superelasticity, the only difference being whether the formed martensite is stable or not in the absence of external stress.

It is clear from the above that both superelasticity and shape memory effects occur in the same specimen, and which occurs depends only upon the test temperature. This situation is illustrated in Fig. 47, in which two solid lines and a broken line are drawn. The line with a positive slope represents the critical stress to induce martensite, which is essentially the same as the one upon loading with a positive slope in Fig. 46. The lines with a negative slope represent the critical stress for slip. If the critical stress is very low as in the case (B), we cannot expect good or complete superelasticity, because slip, which is an irreversible process, is easily introduced below the critical stress for stress-induced transformation. Thus we assume that the critical stress for slip is high enough here as is the case for (A), and the case for (B) will be discussed in the later sections. Then we see that superelasticity appears at temperatures above $A_{\rm f}$ in the shaded region, because if we apply a stress at temperatures above $A_{\rm f}$ the stress-induced transformation occurs at a stress above the critical stress for inducing martensite. However, the reverse transformation must occur upon unloading, since the formed martensite is completely unstable at temperatures above $A_{\rm f}$ in the absence of stress. Thus we obtain superelasticity upon unloading as far as the reverse transformation is crystallographically reversible, which will be discussed in later section. Similarly, at temperatures below A_s the deformed martensites are stable, and thus the martensites stay deformed (or bent) after the release of stress, and the strain can recover only by reverse transformation. In the temperature regime between $A_{\rm s}$ and $A_{\rm f}$ the martensites are partly unstable, and thus both superelasticity and shape memory effects coexist.

In the following two sections we discuss the mechanisms of superelasticity and shape memory effect separately, since the mechanisms are different, although the driving force is the same (i.e. the free energy difference between the parent phase and martensite). The mechanisms of superelasticity and shape memory effect were studied most actively for β -phase alloys other than Ti–Ni alloys, because single crys-



Fig. 47. Schematic representation for the appearance of shape memory effect and superelasticity, which is termed as "Transformation Pseudoelasticity" here, in temperature–stress space [229].

tals are not easily made and martensite plates are very small in Ti–Ni-based alloys, while in other β -phase alloys single crystals are easily available and martensite plates grow quite large, and different variants of martensite appear with different color under polarized light for β -phase alloys with large optical anisotropy. Thus generally speaking, it is easier to draw important conclusions in β -phase alloys. Thus we may refer frequently to the results obtained for β -phase alloys in the following two sections, because both superelasticity and shape memory effects are common phenomena, which can be understood from a general point of view. Those characteristic of Ti–Ni-based alloys will be discussed in the subsequent Section 6.4.

6.2. Mechanism of superelasticity effect

We first discuss the mechanism of superelasticity, because it is simpler than that of shape memory effect. Because the martensitic transformation is a shear-like mechanism, stress assists the martensitic transformation. Thus, it is possible to stress-induce martensite even at temperature above M_s which is the highest temperature for the martensite to appear upon cooling. The stress-induced martensitic transformation can be analyzed by the Patel–Cohen theory [230], in which the work done by an external stress on the system is treated to be equal to the change of the free energy of the system, and/or by the thermodynamic Clausius–Clapeyron relationship [3,231], but the latter may be more easy to use, because it is summarized in the following simple mathematical form:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}T} = -\frac{\Delta S}{\varepsilon} = -\frac{\Delta H^*}{\varepsilon T},\tag{23}$$

where σ is a uniaxial applied stress, ε a transformation strain, ΔS the entropy of transformation per unit volume, and ΔH^* the enthalpy of transformation per unit volume. The above Clausius–Clapeyron equation can be easily derived by equating the generalized free energy of parent phase and that of martensite [231]. In the above expression readers should note the presence of minus sign on the right-hand side of that expressions, because the minus sign is some times dropped off in some references, e.g. [3]. If we consider the forward transformation from parent to martensite, ΔS and ΔH^* are negative. Thus the slope of $d\sigma/dT$ must be positive for stress-induced transformation (similarly we can consider the opposite way for the reverse transformation, but we result in the same conclusion). Thus the positive slope observed in Figs. 46 for $T > M_s$ indicates that the behavior of the critical stress in that temperature region is due to the stress-induced transformation, because temperature dependence of the critical stress for slip is just opposite, as shown in Fig. 47.

The transformation strain associated with the stress-induced transformation, which depends upon the orientation of a crystal, may be calculated in two ways. Otsuka et al. [232] gave the following expression by using the shape strain obtained by the phenomenological crystallographic theory explained in Section 4.

$$\varepsilon_{\rm c} = \sqrt{\left(m_1^{\rm p} \sin \chi\right)^2 + 2m_1^{\rm p} \sin \chi \cos \lambda + 1 - 1 + m_1^{\rm n} \sin^2 \chi},\tag{24}$$

where λ is the angle between the tensile axis and the shear direction d_1^p , χ the angle between the tensile axis and the habit plane (for the meaning of other symbols, see Fig. 17). This equation is similar to the Schmid-Boas relation [233] describing the relation between shear strain and elongation for slip, but the normal component of the shape strain is also taken into account in the above equation. In thermoelastic alloys, usually $m_1^n (= \Delta V/V) \ll m_1^p$ and $(m_1^p \sin \chi)^2 \ll 1$. Thus,

$$\varepsilon_{\rm c} \sim m_1^{\rm p} \sin \chi \cos \lambda,$$
 (25)

This means that ε_c is nearly proportional to the Schmid factor for the shape strain.

On the other hand, Saburi et al. [141] calculated the transformation strain from the lattice deformation matrix B as follows. According to the lattice deformation, any vector [uvw] is changed into [UVW] upon martensitic transformation such that

$$\begin{pmatrix} U\\V\\W \end{pmatrix} = \boldsymbol{B} \begin{pmatrix} u\\v\\w \end{pmatrix},$$
(26)

where B is the lattice deformation matrix with respect to the parent lattice. Thus the transformation strain is given by the following equation:

$$\varepsilon_{\rm c} = \sqrt{\frac{U^2 + V^2 + W^2}{u^2 + v^2 + w^2}} - 1.$$
(27)

In the former calculation, the lattice invariant strain is present in the martensite, while in the latter, it is not. Thus, the difference between the two treatments lies in whether the lattice invariant strains are present or not at the end of the plateau region in the S–S curve. If the lattice invariant strain does not move under the stress, the first equation should hold, while if the stress-induced martensite becomes a single crystal by detwinning for example, the second equation should hold. Thus, the former equation gives the minimum transformation strain, while the latter gives the maximum. Thus, which equation is better depends upon the alloy system and stress level.

Among early investigations [234,235] on the mechanical properties of Ti–Ni alloys, to the authors' knowledge Wasilewski [236] and Honma [237] were the first to observe superelasticity in Ti–Ni alloys, although both experiments and descriptions were very brief. It was stated in the previous section that the superelasticity is due to the stress-induced martensitic transformation upon loading, and the subsequent reverse transformation upon unloading. In fact there are direct evidences to show that in other β -phase single crystals; e.g. it is clearly shown for a Cu–Al–Ni single crystal that the particular variant of martensite are stress-induced with the same habit plane, which is most favorable under stress, and the parent single crystal changes into a single crystal of that martensite variant at the end of the stress plateau of the first stage (as will be shown later for Ti–Ni alloy in Fig. 48), and upon unloading the reverse transformation occurs with the same habit plane, thus the strain recovering completely upon unloading [232]. It was also confirmed that the observed recoverable strain was consistent with that predicted by Eq. (24) in this case [232]. On the contrary, such direct observation has not been made for Ti–Ni alloys, and the evidences are rather indirect in this case. The positive slope of the critical stress as a function of temperature in Fig. 46, and the closed S-S curves at temperatures above $A_{\rm f}$ support the above mechanism. The choice of the h.p.v. under stress observed with respect to Fig. 24 also supports the mechanism (strictly speaking, the Schmid factors were the largest or the second largest in this case [131].). As the other checkpoint, we may compare the amount of the recoverable strain with experiment. However, it is almost impossible to observe superelasticity in single crystals of Ti-Ni alloys ¹¹ in solution-treated condition, because the critical stress for slip is so low in the single crystals under such condition. i.e. The critical stress for slip for Ti-Ni single crystals corresponds to the case (B) in Fig. 47. Thus, when a specimen is subjected to an applied stress at a temperature above A_f slip occurs before the onset of the stress-induced transformation, and thus the superelasticity does not appear. In fact this is one of the characteristics of Ti–Ni alloys compared to other β -phase shape memory alloys. So, superelasticity usually observed in single crystals is for aged Ni-rich Ti-Ni alloys (e.g. see Ref. [239]), for which the critical stress for slip is strengthened by precipitation hardening (this point will be discussed in Section 9). However, the aged samples do not give accurate recovery strain, because untransformed regions are left due to precipitates. Thus the critical comparison of the recovery strain is more suited to be done with respect to the shape memory effect, because the maximum recovery strain for superelasticity is the same as that for the shape memory effect, as will be discussed in the following section.

We will add one more point with respect to Fig. 45. In this figure, the first stage in the S–S curves of (h)–(m) are very flat and associated with serrations. The flatness seems to indicate as if the S–S curves are from a single crystal, but of course they are the data of polycrystals, whose grain size is as small as several tens of μ m. It is clearly shown by optical microscopy that the deformation proceeds in quite an inhomogeneous manner such that it starts from one end of the specimen and proceeds to the other end with increasing strain [240]. This was the first observation to show that the stress-induced transformation in fine grained Ti–Ni polycrystals proceeds as Lüders deformation. This means that the propagation of the stress-induced transformation is much easier in the stressed neighboring transformed region compared to nucleating martensite in untransformed region in such small grains, the boundaries of which constrain the martensitic transformation.

We will discuss more experimental data in Section 6.4, especially with respect to superelasticity associated with R-phase etc.

6.3. Mechanism of the shape memory effect

Since the shape memory effect is a universal effect as well as superelasticity, and most of the important critical tests/observations were carried out for other β -phase

¹¹ To the authors' knowledge, complete superelasticity in a Ti–Ni single crystal in solution-treated condition was observed only once for the most favorable orientation for the Schmid factor under compression for Ti–50.8Ni alloy [238].

shape memory alloys, we discuss it here in a rather broad viewpoint. As was pointed out in Section 6.1, the deformation process in the shape memory effect may be either the deformation of martensite or the stress-induced transformation, and the mechanisms are different in the two cases [241]. Since the mechanism in the latter is essentially the same as that of superelasticity, we discuss here only for the former case. There is a consensus that both shape memory and superelasticity effects are characteristic of thermoelastic alloys [242–247]. ¹² It is also observed in the early stage investigation that the deformation of martensite must be twinning in order for the shape memory effect to be realized, because slip is an irreversible process [241].

We now describe the general mechanism of the shape memory effect mostly after Saburi et al. [141], who carried out detailed analysis for various types of transformations in β-phase alloys such as Cu–Zn–Ga, Cu–Zn–Al, Ag–Cd etc., including observations of deformation process in martensites by using single crystals. We consider here a solution-treated single crystal fully transformed just for simplicity, although the same discussion may apply equally to polycrystals. Now, there is no change in shape upon the martensitic transformation upon cooling, because the transformation occurs in a self-accommodating manner. If such self-accommodated martensite is deformed, the deformation proceeds by the twin boundary motion, which is equivalent to the conversion of one martensite variant to the other. More strictly speaking, there are two types of boundaries; twin boundaries, which separate c.vs. in each martensite plate, and the boundaries between h.p.v.'s (i.e. junction plane which we discussed in the section of self-accommodation). Saburi et al. showed that the most favorable correspondence variant, which gives the largest strain under the given stress condition, grows at the expense of the others, and that the specimen finally becomes a single crystal of the most favorable martensite variant under the stress. Upon heating to a temperature above $A_{\rm f}$ the martensite transforms back to the parent phase in the original orientation, because of the lattice correspondence. Because the martensite becomes a single variant of the most favorable orientation at the end of the deformation, the maximum recoverable strain is the same as that obtained for superelasticity in Eq. (27), and this was experimentally confirmed too [141].

We now discuss the basic requirements for shape memory effect as well as superelasticity. Otsuka and Shimizu [241,242] once proposed three requirements for the effects; thermoelastic nature of the transformation, ordering, and twinning as a deformation mode, although they noticed later a disordered case for In–Tl, as will be discussed later [249]. The thermoelastic transformation [250,251] is character-

¹² There may be some argument that the shape memory effect occurs even in non-thermoelastic alloys, such as the so-called Fe-based shape memory alloys including Fe–Mn–Si [248]. However, in these cases the shape memory effect appears only when specimens are deformed by the stress-induced transformation, and no shape memory effect appears when they are deformed in the fully martensitic state [246]. Here we recognize the shape memory effect as a universal effect, such that both shape memory (including in fully martensitic state) and superelasticity effects can occur concurrently in the same specimen depending upon the test temperature. If we recognize the shape memory effect in this way, it appears only in thermoelastic alloys.

ized by the mobile boundary between parent and martensite, and a small temperature hysteresis, which indicates a small driving force for the forward/reverse transformation, and thus indicating negligible possibility of introducing irreversible process such as slip. The transformation usually is also associated with the crystallographic reversibility, leaving any macroscopic debris on the surface after the reverse transformation. On the contrary, it is known for the non-thermoelastic transformation such as Fe-Ni alloys that the martensites grow very rapidly (i.e. about 1/3 of the sound velocity), and stop growing after reaching a specific size, possibly because of the introduction of irreversible plastic deformation. Since mobile boundary upon changing temperature/stress is necessary for superelasticity and the shape memory effect, which occurs at a temperature above A_s , thermoelastic nature is a required condition for the shape memory effect/superelasticity. Twinning as a deformation mode is also a necessary condition, because slip is an irreversible process. Besides, the characteristic of the twinning in martensite, which is equivalent to the change of correspondence variant, promotes the strain attained by twinning/detwinning of martensite to recover upon the reverse transformation. The condition, that twinning/detwinning is equivalent to the change of correspondence variant, is usually met, because twins introduced as a lattice invariant shear have this characteristic, and there are such twinning modes with small twinning shears, as shown in Table 4. However, if such a condition is not satisfied, the strain attained by such twinning/detwinning cannot be restored. e.g. $\{20\overline{1}\}_m$ twinning in the table is not a lattice invariant shear, and thus it is not recoverable. Then the reversibility of the transformation is left as the last key point. As discussed just in the above, the strain recovers by the lattice correspondence upon reverse transformation, as far as the lattice correspondence is unique. Otsuka and Shimizu [249] proposed that ordering and/or unique lattice correspondence restricts the reverse path from martensite to the parent phase uniquely, and guarantees the reversibility of the thermoelastic transformation, where the disordered case of In-Tl was explained on the basis of the unique lattice correspondence between FCC and FCT. Although this proposal was replaced by a more general theory described below, we point out another importance of ordering. Usually ordering, which depends upon the structure though, requires the dislocations to be superdislocations, which have larger Burgers vectors. Thus if the crystal is ordered, the critical stress for slip increases compared to the disordered case, and thus we can expect better shape memory/superelasticty characteristics.

More recently Bhattacharya et al. [252] proposed a more general mathematical theory, according to which the martensitic transformation is divided into two groups: weak transformation and reconstructive transformation. Since they use a different terminology, it may cause some confusion. Especially the reconstructive transformation is confusing, because it usually represents the diffusional transformation in physical metallurgy, but here it presents a non-weak transformation, which is explained soon below in the framework of the diffusionless transformation. Their theory is based on the change in crystal symmetry during the transformation, and they call the transformation "weak", when parent and martensite are related by group and the sub-group relation. Then they state that the necessary

condition for a martensitic transformation to be reversible (i.e. without introducing plastic strains such as dislocations during transformation) is that the transformation is weak. In another words, unless the parent phase and martensite are related by group and the sub-group relation, it cannot exhibit shape memory effect. i.e. According to this theory, neither FCC–BCC nor FCC–HCP transformations cannot exhibit shape memory effects since they are not in the group and the sub-group relation. This is in accord with the previous discussions. It is also to be noted that this is a *necessary condition*, but not a sufficient condition, as is easily recognized by the case of Ti–50Ni alloy. In that case no superelasticity appears and shape memory effect and superelasticity effects are realized only after the alloy is subjected to proper thermomechanical treatment, as is discussed in detail in Section 9, because slip is easily introduced in solution-treated condition.

6.4. Comparison with experiments in Ti–Ni-based alloys

We will compare experimental results with theory for superelasticity and shape memory effects together in this section, because both effects appear in the same S– S curves diagram as shown in Fig. 45. In order to discuss them in a quantitative manner, it is best to use single crystals data, but there are not many such data, since it is difficult to grow single crystals of Ti–Ni-based alloys. Besides, the critical stresses for slip for single crystals of solution-treated Ti–Ni-based alloys are so low, as described earlier, most of the data were taken for aged specimens. However, such aged specimens give rise to untransformed regions in specimens, and thus there are some limitations in the critical test. We will also discuss the results for polycrystals as well, because single crystals are not always available, and on the other hand polycrystals are important from practical point of view.

6.4.1. Comparison with experiments: B2–B19' transformation

Since the observation of twin boundary movements are possible only by electron microscopy for tiny Ti–Ni martensites, such observations are very few [253]. Thus we first compare the recovery strain due to shape memory effect with the theoretical value for solution-treated (1273K×1h WQ)¹³ Ti–50.5Ni single crystals as well as aged (1273K×1h WQ, 673K×1h WQ)¹⁴ single crystals [139]. One such example is shown in Fig. 48 for a single crystal near $[11\bar{1}]_p$ orientation. We see that the S–S curves are divided into three stages, which is similar to those in polycrystals, as we will discuss it in Section 7. In this figure the dashed lines represent recovered strains after heating to temperatures above A_f . If we plot the recovered strain as a function of total strain, we obtain Fig. 49. Thus we see that the recovered strain increases with increasing to

 $^{^{13}}$ This abbreviation means that the specimen was solution-treated at 1273 K for 1 h followed by quenching into ice water.

 $^{^{14}}$ This abbreviation means that the specimen was aged at 673 K for 1 h after the above solution-treatment, followed by quenching into ice water.



Fig. 48. Stress-strain curve of a solution-treated Ti–50.5Ni single crystal. The curve is divided into three regions according to the deformation modes. Dashed lines show the strain recovery upon heating after unloading. See text for details [139].



Fig. 49. Plots of recovered and permanent strains vs. total strain for a solution-treated Ti–50.5Ni single crystal [139].

tal strain, and that the former increases even in Stage II, the strain recovering completely by the end of Stage II. We see from Fig. 49 that the permanent strain sets in from nearly the maximum recovered strain. Upon comparing the recovered strain with theoretical value, the strains calculated from the lattice deformation matrix (i.e. Eq. (27)) were used, because the recovered strains in the stage I were always larger than those calculated from the shape strain, implying that detwinning occurs during the Stage I. The result of the comparison of observed ε_{max} (indicated by the numbers in parentheses) for various orientations with the theoretical ones (indicated by the contour lines) is shown in Fig. 50. We see very good agreement between theory and experiments. This implies indirectly that the mechanism of shape memory effect described in Section 6.3. holds true for Ti–Ni alloys as well. The figure also shows that the maximum recoverable strain can be obtained near $\langle 111 \rangle_p$ orientation, as Saburi et al. [141] predicted. Similar experiments were also carried out for aged specimens (1273K×1h WQ, 673K×1h WQ), and the results were compared with solution-treated ones in Table 13. We see that ε_{max} for aged specimens are much smaller



Fig. 50. Orientation dependence of shape memory strain. Numbers in parentheses represent the experimental results (ϵ_{max}), and contour lines calculated ones [139].

Table 13 Comparison of observed transformation strains with calculated ones [139]

Spec. No.	Aged ϵ_{\max}	Solution-treated		
		ε _L	ε_{\max}	$\varepsilon_{\rm cal}$
1	4.5	4.2	4.6	4.6
2	3.8	7.2	7.8	7.9
3	5.9	8.9	10.6	10.0
4	5.5	9.1	10.5	10.3
5	5.9	8.4	10.0	10.3
6	5.4	8.3	9.4	9.4
7	_	4.0	6.5	6.3

than the theoretical values (except for Spec. No. 1). We also note that the recovered strain in Stage I is always smaller than the theoretical values, as noted earlier. Saburi et al. [138] carried out a similar work and obtained the similar result, but they used aged specimens.

Fig. 51 is a series of S–S curves for an aged Ti–50.3Ni single crystal. We clearly see that good shape memory effect and superelasticity are obtained even in single crystals, if it is properly aged. Fig. 52 is a critical stress plot as a function of test temperature for Fig. 51. The departure of the critical stress from the linear relation as indicated by dashed lines in the stress-induced transformation temperature region represents the set in of slip [228]. In this experiment the critical comparison of recovery strains was not carried out, because the aged specimens give rise to serious errors, as explained in the above.

6.4.2. Comparison with experiments: B2–R transformation

The B2–R transformation is also a martensitic transformation as described in an earlier section, and thus the shape memory and superelasticity effects are expected to occur associated with this transformation, although the associated strain is very small. The mechanical behavior associated with the R-phase was first observed by Khachin and co-workers [99,100] by tensile tests on binary Ti–Ni alloys. They



Fig. 51. Stress–strain curves as a function of temperature of a Ti–50.3Ni single crystal, which was solution-treated at 1273 K for 1 h followed by aging at 673 K for 1 h. Dashed lines show the strain recovery upon heating after unloading [239].



Fig. 52. Critical stress for inducing martensites and for reverse transformation of a Ti–50.3Ni single crystal, which was solution-treated at 1273 K for 1 h followed by aging at 673 K for 1 h [239].

observed two-stage yielding in the S-S curve, and ascribed the first stage due to the rearrangement of R-phase variants, and the second stage to the stress-induced

martensitic transformation from the R-phase to B19' martensite. They also observed the strain recovers by heating to a temperature above R_s . Ling and Kaplov [101,102] then studied the shape memory effect associated with this transformation in bent specimens coupled with X-ray diffraction measurement. More systematic works for superelasticity as well as shape memory effect were done by Miyazaki et al. by tensile tests using both Ti₅₀Ni₄₇Fe₃ polycrystals [67] and aged Ti–50.5at.%Ni single crystals [105].

We will discuss first the results for Ti–50.5Ni single crystals, which were aged to introduced R-phase transformation (1273K×1h WQ, 673K×1h WQ) [105]. Before we discuss the experimental results, we calculate the transformation strain using lattice deformation matrix. Although the structure of R-phase is trigonal, as described in Section 3.4, it is more convenient to use orthonormal axis system. With referring to Fig. 13, we will choose principal axes as shown in the figure, i.e. $[110]_p$ as $[100]_d$, $[\bar{1}1\bar{2}]_p$ as $[001]_d$, $[\bar{1}11]_p$ as $[001]_d$. Then the coordinate transformation between the parent phase and the principal axes are written as follows:

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix}_{p} = \mathbf{R} \begin{pmatrix} U \\ V \\ W \end{pmatrix}_{d} = \begin{pmatrix} 1/\sqrt{2} & -1/\sqrt{6} & -1/\sqrt{3} \\ 1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\ 0 & -2/\sqrt{6} & 1/\sqrt{3} \end{pmatrix} \begin{pmatrix} U \\ V \\ W \end{pmatrix}_{d}.$$
 (28)

In the principal axis system, the lattice deformation matrix \boldsymbol{B}_{d} is written as

$$\boldsymbol{B}_{\rm d} = \begin{pmatrix} \sqrt{2}\sin(\alpha/2) & 0 & 0\\ 0 & \sqrt{2}\sin(\alpha/2) & 0\\ 0 & 0 & [3 - 4\sin^2(\alpha/2)]^{1/2} \end{pmatrix},\tag{29}$$

where α is the angle defined in Fig. 13. Thus, the lattice deformation matrix relative to the parent phase is given as

$$\boldsymbol{B} = \boldsymbol{R}\boldsymbol{B}_{\mathrm{d}}\boldsymbol{R}^{\mathrm{T}},\tag{9}$$

where \mathbf{R}^{T} is the transpose of \mathbf{R} . By the operation of deformation matrix, a given vector \mathbf{x} in the parent phase changes into a vector \mathbf{x}' upon the R-phase transformation such that

$$\mathbf{x}' = \mathbf{B}\mathbf{x} = \begin{pmatrix} m & n & n \\ n & m & -n \\ n & -n & m \end{pmatrix} \mathbf{x},$$
(30)

where

$$m = (2\sqrt{2}/3)\sin(\alpha/2) + [3 - 4\sin^2(\alpha/2)]^{1/2}/3,$$
(31)

and

$$n = (\sqrt{2}/3)\sin(\alpha/2) - [3 - 4\sin^2(\alpha/2)]^{1/2}/3.$$
(32)

Thus, the tensile (or compressive) strain is given by the following equation:

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$$\varepsilon = \frac{|x'| - |x|}{|x|} \times 100(\%). \tag{33}$$

Because α is a function of temperature, as shown in Fig. 14, it is possible to calculate the maximum recovery strain as a function of temperature and orientation by using such data. In the following calculations, the data by Ling and Kaprov [101] was used.

Miyazaki et al. [105] measured S–S curve associated with R-phase transformation as a function of temperature for various orientations. One example of such S–S curves is shown in Fig. 53. We see both superelasticity and shape memory effect. It is interesting to note that the recovered strain increases with decreasing temperature, i.e. the shape memory strain is a function of deformation temperature. This is quite distinct from the behavior of ordinary shape memory alloys, in which lattice parameters of martensite do not change appreciably with temperature. On the contrary, the lattice parameters of R-phase changes sharply with temperature, as shown as the change in α -angle in Fig. 14. Thus, the change in α -angle reflects to the change in recovery strain through Eqs. (28)–(33). If we plot the critical stress as a function of temperature, we obtain Fig. 54. We see that the critical stress for stress-induced transformation increases quite rapidly with increasing temperature. This occurs because the recovery strains is so small as shown in Fig. 53(h)–(j), the slope of $d\sigma/dT$ becomes very large by the Clausius–Clapeyron relation of Eq. (23). The extrapolation of the straight Clausius–Clapeyron line to zero stress is slightly displaced with



Fig. 53. Stress-strain curves as a function of temperature of a Ti-50.5Ni single crystal, which was aged at 673 K for 1 h after solution-treatment. The S-S curves are related with R-phase transformation or deformation of R-phase. $T'_{\rm R} = R_{\rm s}$. See text for details [105].

600



Fig. 54. (a) Critical stresses for the first stage yielding, and (b) the recovered strain of R-phase, along with the calculated strain shown by a dashed line. These were plotted from the data in Fig. 53. See text for details [105].

 $T'_{\rm R}$, which is defined to be equal to $R_{\rm s}$. The recovery strain in Fig. 53 is plotted in Fig. 54(b). The data fit very well with the calculated values (dashed lines in the figure) through Eqs. (28)–(33). The measured recovery strains in various orientations at a temperature ($T_{\rm R} - 35$) K are plotted in Fig. 55, where $T_{\rm R}$ is defined as the critical temperature at which α -angle starts deviating from 90° in Fig. 14, in comparison with



Fig. 55. Orientation dependence of strain recovery associated with R-phase transformation, which were obtained at a temperature ($T_{\rm R} - 35$) K. Closed circles indicate the experimental data, while contour lines are calculated. Ti–50.5Ni single crystals, which were aged at 673 K for 1 h after solution-treatment [105].

the theoretical values (contour lines). We see very good agreement with theory and experiment. This figure also shows that the maximum recovery strain is obtained at $\langle \bar{1} 1 1 \rangle_p$ orientation as expected.

The shape memory and superelasticity effects were also studied in detail for Ti– 49.8 Ni polycrystals, which were cold-worked followed by annealing at 673 K, and for Ti–50.6Ni polycrystals, which were aged at 673 K after solution-treatment, and superelasticity due to R–B19' transformation was observed for the former [66]. One interesting point in this study is that a big difference in the flow stress for detwinning/twinning of R-phase. i.e. The critical stress for the former is much higher than that for the latter. This means that high density of dislocations are more resistant for twin boundary movement of R-phase compared to precipitates.

The available shape memory strain for R-phase transformation, which is also a function of temperature due to α -angle dependence, is very small (the maximum for polycrystals are about 1%). However, the temperature hysteresis associated with the transformation is also very small (1–2 K). The main reason for the small temperature hysteresis is probably due to the extremely small transformation strain at the transformation temperature, as will be discussed in Section 8.4.1. Thus, despite the fact of small shape memory strains, the R-phase transformation is very useful for actuator applications, as actually used for practical applications [17].



Fig. 56. Stereographic representation of calculated shape memory strains associated with B2–B19 transformation in a $Ti_{50}Ni_{40}Cu_{10}$ alloy (after Nam et al. [91] reproduced with permission of Japan Institute of Metals).

6.4.3. Comparison with experiments: B2–B19 transformation

The recovery strain associated with B2–B19 transformation was calculated for $Ti_{50}Ni_{40}Cu_{10}$ alloy as a function of orientation by Nam et al. [91], as shown in Fig. 56. However, there is no critical comparison with the theoretical calculation, although there is a brief report on the S–S curves of Ti–Ni–Cu single crystal [254]. According to the figure, the maximum recoverable strain of 5.3% is obtained for $\langle 110 \rangle_p$ orientation. This value is much smaller than that (10.5%) for B2–B19' transformation in Fig. 50. Since no more information is available for single crystals, we discuss the results for polycrystals in the following.

Fig. 57 shows a series of S–S curves as a function of temperature for a solutiontreated $Ti_{49.5}Ni_{40.5}Cu_{10.0}$ alloy [255]. We can see complete shape memory and superelasticity effects within the strain limit of 4%. We notice that stress hysteresis of superelasticity is very small compared with those in binary Ti–Ni alloys (compare



Fig. 57. Stress-strain curves of $Ti_{49.5}Ni_{40.5}Cu_{10.0}$ alloy quenched from 1123 K (after Saburi et al. [255] reproduced with permission of Materials Research Society).



Fig. 58. Effect of Cu addition on the yield stress (0.5% offset stress). The specimens were quenched from 1123 K (after Saburi et al. [255] reproduced with permission of Materials Research Society).

with Fig. 45). We also notice that the flow stress or the critical stress in the martensitic state (i.e. the stress to move twin boundaries in martensite) is very low. This is more clearly shown in Fig. 58, which represents the critical stress as a function of temperature for other compositions as well as that for binary Ti–Ni alloy. i.e. Ti–Ni–Cu alloys are much easily deformed in the martensitic state compared with binary Ti–Ni alloys. This can be understood by comparing the twinning shear of B19' martensite with those of B19 martensite in Tables 4 and 8, respectively. That is, the twinning shear of $\langle 011 \rangle_m$ type II twinning, which is the main lattice invariant shear in B19' martensite, is 0.280, while those of $\{011\}_o$ compound or $\{111\}_o$ Type I twinning of B19 martensite are either 0.11 or 0.17, respectively. Thus the twinning/ detwinning will be much more easier for the B19 martensite.

The temperature hysteresis of B2–B19 transformation as a function of composition is shown in Fig. 59 [68]. We notice that they are smaller than those in binary alloys in all compositions, and further that the temperature hysteresis decreases with increasing Cu content, the minimum being 4 K for 20Cu. To understand the reason for the small temperature hysteresis of Ti–Ni–Cu alloy, Nam et al. [91] examined the



Fig. 59. Elongation vs. temperature curves under 40 MPa load for Ti–Ni–Cu alloys with various compositions indicated. $M'_s = O_s$, $M'_f = O_f$, $A'_s = AO_s$, $A'_f = AO_f$ etc. (after Nam et al. [68] reproduced with permission of Japan Institute of Metals).

volume change $(\Delta V/V)$ as a function of composition, and found that it decreases with increasing Cu content up to 12.5 at.%Cu with the minimum value of -0.1%, then increases again with further increasing Cu content. Thus the small volume change may be one factor for the small temperature hysteresis, but that alone cannot explain the composition dependence. Thus they proposed the main reason for the small temperature hysteresis is the strengthening of the parent phase by increasing Cu content as experimentally observed [256], since the frictional stress for twin boundary movement will be suppressed if the introduction of dislocations are avoided by the increase of Cu content.

The low flow stress in the martensitic state, the small temperature hysteresis, and the appreciably higher transformation temperatures, which are observed in Fig. 59, make the Ti–Ni–Cu alloys very attractive for actuator applications, and they are actually used for practical applications. However, one disadvantage of the alloys is the poor workability, if Cu content exceeds 10 at.%Cu [257].

6.5. Mechanism of two-way shape memory effect

In the shape memory effect discussed in the preceding section, what is remembered was the shape of the parent phase only. Then, is it possible to remember the shape of the martensitic phase also? Yes, it is possible to remember the martensitic phase also under certain conditions to be discussed below. This effect was first called "the reversible shape memory effect" [258,259], but now it is called "two-way shape memory effect", while the ordinary shape memory effect in the preceding section is sometimes called "one-way shape memory effect", in contrast to two-way. To the authors' knowledge, the first report of two-way shape memory effect is due to Wang and Buehler [260] for a Ti–Ni alloy, but the condition to realize the effect is too complex and it is hard to know what is essential, as criticized by Nagasawa et al. [258]. The behavior reported by Tas et al. [261] as "the reversible linear change on transformation" is also related to this effect. However, more clear report on this effect is due to Nagasawa et al. [258] and Saburi and Nenno [259]. Nagasawa et al. reported that reversible shape memory effect is obtained when specimens are severely deformed below M_s temperature, and they observed the effect for Ti–Ni, Cu–Zn and Ni–Al alloys. Saburi and Nenno also found the same effect by sever deformation of Cu-Zn-Ga alloy in a persistent manner. Thereafter many reports appeared how to realize two-way shape memory effect including the above: (1) introduction of plastic deformation described above, (2) constraint aging [262], (3) thermal cycling [263], (4) utilization of precipitates [264,265], (5) martensite aging due to symmetry-conforming short range order (SC-SRO) [266] etc. It will be easily expected that in order to realize the shape of martensitic phase, certain martensite variants need to be selected. Since the martensitic transformation strongly interacts with stress, the stress selects certain variants of martensite in the nucleation process in order to lower the energy of the system, e.g. [267], and contributes to create the certain shape of martensite. In the above process (1)–(4), certain stress sources are created during the processes such as dislocation configurations, precipitates etc., which produce internal stress fields to choose specific martensite variants. The case of (5) is slightly different from the above ones. In this case, a specimen such as Au-Cd, in which diffusion is rather easy, is aged in the martensitic state. Then SRO called SC-SRO is developed in each variant of martensite. If such a specimen is reverse transformed by heating, and quickly cooled to martensite again, the specimen returns to the original configuration of martensite variants, since it gives the lowest energy state. As is clear from the above explanation, if the above mechanism (i.e. the selective nucleation of martensite variants) is correct, we can expect one-to-one (or nearly one-to-one) correspondence between two-way shape memory effect and "microstructure memory effect", in which the specimen exhibits the same variant configuration upon heating and cooling. Such a perfect one-to-one correspondence was found for a Au–Cd alloy described in the above [266], but such correspondence has not been observed for Ti-Ni alloys as yet. It is clear from the above that two-way shape memory effect is a rather weak effect compared to one-way shape memory effect, since the former is due to the selective nucleation of certain martensite variants, while the latter is due to the strong reversibility and unique lattice correspondence upon reverse transformation. In the following we discuss two-way shape memory effect in Ti-Ni alloys more in detail.

A most remarkable two-way shape memory effect in Ti-Ni alloys will be the one reported by Nishida and Honma as "all-round shape memory effect" [63], as shown in Fig. 60. They used Ti-51Ni alloy, in which the precipitates of Ti₃Ni₄ phase can be utilized. The strips of the alloy were solution-treated at 1073 K for 7.2 ks. Then they were subjected to constrained-aging at 773 K for 3.6 ks as a half-circular form as shown in Fig. 60(a). This is the aging process to produce Ti₃Ni₄ precipitates, as will be discussed later. Thus the form of the parent phase is prepared as shown in Fig. 60(a). If the specimen is cooled as indicated in the lower part of the figure, down to 77 K, the shape changes from Fig. 60(a)–(e). That is, the shape changed dramatically just by cooling. Upon heating just reverse change of the shape was observed from Fig. 60(e)-(a). Upon further cooling-heating the same behavior was observed. This is the two-way memory effect, and Nishida and Honma called this "all-round shape memory effect", because it occurred in a dramatic fashion. They also measured the change of electrical resistivity and the change of shape as a function of temperature using a parameter $r_{\rm L}/r$, where $r_{\rm L}$ is the bending curvature attained at the lowest temperature, and r is the bending curvature at each temperature (Fig. 61). The plus and minus sign of the curvature ratio indicates the downward and upward curvature, respectively. With respect to the temperature regime in the figure related with resistivity behavior indicates that: (I) R-phase transformation, (II) the change of α -angle in the R-phase, and (III) transformation from R-phase to B19' martensite. Thus we notice that most of the shape change upon cooling is realized by the R-phase transformation, and subsequent change in α -angle upon further cooling of the R-phase, and the contribution of R-B19' transformation in Region III to the shape change is rather small. This was also confirmed by Fukuda et al. [268] by a uniaxial experiment to be discussed later. This interesting behavior was explained by Kainuma et al. [269], as shown in Fig. 62. As was explained with respect to Fig. 6, Ti₃Ni₄ phase precipitates along the $\{1\,1\}_p$ plane of the parent phase, and exerts tensile stress normal to the habit plane of the precipitates when the precipitates are coherent, as



Fig. 60. Demonstration of "all-round shape memory effect" in Ti–51Ni alloy. $R_s = 325$ K, $R_f = 280$ K, $M_s = 275$ K, $M_f = 250$ K, $A_f = 345$ K, $AR_s -$, $A_f -$, $A_s = 320$ K. See text for details (after Honma, referred in [229] reproduced with permission of Institute of Materials, Minerals and Mining).

shown in the figure. Now if the specimen is bent as shown in the figure, compressive stress and tensile stress arise in the lower part and upper part, respectively. Thus if the precipitates are formed normal to the compressive stress, and parallel to the tensile stress, respectively, as shown in the figure, the bending stress will be relieved. The fact that precipitates are formed in such a way by constrained-aging was confirmed by TEM observations [269,268]. Because of these special microstructure and stress field, special variant of R-phase will be selected upon B2–R transformation. Indeed they observed by TEM that a single variant of R-phase was formed corresponding to the microstructure. The line up of the R-phase will further lead to the further shape change upon the transformation from R-phase to B19' martensite, as is actually observed in Fig. 60.



Fig. 61. Shape change and corresponding electrical resistivity for Ti–51Ni alloy aged at 773 K for 1 h under constraint (after Nishida and Honma [63] reproduced with permission of Elsevier).



Fig. 62. Mechanism of "all-round shape memory effect". See text for details (after Kainuma et al. [269] reproduced with permission of Japan Institute of Metals).

Meanwhile, Fukuda et al. [268] carried out a similar work using a uniaxial tensile stress, which is easier to analyze. The specimens of Ti–51Ni alloy were aged at 773 K for various times (both with/without constraining load) after the solution-treatment at 1123 K for 3.6 ks. They used *tensile* stress both for the constrained aging, and for

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Fig. 63. Strain vs. temperature curves obtained by thermal cycling tests made under various applied stresses (σ_{test}) of Ti–51Ni specimens (a) aged under no applied stress ($\sigma_{age} = 0$ MPa), (b) aged under an applied stress of 300 MPa (after Fukuda et al. [268] reproduced with permission of Japan Institute of Metals).

measuring strain vs. temperature curves under constant load to be described below. Fig. 63 shows an example of such curves. Fig. 63(a) shows the case for a specimen, which was aged under no constraint. We see a transformation strain in the positive direction (elongation), as expected. On the contrary, in Fig. 63(b), in which the specimen was constrained-aged under the stress of 300 MPa, we see the transformation strain in the negative direction, which is opposite to the applied stress. This is the two-way shape memory effect for R-phase transformation.¹⁵

It is interesting to note that the two-way shape memory effect occurs against the applied stress, although the effect is very much weakened when the applied stress is increased to 127.9 MPa. Although the reason why the two-way shape memory effect is in the negative direction under the present experimental condition is not described in the original paper, this may be explained in the following way. Since the specimen was aged under tensile stress, the precipitates will be formed in parallel to the tensile axis as discussed in the above, and this is confirmed by TEM observations [268]. According to Kainuma et al. [269], the orientation relationship between the precipitate and the R-phase is the following:

 $[111]_{B2} \| [111]_{Ti_3Ni_4} \| [111]_R ([0001]_H)$

¹⁵ Readers may think that the curves in Fig. 63(a) also represent two-way shape memory effect, but this is not the case. This is simply the result of stress-induced transformation under the stress of 55.0 MPa or 104.4 MPa. This is quite clear from the fact that no transformation strain is available when the applied stress is 6.4 MPA, which is too small to affect the transformation.



Fig. 64. Two-way shape memory effect obtained after a single deformation by 6.2% of Ti–50.0Ni alloy, which was annealed at 938 K for 0.5 h. See text for details (after Liu et al. [274] reproduced with permission of Elsevier).

If we follow this orientation relationship, $[111]_R$ axis of the R-phase is aligned normal to the tensile axis. Since the α -angle decreases with decreasing temperature, as shown in Fig. 14, the specimens thickens in radial direction, resulting in the contraction of the specimen in the tensile axis. As a result of these measurements Fukuda et al. reports that the strain due to the two-way memory is about 0.5%. Thus even if we add the strain due to the change of α -angle upon further cooling, as shown in Fig. 61, the two-way memory strain due to R-phase will be lower than 1%. They further studied two-way shape memory effect for the transformation from R-phase to B19', but found that it is not effective.

The above two-way shape memory effect utilizing Ti_3Ni_4 precipitates were very interesting, especially from scientific point of view, because the mechanism of the two-way shape memory effect was rather clear. However, the available two-way memory strain was not so large (less than 1%), and the increase of Ni to form Ti_3Ni_4 precipitates results in the lowering of M_s temperature (especially below ambient temperature), as will be described in Section 8. These are not advantageous for applications. Thus researchers, especially in the field of applications, are interested in creating two-way shape memory effect by sever deformation and/or cycling technique of Ti–Ni alloys near equiatomic composition, in order to obtain optimum processing conditions [270–274]. We will briefly discuss the results here. ¹⁶ However, readers should note that the results are strongly dependent upon composition, heat-treatment and deformation method etc. Thus, if they want to know the details they should refer to the original papers, although there are some important guide-lines to understand them. Fig. 64 shows an example to exhibit that two-way shape memory effect can be obtained by a single deformation process [274]. In this case

¹⁶ Since this part is related with heavy deformation of polycrystals and heat-treatment, it may be easier for readers to read this after Sections 7 and 9. We may also refer to some figures in these sections.

the specimen was preliminary deformed to 6.2% (which corresponds to the end of the first stage (plateau stage) in Fig. 69). Then the measurement of the shape memory strain was carried out by TMA (thermomechanical analyzer), first by heating it to cause the reverse transformation up to 375 K. Then it was cooled and heated to experience one cycle of transformation. We see that the two-way memory strain (ε_{tw}) of 1.44% is available by this tensile deformation. Usually two-way shape memory effect does not stabilize in a cycle, but it tends to stabilize with cycling, although there may be a condition that it tends to stabilize in a few cycle [271]. It is also known that heattreatment affects greatly two-way memory strain; usually the heat-treatment, which cause the direct transformation from B2 to B19', gives larger two-way memory strain, while that, which causes B2-R-B19' transformation, is not good for twoway memory effect [270,271]. One reason for this is that the parent phase is hardened when R-phase is introduced, and thus the introduction of dislocations becomes more difficult, although the kind of dislocations must also be related with two-way memory effect. With respect to the stressing condition, the stress-induced transformation is known to be more effective than the deformation of martensite [263]. This is probably because the same variants of martensite are more easily aligned in the former, when stress is applied. This is probably related with the way or kind of dislocations introduced, as we will discuss soon in the following. The maximum two-way memory strain for equiatomic Ti-Ni alloy is about 4%, as shown in Fig. 65 [274]. The maximum two-way memory strain is usually obtained for the pre-strain, for which the maximum one-way memory strain is attained [275–278]. In the figure η_{tw} is defined as the ration of $\varepsilon_{tw,max}$ and the corresponding value of one-way memory strain, ε_{tr} . We see that η_{tw} is also attained maximum at similar pre-strain for maximum ε_{tw} . The origin of two-way shape memory effect by heavy deformation and cycling is usually believed to be due to dislocations specially arranged, whose stress field causes preferential nucleation of martensite variants, but the details are not clear. In this respect an experiment by Miyazaki and Kimura [273] is interesting. By using a solution-trea-



Fig. 65. Effect of martensite reorientation deformation on the development of two-way shape memory effect. The specimens were Ti–50.0Ni alloy, which was annealed at 938 K for 0.5 h (after Liu et al. [274] reproduced with permission of Elsevier).

ted Ti–51Ni alloy, they measured two-way memory strain after they introduced dislocations in the parent phase and in the martensitic state, respectively, by changing deformation temperature. As a result they found a substantial ε_{tw} (~2%) when dislocations are introduced in the martensitic state, while ε_{tw} was negligible when dislocations are introduced in the parent phase. This result may imply that the former dislocations are effective to nucleate martensite variants preferentially, because the stress field is favorable to nucleate formerly present martensite variants, while the latter does not nucleate them preferentially.

7. Deformation mechanisms and related behaviors

Deformation mechanisms were already discussed with respect to shape memory and superelasticity effects as a function of temperature in Section 6. In this section we discuss them as a function of strain (up to fracture strain) *for polycrystals*, and other related behaviors.

7.1. Identification of each stage in stress-strain curves

The deformation behavior is different depending upon test temperatures, as we discussed in Section 6. Thus we discuss them separately for two temperature regimes in the following.

7.1.1. Identification of stages in stress-strain curves for $T > A_f$

Fig. 66(a) shows a typical S-S curves of solution-treated Ti-50.6Ni wire for this temperature regime, and Fig. 66(b) shows the superelastic strain (ε_{s}), residual strain (ε_r) and permanent strain (ε_n) , which were measured from Fig. 66(a). Miyazaki et al. [228] divided the S–S curve into three stages as indicated in the figure. The stage I is characterized by the initial linear portion due to elastic deformation of the parent phase, and the plateau stage with serrations, which is due to stress-induced martensitic transformation. They further found that the deformation at the plateau is the "Lüders deformation", which occurs inhomogeneously, by direct observation and by partial cyclic deformation [240]. Later this was also confirmed by Shaw and Kyriakides [279], who made detailed observations coupled with an infrared imaging radiometer, as shown in Fig. 67. In Fig. 67(a) the black part represents the parent phase and gray part martensite. We see that a martensite is nucleated near the left grip in (O) at time t_1 , and then grows with time, while another martensite is nucleated at time t_3 near the right grip in (③), which also grows with time. This behavior looks like a martensitic transformation process in a single crystal, but remember the specimen was polycrystals. This is characteristic of Lüders deformation, in which the stress concentration at the interface between deformed and undeformed regions causes the stress-induced transformation only at the neighboring region of the deformed one, because the required stress for nucleation is higher than that for growth in these materials. In Fig. 67(b), which was simultaneously taken with Fig. 67(a), we



Fig. 66. (a) Stress–strain curves of Ti–50.6Ni alloy, which was deformed at 243 K (> A_f). The alloy was solution-treated at 1273 K for 1 h. Dashed lines represent the recovered strain upon heating to 373 K. The symbol (X) represents the fracture point. (b) Plots of various strains in (a) as a function of total strain [228].

see the stress drops at the times t_1 and t_3 , which indicates that the required stress for nucleation is higher than that for growth.

We now return to Fig. 66(a) again. The stage II is characterized by a rapid strain hardening. By comparing with Fig. 66(b), we also notice that superelastic strain has not finished in stage I but it is still increasing in stage II. This indicates that stress-induced transformation, detwinning or twinning to more favorable orientations are still occurring with increasing stress. However, we also notice from Fig. 66(b) that the permanent strain by slip also sets in from the total strain of 8%. So, we can summarize that stage II is characterized by stress-induced transformation (including detwinning and twinning) and slip. In stage III the strain hardening saturates, and recovery strains decreases. Thus this stage is characterized only by slip and twinning, which is described soon below.

Upon discussing permanent deformation modes, it is probably appropriate to discuss them in the B19' martensitic phase, since specimens become almost martensitic state by stages II and III even though they started from the parent phase. The slip system in B19' martensite is probably $[100](001)_m$, but this is not confirmed as yet [81]. The twinning mode in stage III is most likely to be $\{20\bar{1}\}\langle\bar{1}0\bar{2}\rangle_m$ with twining shear of 0.4250 [128]. This twinning mode is very efficient for large deformation,



Fig. 67. (a) Observation of Lüders deformation by photography for Ti–50.5Ni alloy. Black regions represent the parent phase, and lighter colored regions martensite. The strain increases with increasing numbers from O to O. (b) shows stress as a function of time. See text for details (after Shaw and Kyriakides [279] reproduced with permission of Elsevier).

since it is associated with large twinning shear. The strain introduced by this twinning mode cannot be recoverable, since it is not the lattice invariant shear, as pointed out previously in Section 4.1.1, and thus it is consistent with permanent deformation in stage III.

Apart from the three-stage transformation in the above, Moberly et al. [280] studied the deformation behavior in the parent phase by using a Ti₅₀Ni₄₇Fe₃ alloy, which has a very low M_s temperature, and thus no martensites are stress-induced at ambient temperature. They report that the slip system in the parent phase is confirmed to be $\langle 100 \rangle \{011\}_p$, which is consistent with the report by Miyazaki et al. [281]. They also confirmed that the operative twinning mode in the parent phase is $\{114\} \langle 22\bar{1} \rangle_p$ with twinning shear of 0.707, which was found by Goo et al. [282]. This



Fig. 68. High resolution electron micrograph exhibiting that $(20\bar{1})_m$ twin in B19' martensite inherits to $(41\bar{1})_p$ twin in the parent phase upon reverse transformation. The specimen was Ti–50.6Ni alloy, which was deformed first in fully martensitic state, and then partially reverse transformed (after Ii et al. [283] reproduced with permission of Elsevier).

twinning mode corresponds to $\{20\bar{1}\}\langle\bar{1}0\bar{2}\rangle_{m}$ twinning mode in B19' martensite described in the above. Actually Ii et al. [283] directly observed that $\{20\bar{1}\}_{m}$ twin remains as $\{114\}_{p}$ twin after reverse transformation, as shown in Fig. 68, in which $\{20\bar{1}\}_{m}$ twin changes into $\{41\bar{1}\}_{p}$ twin continuously. This also serves as an evidence to show that $\{20\bar{1}\}_{m}$ is not recoverable upon reverse transformation, as was pointed out in Section 6.3. In Moberly et al.'s report they argue that the number of independent slip system of $\langle 100 \rangle \{011\}_{p}$ is only three, which is insufficient for Taylor's criterion. Strictly speaking, however, this argument will not be appropriate, because the number of slip systems for $\langle 100 \rangle \{011\}_{p}$ is 12 (6 planes × 2 directions), and is larger than 5, which is required by Taylor's condition, although the introduction of twinning systems surely assist to increase the ductility.

7.1.2. Identification of stages in stress–strain curves for $T < M_s$

Miyazaki et al. [228] carried out a similar experiment for a temperature well below M_s as shown in Fig. 69. Again the S–S curves are similar to the previous case except for stage I. This time the plateau region is very smooth without serrations, and initial part is more gradually change as if elastic deformation is absent. According to them, stage I represents detwinning or twinning of martensites (the detwinning or twinning is also called "reorientation of martensites", because detwinning/twinning is equivalent to the conversion of martensite variants, as discussed in Section 6.3), and stage II detwinning/twinning and slip, while stage III slip and twinning. (Strictly speaking, twinning was not included in their original paper, since $\{20\bar{1}\}\langle\bar{1}0\bar{2}\rangle_m$ was found later, but obviously it should be included.)

More recently Liu et al. [284] carried out detailed study on the deformation behavior in martensitic state by using specimens of Ti–50.0Ni plate, which is slightly different from that of Fig. 69. According to them, they divide the previous stage I into two stages; i.e. stage I and stage II. Their stage II is plateau region, which is characterized by the stress drop. (Note we do not see a stress drop at the beginning



Fig. 69. (a) Stress–strain curves of Ti–50.6Ni alloy, which was deformed at 173 K ($<M_s$). The alloy was solution-treated at 1273 K for 1 h. Dashed lines represent the recovered strain upon heating to 373 K. The symbol (x) represents the fracture point. (b) Plots of various strains in (a) as a function of total strain [228].

of the stress plateau in Fig. 69(a).) They claim that stage I represents a non-linear uniform deformation of martensite, and stage II represents Lüders deformation. Since the stage II is associated with the stress drop, their interpretation seems reasonable, as far as their data are concerned, although the stress drop is not observable in Fig. 69(a). Since they divided previous stage I into two, previous stage II becomes stage III in their new notation.

7.2. Effect of deformation on transformation temperatures

The control of transformation temperatures is important for applications of shape memory alloys, as is discussed in the following section, and the use of deformation is another way to control them. This was first explored by Melton et al. [285,286] for the need of expanding transformation temperature hysteresis for pipe coupling applications of Ti–Ni alloys, because expanded couplings must be stored in liquid nitrogen before inserted over pipes in the then technique. After extensive research they found that Ti–Ni–Nb alloys exhibit significant increase of A_s/A_f temperature after severely deformed in the martensitic state. Lin et al. [287] found the similar effect for a Ti–Ni alloy. The effect is now shown for a Ti–50Ni alloy in Fig. 70, which represents elec-



Fig. 70. Effect of deformation on electrical resistance vs. temperature curve for Ti–50Ni alloy solutiontreated at 1173 K. A_s^d represents A_s temperature after deformation in martensitic state. ε_t and ε_p are total strain and permanent strain, respectively [288].

trical resistance vs. temperature curves for the solution-treated alloy, which were subjected to tensile deformation at various degrees in the martensitic state [288]. Here ε_t represents a total strain, ε_p a permanent strain, and A_s^d the A_s temperature after deformation in the martensitic state. The first curve represents without deformation. The second curve exhibits the following; after deformation, the specimen is heated until the reverse transformation is completed, which is confirmed by the reduction of electrical resistance (which is caused by the shortening of the specimen by the reverse transformation). Then it is cooled to cause a forward martensitic transformation, and then heated again to cause the reverse transformation. This makes a cycle of deformation: first heating-cooling; second heating in each curve in that figure. From this figure we immediately notice that A_s temperatures increase with increasing total strain. This means "martensite stabilization" by deformation in martensitic state. It is also important to notice that the increase of A_s is one-time effect, because A_s temperature in the second heating is almost the same as the original one without deformation. This characteristic must be explained when we discuss the mechanism for this effect.

We now discuss the mechanism for the martensite stabilization. Lin et al. [287] stated that the possible mechanism comes from deformed structures and deformation induced dislocations/vacancies. They seem to suggest the pinning effect of mar-

tensite boundaries by dislocations/vacancies, but they did not elaborate. On the other hand, Piao et al. [288] proposed more clear mechanism as follows. They focus attention on the stored elastic energy in thermoelastic alloys, which arise upon cooling against the forward transformation. Thus it assists the reverse transformation, in such a way that the reverse transformation starts at a lower temperature under the presence of such elastic energy. Thus, if such elastic energy is relaxed by some means, A_s/A_f temperatures will be increased. This is their essential idea. Actually Olson and Cohen [289] formulated the stored elastic energy as follows:

$$\Delta g_{\rm ch} + 2\Delta g_{\rm el} = 0, \tag{34}$$

where $\Delta g_{ch} = g_M - g_P$ is the chemical free energy change between parent and martensite, and Δg_{el} is the elastic strain energy stored around the martensite plate. The above equation means that the half of the chemical free energy change is stored as the elastic energy in the specimen. Under the above idea, Piao et al. carried out an experiment using a single crystal of Cu–Al–Ni alloy, and found out the A_s actually increase by the deformation in martensitic state. They also observed that the initial multi-variant state in martensite changed into a single variant state by tensile deformation. That is, the stored elastic energy was relaxed by tensile stress from the surface in this case, and as a result A_s temperature increased. This A_s increase returned to a normal value after experiencing the reverse transformation in the first heating cycle, because the martensite appeared upon cooling was multi-variant. Thus the one-time effect of the martensite stabilization was also explained by the same mechanism. Then they carried out similar experiments using Ti-Ni polycrystals. In this case many dislocations were observed by TEM after the deformation in martensitic state, and they interpreted the results in the following way. In polycrystals elastic strain cannot be relaxed by twin boundaries movement alone, because of grain boundary constraints. Thus elastic strains are relaxed by slip by the movement of dislocations in this case. One-time effect of the martensite stabilization can be explained in the same way as for the single crystal. Thus this mechanism can explain all aspects of this phenomenon as far as qualitatively. However, Liu et al. [290,291] carried out DSC measurements for the effect, and criticized the mechanism from their heat measurement from the DSC curves. They calculated the stored energy from $\sigma^2/(2E)$, where σ is the macroscopic stress and E Young's modulus. As a result they claim that the calculated elastic energy is too small compared with the heat measured from DSC curves. One controversial point in their calculation is the estimation of σ . They use ordinary macroscopic stress, but in heavily deformed state microscopic stress will be much higher than the macroscopic one. Anyway it is anticipated for a theory to appear, which can account for all aspects of this curious effect quantitatively.

In the above discussion the A_s increase for Ti–50Ni alloy was about 40 K or so (Fig. 70). However, if the deformation mode becomes more complex than uniaxial stress and heavier, it is possible to extend A_s temperature increase further. In fact such a request arise upon the application of SMA to smart composites, which consists of SMA and polymers, because curing process (e.g. at 130 °C or 180 °C) is required in such applications. Fig. 71(a) shows a DSC curve of cold-drawn ultra-thin


Fig. 71. DSC curves of a cold-drawn Ti-50.0Ni wire (35% cold-drawn). (a) shows the result in the first heating cycle after cold-drawing. The upper inset is an enlarged DSC curve from the dotted area in (a). The enlarged DSC curve clearly shows the presence of endothermic heat. (b) shows the result after the first heating-cooling cycle [292].

wire of 50 µm, which was subjected to a complex and heavy deformation (cold-drawing rate = 35% [292]. From such curve we cannot observe the reverse transformation, but the inset figure in the above, which was compressed horizontally and expanded vertically, clearly shows the presence of endothermic reaction due to the reverse transformation. This means that the reverse transformation covers a very wide temperature range, reflecting a wide strain inhomogeneity in the specimen. Upon the second heating we observe a normal reverse transformation behavior (Fig. 71(b)) as we have seen before. The A_s temperature (here it is written A_{s1} , implying first heating) of the same cold-worked specimen is more clearly seen by TMA (thermomechanical analyzer) measurement, as shown in Fig. 72(a). In the figure four TMA curves are shown, which correspond to low temperature annealing or without annealing, as indicated in the inset. The A_s temperature of as-cold-drawn wire is 105 $^{\circ}$ C. It is interesting to note that A_{s} temperature increases by low temperature annealing such as 130 °C or 180°C for 2 h, although the recovery strain decreases correspondingly. Furthermore, it is interesting to note that if the curves are redrawn by displacing the origin by the amount of ϵ , which corresponds to the loss of recovery strain, as shown in Fig. 72(b), all curves fit to the master curve of as-cold-drawn wire. This interesting behavior is easily explained in the following way, by taking the example of the wire, which was subjected to 130 °C for 2 h annealing. As noted earlier, the wire has a great inhomogeneity in strains, and thus the reverse transformation temperature is different from one place to the other. If such wire is annealed at 130 °C for 2 h, the portions, whose A_s is lower than 130 °C, reverse transform. If such wire is subjected to the second heating, nothing happens by 130 °C, and the reverse transformation occurs above this temperature. Since the strain recovery in the



Fig. 72. (a) TMA curves of Ti–50.0Ni wires either in as cold-drawn state or after heat-treated state at various low temperatures, the conditions of which being shown in the inset. Each curve starts from 0 recovery strain, and each specimen is subjected to heating–cooling–heating cycle. The curves for a specimen subjected to heat-treatment at 300 °C for 5 min consist of two-loops, larger one corresponding to the first cycle and smaller to the second cycle. (b) When each curve is superimposed to the as cold-drawn one by displacing it downward relative to that for as cold-drawn one by the amount of the difference in recovery strain (e.g. ε in the figure), they fit well to the master curve of as cold-drawn one. See text for details [292].

first heating to 130 °C is displaced in Fig. 72(b), the rest of the curve fit to the master curve. Thus we can understand the whole behavior in Fig. 72(b). Anyway it is interesting and useful to note that A_s temperature can be increased by low temperature annealing, although the martensitic transformation is diffusionless.

7.3. Amorphisation by heavy deformation

The amorphisation of Ti–Ni is interesting, because the grain size of specimens made via amorphous state followed by crystallization can be much smaller compared to those fabricated by ordinary method, which may improve mechanical properties. This problem of amorphisation of Ti–Ni alloys will be discussed in detail in Section 10, with respect to sputtering and rapid quenching methods. However, we will introduce reports here that amorphisation of Ti–Ni is possible by heavy deformation as well. This problem is interesting, because amorphous state is available in bulk state



Fig. 73. TEM images and corresponding diffraction patterns of Ti–50.8Ni sheet; (a) as-received, (b) 30% reduced, and (c) 60% reduced. " α " and "x" in (c) indicates amorphous area and heavily deformed area, which consists of crystalline diffraction spots and diffuse ring. See text for details (after Koike et al. [293] reproduced with permission of Materials Research Society).



Fig. 74. The amorphous volume fraction vs. the true strain of cold-rolled and compressed Ti–50.8Ni and Ti–50.8Ni–0.6Cu alloys. The deformation was performed at room temperature. See text for details (after Ewert et al. [295] reproduced with permission of Elsevier).

rather than in thin films, if we follow this method. Koike et al. [293,294] found that crystal-amorphous transformation occurs in Ti-50.8Ni alloy by cold-rolling at room temperature by as large as 60% reduction. This was also confirmed by Ewert et al. [295] and Nakayama et al. [296] later. One typical example is shown in Fig. 73. Fig. 73(a) shows martensite twin structures before deformation, the state of which is easily confirmed by the associated diffraction pattern. Fig. 73(b) shows the structure when the sample is deformed by 30%. A detailed analysis shows that the structure contains amorphous state partly, as might be seen from the diffuse arcs in the associated diffraction pattern. When the sample is subjected to 60% reduction, Fig. 73(c) is obtained, which clearly indicates banded structure like "shear-band". From the associated diffraction pattern the band designated as " α " is known to be amorphous, whereas the area designated as "x" is heavily deformed area. By the detailed analysis of dislocation density in the region nearby amorphous state, they obtained the dislocation density of 10^{13} - 10^{14} /cm², which is equivalent to the crystallization energy. Thus they conclude that a major driving force for amorphisation is dislocation accumulation. Furthermore, since the amorphous state appears in the shear band, they suggest that an amorphous state is caused by the shear instability associated with a high dislocation density.

Although the phenomenon is quite interesting, one of the disadvantages upon application is that amorphisation occurs only partially by this method. Ewert et al. [295] studied the amorphisation of Ti–50Ni (TiNi-I) and Ti–50.2Ni–0.6Cu (TiNi-II) alloys by changing strains widely, but obtained amorphous fraction of 30% at maximum at the true strain of 2.0, which corresponds to 86% reduction in the usual expression, as shown in Fig. 74. They also studied the effect of deformation temperature, and obtained the result that the amorphous fraction increases with decreasing temperature. This seems to indicate that amorphisation occurs more easily in martensitic state rather than in the parent phase.

7.4. Origin of high ductility of Ti–Ni alloys as intermetallic compounds

As shown in Figs. 66 and 69, Ti–Ni alloys exhibit very high ductility with elongation more than 50%, despite the fact they are intermetallics. Actually, this is the main reason why Ti-Ni alloys serve as good practical shape memory alloy among many other such alloys. The inquiry to know the origin for such a high ductility may be useful to improve the ductility of other intermetallics as well. Although there are several factors, which affect the ductility of Ti-Ni alloys to be discussed below, one of the important factors lies in the low critical stress, which is as low as less than 150 MPa for a solutiontreated Ti-50.3Ni single crystal [145]. Actually we recall that there was no superelasticity, and only very poor shape memory effect, when single crystal specimens are solution-treated, as we discussed in Section 6.4. Good superelasticity and shape memory effects were realized only by utilizing precipitation hardening or work-hardening followed by proper annealing, as we discuss more in detail in Section 9. We think this low critical stress for slip originates from the low values of elastic constants c' and c_{44} in the alloys, as we remarked in Section 5.3, and the lattice softening in both c' and c_{44} contributes to lower the critical stress near M_s temperature, because the stress necessary to move dislocations (the so-called Peierls stress) is proportional to the rigidity of the alloys [297,298]. In Table 12, we observed that the c_{44} is as low as $1/3 \sim 1/2$ of ordinary intermetallics. The low critical stress for slip is probably also related to the degree of order. As shown in Fig. 2, these alloys exhibit order-disorder transformation at 1090 °C, and thus the parent phase of the alloys are ordered phase rather than intermetallics in a strict sense. This fact may contribute partly to the low critical stress for slip, although the degree of order is yet to be determined experimentally. The low elastic anisotropy as low as 2 (see Fig. 38) is also responsible for high ductility, because it avoids the fracture at grain boundaries due to elastic anisotropy [299].

Various factors, which affect the ductility of the alloys, were investigated by Miyazaki et al. [300,301], and the result on the deformation temperature is shown in Fig. 75. We recognize that the elongation is the maximum at the temperature near M_s , and is higher in the lower temperature range of the martensitic state, and the lowest in the higher temperature range of the parent phase. Although this was shown for



Fig. 75. Temperature dependence of the elongation of Ti-51.0Ni alloy, which was solution-treated at 1273 K for 1 h [301].

solution-treated Ti–51Ni alloy, the tendency was the same for other compositions. This result will be understood in the following way. The elongation is high in the martensitic state, because many twinning modes are available in the martensitic state, as shown in Table 4, in addition to the possible slip mode of $[100](001)_m$. Near the M_s temperature, the stress-induced transformation (theoretically 24 variants are possible) is further available as additional deformation modes, and thus the elongation becomes the maximum in the temperature range. On the contrary, in the parent phase at high temperature, where stress-induced transformation is not possible, only the slip mode by $\langle 100 \rangle \{011\}_p$ and twinning modes $\{114\} \langle 22\bar{1} \rangle_p$ are available, and thus the elongation decreases at high temperatures. The above paper also shows the strong composition dependence with maximum at the equiatomic composition, but we do not discuss it here.

To summarize, the origin of the high ductility of Ti–Ni alloys is twofold; elastic behavior and the use of martensitic transformation. The first is the low value of elastic constants of c' and c_{44} , which leads to low critical stress for slip. The low elastic anisotropy ($A \sim 2$) and the lattice softening toward M_s temperature also contributes to the high ductility. The second is related with the martensitic transformation itself in the following way, with respect to Taylor's condition of available deformation modes. Because of the low symmetry of the martensitic phase more ductile compared to the parent phase. In addition to the twinning modes, many modes of stressinduced transformation (24 h.p.v.'s) make the ductility near M_s the maximum. This guiding principle is actually useful in the practical fabrication of shape memory alloys, because cold-working at temperatures near M_s is most efficient.

8. Effect of composition and Ti₃Ni₄ precipitates on martensitic transformation

As shown in Section 4, martensitic transformation determines almost all important properties of shape memory alloys, including shape memory effect and superelasticity. Transformation temperature determines at what temperature (range) such effect can be observed. This is very important for practical applications [302]. For example, if room-temperature application of superelasticity effect is desired, it is necessary to make the alloy to have subzero transformation temperature; but the transformation temperature cannot be too low; otherwise it is too hard to induce the transformation and the associated large strain. For shape memory applications, the transformation temperature control is often more stringent. In this section, we shall first briefly discuss the alloy chemistry (i.e., site occupancy of alloy elements in TiNi) and then show two ways of changing/controlling transformation temperature, i.e., by composition and by aging treatment.

When adding alloying element or thermomechanical treatment (that introduces precipitates/dislocations), not only the transformation temperature is changed, but also the transformation paths and the transformation product can also be changed. For example, the addition of Fe changes B2-B19' one-stage transformation to B2-R-B19' two-stage transformation, as discussed in preceding sections. In the last part

of this section we shall give a thermodynamic explanation for the effect of alloying elements as well as thermomechanical treatment on transformation paths. Sometimes the intermediate phase like R or B19 martensite show superior properties over conventional martensite B19'. Therefore, this subject is also of much importance.

8.1. Alloy chemistry and site occupancy of alloying elements

As will be seen later, martensitic transformation temperature is strongly dependent on composition and alloying. Then the first question concerning alloying effect is: to which site does a given alloying element go? The answer to this key question is unfortunately still not very clear. At present, it is known that there are several important factors determining the site occupancy of alloying elements.

The first factor is electron configuration of the alloying element. It is natural to consider that alloying element tends to substitute for electronically similar atoms. It can be seen that Zr and Hf have similar electron configuration in the outer shells to Ti, all have a nd^2 configuration at the outer shells. Therefore, it is expected that Zr and Hf will substitute for Ti, rather than Ni. On the other hand, Fe and Co are close to Ni in the periodic table; thus it is expected that Fe and Co will substitute for Ni in Ti–Ni alloys.

Experimental effort to determine the site occupancy of alloying element in Ti–Ni has been made by Nakata et al. [303–305]. They employed "atom location by channeling enhanced microanalysis (ALCHEMI)" method to determine the site preference of alloy element Cr, Mn, Fe, Co, Cu, Pd. They found that Fe, Co and Pd prefer substituting for Ni, while Mn, Cr, and Cu seem to substitute for both Ti and Ni with similar preference. Table 14 [305] shows the occupation fractions of various alloying elements at Ni-site determined experimentally. Three formulas of adding alloying element are shown in the first row of the table as: $Ti_{0.5-c}Ni_{0.5}X_c$, $Ti_{0.5-c/2}Ni_{0.5-c/2}X_c$, $Ti_{0.5-c/2}X_c$. These three formulas give prior preference for the alloying element to go to Ti-site, both sites, and Ni-site, respectively. If a given

anoying formulas, $110.5-c110.5-c/2110.5-c/2110.5-c/21x_c$, $110.5-c/2x_c$, $110.5-cX_c$			
Х	$\mathrm{Ti}_{0.5-c}\mathrm{Ni}_{0.5}\mathrm{X}_{c}$	$Ti_{0.5-c/2}Ni_{0.5-c/2}X_c$	$Ti_{0.5}Ni_{0.5-c}X_c$
Sc	0.01 ± 0.08	-0.08 ± 0.11	0.04 + 0.09
V	0.13 ± 0.10	0.54 ± 0.06	0.78 ± 0.06
Cr	0.51 ± 0.12	0.50 ± 0.11	0.89 ± 0.05
Mn	0.24 ± 0.07	0.55 ± 0.11	0.66 ± 0.09
Fe	0.91 ± 0.08	0.89 ± 0.07	_
Со	1.01 ± 0.06	1.00 ± 0.07	_
Cu	0.34 ± 0.23	0.52 ± 0.18	1.11 ± 0.13
Pd	0.92 ± 0.06	0.94 ± 0.06	0.90 ± 0.08
Au	0.14 ± 0.07	0.55 ± 0.07	0.64 ± 0.06

Experimentally-determined occupancy fractions of various alloying elements on Ni-site for three kinds of alloying formulas, $Ti_{0.5-c}Ni_{0.5}X_c$, $Ti_{0.5-c/2}Ni_{0.5-c/2}X_c$, $Ti_{0.5-c/2}X_c$, $Ti_{0.5-c/2}X_c$

Table 14

These three formulas give prior preference for the alloying element to go to Ti-site, both sites, and Ni-site, respectively [305].

alloying element has strong preference for going to a given site, the occupancy fraction will not be affected by the formula of adding third element; on the other hand, if the preference is not strong the occupancy fraction will be dependent on the formula of adding the third element. From Table 14 Nakata et al. summarized the following:

- (i) Fe, Co and Pd have strong preference for entering into Ni-site, irrespective of the formula of adding alloying element.
- (ii) Sc has strong preference for entering into Ti-site, irrespective of the formula of adding alloying element.
- (iii) V, Cr, Mn, Cu and Au seem to have less preference for a particular site; their occupancy fractions are strongly affected by the formula of adding alloying element. For example, if adding Cu with formula $Ti_{0.5}Ni_{0.5-c}X_c$ (i.e., giving prior preference for entering into Ni-site), from Table 14 we can see that Cu occupies only Ni-site; but if adding Cu with formula $Ti_{0.5-c}Ni_{0.5}X_c$ (i.e., giving prior preference for entering into Ti-site), there is only about 34% Cu entering into Ni-site. This is quite different from the well-accepted postulation that Cu only goes to Ni-site.

The above results imply that although electron configuration play certain role in site preference, other factors may also be important, such as chemical affinity and atomic size effect.

Relative chemical affinity of alloying element to Ti and Ni is another important factor. If an alloying element has strong affinity to Ti (represented by a large negative formation enthalpy) but has only weak affinity to Ni, this element tends to substitute for Ni, as it has similar chemical property as Ni [303]. Co and Fe satisfy this condition and thus substitute for Ni. Besides, atomic size factor is another factor in determining site preference. If other factors are the same, alloying element tends to substitute for species of the similar size.

8.2. Composition dependence of transformation temperatures

Experimentally it is known that martensitic transformation temperature is strongly dependent on composition and alloying elements. In many cases, one percent change in composition can change transformation temperature by more than 100 K. Therefore, the most effective way of changing transformation temperature is by changing composition. In the following, we shall discuss firstly the composition dependence of transformation temperature in binary Ti–Ni alloy and followed by the effect of alloying element on transformation temperature(s) in ternary alloys.

8.2.1. Ni content dependence of M_s temperature in binary Ti–Ni alloys

As stated in preceding sections, binary Ti–Ni alloy is actually not a common disordered alloy; it is an intermetallic compound with B2 order. But it is not a line-compound with a fixed composition. It shows certain solubility of excess Ni on Ni-rich side but cannot dissolve excess Ti. Fig. 2 shows the phase diagram of Ti–Ni. One can



Fig. 76. M_s temperature as a function of Ni content for binary Ti–Ni alloys. Different data symbols represent data from different authors. The solid line is given by thermodynamic calculations (after Tang [306] reproduced with permission of ASM International).

see Ti-rich side is almost vertical but Ni-rich side has some solubility at high temperature (up to about 6 at.% at 1000 °C as discussed previously). Quenching from high temperature (say 1000 °C) can preserve the solid solution to room temperature without precipitation. This makes possible to study the effect of Ni content on martensitic transformation temperature.

Quenched Ti–Ni alloys show one-stage B2–B19' transformation, as discussed in the preceding sections. The transformation temperature is strongly dependent on Ni concentration, as shown in Fig. 76 [306]. On Ti-rich side the transformation temperature is almost composition independent being about 60 °C; this may be due to the fact that the solubility limit of TiNi phase on Ti-rich side is almost vertical and thus it is not possible to get Ti-rich Ti–Ni solid solution. So the Ti-rich alloys show a behavior being the same as Ti–50Ni alloy. On Ni-rich side, increasing Ni causes a drastic decrease in transformation temperature. Martensitic transformation temperature almost drops to 0 K for Ni content exceeding 51.5 at.%, but experimental data show a large scattering.

¹⁷ In systems (like Ti–Ni-based alloys) where both c' and c_{44} play important role, there is a possibility that this condition may not hold. For example, for Ti–Ni–Cu system that has double instability towards B19 and B19' martensite, Fig. 38(c) shows that Ti–40Ni–10Cu and Ti–30Ni–20Cu takes different c' at transformation temperature.

The reason why there is a strong composition dependence of martensitic transformation temperature can be understood in the following way [221]. Prior to martensitic transformation there exist a softening in elastic constant c' with lowering temperature. Experimentally there has been evidence [307–309,72] showing that there is a critical value of elastic constant c' at which transformation occurs; this *crit*ical value seems not sensitive to compositions. ¹⁷ On the other hand, elastic constant c' is dependent on both temperature and composition. For first order transformation softening in c' is only partial, so the temperature dependence of c' is small. On the other hand, elastic constant is strongly dependent on composition in martensitic alloys [170] due to the fact that alloying alters lattice dynamic properties significantly (this can be seen from Fig. 39 where alloying leads to significant change in phonon dispersion curve). In order to keep a constant c' at transformation temperature, a small change in composition (which creates large change in c') must be compensated by a large change in transformation temperature. This explained why there is a strong composition dependence of transformation temperature. For a semi-quantitative treatment of this problem see Ref. [221].

8.2.2. Effect of alloying element on transformation temperature

There has been much effort to modify Ti–Ni shape memory alloys by adding various alloying elements to the binary system. It was found alloying elements often alters transformation temperature greatly. Fig. 77 summarize the effect of third element on transformation temperature reported in the literature [310–314]. It is found that most alloying elements lower transformation temperature; but there are only a few, notably Pd, Pt, Au, Zr and Hf, which increase transformation temperature. Therefore, Ti–Ni–Pd, Ti–Ni–Zr and Ti–Ni–Hf are considered as candidates for high temperature shape memory alloys. See Ref. [315] for a review of high temperature shape memory alloys.

8.2.3. Effect of alloying element on the structure of martensite

Alloying elements not only change transformation temperature, but also often change the product of the transformation or the transformation route. A typical example is that Ti–Ni undergoes a direct B2–B19' transformation; but with the addition of Fe, Ti–Ni–Fe alloy shows a two-stage transformation B2–R–B19' [316], as shown in Fig. 78. It can be seen that with increasing Fe content, B2–R transformation becomes more and more separated from the R–B19' transformation. This feature enables a characterization of R-phase over wide temperature range without being interrupted by the second transformation R–B19'.

Another important system is Ti–Ni–Cu. As having been explained in detail in Section 6.4.3, addition of Cu makes the transformation temperature much less sensitive to composition change, as shown in Fig. 8. This makes the control of shape memory properties easier. Another good feature of adding Cu is that the transformation temperature is relatively high (above room temperature); this makes possible to realize shape memory effect around room temperature. Addition of Cu exceeding 5 at.% can change the transformation route into B2–B19–



Fig. 77. The effect of alloying element Fe, Pd, Pt, Hf, Co, V, Mn Au, Zr, Al and Cr on martensitic transformation temperature of Ti–Ni system: (a) wide alloying range, (b) narrow alloying range (low alloying level). The data were compiled from the data in references indicated in the figure.

B19'. B2–B19 transformation is associated with a small transformation hysteresis (about 4 K at 20 at.%Cu), which is similar to B2–R transformation, and being



Fig. 78. Effect of Fe addition on the martensitic transformation temperature and transformation paths. I, II and III regime represents parent B2 phase, R phase and B19' martensite, respectively (after Honma et al. [316] reproduced with permission of TMS).

much smaller than that for B2–B19' transformation (about 30 K). The above good features make Ti–Ni–Cu alloy an important candidate for shape memory applications.

Addition of Pd to substitute for Ni in Ti–Ni alloy leads to an initial decrease of transformation temperature with increasing Pd content; but at higher Pd concentrations, transformation temperature increases with increasing Pd [317]. At the same time, the transformation changes into B2–B19 instead of B2–B19'. The ternary Ti–Ni–Pd as well as the terminal Ti–Pd systems has been studied as high temperature shape memory alloys [315].

8.3. Control of transformation temperatures by aging treatment

In the above, we have seen that transformation temperature is very sensitive to composition. This high composition sensitivity of the transformation temperature is undesirable in most cases, since it simply means that very precise composition control of the alloy is necessary in order to get desired transformation temperature or properties. This is technically difficult in most cases. It is ideal to have an alloy system whose transformation temperature is insensitive to composition; or even the better, to have a way to adjust transformation temperature after the alloy has been produced.

There is a very good way to adjust the transformation temperature of Ti–Ni alloys for Ni-rich alloys even after the alloys have been made. It was first found by Horikawa et al. [322] although the underlying mechanism was not clear at that time. They reported that there is an alternating change in transformation temperatures (R_s and M_s) when Ni-rich Ti–Ni alloy is alternatively aged between two aging temperatures, and the transformation temperature seems to be controlled by aging temperature alone, essentially independent of the number of cycles. They also confirmed that



Fig. 79. Transformation temperatures as a function of the number of alternate aging cycles between 713 K and 823 K for Ti–51Ni alloy. The aging time at 713 K is fixed to be 86.4 ks, while those at 823 K are (a) 0.6 ks, (b) 3.6 ks, (c) 86.4 ks and (d) 172 ks, respectively [318].

equiatomic Ti–Ni does not show this behavior. This work provides a new way to finely tune the transformation temperature just by changing aging temperature. But the reason for such an interesting behavior was unclear. Recently Zhang et al.'s work [318,319] clarified the origin of this phenomenon. They systematically investigated the alternating aging phenomenon and found that the phenomenon seem essentially independent of the aging time at each temperature, as shown in Fig. 79. They realized that such a behavior stems from the equilibrium between TiNi phase and Ti₃Ni₄, as illustrated in Fig. 80. Alternating aging between two aging temperatures causes an alternating change in B2 matrix composition. Such an alternating change in B2 composition naturally causes an alternating change in R_s and M_s temperature. But M_s



Fig. 80. Schematic of the origin of the reversible change in transformation temperatures, which is based on the equilibrium between TiNi matrix and $T_{i_3}N_{i_4}$ precipitate. Higher aging temperature causes higher Ni content in the TiNi matrix and consequently leads to lower transformation temperatures; lower aging temperature produces a TiNi matrix of lower Ni content and consequently leads to higher transformation temperatures [318].

show some cycle dependence, since M_s is also dependent on the size and density of Ti_3Ni_4 precipitates, which are dependent on the number of cycles.

Therefore, the key idea in the above is to use the precipitation reaction of the quenched supersaturated Ti–Ni solid solution to finely adjust the composition of the Ti–Ni matrix and hence give a precise control of transformation temperature [319]. The principle behind this method is the (metastable)-equilibrium between TiNi and Ti₃Ni₄ precipitates. Although Ti₃Ni₄ is considered as a metastable phase compared with the equilibrium TiNi₃ precipitate, it is quite stable at temperature below 600 °C and under normal aging condition only Ti₃Ni₄ is observed. Therefore, it is important to establish a phase diagram between TiNi and Ti₃Ni₄. Fig. 81 shows a primitive form of this phase diagram [319]. One will note from this diagram that when precipitation reaction occurs, formation of Ti₃Ni₄ precipitates is accompanied by a decrease in Ni content of the TiNi matrix; as the result R_s and M_s temperature

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Fig. 81. Preliminary phase diagram between TiNi (B2) phase and metastable Ti₃Ni₄ precipitate. Phase equilibrium between TiNi (B2) and TiNi₃ is also shown (after Zhang [319]).



Fig. 82. Effect of aging time on R_s and M_s temperatures of two Ni-rich Ti–Ni alloys, Ti–51Ni and Ti– 52.6Ni. It is noted that at given aging temperature R_s is almost independent of aging time and the composition. M_s is dependent on aging time and composition at short aging time, but gradually reaches a constant value after long aging time, being independent of aging time and composition [320].

will increase with aging time until finally reach a constant value that corresponds to the equilibrium composition at that temperature. Most importantly, this "saturated" transformation temperature after long aging is independent of alloy composition, and dependent only on aging temperature. This is a natural result of the equilibrium between the two phases.

Fig. 82 shows the aging time dependence of R_s and M_s for two Ti–Ni alloys with 51Ni and 52.6Ni, respectively [320]. The first striking feature is that after long-time aging, $R_{\rm s}$ and $M_{\rm s}$ become constant, being independent of alloying composition. This provides a powerful way of precisely controlling transformation temperature solely by aging treatment without being affected by alloying composition. In other words, it is possible to use aging treatment to rectify the transformation temperature due to incorrect initial composition. This important method is the direct result of the phase equilibrium between TiNi and Ti₃Ni₄. Secondly it is found that R_s is almost constant from very short aging time (1 h). This suggests that the TiNi matrix reaches equilibrium very rapidly. But M_s show gradual increase before reaching the saturation value. This aging time dependence comes from the evolution of the density and size of Ti₃Ni₄. Ti₃Ni₄ provides a strong resistance to transformations associated with large deformation like R-B19' but much less to transformations associated with small deformation like B2–R. As the result, B2–R transformation is insensitive to the density and size of the precipitates, and depends mainly on the composition of TiNi matrix. This is why B2-R transformation shows very weak aging time dependence. On the other hand, for R-B19' transformation, which involves a large deformation, the resistance to the transformation is large when there is a high density of Ti_3Ni_4 particles and becomes less when the density of the particles is low. This explains why there is a gradual increase with aging time for R-B19' transformation. Aging temperature dependence of R_s is shown in Fig. 83 [321]. This is an important figure for precisely control transformation temperature by choosing suitable aging temperature. It can be seen that higher aging temperature leads to lower transformation



Fig. 83. Effect of aging temperature on R_s temperature, which is almost independent of aging time (when aging temperature is above 573 K). This curve is also independent of alloy composition. This is due to the phase equilibrium between TiNi (B2) matrix and Ti₃Ni₄ precipitates, which results in a decrease in Nicontent of the B2 matrix (hence an increase in R_s temperature) as aging temperature lowers (after Zhou [321]).

temperature. This can be easily understood from the change in Ni content in B2 matrix with aging temperature.

Aging effect was also found in ternary Ti–Ni–Cu alloys with Ti-poor compositions (less than 50 at.%) [323,324]. In such a case, a new kind of precipitate Ti(Ni-Cu)₂ with tetragonal Cl1_b(MoSi₂)-type structure was found [323]. During the precipitation of such particles by aging treatment, it was found that martensitic transformation temperature increases to some extent.

From the above, we note that although we use *diffusionless* martensitic transformation to realize the functionality of Ti–Ni shape memory alloys, the control of such behavior is by a *diffusional* precipitation reaction. This is in much analogy to many other important alloy systems like Fe–C and Al–Cu etc. in which similar aging reaction is used to control the mechanical properties of these structural materials.

8.4. Thermodynamic explanation of different paths of martensitic transformation

8.4.1. A general rule for the sequence of multi-stage martensitic transformation

From the above one can find alloying addition or aging not only changes transformation temperature, but also transformation paths and products. Section 9 will show that introducing dislocations through thermomechanical treatment also has the same effect. Thus it is of fundamental interest why this can happen.

Experimentally it has been found that addition of Fe will change the transformation into B2–R–B19', and addition of Cu will change the transformation into B2– B19–B19'. But there has been no report of a "reverse order" in the transformation sequence, such as a "B2–B19'–R transformation". This fact indicates there is a certain rule for the possible or impossible sequence of multi-stage transformation. The general rule governing the possible sequence of multi-stage transformation is proposed by Ren et al. [72]. This rule will lay a basis for understanding why and how transformation path can be changed by various factors. As this is important for explaining the effect of alloying and thermomechanical treatment on martensitic transformation, we give a detailed deduction of this rule.

Consider the Landau free energy of a martensitic alloy undergoing first order transformation with no external stress. The simplest generic form of Landau free energy for first order transformation can be written as an appropriate 2–4–6 potential [162] (as explained in Section 5)

$$F = a(T - T^*)\eta^2 - b\eta^4 + c\eta^6,$$
(22)

where η is the order parameter, usually taken as a characteristic lattice distortion; *a* (>0), *b* (>0), *c* (>0) are coefficients not very sensitive to temperature, but dependent on composition. *T** is the harmonic instability temperature, as explained in the previous sections. For first order transformation, transformation occurs always above this temperature [222,223].

By simple manipulation it is easy to find the entropy change associated with martensitic transformation is

$$\Delta S = -a\eta_{\rm M}^2,\tag{35}$$

where η_{M} is the lattice distortion (or transformation strain) at transformation temperature.

The minus sign of Eq. (35) clearly shows that martensitic transformation always leads to entropy decrease. Eq. (35) also leads to an important conclusion: *the magnitude of entropy change associated with martensitic transformation is proportional to the square of lattice distortion (or transformation strain)*, i.e., the larger the transformation strain the larger the entropy change is. Strictly speaking, the quantitative relations of Eq. (22) and Eq. (35) depend on the exact symmetry of martensite; nevertheless, the major contribution to entropy comes from harmonic energy, which is related to the square of strain (plus some other terms), therefore we can expect that the qualitative conclusion holds for all the cases. Indeed, it is also a clear manifestation of a well-known fact: transformation heat (which is proportional to entropy change) decreases with decreasing transformation strain, and vanishes for second order transformation where transformation strain becomes zero. Therefore, transformation entropy is mainly determined by transformation strain.

If we roughly approximate free energy vs. T relation for the parent phase as a straight line F = U - TS, entropy S is the slope of this line. Then it follows that entropy change ΔS on martensitic transformation means the slope difference between the free energy lines of martensite and parent phase. The smaller ΔS the closer is the martensite free energy line to that of the parent phase. Consequently, if knowing ΔS we can deduce the slope of free energy of martensite relative to that of the parent phase.

As shown in Section 5, there may exist several possible candidates of martensite in a given alloy system, being determined by lattice dynamics. Now let us show that there exists a general rule for the sequence of these candidates to appear. We take Ti–Ni-based alloys as an example; but the conclusion applies to all martensitic systems because only transformation strain is of relevance.

In Ti–Ni-based alloys, there exist three possible martensite candidates, R, B19, and B19', as discussed above. The transformation strain for R-phase is very small (~1%), next is the B19 (~8%), B19' is the largest (~10%). From Eq. (35) we can deduce that $|\Delta S_{B19'}| > |\Delta S_{B19}| > |\Delta S_R|$. Since the entropy change means slope change of martensite (including R-phase) relative to that of the parent phase in free energy vs. temperature line, we can deduce that R-phase line makes the smallest angle from the B2 line, next is the B19 line, while B19' line makes the largest angle, as shown in Fig. 84. Depending on the relative stability of these three candidates, it is possible to have three situations, as shown in Fig. 84(a)–(c).

The first case is shown in Fig. 84(a), where B19' is more stable than the other two candidates, R and B19. Due to the large angle of the B19' line from B2 line (or smaller temperature dependence), which stems from the large entropy change, there is no chance for other two phases to appear below the transformation temperature M_s (B19'). Then there appears a single transformation B2–B19' at M_s (B19').

The second case is shown in Fig. 84(b), where B19' line is moved up (unstable); then R-phase appears first at R_s temperature. However, due to the small angle between R line and B2 line (due to the small entropy change), R line is above B19' line



Fig. 84. Schematic of the three possible transformation paths of Ti–Ni-based alloys in relation to the relative stability of three competing martensite candidates, R, B19 and B19', with respect to B2 parent phase. (a) B2–B19' one-stage transformation, (b) B2–R–B19' two-stage transformation, and (c) B2–B19–B19' two-stage transformation. The dotted lines indicate martensite(s) that is unstable at any temperature [72].

below a temperature M_s (B19'), then R-phase transforms into B19' to further lower free energy. This results in a two-stage transformation B2–R–B19'.

The third case is shown in Fig. 84(c), where B19' line is moved up (unstable) but B19 line is move down (stable). Then B2–B19 transformation occurs first at M_s (B19). However, due to the smaller angle between B19 line and B2 line (due to small entropy change), B19 becomes unstable relative to B19' below M_s (B19'). Then this situation results in another two-stage transformation B2–B19–B19'.

From Fig. 84, we can draw an important general conclusion: the necessary condition for an intermediate martensite to appear before the formation of final product is that the intermediate phase must have smaller transformation strain (or smaller entropy change during transformation) than the final product, or in other words, the intermediate martensitic transformation must be more weakly first order transformation than the final transformation. We can summarize this important conclusion in a simple statement: *multi-stage martensitic transformation occurs in the sequence of increasing transformation strain.* Considering the relationship between transformation strain and entropy change shown in Eq. (35), we can restate this conclusion in an equivalent form: *multi-stage transformation occurs in the sequence of increasing transformation entropy.*

The above conclusion holds for all martensitic alloys. In Ti–Ni-based alloys, the intermediate R-phase or B19 phase has smaller transformation strain than the final product B19'. In Ni–Mn–Ga alloys, an intermediate phase (often called premartensitic phase) with very small transformation strain (as evidenced by very small transformation hysteresis) appears before transforming into the final martensite [325]. Equivalently, if considering entropy one can also find that in Ti–Ni(Fe) system the entropy change associated with B2–R transformation [108,326] is smaller than that with B2–B19' transformation [327]; in Ni–Mn–Ga alloys the first-stage (premartensitic) transformation has smaller entropy change than the second (martensitic) transformation, as evidenced by the difference in transformation heat production [325].

8.4.2. Effect of alloying and precipitation/dislocation-network on transformation path

Based on the above sequence rule for multi-stage transformation, it is easy to understand why alloying and thermomechanical treatment changes the transformation path by considering their effect on relative stability of three martensite candidates, R, B19 and B19'. For quenched Ti–Ni alloys, the free energy of three candidates can be schematically illustrated in Fig. 84(a). Due to the high stability of B19', there occurs only one stage transformation B2–B19'. In the following, we shall show how alloying or other factors alter this basic transformation pattern.

We first consider why Fe addition can induce an intermediate R phase. From elastic constants of Ti–Ni–Fe alloy shown in Fig. 38, we can find that Fe addition increases c_{44} appreciably. Since c_{44} is crucial for B19' formation, the hardening of c_{44} indicates that B19' is more unstable, thus the B19' line in Fig. 84(b) moves up compared with binary alloys in Fig. 84(a). The result of such a change is shown in Fig. 84(b), the B2 parent phase first transforms into R-phase at R_s and followed by a second transformation to B19' at M_s (B19'). Therefore, Fe addition changes the transformation path from B2–B19' into B2–R–B19'.

Following the same reasoning, we can easily understand a long-standing puzzle as to why introduction of fine precipitates Ti_3Ni_4 (by aging) or introduction of dislocation network by deformation/transformation-cycling can change the transformation path from B2–B19' into B2–R–B19'. Elastic constant measurement [72] showed that there is little change in either *c'* or in *c*₄₄ for aged Ti–Ni alloys (i.e., with fine Ti₃Ni₄ particles) compared with the quenched counterparts. This indicates that the intrinsic stability of R or B19' does not change with aging. Therefore, it seems that there is no reason for a change in transformation path. However, the precipitation of fine particles induces additional energy to affect the relative stability of R and B19', that is, the coherency strain energy associated with the lattice distortion during martensitic transformation. It is this additional energy that changes transformation path as discussed in the following.

During martensitic transformation B2 lattice is distorted into martensite lattice. However, the Ti₃Ni₄ precipitates do not transform; thus they do not follow such a shape change. Then strain energy is engendered, which is apparently proportion to the square of transformation strain, $E = K\eta_M^2$, where K is related to elastic constants and distribution density of the particles. It is noted that the transformation strain for R-phase is one order of magnitude lower than that for B19' martensite, as mentioned above; therefore, the energy increase for R-phase is about two order of magnitude smaller than for the B19' martensite; thus R-phase transformation is almost insusceptible to particles while B19' transformation is highly susceptible to particles. Fig. 80 showed that increase in aging time (which lowers the density of the particles) has no effect on R_s temperature, but has quite a strong influence on B19' transformation temperature. This result can be viewed as clear experimental evidence supporting this conclusion. Due to the large additional strain energy for the B19' transformation caused by particles, the B19' line is moved up (Fig. 84(b)) compared with that in quenched counterpart (without particles) (Fig. 84(a)). By contrast, R free energy line shows little change due to the small effect of particles on this transformation. Then naturally we can find R-phase forms first and followed by the B19' transformation as shown in Fig. 84(b).

The effect of dislocation network on transformation path can be understood in the same way. High density of dislocations acts as a resistance to lattice distortion (martensitic transformation), similar to the precipitates. The resistance is much larger for transformation involving large lattice distortion like B19' transformation, while the effect becomes very small for transformation involving small lattice distortion like R-transformation. Then the B19' line is significantly increased but R line remains essentially the same as shown in Fig. 84(b); this is very similar to the case of precipitations discussed above. Therefore, introduction of dislocations by deformation or by transformation cycling gives the same consequence as the introduction of fine precipitates: the transformation path changes from B2–B19' into B2–R–B19'.

Now we discuss the effect of Cu on transformation path. From Fig. 38 we can see that Cu addition increases c_{44} significantly. This suggests that Cu addition destabilize B19'; thus B19' line in Fig. 84(c) moves up. Phonon dispersion curve for Ti–30Ni–20Cu alloy (Fig. 39) suggested that 1/3 TA₂ dip does not exist in this alloy, while there is a strong softening in 1/2 TA₂ mode. Therefore, Cu addition increases R-phase energy but decreases B19 energy (which corresponds to 1/2 TA₂ mode), as shown in Fig. 84(c). Due to the increase in B19' energy and decrease in B19 energy (Fig. 84(c)) the Ti–Ni–Cu system undergoes B2–B19–B19' transformation.

From the above discussion, we can clearly see that there is a thermodynamic requirement that intermediate martensite phase must have smaller transformation strain than the final product. However, whether or not the intermediate phase appears or which intermediate phase is realized depends on competition in both intrinsic and extrinsic energies. The intrinsic energy is governed by lattice dynamics (phonon softening and elastic softening), while the extrinsic energies arise from resistance to lattice distortion (i.e., transformation) by precipitates or dislocations. With this basic principle all facts about the effect of alloying and the precipitation/dislocation-network can be easily understood.

9. Effects of thermomechanical treatment on shape memory characteristics and some strange aging effect

Although the main theme of the present review is the martensitic transformation and the associated shape memory behaviors in Ti–Ni-based alloys, we have seen already in Section 8 that a diffusional transformation can be successfully utilized to control the transformation temperatures of the shape memory alloys. In this section we will see that diffusional transformations and/or thermomechanical treatments are also very useful to improve shape memory characteristics. We will also discuss a current controversial problem, which is called "abnormal 3-stage transformation" in Ni-rich Ti–Ni alloys, which is related with inhomogeneous precipitation of Ti₃Ni₄ phase upon aging. Readers will encounter another important case of precipitation in Ti-rich Ti–Ni alloys in thin films in Section 10. Thus readers will see that not only martensitic transformations but also diffusional transformations and/or thermomechanical treatments are important in order to fully utilize Ti–Ni-based shape memory alloys from the viewpoint of physical metallurgy.

9.1. Effects of thermomechanical treatment on shape memory and superelastic characteristics

As we discussed in Section 6.3, thermoelastic transformation exhibits crystallographically reversible transformation. Thus shape memory and superelastic effects are expected in thermoelastic alloys. On the other hand, plastic deformation such as slip or deformation twinning (such as $\{20\bar{1}\}_m$ twinning in B19' martensite) are irreversible, and such strains cannot be restored even upon heating. Thus it is most important to increase the critical stress for slip in order for shape memory alloys to realize good shape memory and superelastic characteristics. In order to achieve a high critical stress for slip, four methods are known in physical metallurgy; i.e. work-hardening, precipitation hardening, alloy-hardening, and grain refinement. Historically there were some preliminary investigations on the effect of thermomechanical treatment on improvement of shape memory characteristics such as in Refs. [328–334]. However, a systematic investigation based on the above principle was initiated by Miyazaki et al. [332], as will be described below. The increase of the critical stress is especially important for Ti-Ni alloys, because slip is so easily introduced in Ti-Ni alloys, as was pointed out in Section 6. In the following, we will discuss the effects of work-hardening and precipitation-hardening, but not of alloy-hardening, because practical use of shape memory alloys is also related with the transformation temperatures. The effect of grain refinement is treated in Section 7.3 and in Section 10. Although thermomechanical treatments affect not only B2-B19' and R-B19' transformations but also B2-R transformation, we will discuss only the former two transformations, which are associated with large strains, the effect being larger, and we will not discuss the latter in the following, because it was already treated in Section 6.4.2.



Fig. 85. Effect of thermomechanical treatment on the stress–strain curves as a function of deformation temperature for Ti–49.8Ni alloy. (a) Solution-treatment at 1273 K for 1 h followed by annealing at 673 K for 1 h. (b) annealed at 673 K for 1 h immediately after cold-working [332].

9.1.1. Effect of cold-working followed by annealing on shape memory and superelastic behavior

Fig. 85(a) shows a series of S–S curves for solution-treated Ti–49.8Ni wire. Strictly speaking, the specimen was annealed at 673 K after solution-treatment, but it is essentially the same as solution-treated one, because there is no aging effect due to precipitation in this composition. The dashed lines below the horizontal lines represents the strain recovered by heating the specimen above A_f temperature. Thus the difference between the recovered strain and origin represents a permanent strain. The tensile tests were carried out for the same specimen successively from low temperatures to higher temperatures. Thus the permanent strains are accumulated from low temperatures to higher temperatures. From the figure we cannot see superelasticity in any temperature region, because slip is easily introduced in solution-treated condition.

On the contrary, Fig. 85(b) represents a series of S–S curves for the wire with the same composition, which was heavily cold-drawn and annealed at 673 K for 1 h without solution-treatment. Now, we see very good superelasticity as well as shape memory effect, and no plastic strains are practically observed. By plotting the yield stress upon loading ($\sigma_{\rm M}$), and the critical stress upon unloading ($\sigma_{\rm R}$), we obtain Fig. 86. We see from the figure that the best superelasticity and shape memory character-



Fig. 86. Effect of annealing temperature on the critical stresses for inducing martensites ($\sigma_{\rm M}$) and for reverse transformation ($\sigma_{\rm R}$) in Ti–49.8Ni alloy specimens, which were annealed at each temperature without prior solution-treatment after cold-working [332].

istics are obtained, when the specimen is annealed at 673 K right after cold-working. The reason for the above behaviors are easily understood by the TEM observations in Fig. 87, and the associated electron diffraction patterns in Fig. 88. Although the TEM observations were done for plate specimens, since wires were too thin ($\phi 0.4$ mm) as TEM specimens, they were treated similarly. Fig. 87(a) represents an electron micrograph in as cold-rolled state, which contains high density of tangled dislocations, and the corresponding diffraction pattern in Fig. 88(a') exhibits diffuse spots with arcs, which represent the presence of strains due to high density of dislocations. Fig. 87(b) taken from a specimen annealed at 673 K after cold-rolling, still shows the presence of rearranged dislocations, but the corresponding diffraction pattern in Fig. 88(b') shows sharp round diffraction spots. Thus we know that the specimen is in recovered but un-recrystallized state. Thus we know that the specimen in this condition exhibits a smooth martensitic transformation upon cooling and heating, but still hold high strength by the presence of rearranged dislocations. Fig. 87(c) represents a micrograph of a specimen annealed at 773 K after cold-working, which clearly shows that the specimen is recrystallized. The recrystallization is also confirmed by the corresponding diffraction pattern in Fig. 88(c'), which is characterized by the presence of various grains in different orientations. We can identify the difference in the microstructures between those annealed at 673 K and at 773 K in the mechanical behaviors in Fig. 86. Those annealed at 673 K exhibit much superior superelastic behavior compared to those annealed at 773 K. Fig. 87(d) shows the micrograph of a specimen annealed at 873 K, which exhibits the rapid growth of grains by recrystallization, and the corresponding diffraction pattern in Fig. 88(d') shows a single crystal diffraction pattern, since the selected area for diffraction was a part of the large grain. This explains why the mechanical behavior in solution-treated specimens are so worse in Figs. 85(a) and 86.



Fig. 87. TEM micrographs of Ti-49.8Ni alloy, which were annealed for 1 h at various temperatures indicated after cold-working; (a) as cold-worked, (b) at 673 K, (c) at 773 K and (d) at 873 K [333].

9.1.2. Effect of age-hardening on shape memory and superelastic behaviors

Age-hardening by the precipitation of Ti_3Ni_4 phase also affects shape memory effect and superelasticity greatly [332,334]. In this case the data for solution-treated one for the same specimen is not available unfortunately, and thus we compare two cases for those aged at 573 K and 673 K for 1 h, respectively. Fig. 89 shows a series of S–S curves of Ti–50.6Ni wire, which was solution-treated at 1273 K followed by aging at 773 K. We observe that although superelasticity is available, it is in a very narrow temperature range. Shape memory effect is also observed but not in a



Fig. 88. Electron diffraction patterns corresponding to each of Fig. 87; (a') as cold-worked, (b') at 673K, (c') 773 K and (d') 873 K [333].

perfect manner. Some permanent strains are introduced in figures from (h) to (m). On the contrary, the result is shown in Fig. 90, when the specimen is aged at 673 K for 1 h after solution-treatment. We now see very good superelasticity and shape memory effect. By plotting the yield stress upon loading (σ_M) and the critical stress upon unloading (σ_R), we obtain the result shown in Fig. 91, which also contains the results for that aged at 573 K for 1 h. From this figure we can see easily that the one aged at 673 K gives the best shape memory and superelastic characteristics, because



Fig. 89. Stress-strain curves as a function of deformation temperature of Ti-50.6Ni alloy, which was aged at 773 K for 1 h after solution-treatment at 1273 K for 1 h (after Asai [335]).

it gives the recoverable strain up to the highest stress level, which is recognized by the deviation from the linear stress-strain relationship (i.e. Clausius-Clapeyron relationship), as was discussed in Section 6.4. Besides it exhibits superelasticity in a wide temperature range. These behaviors are easily understood from the physical metallurgy principle that the effect for increasing critical stress for slip is most effective, when high-density small precipitates are available. This is easily understood from the TEM observations in Fig. 92. When aging temperature is higher than 873 K, no precipitates appear for the composition of Ti-50.6Ni (Fig. 92(c)). When the aging is conducted at 773 K for 1 h, the precipitates are larger and the density is low (Fig. 92(b)). Thus the effect of aging on shape memory and superelasticity characteristics will be low, as was shown for Figs. 89 and 91. On the contrary, the precipitation at 673 K for 1 h occurs with very high density with very small size (Fig. 92(a)). Thus the shape memory and superelasticity characteristics in Figs. 90 and 91 are rationalized. For the case of aging at 573 K, TEM observation was not carried out, but in this case the transformation is suppressed to lower temperature side, and the shape memory and superelastic characteristics is worse than the previous case (see Fig. 91).

9.1.3. Combined effects of cold-working and aging on shape memory and superelastic behaviors

Combined use of work-hardening and age-hardening is more effective to increase the critical stress for slip. This is shown in Fig. 93, in which cold-worked Ti–50.6Ni wire is aged at 673 K without solution-treatment. If we compare the data in Fig. 90 and those in Fig. 93, we see that complete superelasticity is available at higher stress



Fig. 90. Stress-strain curves as a function of deformation temperature of Ti-50.6Ni alloy, which was aged at 673 K for 1 h after solution-treatment at 1273 K for 1 h [336].



Fig. 91. Effect of aging temperature on the critical stresses for inducing martensites (σ_M) and for reverse transformation (σ_R) in a Ti–50.6Ni alloy, which was aged at various temperatures for 1 h after solution-treatment [332].

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Fig. 92. TEM micrographs and corresponding diffraction patterns of Ti–50.6Ni alloy specimens, which was aged at various temperatures after solution-treatment at 1273 K for 1 h; (a and a') at 673 K, (b and b') at 773 K and (c and c') at 873 K [333].

level in the latter. Besides, combined use of work-hardening and age-hardening is especially useful for increasing stability of superelastic curves [337]. Furthermore, we can point out another advantage of the combined use, because we can omit one heat-treatment of solution-treatment in that case, which is quite advantageous economically in practical productions.

9.2. Strange multi-stage transformation in aged Ni-rich Ti–Ni alloys

As discussed in previous sections, in Ni-rich alloys aging creates finely dispersed Ti_3Ni_4 precipitates in B2 matrix. In systems with Ti_3Ni_4 particles it has been known



Fig. 93. Stress-strain curves as a function of deformation temperature of Ti-50.6Ni alloy, which was aged at 673 K immediately after cold-working [336].

that 2-stage transformation B2–R–B19' occurs instead of 1-stage B2–B19' transformation for quenched sample (without Ti_3Ni_4 particles). The reason why there is a change from 1-stage transformation to 2-stage transformation is that fine precipitates have strong resistance to transformation with large transformation strain like B2–B19', but has much less resistance to transformation with small transformation strain like B2–R. Considering R phase is another martensite candidate of the Ti–Ni system and B19' is the ground state of the system at low temperature, we can understand that there is a B2–R–B19' 2-stage transformation in the presence of fine precipitates. This has been discussed in detailed in Section 8.4. This behavior is known as the normal 2-stage transformation behavior.

However, it has been frequently observed in some aged Ni-rich Ti–Ni alloys, there are sometimes three DSC peaks [338–341] during cooling. No new kind of martensite was detected by diffraction studies [341,342]. It is unclear why two kinds of transformations (B2–R–B19') can result in three DSC peaks.

This abnormal 3-stage transformation behavior has attracted much interest in recently years. Several very different explanations have been given based on different experimental observations as follows:

(1) Local stress inhomogeneity around Ti₃Ni₄ particles

Bataillard et al. [339,342] suggested that 3-stage transformation stems from an inhomogeneous stress distribution in the B2 matrix around Ti_3Ni_4 particles. Such stress inhomogeneity arises from the coherency between the precipitates and B2 matrix. They proposed that in such a stress-inhomogeneous system R-phase transformation occurs in one step but R–B19' transformation occurs in two steps, corresponding to the high stress region (near precipitate) and low stress region (away from precipitate), respectively. Apparently, this mechanism is based on small-scale stress inhomogeneity around Ti_3Ni_4 particles and thus it follows that 3-stage transformation should also occur even in single crystal of Ti–Ni.

(2) Local composition inhomogeneity around Ti_3Ni_4 particles

Allafi et al. [343] performed a systematic investigation of the evolution of transformation behavior with aging temperature and time by means of DSC measurement. They proposed that 3-stage transformation is due to the composition inhomogeneity in matrix B2 phase between Ti_3Ni_4 particles. Such composition inhomogeneity is a result of the kinetics of precipitation process out of a supersaturated solid solution. They suggested that the Ti–Ni system with composition inhomogeneity between Ti_3Ni_4 particles would create one B2–R transformation and two R–B19' transformation, the latter corresponding to the transformation at low Ni region (near Ti_3Ni_4) and high Ni region (away from Ti_3Ni_4), respectively. Apparently, this mechanism is also based on small-scale (chemical) inhomogeneity between Ti_3Ni_4 particles; it suggests 3-stage transformation should also occur in Ti–Ni single crystals.

(3) Large scale inhomogeneity between grain boundary region and grain interior

Allafi et al. [344] and Dlouhy et al. [345] studied microstructures of Ni-rich Ti–Ni alloys after aging treatment and found that precipitation of small lenticular Ti_3Ni_4 precipitates occurs preferentially at grain boundaries. The major part of the grain interior is free of precipitates. They suggested from their in situ TEM observation that the first DSC peak corresponds to the formation of R-phase at grain boundary regions containing precipitates and the second DSC peak corresponds to the formation of B19' in the same regions, the third distinct peak corresponds to B2–B19' transformation in precipitate-free grain interior regions. This mechanism points out the importance of large-scale inhomogeneity in precipitation between grain boundary and interior.

All the above explanations imply that 3-stage transformation is the normal case rather than special case, as the inhomogeneity (due to stress distribution, composition inhomogeneity and grain boundary effect) required by the above mechanisms is always present. But as a matter of fact, the majority of the reported DSC curves show normal 2-stage transformation (B2–R–B19'), rather than the 3-stage transformation. Therefore, the above mechanisms cannot explain why 3-stage transforma-



Fig. 94. DSC curves for Ti–50.6Ni single crystals: (a) solution-treated at 1273 K for 1 h followed by water quenching, (b)–(f) aged at 723 K for 1, 10, 24, 73, 150 h, respectively, after solution-treated at 1273 K for 1 h [347].

tion does not occur all the time. Furthermore, it was recently found that the appearance of 3-stage transformation depends on heat-treatment atmosphere [346]. Normal 2-stage rather than 3-stage transformation occurs when the specimens are protected from oxidation by Ti and Zr getter during solution-treatment. This result is also difficult to explain by these mechanisms.

Very recently, by a comparative investigation of the behaviors of single crystals and the corresponding polycrystals Fan et al. [347] provided a simple explanation for this puzzling phenomenon. Figs. 94 and Fig. 95 show, respectively, DSC curves for Ti–50.6Ni single crystal and polycrystals. It is clear that single crystal does not show 3-peak behavior while polycrystal shows 3-peak behavior. This seems to suggest that grain boundary play a central role for this behavior, as proposed by Allafi et al. [344]. Further study found that single crystal of different composition also exhibit normal 2-stage transformation, being consistent with the above reasoning. However, DSC result of high Ni polycrystalline alloy (51.5Ni) shows normal 2-stage transformation. This cannot simply be understood with the grain boundary argument.

TEM observation of those polycrystalline samples showing normal 2-stage transformation and those showing abnormal 3-stage transformation revealed remarkable difference in the distribution of Ti_3Ni_4 particles. Fig. 96 shows the distribution of Ti_3Ni_4 particles for (a) polycrystal of 50.6Ni and (b) polycrystal of 51.5Ni. The low-Ni 50.6Ni alloy, which shows 3-stage transformation, reveals that Ti_3Ni_4 parti-



Fig. 95. DSC curves for Ti–50.6Ni artificial polycrystals: (a) solution-treated at 1273 K for 1 h followed by water quenching, (b)–(f) aged at 723 K for 1, 11, 24, 73, 150 h after solution-treated at 1273 K for 1 h [347].

cles form preferentially around grain boundary and much less in grain interior; but in the high-Ni 51.5Ni alloy, which show normal 2-stage transformation, a large number of small Ti_3Ni_4 particles were evenly distributed across the sample and they do not show preference at the grain boundary.

Therefore, it becomes clear that the presence of grain boundary is a necessary condition for 3-peak behavior, but it is not a sufficient condition. The transformation behavior is dependent on how Ti_3Ni_4 particles are distributed between grain boundary and grain interior. Then the central question is: "what determines a homogeneous or heterogeneous distribution of Ti_3Ni_4 precipitates in polycrystals?" The answer to this question will naturally explain the origin of the 3-stage transformation.

Fan et al. [347] showed that the key to understanding all the above facts lies in the nucleation kinetics of Ti₃Ni₄ particles in polycrystalline Ti–Ni alloys. In Ni-rich (supersaturated) Ti–Ni alloys, Ti₃Ni₄ precipitates in B2 matrix during aging, and Ni content of matrix decreases until reaching equilibrium Ni content [318]. Accord-



Fig. 96. TEM micrographs of artificial polycrystal samples after aging at 723 K for 1 h: (a) Ti–50.6Ni artificial polycrystal; (b) Ti–51.5Ni artificial polycrystal [347].

ing to the theory of phase transformation kinetics [348], nucleation rate I (the number of stable nuclei formed in the assembly in unit time) can be

$$I \propto \exp(-\Delta G_{\rm c}/kT),$$
(36)

where ΔG_c is the critical free energy to form a nucleus (i.e., nucleation barrier); k is the Boltzmann constant; T is transformation temperature. This equation shows that nucleation rate is determined by nucleation barrier ΔG_c .

The nucleation barrier ΔG_c for coherent nuclei is given by [349]

$$\Delta G_{\rm c} = 16\pi\sigma^3 / [3(\Delta G_{\rm v} + \varepsilon)^2], \tag{37}$$

where ΔG_v is the chemical free energy change associated with the precipitation reaction, ε is the strain energy per unit volume associated with the formation of a nucleus, σ is the interfacial energy associated with the formation of the new interface. Here it should be noted that ΔG_v is the driving force for the formation



Fig. 97. Schematic illustration for the relation between nucleation rate and supersaturation degree in grain interior region and grain boundary region. Supersaturation degree ΔX is defined by the solute (Ni) concentration beyond its solubility limit in B2 TiNi phase at given aging temperature. The nucleation rate at grain boundary and at grain interior is indicated by I_{GB} and I_{GI} , respectively [347].

of new phase and thus must be negative to enable the precipitation to happen. This requires that the solid solution must be supersaturated, i.e., solute concentration must be beyond its solubility limit in the solid solution (this situation is produced by rapid cooling of more concentrated solid solution from higher temperature, as being the case for our quenched Ti-Ni alloys). The larger the degree of supersaturation (i.e., the excess solute concentration beyond solubility limit) the more negative is the driving force $\Delta G_{\rm v}$ for precipitation. According to Eq. (35), at small supersaturation or small driving force $\Delta G_{\rm v}$ the nucleation barrier $\Delta G_{\rm c}$ will reach infinite; thus from Eq. (22) we know that nucleation rate is virtually zero. At very large supersaturation or large driving force $\Delta G_{\rm v}$ the nucleation barrier $\Delta G_{\rm c}$ is almost zero and thus the nucleation rate will reach a high plateau following Eq. (22). Therefore, the typical form of nucleation rate as a function of supersaturation or driving force will be a step-like curve as schematically shown in Fig. 97. It is characterized by an almost zero nucleation rate at small supersaturation/driving-force and rapid increase with increasing supersaturation until reaching a constant level at large supersaturation.

Now we consider the effect of grain boundary. In the case of polycrystals, at grain boundary (or similar defect) nucleation barrier is much reduced compared with that at grain interior. It was shown that nucleation barrier could become a fraction of that for homogeneous nucleation [349]. For a qualitative evaluation of the effect of grain boundary, let us assume there is a half reduction of the nucleation barrier, $\Delta G_c^{GB} = (\Delta G_c)/2$; then one can easily conclude from Eq. (22) that the nucleation rate curve for grain boundary (I_{GB}) will be shifted to left side compared with that for grain interior (I_{GI}), where homogeneous nucleation occurs. Fig. 97 shows that at low supersaturation grain boundary nucleation rate is significantly larger than that of grain interior; but at high supersaturation there is not a large difference. Fig. 97 answers the question about what determines whether there should be a preferential precipitation at grain boundary or an essentially homogeneous precipitation. When Ni content is low (50.6Ni), the nucleation rate is very small and thus precipitation of Ti_3Ni_4 is very sensitive to the presence of grain boundary. In this case, nucleation rate at grain boundary is much larger than at grain interior, as shown in Fig. 97. As a result, precipitate-free. When Ni content is high (51.5Ni), the difference in nucleation rate between grain boundary and interior is small; thus precipitation occurs homogeneously without being affected by grain boundary, as shown in Fig. 97. As a result, high supersaturation or high Ni content favors a homogeneous distribution of precipitates.

Therefore, there are two competing factors, which control the resultant distribution of precipitates in Ni-rich Ti–Ni alloys. The first factor is the presence of grain boundary or similar defects, which favor a preferred precipitation along grain boundaries. The second factor, which has an opposite effect, is the degree of



Fig. 98. A unified model for explaining the microstructure evolution at low Ni supersaturation (a and b) and high Ni supersaturation (c and d). It also explains both 3-stage and 2-stage transformation behavior of supersaturated Ti–Ni solid solution. In the figure, C_{initial} and C_{aged} curves represent the Ni profile of initial (as-quenched) state and that after aging, respectively. GB denotes grain boundary [347].
supersaturation of Ni (or Ni content). The competition between the two factors determines whether there will be a heterogeneous or a homogeneous distribution of precipitates.

After understanding what determines whether there will be a heterogeneous or homogeneous distribution of Ti_3Ni_4 , it is very easy to understand the different transformation behaviors of low Ni and high Ni Ti–Ni polycrystals. This is shown in Fig. 98. For low-Ni samples, the low supersaturation leads to a preferential precipitation along grain boundary (Fig. 98(a) and (b)) where leaving grain interior essentially precipitate-free, as discussed above. So grain boundary portion undergoes B2-R-B19' 2-stage transformation while the grain interior, being free of precipitates, undergoes a direct B2-B19' transformation and this gives rise to totally 3-stage transformation. For high Ni content alloys, as the supersaturation is high there is no much difference in nucleation rate between grain boundary and grain interior; thus an essentially homogeneous distribution of precipitates. So the whole sample undergoes normal 2-stage transformation. Therefore, both abnormal 3-peak behavior and normal 2-peak behavior can find a unified and natural explanation by the theory of precipitation kinetics.

Therefore, in low Ni samples the three peaks during cooling corresponds to the following:

- Peak-1 (first peak upon cooling): B2–R transformation of grain boundary region, where there is a high density of Ti₃Ni₄ particles.
- Peak-2 (second peak upon cooling): B2–B19' transformation of the grain interior region, where Ti_3Ni_4 particles are essentially free.
- Peak-3 (third peak upon cooling): R-B19' transformation of the grain boundary region.

The new mechanism gives a unified explanation for different transformation behaviors of both single crystals and polycrystals and their dependence on composition.

10. Thin films: process via amorphous state

Ti–Ni thin films attracted much attention with respect to possible applications to microactuators and "Micro Electro Mechanical Systems" (MEMS) [350]. The use of shape memory alloys in thin films has advantage not only for small size applications but also for improving response speed. The slow response speed is one of the short-comings of SMA applications, but cooling will be faster in thin films. The first Ti–Ni thin film was produced by Sekiguchi et al. [351] by using vacuum deposition method, the film being deposited in a crystalline state, and the shape memory effect was confirmed in 1983. However, we are interested in thin films via amorphous state, which is a *non-equilibrium state*, in order to obtain extremely fine grain sizes, with good mechanical properties, as it will turn out later. So, in the following, we restrict our-

selves to thin films, which are produced via amorphous state. The first amorphisation of Ti–Ni alloys was found by Thomas et al. [352] in 1982 by electron irradiation by using high voltage electron microscope (1–2 MeV). In 1986 Kim et al. [353] obtained amorphous films of Ti-Ni alloys with three compositions by magnetron sputtering method, and observed R-phase and X-phase precipitates (now known as Ti₃Ni₄ phase) in Ti-56Ni alloy after crystallization. However, they did not observe the martensitic transformation, because they did not hit near equiatomic composition. In 1990 many papers appeared on Ti-Ni thin films made by sputter deposition, which is a convenient method for fabricating MEMS [354–360]. Among these Walker et al. [354] and Busch et al. [355] recognized the importance of crystallization process to realize martensitic transformations, and observed shape memory effect. They also made prototype microactuators of thin films by using patterning of photoresist. Thereafter the investigations on sputter deposited thin films became quite active. In 1992 Miyazaki et al. [361] reported the shape memory effect by taking strain-temperature curves under constant load and DCS measurements for Ti-50.4Ni and Ti-51.4Ni alloys in a well-characterized manner. Chang and Grummon [362] studied two-step $B2 \rightarrow B19 \rightarrow B19'$ transformations in Ti–Ni–Cu thin films by TEM observations in the same year. Su et al. [363] studied damping effect in Ti-Ni film on Si substrate. Saburi et al. [364] observed R-phase transformation in near equiatomic but slightly Ti-rich Ti-Ni alloy. In the following we will discuss the developments thereafter. Before moving to the following section, let us discuss briefly on why TiNi has a tendency to become amorphous by sputter deposition or rapid quenching to be discussed later. Inoue [365] proposed an empirical rule on glass forming ability of metals as follows: the constituent elements more than three kinds with large atomic size ratios above 12%, and negative heat of mixing. In the case of TiNi, the number of elements are only two, instead of three, but the atomic size difference are 19% (used atomic radii were: $r_{\text{Ti}} = 0.147 \text{ nm}$, $r_{\text{Ni}} = 0.124 \text{ nm}$) [366,367], and standard enthalpy of formation is -33.1 kJ/mol atom [368]. Thus it may be appropriate to understand amorphisation of TiNi along this line.

10.1. Thin films formed by magnetron sputtering

Ti–Ni alloys may be divided into two categories; Ni-rich and Ti-rich alloys. In bulk state, Ti_3Ni_4 precipitates can be used to improve shape memory characteristics in Ni-rich side unless Ni content is very close to 50% (say <50.5%), as was discussed in the previous section. On the other hand, in Ti-rich side Ti_2Ni precipitates cannot be utilized, because the solubility limit on this side is almost vertical, as was pointed out in Section 2. However, this situation changes in crystallized thin films via amorphous state, which is a non-equilibrium state, as will be discussed in detail later. From this reason we mostly discuss Ti-rich thin films in the following, in which microstructures quite different from those of bulk materials appear. As-deposited films are amorphous when the substrate (glass or quartz) temperature is lower than 473 K (e.g. see Fig. 106(f)). Crystallization temperature may depend upon composition, and that of Ti–50.4Ni and Ti–51.1Ni is reported to be 756 K [361]. The grain size of crystallized films, which depends upon heat-treatment, are usually less than 4



Fig. 99. Strain-temperature curves of Ti-Ni thin films under constant stresses: (a) near equiatomic composition, (b) Ni-rich composition. Films were crystallized by the heat-treatment at 773 K for 1 h. (a) shows one-stage transformation, while (b) shows two-stage transformation. See text for details (after Ishida et al. [371] reproduced with permission of Materials Research Society).



Fig. 100. Variation of transformation behavior due to the variation in composition and heat-treatment for near-equiatomic and Ni-rich Ti–Ni thin films (after Gyobu et al. [372] reproduced with permission of Elsevier).

 μ m [369], and mostly 1 μ m or so, which is one order of magnitude smaller than those of bulk materials.

10.1.1. Ni-rich Ti–Ni thin films

As a result of extensive researches in the above and below, it is already established that Ti–Ni thin films exhibit good mechanical properties, since grain size is extremely fine [370]. The transformation behavior as a function of composition is also very similar to that in bulk materials, as typically shown in Fig. 99, where near equiatomic Ti–Ni in Fig. 99(a) exhibits a single $B2 \rightarrow B19'$ transformation, while Ni-rich Ti–Ni in Fig. 99(b) exhibits two-stage $B2 \rightarrow R \rightarrow B19'$ transformation, because Ti₃Ni₄

precipitates suppress $B2 \rightarrow B19'$ transformation relative to $B2 \rightarrow R$ transformation, as in the case for bulk materials. This behavior is shown more in detail as a function of composition and heat-treatment temperature in Fig. 100. Since the microstructures [373,374], transformation behavior and mechanical behavior for Ni-rich Ti–Ni thin films are essentially the same as those in bulk materials, superelasticity [375,376], 2-way shape memory effect [359,377,372], in addition to one-way shape memory effect were all found, and transformation and shape memory characteristics were investigated in detail in Ni-rich alloys. Thus, readers are referred to good reviews [370,378,369], and other papers referred therein for the details for Ni-rich Ti–Ni alloys.

10.1.2. Ti-rich Ti-Ni thin films

In contrast to Ni-rich thin films, behaviors in Ti-rich thin films are quite interesting, as expected from the phase diagram discussed in Section 2. Since the solubility limit on Ti-rich side of the binary Ti–Ni alloy (Fig. 2) is almost vertical, precipitation of Ti₂Ni phase appears only at grain boundaries for Ti-rich alloy in bulk, and thus it is impossible to use the precipitation to improve shape memory characteristics. However, if such alloys are prepared via amorphous state, it becomes possible to form precipitates rather uniformly in an intergranular manner, because amorphous film can supersaturate Ti atoms in it, and excess Ti may precipitate upon crystallization or thereafter. This aspect of Ti-rich films is discussed below.

Investigations of Ti-rich Ti–Ni alloys seem to have started around 1995. As it will turn out soon below, the precipitation behavior of Ti-rich alloys depends upon heat-treatment temperature. In 1995 Nakata et al. [379] found thin plate precipitates, which is accompanied by heavy strain contrast, very similar to G.P. zones in Al–Cu alloy, by heat-treating amorphous $Ti_{51.5}Ni_{48.5}$ film at 773 K for 600 s, which is rather low as heat-treatment temperature, as shown in Fig. 101. They observed that the plates form along $\{100\}_{B2}$ plane uniformly, and also observed streaks in the diffraction patterns normal to the $\{100\}_{B2}$ plates. Thus they termed them as G.P. zones



Fig. 101. TEM observation of G.P. zone precipitates in 51.5Ti–48.5Ni thin film, which was heat-treated at 500 °C. (a) TEM image showing thin plate morphology, (b) corresponding diffraction pattern with streaks in $\langle 100 \rangle^*$ direction, which is normal to thin plates in (a) (after Nakata et al. [379] reproduced with permission of Nakata).



Fig. 102. High resolution TEM image of G.P. zones in 51.5Ti–48.5Ni thin film, which was heat-treated at 500 °C (after Nakata et al. [382] reproduced with permission of TMS).

with mono or a few atomic layers in B2 matrix. In 1996 Kajiwara et al. [380] observed similar thin plate precipitates in Ti_{51.8}Ni_{48.2} film by heat-treating it at 745 K, which is near crystallization temperature of the film. They observed by high resolution electron microscopy (HRTEM) that the lattice of the precipitate and B2 matrix is continuous, implying the precipitate is coherent, and that interplanar distance parallel to $\{100\}_{B2}$ habit plane is larger in the precipitate, and $\{110\}_{B2}$ plane in the precipitate is bent by 6° from that in the matrix. Thus they deduced that the structure of the precipitate is body-centered tetragonal (BCT) [381]. This imply that the BCT structure is a result of the precipitation of excess Ti atoms on $\{100\}_{B2}$ plane, because Ti atoms are larger than Ni atoms by 19%. In a little later works Nakata et al. [382,383] take a similar view on the structure of the precipitates, but in a strict sense they have different view in the following. They pay attention to the bright contrast of the precipitate, as shown in Fig. 102, because they always appear bright compared to that of the matrix. (This is also true for HRTEM of Kajiwara's group as well.) They carried out computer simulation of the image of the precipitates based on the model that Ti atom layers precipitates on $\{100\}_{B2}$ planes. However, they obtained only dark contrast instead of bright one for this model, and bright contrast was obtained only when they introduced vacancies in addition to Ti atoms. Thus they consider that about 20% Ti atoms are substituted by vacancies in the precipitates. This is the essential difference on the structure of precipitates between the two groups. Con-

¹⁸ Crystallization below the crystallization temperature may seem to be strange for readers, but of course it depends upon the definition of crystallization temperature. Obviously crystallization is a function of not only temperature but also time. The crystallization temperature used in the related literature here is defined as the temperature of the maximum heat evolution in DSC curves at a constant heating rate [380].



Fig. 103. Strain-temperature curves under constant stresses for 51.8Ti-48.2Ni thin film, which was heattreated at 745 K for 1 h, the crystallization temperature being 737 K. See text for details (after Kajiwara et al. [380] reproduced with permission of Taylor and Francis Ltd.).

cerning the formation mechanism of the precipitates, Kajiwara et al. [381] consider that precipitation occurs after the crystallization, because the distribution of precipitates is homogeneous. In this mechanism the excess Ti is presumed to be still held in the matrix somehow even after crystallization. This point is to be compared with another case of precipitation to be discussed below.

Kajiwara et al. [381] found another morphology of plate precipitates, when amorphous films of the same composition was heat-treated at temperatures lower than crystallization temperature by about 50 K.¹⁸ In this case crystallized films consists of many particles with the size in the range of $0.1-1 \mu m$, and each particle contains many nanocrystals with diameters of 20–40 nm. These nanocrystals have the same orientation in each particle, and is surrounded by the above precipitates on $\{100\}_{B2}$ planes, which are thicker than the above case. They consider the formation mechanism of this morphology in the following way. Upon crystallization, a nanocrystal with B2 structure is formed first. Then excess Ti are pushed out in the amorphous phase surrounding the nanocrystal, creating thin plates on $\{100\}_{B2}$ planes,

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Fig. 104. (a) Variation in critical stress for slip as a function of heat-treatment temperature. (b) Variation in the maximum recoverable strain as a function of heat-treatment temperature. Specimens are 51.8Ti–48.2Ni thin films (after Kajiwara et al. [380] reproduced with permission of Taylor and Francis Ltd.).

because excess Ti can not be held in B2 matrix. By repeating this process, this morphology is thought to be created in their mechanism. They also investigated mechanical properties of thin films, and showed that the films with thin plates exhibit very good shape memory characteristics, as shown in Fig. 103 as an example, in which 5.5% recovery strain is available at 240 MPa without introducing any plastic strain. Similarly, Fig. 104(a) shows that the critical stress for slip increases rapidly with decreasing heat-treatment temperature of amorphous films, and the critical stress levels off at temperatures above 820 K. This temperature of 820 K corresponds to the critical temperature, where the shape of precipitates changes from thin plate to granular Ti₂Ni particles, which will be described soon below. Fig. 104(b) shows that the recoverable strain as a function of heat-treatment temperature. This also shows that the recoverable strain is larger at low heat-treatment temperature, because the recoverable strain at 687 K increases by increasing heat-treatment time



Fig. 105. Various precipitates in the Ti–Ni matrix of Ti-rich Ti–Ni thin films heat-treated at various temperatures for 1 h: solid squares (\blacksquare) are Ti₂Ni particles with random orientation (a); open squares (\square) are Ti₂Ni precipitates with the same orientation as that of the matrix (b); open triangles (\triangle) are plate precipitates and oriented Ti₂Ni precipitates (c); solid circles (\bullet) are plate precipitates (high temperature form) (d) and plate precipitates (low temperature form) (e); open circles (\circ) indicate no precipitates; and solid triangles (\blacktriangle) indicate amorphous films (f). The above alphabets a–f correspond to those in the next figure of Fig. 106 (after Saburi and Ishida [369] with permission of Materials Research Society).

from 1 h (closed circle) to 2 h (open circle). This means that thin plate precipitates are much more effective to increase mechanical properties.

The studies on crystallization behavior at temperatures above crystallization temperature also started around 1995 [373,379,384], and granular Ti₂Ni precipitates in B2 matrix were found in this temperature regime. In this case there are two categories with respect to orientation relationship with B2 matrix. When Ti content is lower than about 53%, Ti₂Ni precipitates have specific orientation relationship with B2 matrix, as typically shown in Fig. 106(b) and (c), because the precipitates are formed after the crystallization of B2 matrix. The orientation relationship was determined by Ishida et al. [385] as: $040_{Ti_2Ni} \| 010_{B2}, 004_{Ti_2Ni} \| 001_{B2}$; i.e. the crystal axes of Ti_2Ni and those of B2 are parallel to each other. On the other hand, when Ti content is higher than about 53%, Ti₂Ni phase are formed first, and then crystallization occurs. Thus Ti₂Ni phase and B2 matrix have no orientation relationship [373]. More details on the relation between composition, heat-treatment temperature and resulting microstructures are shown for a fixed time of 1 h for heat-treatment in Figs. 105 and 106. Fig. 105 was originally made by Kawamura et al. [386], and was then refined further by Ishida [369]. In the composition regime of Ti less than 53%, plate morphology is taken over by granular morphology of Ti₂Ni with increasing heattreatment temperature, but there is a region where plates and granular one coexist (indicated by a symbol \triangle) in between. In Fig. 106(b) and (c), we observe grid-like patterns along $\langle 110 \rangle$ directions. These are moiré fringes due to granular Ti₂Ni and B2 matrix. We also notice that there are two morphologies (Fig. 106(d) and



Fig. 106. TEM micrographs and corresponding electron diffraction patterns, which correspond to various compositions and heat-treatment, which are indicated in Fig. 105. The alphabets a–f correspond to those in the previous figure (after Ishida and Saburi [369] with permission of Materials Research Society).

(e)) in the G.P. zone region (indicated by symbol \bullet). These correspond to thin plates heat-treated at temperatures near crystallization temperature and at those below the temperature, respectively, as we described in the above. There is also a composition range near equiatomic composition, where no precipitates appear.

Since good microstructures are available in Ti-rich Ti–Ni thin films as described in the above, two-stage transformation via R-phase (e.g. see Fig. 103), superelasticity (although not complete) [387], two-way shape memory effect [388] are all realized in these films as well. See review papers for these and references cited therein [370,378,369]. One of the advantages of Ti-rich films is that the transformation tem-

peratures are higher than those of Ni-rich ones, even though micro precipitates are introduced [389], because M_s temperature of Ti–Ni alloy has a tendency such that M_s decreases with increasing Ni content in Ni-rich side, while M_s is nearly constant on Ti-rich side, as we discussed in Section 8 (see Fig. 76).

In addition to the above binary thin films, the investigations on ternary alloy thin films are also quite active. Among these Ti–Ni–Cu [390–393], Ti–Ni–Pd [390,394,396] and Ti–Ni–Hf [395] thin films are most attractive. The former is interesting for actuator applications with small temperature hysteresis, and the latter two are interesting as high temperature shape memory thin films, as is the case for bulk materials. See review papers [370,378] and references cited therein for those.

10.2. Thin ribbons formed by rapid quenching

Another way to obtain fine grains is to use rapid quenching such as by melt-spinning technique, which does not necessarily pass through amorphous state. Thus we discuss it here just briefly. Since melt-spinning is a non-equilibrium technique, the result may strongly depend upon the cooling rate. However, the cooling rate is not specified in literature in many cases. Instead they are described by the roll speed (rpm) or surface velocity etc. Thus it is difficult to characterize or compare them in a unified manner in the present situation, and thus readers are referred to the original papers when necessary. Furuya et al. [397,398] investigated the shape memory characteristics of melt-spun ribbons of $Ti_{50}Ni_{50-x}Cu_x$ (x = 0–20) alloys in early 1990. The choice of Ti–Ni–Cu is probably due to the small temperature hysteresis of the alloys, which is good for actuator applications. The obtained ribbons with 1 mm width and 30 μ m thickness were all crystalline in as-spun condition with grain size of 2–3 μ m. After suitable heat-treatment, they obtained good shape memory characteristics both in shape memory strains and transformation strains, which depends upon Cu-content as expected from bulk characteristics. The obtained large transformation strains (compared to those of bulk materials) is due to the texture of the ribbons, and this was confirmed to be due to $\{200\}_{B2}$ texture of the melt-spun ribbons [399]. This is reasonable because crystals grow normal to the ribbon surface in melt-spinning technique, and growth direction with high growth rate in cubic system is usually $\langle 100 \rangle_{\rm c}$.

In 1997 Xie et al. [400] studied melt-spun ribbons of $Ti_{50}Ni_{25}Cu_{25}$, which is brittle in bulk state, by TEM observations. They found that most of the ribbons are amorphous with a small amount of spherical crystalline particles of $\phi 3 \mu m$ to $\phi 22 \mu m$, which consist of either (011)_o and (111)_o twins of B19 martensite. Thereafter the research on $Ti_{50}Ni_{25}Cu_{25}$ melt-spun ribbons became quite active [401–411]. Rösner et al. [401,402] found plate-like precipitates by heat-treating the ribbons at 410 °C for 22–48 h, which is 45 °C lower than the crystallization temperature of 455 °C, as shown in Fig. 107. So, the situation is similar to G.P. zone type precipitates in sputter-deposited Ti-rich Ti–Ni films discussed above. The habit planes of the precipitates were found to be {100}_{B2} (see Fig. 107) or {011}_o when the matrix is in B19 martensitic state. They reported the structure of the precipitate is tetragonal B11 with Ti_{50} Cu₅₀ composition, which is different from the C11b structure with



Fig. 107. TEM bright field (a) and two dark field micrographs (b,c) of the same area of a melt-spun $Ti_{50}Ni_{25}Cu_{25}$ ribbon annealed at 410 °C for 48 h. The precipitation takes place within the same grains. Beam direction $|| [100]_{B2}$ direction of the parent B2 phase for all three micrographs. Note that only the variant of platelets perpendicular to the encircled streak which marks the corresponding *g*-vector is visible in (b) and (c), respectively (after Rösner et al. [401] with permission of Elsevier).

 $\{100\}_{B2}$ habit plane and composition Ti(Ni,Cu)₂ [323]. Since the precipitates were too thin for EDS analysis, they used thick precipitates in bulk materials, which were annealed at 600 °C for 48 h. Since the structure of a G.P. zone and that of metastable precipitates are sometime different, there may remain some ambiguity on this point. Besides since the precipitation of Ti₅₀Cu₅₀ phas leaves high concentration of Ni in the matrix, this may cause significant lowering of M_s temperature. This point need to be checked. Rösner et al. reported that the formation of plate-like precipitates lead to embrittlement, but they did not show S-S curves. Thus it is not known whether or not the precipitates are useful for mechanical properties at all. For the alloy with the same composition Liu [409] reported good superelasticity for ribbons without plate-like precipitates, being annealed at 500 °C for 15 min, but the superelasticity does not exhibit stress-plateau, and the S-S curves change greatly in the first 10 cycles or so. Some curious structures and morphologies are also found in the partially crystallized ribbons such as "twinned BCC spherical particles" [411], which manifest the non-equilibrium state of the ribbons. It is also important to note that melt-spun ribbons are not completely amorphous, but the so-called "free side" of the ribbons are crystalline [402,403]. Thus Rösner et al. state the above-mentioned surface layer must be removed to obtain proper results. In the above alloy, the number of alloying elements was three, and the condition is more close to the empirical rule proposed by Inoue [365] to form amorphous state. This is probably one of the reason why Ti–Ni–Cu alloy was chosen as a target of melt-spun ribbons. In this respect Kolomytsev et al. [412] are studying melt-spun shape memory ribbons in wide variety of alloys.

More recently some interesting behavior was also reported by Khantachawana et al. [413] for Ti-Ni binary melt-spun ribbons, which were made under cooling rates possibly higher than before (roller surface velocity is 42 m/s, the ribbons being 15 µm thick and 1mm wide). They used Ti-49.0Ni, -50.0Ni, -51.0Ni alloys in nominal composition. All ribbons were fully crystallized in as-spun condition. Although Ti-51.0Ni did not exhibit shape memory effect, the former two ribbons exhibited good recovery strains of 5.5% and 5.0%, respectively. Both ribbons exhibited R-phase/2stage transformation. It is surprising that even Ti-50.0Ni ribbon exhibited R-phase transformation, but this may need justification by accurate chemical analysis, because the composition is described only by nominal composition. They also observed disc precipitates on $\{100\}_{B2}$ plane of the matrix by TEM in all ribbons, in addition to Ti₂Ni precipitates at grain boundaries for Ti-51.0Ni ribbons. The precipitation of Ti_2Ni phase in Ni-rich alloy is unusual, and the mechanism is not understood as yet, and the structure of disc precipitates inside grains is not identified yet. All the above rather unusual behaviors both in Ti-Ni-Cu and Ti-Ni alloy systems seem to indicate non-equilibrium characteristics of melt-spun ribbons under rapid quenching processes.

Finally we close this section by comparing the sputter deposition technique and the melt-spinning one.

- Sputter deposition is much more suited to MEMS, because Ti–Ni films can be directly deposited to semiconductors or IC, and patterning is also easily incorporated by photoresist technique.
- (2) Sputter deposition process is much more expensive than melt-spinning one, because the former needs high vacuum (base pressure: 2.1×10^{-5} Pa [377]), and it will take a rather long time for film forming (~2 h for 8 µm thick film).
- (3) In melt-spinning process, microstructure strongly depends upon cooling conditions. Thus it may be difficult to obtain reproducible results among different apparatus or among different researchers. On the contrary, sputter deposition process is a more stable one, and the starting as-deposited films are usually in completely amorphous state (which of course depends upon the substrate temperature). It was also mentioned in the above for $Ti_{50}Ni_{25}Cu_{25}$ ribbons that the as-melt-spun ribbon always contains crystalline surface layer on "free" side, other parts being amorphous.
- (4) There is no limitation in the thickness of sputter-deposited films. On the other hand, there is a limitation in those of ribbons. Usually the thickness of melt-spun ribbons is 30–40 μm, and the minimum thickness reported so far is 15 μm [413].
- (5) Concerning the uniformity of composition, there are reports that it strongly depends upon the position on the substrate in sputter deposition method [389,414]. This is a serious problem, because transformation temperature of

Ti–Ni alloys has a strong composition dependence, as discussed in Section 8. On the contrary, the uniformity of composition in melt-spun ribbons is expected to be high, although such data are not available as yet.

Thus both processes have some advantages and disadvantages respectively, but from the viewpoint to the applications to MEMS, sputter deposition technique will be much more suitable. By the way, it is now possible to make strips of Ti–Ni alloys with the thickness of 30 μ m by cold-rolling [415], and thus the melt-spinning technique and rolling technique may become competitive in the future. It is expected that some of the disadvantages pointed out in the above will be overcome by the advancement of the technology in the future.

11. Summary

In the above we have discussed various aspects of Ti–Ni-based alloys, including crystallographic mechanism of martensitic transformations, mechanisms of shape memory and superelastic effects, effects of aging on martensitic transformations and on shape memory/superelastic characteristics etc. It is now clear they are mostly understood in the framework of standard physical metallurgy. We also discussed some important "non-classical" issues like precursor phenomena. It turned out that Landau theory is useful to understand the relation between the parent phase and martensite through their symmetry relation and to understand premartensitic behavior. Since the present review is devoted to the unified understanding of fundamentals of these alloys, applications of these alloys were not treated at all, but the authors believe that these basics are useful for applications as well, as typically shown in Sections 8 and 9, in which how the aging and thermomechanical treatment can be effectively utilized to change transformation temperatures and to improve shape memory characteristics of the alloys concerned.

Ti–Ni-based alloys are quite unique alloys compared with other β -phase shape memory alloys, as is typically seen in the following points:

- (i) Elastic anisotropy A is close to 2, which is quite isotropic.
- (ii) c_{44} in the parent phase softens with decreasing temperature toward the transformation temperature, in contrast to that of other β -phase alloys. This soft c_{44} has special roles, as discussed in Sections 5 and 7.
- (iii) The shape memory/superelastic characteristics are not good in the solutiontreated condition, but become very good by proper thermomechanical treatments.
- (iv) The ductility of the alloys is quite high compared with other β -phase alloys or other intermetallics.
- (v) The alloys have a potentiality to amorphisation, as actually observed.

Among these the characteristics (iii) and (iv) are actually the main reasons for the fact that almost only Ti–Ni-based alloys are *practical* shape memory alloys, although other β -phase alloys also exhibit shape memory/superelastic effects as well. These two characteristics originate from the first two characteristics (i) and (ii), as we discussed in the previous sections. It is interesting to note that the fact that the shape memory/superelatic characteristics are worse in the solution-treated condition is also the cause for the good ductility, and this can be improved by proper thermomechanical treatment. This means that the superior mechanical properties of the alloys are based on the delicate balance of the physical properties, which indicates that Ti-Ni-based alloys are really interesting materials from both fundamentals' and applications' point of view. Although we did not discuss in the preceding sections, there is also another important characteristic, which makes Ti-Ni-based alloys practical shape memory alloys; that is the absence of martensite aging effect. i.e. In many other β -phase alloys transformation temperature changes during aging in martensitic state at ambient temperature (i.e. their transformation temperatures may change with time just by leaving them at ambient temperature.), but Ti-Ni-based alloys does not show this effect, because the melting temperatures are high and the diffusion of point defects is not allowed. Interested readers may refer to Refs. [416–418]. The potentiality to amorphisation adds another interest to applications, such as to MEMS. Although we have not discussed, high abrasion resistance and high corrosion resistance are another advantages of the alloys.

Among the issues, which were not treated in the above, damping properties of the allovs are important, because Ti-Ni-based alloys exhibit quite high damping capacity. Generally speaking, two internal friction peaks appear depending upon experimental conditions. The first one is the so-called "transient peak", which appears at martensitic transformation temperatures (i.e., $\sim M_s$ or $\sim A_f$ depending upon either forward or reverse transformation). This peak appears only when temperature is continuously changed, and it disappears when the temperature is kept constant. This is the reason why it is called a "transient peak". It is clear that the peak is related with the martensitic transformation or its reverse transformation, although the mechanism how the peak is associated with the martensitic transformation is not understood yet. The second "broad" peak often appears at a temperature below that of the transient peak (i.e. in the martensitic state). It is sometimes called the "relaxation type peak", but whether it is really relaxation type or not is not clear as yet. It is generally believed that it originates from the back and forth twin boundary motion under stress. However, the mechanism, including the temperature and frequency dependence of the peak is not understood at all. In fact this was the reason why this was not treated in the previous sections. It is, however, to be mentioned that the internal friction of Ti–Ni-based alloys are quite high, especially $Ti_{50}Ni_{40}Cu_{20}$ alloy exhibits remarkably high value of internal friction $Q^{-1} = 0.2$ [419]. Thus they are important as high damping materials with high strength. The Ti-Ni-based alloys await the clarification of damping mechanism as well as applications as high damping materials. Interested readers are referred to Refs. [420-423] and those cited therein. There are some other interesting issues to be solved, as was pointed out in Section 5.9, as unsolved issues. Thus Ti–Ni-based alloys still remain as a treasure island to materials scientists.

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