

RECENT ADVANCES IN UNDERSTANDING THE ORIGIN OF MARTENSITE AGING PHENOMENA IN SHAPE MEMORY ALLOYS

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The martensite aging phenomena (martensite stabilization and rubber-like behavior) found in many shape memory alloys have puzzled material scientists for over 60 years without a definite answer. In this article we critically reviewed previous models to understand the aging phenomena, which include pseudotwin-type model, LRO model, SRO model, twinning dislocation model, and domain (twin) boundary pinning model. We showed that these models failed to meet generality criterion, although being able to explain the phenomena to some extent. Then we focused on a very recent general model (Ren and Otsuka, *Nature*, **389**, 579–582, 1997) which makes use of only two common features of martensitic transformation and aging, i.e., diffusionless symmetry change during martensitic transformation and diffusion during aging. This model appears to be able to explain all of the available experimental observations on the aging phenomena. In view of recent development in this field, we have reason to believe that we are approaching the final solution to the aging problem.

Keywords: Aging effect; Martensitic transformation; Shape memory alloys; Martensite stabilization; Rubber-like behavior; Diffusion

1. INTRODUCTION

Since the discovery of the rubber-like behavior in Au–47.5Cd by Ölander (1932) 65 years ago, aging phenomena have been found in martensitic state of most shape memory alloys, which are either ordered

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or disordered. The examples of martensite aging for ordered martensites are γ_2' -Au-Cd (Ölander, 1932), ζ_2' -Au-Cd (Nakajima *et al.*, 1994), Au-Cu-Zn (Miura *et al.*, 1974), Cu-Zn-Al (Rapacioli *et al.*, 1975), Cu-Al-Ni (Sakamoto *et al.*, 1977), and that for disordered martensite is In-Tl (Burkart and Read, 1953; Basinski and Christian, 1954). Aging phenomena include two closely related time-dependent effects. One is the so-called "martensite stabilization", by which martensite becomes more stable with aging, such that the reverse transformation temperature (A_f) increases with aging time (Fig. 1). Another is "rubber-like behavior (RLB)", in which that martensite exhibits recoverable or pseudo-elastic deformation behavior after being aged for some time (Fig. 2). Early studies on RLB were reviewed by Otsuka and Wayman (1977), Christian (1982), and Otsuka *et al.* (1997), and a review on the stabilization of Cu-Zn-Al martensite was given by Ahlers (1986). Because the time-dependence of aging is a clear signal of atomic diffusion, it is reasonable to consider that the stabilization and RLB possess the same origin which is related to some kind of diffusion. This means that if a martensite exhibits a stabilization effect, it also shows RLB, and vice versa. This is true for all martensites exhibiting the aging effect. The RLB of In-Tl martensite seems not to require aging, and no stabilization has been reported in this alloy. As will be discussed later, this arises

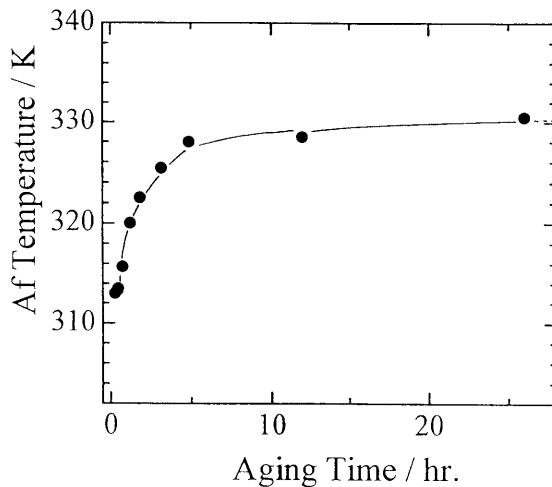


FIGURE 1 Martensite stabilization in Au-49.5at% Cd alloy. After Murakami *et al.* (1994).

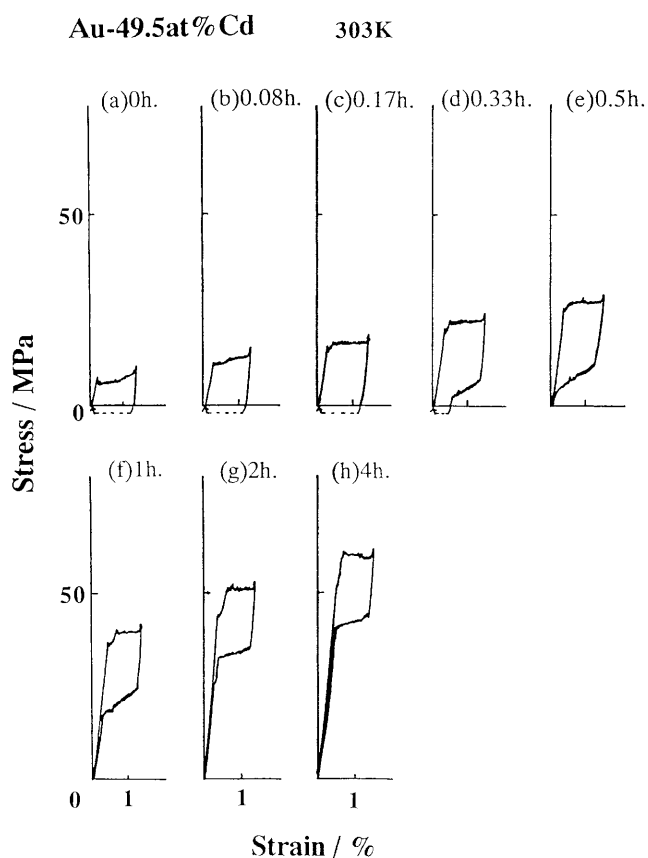


FIGURE 2 Development of RLB during aging at 303 K for Au-49.5at% Cd martensite. After Murakami *et al.* (1997).

from the extremely high aging (diffusion) rate in martensite due to its extremely high M_s/T_m value so that martensite is stabilized immediately when being formed from the parent phase, thus the time-dependence cannot be observed. Here M_s and T_m represent the martensite start temperature and the melting temperature of the alloy, respectively. The study of martensite aging phenomena is not only of fundamental importance, but also of great technological significance, because aging effect is generally an unwanted effect in the application of shape memory alloys (Miyazaki and Otsuka, 1987), and a deep understanding of the origin of the aging is crucial for controlling it.

Let us look into the aging phenomena microscopically. The relationship among martensitic transformation, martensite aging, stabilization effect and RLB is schematically shown in Fig. 3. The common feature of all martensitic transformation is diffusionlessness and symmetry-lowering. By a martensitic transformation a high symmetry (mostly cubic) parent phase transforms into low symmetry martensite. Let a small cube of parent phase (a) transform into martensite with lower symmetry (b). If this “fresh” martensite is deformed, it appears soft and plastic. This is nothing strange because domain reversal (twinning) occurs easy in order to accommodate the strain (note: twinning in SMA martensites is generally very easy). Since the stress-induced new domain (c) has the same martensite structure and thus the same stability as the original domain (b), the new domain has no reason to go back to the original domain. Macroscopically, we observe plastic behavior. What is puzzling is that after aging the martensite seems different from the fresh one, so that the aged martensite (e) exhibits stabilization effect (aged martensite transforms back to the parent (d) at a higher temperature) and RLB (stress-induced martensite domain

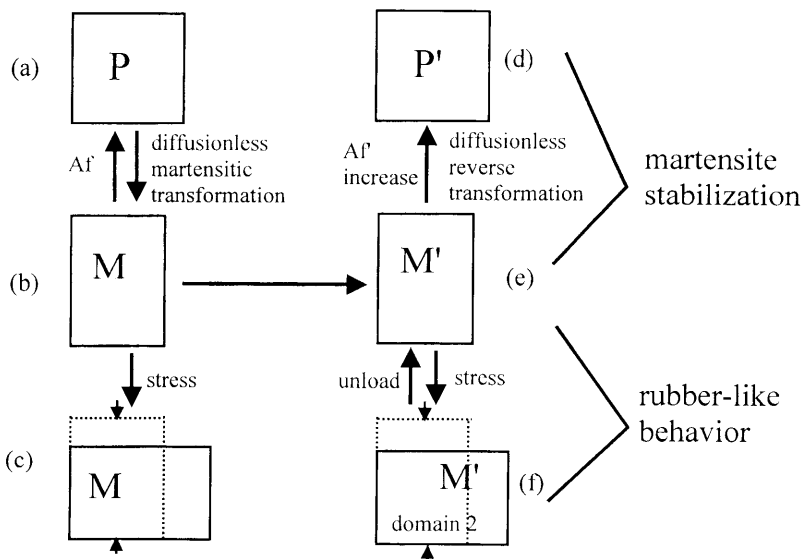


FIGURE 3 Relationship among martensitic transformation, martensite aging, martensite stabilization and RLB. P and M refer to the parent phase and the martensite, respectively.

(f) appears less stable than the original domain (e), thus the original domain (e) is restored after the removal of stress). Since it is aging that causes these significant effects, the key to understanding these phenomena is to know what happens during martensite aging.

In contrast to the RLB, a kind of pseudo-elasticity with unknown origin, there exist two other kinds of pseudo-elasticity with known origin. One is due to the stress-induced martensitic transformation in the parent state, which is usually termed "superelasticity" (Otsuka and Wayman, 1977). Another is due to stress-induced pseudotwin (which can be regarded as a new phase) (Cahn, 1977). In both cases, stress induces a structural transformation and the free energy difference between the two phases provides a restoring force for the pseudoelasticity. One may expect that there might be some obvious structural change during martensite aging and during loading. However, as will be shown below, aging phenomena may occur even without any structural change of martensite. This puzzling feature is in sharp contrast to the significant change in the reverse transformation temperature and mechanical properties during martensite aging. This is the main reason why the aging problem has remained over 60 years without a definite answer.

A. Main Features of the Aging Phenomena

An understanding of aging phenomena depends on how we interpret their common features. Here we list the five most important and general features of martensite aging phenomena.

(1) Aging is a time-dependent process. As mentioned above, this feature suggests that the aging should be related with redistribution of atoms or defects, i.e., diffusion.

(2) Aging is not dependent on a change in average structure of martensite. This is the most striking feature of martensite aging, because it is difficult to imagine why atomic rearrangement during aging does not induce change in the average martensite structure. X-ray diffraction results on Au–Cd martensite (Ohba *et al.*, 1990; Murakami *et al.*, 1997) clearly showed that no detectable change in diffraction peak position and integrated intensity was found during martensite aging (Fig. 4). Ren and Otsuka (1997a) measured the change in electrical resistivity of Au 49.5Cd martensite and parent

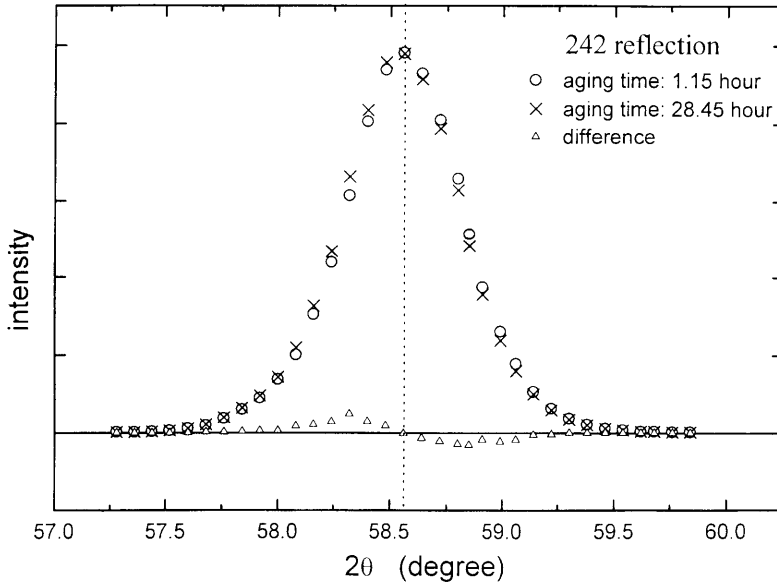


FIGURE 4 X-ray diffraction profile of Au-47.5at% Cd martensite with short and long time aging. After Ohba *et al.* (1990).

phase during aging, and unambiguously proved that aging of both martensite and parent phase does not involve any change of average structure (or long-range order). They pointed out that aging phenomena involves a reconfiguration of lattice defects without altering average structure.

Some of the early studies on martensite aging used metastable martensite (such as Cu–Zn–Al), i.e., such martensite is not an equilibrium low temperature phase and has a tendency to decompose into stable phases. Some change in average martensite structure or LRO during aging was reported in these alloys (e.g., Hashiguchi *et al.*, 1986), and the aging effect has been ascribed to the structure change (Abu Arab and Ahlers, 1988; Tadaki *et al.*, 1990). However, the structure change in such alloys may be simply due to the partial decomposition of the metastable martensite during aging. In stable Au–Cd martensite, no structure change has been found despite the strong aging effect.

(3) Aging appears even in single-domain martensite where no domain (twin) boundary exists (Rapacioli *et al.*, 1975; Barcelo *et al.*, 1978). This feature means that the aging effect is not a boundary effect,

it is related to the rearrangement of atoms or defects throughout martensite. Nevertheless, a recent experiment (Murakami *et al.*, 1995) showed a more complex aspect of the aging effect. They found that the aging effect is much more pronounced in multi-domain martensite than in single-domain martensite. This seems to suggest that a boundary effect (e.g., pinning) also contributes to the aging effect. Therefore, a correct aging mechanism must explain both volume effect and boundary effect. Unfortunately, most of the available aging models cannot explain this dual feature.

(4) Aging effect is sensitive to point defects. There are numerous experimental results (e.g., Nakajima *et al.*, 1994; Murakami *et al.*, 1997) showing that increase of point defects by quenching always leads to an enhanced aging effect. This indicates that aging phenomena are closely related to the reconfiguration of point defects.

(5) Aging phenomena occur both in ordered and disordered martensite. Although the aging effect has been mostly found in ordered martensite such as Au–Cd, Au–Cu–Zn, Cu–Zn–Al, and Cu–Al–Ni, it also exists in disordered martensite such as In–Ti. This fact suggests that the aging effect should be related to a general process common to both ordered and disordered structure. This condition alone has in fact disproved many of the previously proposed LRO-based models.

B. Necessary Condition for a Correct Mechanism of Aging Phenomena

Although the aging phenomena manifests many complex facets, it should be governed by a general and simple mechanism which is capable of explaining all of these facets in diverse martensites. A model cannot be accepted as being correct if it can explain only a part of the experimental facts or is limited to certain alloys. Therefore, generality is the most important criterion for a correct aging mechanism.

In the following, we shall briefly review previous models which can only explain a part of experimental facts, and then focus on a recent general model (Ren and Otsuka, 1997a) that appears to be able to explain all known experimental results. We divide these models into two categories: those demanding a change of average martensite structure and those not demanding such a change. We shall critically discuss these

models with reference to the above-mentioned features of martensite aging.

2. MODELS DEMANDING A CHANGE OF AVERAGE MARTENSITE STRUCTURE

Most of the early models explained the aging effect based on the hypothesis that the average structure of martensite (or its LRO degree) changes to some extent during martensite aging. As discussed above, the change of average martensite structure during aging is absent in stable martensite without a decomposition tendency. Therefore, models demanding a change of average martensite structure do not meet the generality criterion. Nevertheless, during the development of these models the picture of martensite aging phenomena becomes more and more clear, and that helps to develop further our understanding of the aging phenomena.

A. Pseudotwin-type Models

Because this type of models utilized the concept of pseudotwin, we first explain what pseudotwin is before discussing these models. For pure metals or disordered alloys, shearing the lattice produces mechanical twin. The twinned region and untwinned region have strict mirror correspondence and thus the same crystal structure. However, for ordered alloys shearing alone usually cannot produce a strict mirror correspondence between "twinned" and untwinned regions (such a "twinned" structure is called pseudotwin because it does not possess the same crystal structure as the untwinned region). In order to form a "true twin" which has mirror correspondence to the untwinned region, a shuffle, in addition to the shear, is necessary. If the shuffle is somehow prohibited, then pseudotwin is induced to accommodate the strain produced by external stress. This is the Laves–Cahn picture of pseudotwin formation (Laves, 1966; Cahn, 1977), which has been found in some ordered alloys such as FeAl and FeBe. Since pseudotwin has a crystal structure different from that of the untwinned region, it should be regarded as a different phase with higher energy. Therefore, it has a tendency to restore the untwinned structure. This provides a driving force for strain recovery and leads to a macroscopic pseudoelasticity.

This kind of pseudoelasticity is similar to the superelasticity related with stress-induced martensitic transformation. One of the most remarkable features of the pseudoelasticity due to pseudotwin or stress-induced martensitic transformation is that the development of pseudoelasticity is time-independent, because the restoring force develops as soon as stress induces pseudotwin (a less stable phase) or martensite.

Lieberman *et al.* (1975) first proposed a model using the idea of pseudotwin. They suggested that pseudotwin forms if martensite is deformed, and this is the origin of the RLB. They further suggested that if the martensite is aged under stress, a "time-dependent shuffle" occurs. This changes the pseudotwin into true twin, then the restoring force disappears and the strain is no longer recoverable after this restabilization. This explains why strain is not recovered after martensite is aged for some time under load. Similar to Lieberman *et al.*'s idea, a modified pseudotwin-type model was proposed by Zangwill and Bruinsma (1984). This model also reached essentially the same conclusions as above.

Unfortunately, these pseudotwin-based models failed to explain the most important fact of RLB, that is, RLB is absent in fresh (not aged) martensite. According to the above models, the pseudotwin mechanism should equally apply to fresh martensite. Besides, these models cannot explain why aged martensite becomes more stable relative to the parent phase, because martensite structure and stability need not change if martensite is not deformed.

B. Long-range Ordering Model

Abu Arab and Ahlers (1988) proposed that the degree of equilibrium LRO for the parent phase is no longer the equilibrium LRO for martensite when being inherited into the martensite through diffusionless martensitic transformation. Then during aging the as-quenched martensite changes its degree of LRO until reaching the equilibrium value for martensite. They suggested that this is the reason why aging makes martensite become more stable with respect to the parent phase. Tadaki *et al.* (1990) made a detailed ALCHEMI study to identify the change in atomic occupancy during martensite aging. Experimental study (Hashiguchi, 1986) on unstable Cu–Zn–Al alloy also gave some support to such a mechanism.

A primary difficulty that this type of model encountered is that stable martensites such as Au–Cd (Ohba *et al.*, 1990) and Au–Cu–Zn (Ohba *et al.*, 1995) show no evidence of change in LRO during aging, while they still show strong stabilization and RLB. This suggests that this type of model has mistaken the partial decomposition of the unstable martensite (e.g., Cu-based SMA) for the reason for martensite aging. The martensites of Cu-based alloys are not thermodynamic equilibrium phases because they can be obtained only under non-equilibrium conditions (i.e. quenching). Therefore, they have an inborn tendency for decomposition into equilibrium phases, and this occurs whenever diffusion is possible. On the other hand, martensites of Au–Cd and Au–Cu–Zn alloys are obtained by furnace-cooling, thus are equilibrium phases. Since *the average structure (LRO) of an equilibrium phase can by no means be altered by aging* (otherwise it is not an equilibrium phase), the change of LRO cannot be expected to occur in such alloys. Consequently, it is not surprising that the aging of Au–Cd and Au–Cu–Zn martensites brings about no structural change (nor the change in LRO). Thus the origin of aging effect must come from other sources.

Another difficulty for this type of model is that it cannot explain why RLB develops during martensite aging. Following such models, one would deduce that the degree of LRO for different martensite domains (twins) should change into the same equilibrium value during aging, thus reversal of a domain into another one (twinning) by external stress does not involve any change in structure or LRO (as discussed earlier, martensite twinning does not involve pseudotwin formation or structure change). Consequently, there is no energy change for domain reversal and thus no restoring force for RLB. This deduction apparently contradicts the experimental results that martensite stabilization is always accompanied by RLB.

This model also suffers from an insurmountable difficulty in explaining the RLB and stabilization in disordered alloys such as In–Ti, because there is no LRO in disordered alloys at all.

C. Short-range Ordering Model

SRO model was first proposed by Ahlers *et al.* (1978), and was recently extended substantially by Marukawa and Tsuchiya (1995). The SRO model was proposed mainly to explain the RLB, because LRO change

cannot explain RLB. Later the model was also used to explain the stabilization effect of martensite (Marukawa *et al.*, 1995). The essence of this model is as follows: During martensitic transformation, diffusionless lattice distortion brings some 2nd nearest neighbor (2NN) atoms of the parent phase into 1st nearest neighbors (1NN) positions for martensite (for a model martensite structure 3R or L1₀), and this alters the probability of finding a type of atom around the *1NN shell* of a given atom. In other words, martensitic transformation leads to a sudden change in short-range order parameter. This model assumed that despite the structure difference between martensite and the parent, martensite has the same tendency to form more unlike atomic pairs similar to the parent. This tendency is the origin of martensite aging, and consequently the degree of SRO increases during martensite aging. Such a change stabilizes the aged martensite with respect to the fresh one and leads to martensite stabilization. If an aged martensite domain is reverted, the change of martensite crystallographic axes leads to a lowering of SRO (an increase of energy), then a restoring force for RLB engenders.

The SRO model is the first one that explains both stabilization and RLB, as well as the aging effect in disordered alloys, because SRO exists even in disordered alloys. However, there are several shortcomings with this model. The first and the most important one is that this model is in fact a new version of LRO model discussed above. This model depends on the change of pair (bond) probability (which defines the SRO) during martensite aging. However, in an essentially ordered alloy the pair probability also determines the long-range order parameter. Therefore, the change of SRO (or pair probability) in ordered alloys inevitably gives rise to LRO change. This has been illustrated by a computer simulation (Marukawa *et al.*, 1995). Since no LRO change was found in Au–Cd and Au–Cu–Zn alloys in spite of the strong aging effect, one can conclude that the above-mentioned SRO process (leading to LRO change) is not the origin of aging phenomena. The second shortcoming of this model is that if martensite aging were driven by a tendency to increase the probability of favorable atomic pairs (unlike pairs), martensitic transformation would never have occurred because the parent possesses the largest probability of such favorable pairs and thus would have had no reason to transform to martensite. The third shortcoming of this model is the lack of generality. This model is based on a model

martensite structure 3R where transformation from B2 parent into 3R martensite changes some 2NN pairs into 1NN pairs (approximately) by lattice distortion. However, most martensites do not possess such a simple structure, and 2NN atoms in the parent cannot be brought into 1NN positions of martensite by martensitic transformation.

In addition to the above model, Suzuki *et al.* (1995) proposed a different SRO model based on defect pair reorientation similar to Zener ordering (Zener, 1947). They considered that martensite inherits the same configuration of defect-pairs as that of the parent, and such a configuration is not a stable configuration because of the lattice distortion during martensite formation changes the pair lengths, then they try to reorient themselves into a more stable configuration during martensite aging. For aged martensite, a domain reversal by external stress changes some favorably oriented defect pairs into unfavorable pairs, and thus a restoring force for RLB is created. This model is also similar to an earlier model proposed by Christian (1965) that accounts for RLB in disordered In–Ti alloy. However, in ordered martensite free reorientation of defect pairs allowed by the Suzuki model leads to some change of LRO of martensite, thus this model also suffers from the first weakness of the above SRO model, although it appears to be more general.

A recent vacancy ordering model (Ren and Otsuka, 1997b) suggests that vacancy ordering is the origin of the aging effect, this model also has the weakness of requiring some change in LRO of martensite.

In a word, all of the above models require some change of average structure or LRO during martensite aging. This contradicts the experimental fact that aging is not dependent on change of average martensite structure.

3. MODELS WITHOUT DEMANDING A CHANGE IN AVERAGE MARTENSITE STRUCTURE

The above structure-modifying (or LRO-changing) models failed in explaining the most notable feature of martensite aging: martensite aging is not dependent on a change in average martensite structure. Therefore, the aging effect must originate from a process without demanding a change of average martensite structure. The following models belong to this category.

A. Dislocation Model

Birnbaum and Read (1960) proposed that in ordered martensite the existence of order faults hinder the motion of twinning dislocations, and it provides a restoring force for RLB. An obvious shortcoming of this model is the lack of generality, because it cannot explain RLB in disordered alloys. Since the existence of twinning dislocation should not affect the stability of martensite, this model cannot explain why martensite becomes more stable with aging. It is also unable to explain the increase of critical stress with aging, because the interaction of twinning dislocation with order fault is obviously time-independent.

B. Domain Boundary Pinning Model

Because RLB involves reversible motion of domain (twin) boundaries, the dynamics of domain boundaries has been considered to be important for understanding RLB. Internal friction studies by Nakanishi *et al.* (1973) showed that martensite aging leads to a decrease in internal friction and increase of elastic modulus (measured at low frequency). This was interpreted as the pinning of domain boundaries by lattice defects. Because this internal friction result is similar to that for the strain-aging phenomenon of metals where dislocation pinning by defects occurs during aging of metals, it is quite natural to consider pinning force as the restoring force for RLB.

After the discovery of RLB in single domain martensite where domain boundary is absent (Rapacioli *et al.*, 1975; Barcelo *et al.*, 1978), it has been widely believed that a volume effect, not a boundary effect, is the cause of RLB and stabilization effect. However, a recent experiment by Murakami *et al.* (1995) showed that multi-domain martensite has a much stronger aging effect than single-domain martensite does. It seems that the boundary pinning mechanism cannot be simply abandoned, and pinning may be a supplementary, mechanism for RLB.

However, a careful analysis of the pinning mechanism excludes such a possibility. Although domain boundary pinning is highly possible during martensite aging and may contribute to the increase of critical stress, it can never provide a restoring force for RLB which requires the dragging of a macroscopically-displaced (e.g., 1 mm) domain boundary. This is because the pinning force is very short-ranged. Besides, if the

external stress is large enough to change multi-domain martensite into single-domain, there is no domain boundary at all for the pinning source to drag, yet the original domain pattern can still be restored after removing the stress. Therefore, it is clear that domain boundary pinning cannot be a source for RLB, which requires a restoring force of very long range. One may recall the case of dislocation pinning (Cottrell effect) to compare with the RLB of martensite. In that case, pinning of dislocations results in an increased critical stress. However, once a dislocation is depinned by external stress it can never be dragged back to its original position by the pinning force because the pinning force is short-ranged. Therefore, no one has ever observed pseudoelasticity due to reversible motion of dislocations. Because internal friction measurement uses a very small stress which displaces domain boundary only by a very small distance, the result of such a measurement cannot distinguish long-range restoring forces from short-range pinning forces.

Another problem with the pinning model is that it finds difficulty in explaining why martensite needs to become stabilized during aging, because the pinning of martensite domain boundaries does not affect martensite structure, and hence the stability of martensite phase.

Therefore, we can see that although the pinning of martensite domain boundaries is highly possible or may actually happen, it is not a source of martensite RLB and stabilization effect.

C. Symmetry-Conforming Short-Range Order (SC-SRO) Principle and SC-SRO Model

Very recently, Ren and Otsuka (1997a) proposed a general principle concerning the symmetry property of the SRO configuration of point defects in crystals. It is named SC-SRO principle, and is applicable to any crystal containing point defects. The aging phenomena of martensite can be easily understood with this principle. This principle states that *the symmetry of SRO configuration of point defects in equilibrium should conform to the symmetry of the crystal lattice*.

In order to understand this principle, it is necessary to clarify the meaning of SRO parameters. Usually SRO parameters are defined according to the probability of finding one kind of atom in the 1st (or n th) nearest neighbor *shell* of a given atom, as used by previous SRO models. However, such a definition cannot describe atomic

rearrangement within the same shell (or within the same sublattice). We shall show later that it is this kind of rearrangement that is responsible for martensite aging. Therefore, such a definition of SRO parameter is not suitable to describe martensite aging process.

Here SRO is defined in terms of the probability of finding one kind of atom or defect *at some interatomic vector* from a given atom.

$$\alpha_{lmn} = 1 - \frac{P_i^B |^A}{x_B}$$

where lmn is the coordinates of the interatomic vector between site i, j ; $P_i^B |^A$ is the conditional probability that there is a B atom at site i if there is an A atom at j ; x_B is the average concentration of B. Such an SRO concept is consistent with the definition by Warren and Cowley. The averaging of such SRO parameters in the same shell reduces to the SRO concept defined by shell probability. Therefore, such SRO parameters are established on crystal lattice, and it is natural that they should possess certain symmetry properties.

The SC-SRO principle gives a general and simple explanation to the aging phenomena in both ordered alloys and disordered alloys. Since the SRO parameter is completely determined by conditional probability $P_i^B |^A$, we shall discuss aging in terms of the symmetry property of this conditional probability. Let us take an essentially ordered alloy for example. The change of the SRO configuration of a point defect (either anti-site defect or vacancy) during martensitic transformation and aging is considered. Figure 5(a) shows a two-dimensional A-B binary *imperfectly-ordered* parent phase with 4-fold symmetry. Because of the 4-fold symmetry of the structure, the probability of finding a B atom about the A atom (or B atom) must possess the same 4-fold symmetry according to SC-SRO principle, i.e., $P_1^B = P_2^B = P_3^B = P_4^B$, and $P_5^B = P_6^B = P_7^B = P_8^B$, etc., where P_i^B ($i = 1, 2, 3, \dots$) are conditional probabilities, as defined in Fig.5. The martensite has a lower symmetry, thus the equilibrium occupation probability of atoms should have the same symmetry as the structure about the A atom, i.e., $P_1^B = P_3^B \neq P_2^B = P_4^B$ and $P_5^B = P_7^B \neq P_6^B = P_8^B$, as shown in Fig. 5(c). The equalities are due to the centro-symmetry of the schematic martensite structure.

When the parent phase shown in Fig. 5(a) transforms diffusionlessly into martensite, all the probabilities must remain unchanged despite the

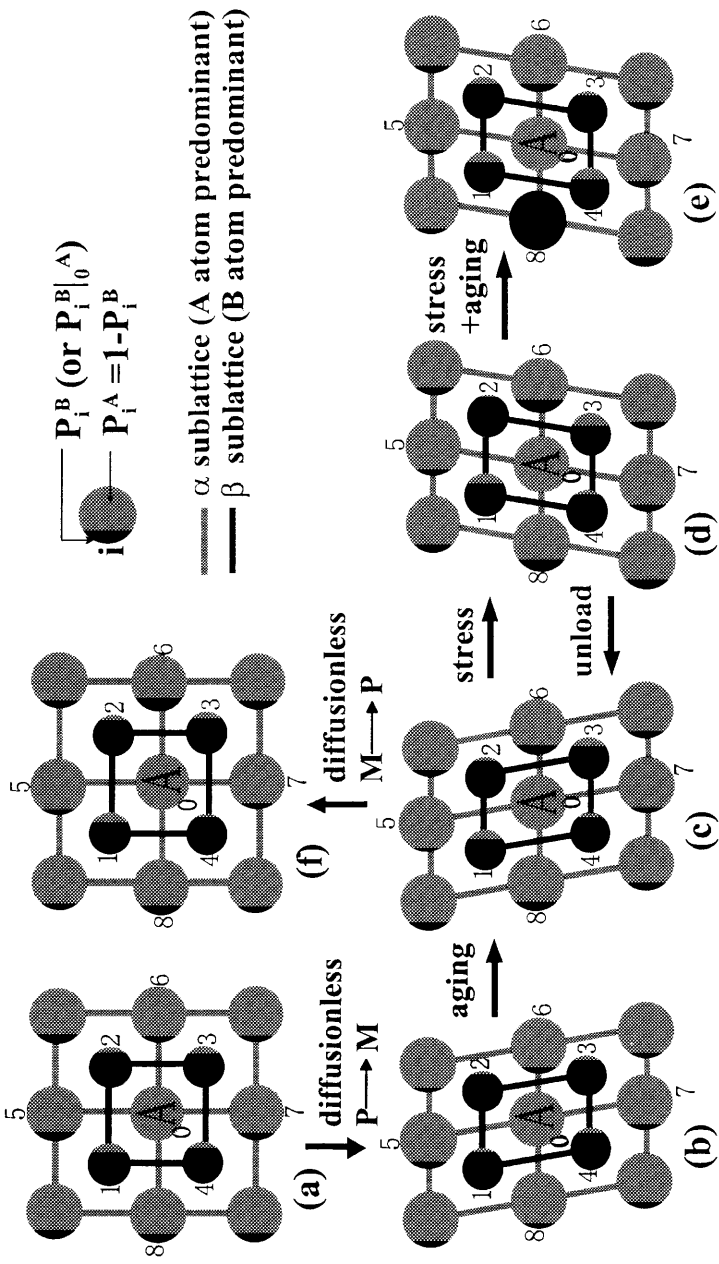


FIGURE 5. Symmetry-conforming short-range order mechanism of martensite aging phenomena. After Ren and Otsuka (1997a). The illustrations show the statistical atomic configuration (conditional probabilities around an A atom) of an *imperfectly-ordered* A-B alloy in (a) equilibrium parent phase; (b) martensite immediately after transformed from (a); (c) equilibrium martensite; (d) stress-induced martensite domain (twin) immediately formed from (c); (e) equilibrium state of the stress-induced domain; and (f) parent immediately transformed from (c), respectively. P: the parent phase, and M: martensite. P_i^B (or P_i^A) is the conditional probability of B atom (or A atom) occupying i -site ($i = 1, 2, 3, \dots, 8$) if an A atom is at 0-site. The relative values of P_i^B and P_i^A are indicated by the black and gray areas, respectively.

symmetry change, as shown in Fig. 5(b). That is $P_1^B = P_2^B = P_3^B = P_4^B$, and $P_5^B = P_6^B = P_7^B = P_8^B$, etc. However, this high-symmetry configuration is no longer a stable configuration for the lower symmetry martensite structure. Then during aging, such a configuration gradually changes into a stable one that conforms to martensite symmetry, as shown in Fig. 5(c). Because the equilibrium martensite structure should be maintained (for stable martensite), this process proceeds by atomic rearrangement or relaxation within the same sublattice. This is the only way that a martensite can lower its free energy without altering the average structure (equilibrium phase). It is obvious that such an atomic rearrangement occurs most easily for atoms close to the A atom, and farther atoms make little contribution. Consequently, *it is a kind of short-range ordering within the same sublattice*. As shown above, this SRO stems from a requirement that the symmetry of the SRO parameters of lattice imperfections in equilibrium conforms to the crystal symmetry, following the SC-SRO principle. The stable SRO configuration for the parent is inherited into martensite during diffusionless martensite formation, but this SRO becomes "unstable" for martensite because it differs from the martensite symmetry. Then atomic rearrangement occurs during aging that results in a correct SRO symmetry for the martensite. The difference between SC-SRO and previously proposed SRO (Ahlers *et al.*, 1978; Marukawa *et al.*, 1995; Suzuki *et al.*, 1995) is that the change of SC-SRO does not alter average structure or LRO. This is because SC-SRO mechanism restricts effective (net) atom exchange only within the same sublattice. In this aspect, such short range diffusion is similar to the diffusion process in conventional ordered alloy where net atomic exchange occurs only within the same sublattice so that LRO structure is maintained (e.g. Hagel, 1967).

When the stabilized (or aged) martensite (Fig. 5(c)) is deformed, it changes into another domain (or twin) as a result of the accommodation of the strain. Because this twinning process is also diffusionless, the atomic occupation probabilities shown in Fig. 5(c) is inherited to the new domain, as shown in Fig. 5(d). Such a configuration, however, is not the stable one for the new domain, which is shown in Fig. 5(e). Therefore, a driving force that tries to restore the original domain (Fig. 5(c)) engenders. This is the long-range restoring force to drag back a displaced domain boundary. When the external stress is released immediately after the loading, this restoring force reverts the new

domain (Fig. 5(d)) to the original one (Fig. 5(c)) by de-twinning. This is the origin of the rubber-like behavior. If the stress is held for some time, the atomic configuration in Fig. 5(d) has enough time to change into a stable configuration (Fig. 5(e)), and no RLB will occur.

When the stabilized martensite (Fig. 5(c)) is heated up and transforms back (diffusionlessly) into the parent, the stable SRO configuration for the martensite is inherited into the parent (Fig. 5(f)). From the above-mentioned symmetry-conforming principle of SRO, it is obvious that Fig. 5(f) is not a stable configuration for the parent. From a thermodynamic point of view, this corresponds to an increased reverse transformation temperature. This is the origin of martensite stabilization.

The SC-SRO model can be easily extended into disordered alloys by considering the existence of only one sublattice. In this case, the present model reduces to Christian's model (Christian, 1965), which was later elaborated by Otsuka and Wayman (1977). This model explained the rubber-like elasticity in disordered alloys such as In–Ti.

The largest advantage of the SC-SRO model compared with previous models is its fulfillment of the generality criterion. It not only explains why aging does not cause a change of average structure of martensite, but also unifies the origin of aging effect for both ordered and disordered martensites. The generality of the model lies in that it makes use of only two general features of martensitic transformation and aging: diffusionless symmetry-change upon martensitic transformation and diffusion of point defects during aging. In line with this reasoning, it can be deduced that the existence of point defects and possibility of diffusion in martensite are two necessary conditions for aging phenomena. The existence of point defects is generally satisfied by alloys, but the possibility of diffusion in martensite depends on the reduced martensitic transformation temperature M_s/T_m . The higher this reduced temperature is, the faster diffusion in martensite becomes. If this value is too low, aging phenomena are too slow to observe; if this value is too high, aging is so fast that aging phenomena actually appear immediately after the martensitic transformation, thus the time-dependence of aging may not be observed. As shown in Table I, TiNi alloy belongs to the former case, and In–Ti belongs to the latter. Other shape memory alloys are in-between. The absence of martensite aging effect in TiNi shape memory alloys (Kozuma *et al.* 1998) is very interesting because this property is desirable for most applications of SMA. The reason, as stated above, is

TABLE I Relationship between the reduced martensitic transformation temperature M_s/T_m and the rate of martensite aging (RLB) at room temperature

Alloy	Ti-Ni	Cu-Al-Ni	Cu-Zn-Al	Au-Cd	In-Tl
M_s/T_m	~ 0.19	~ 0.23	~ 0.27	~ 0.34	$0.50 \sim 0.79$
Aging time for RLB at RT	$\sim \infty$	~ 10 months	~ 5 h	~ 0.5 h	< 1 s

very simple. This reminds us that the most effective way to develop SMA without aging effect is to choose alloys with high M_s/T_m value. This can be realized by (i) using SMA with a low M_s , or (ii) using SMA with high T_m . Since the first method is usually restricted by application purpose, using alloys with high melting temperature becomes the most effective method. Therefore, the development of SMA without aging effect should focus on alloys with high T_m , since it is not possible to stop diffusion in martensite for alloys with low T_m .

One may expect that if the SC-SRO principle or the SC-SRO model is correct, it should not only explain *all* experimental observations without exception, but also be able to find direct experimental evidence. In a preliminary TEM study (Ren *et al.*, 1997), a decisive experimental evidence proving the existence of SC-SRO has been found, this experiment also showed that the SC-SRO model is also able to explain the large difference in aging effect between single-domain martensite and multi-domain martensite, one of the most challenging problems. The details of this study will be published later. At present, the small change in the symmetry of X-ray diffraction profile (Fig. 4) during aging provides support to this model. This result cannot be rationalized by any other model. The change of the symmetry of diffraction profile indicates that the symmetry-conforming SRO rearrangement of defects occurs, which leads to a slight change in atomic displacement field and results in the change in the symmetry of the diffraction profile without altering peak position and intensity.

Since SC-SRO is a general property of point defects in crystalline solids, we predict that the aging effect is no more than one of many effects it produces. For example, if crystal symmetry is changed (slightly) by elastic deformation, not by diffusionless transformation, we can similarly expect that short-range rearrangement of atoms or defects occurs to conform to the new symmetry. This process has really been found in both disordered (Zener, 1947) and ordered alloys (Birkenbeil and Cahn, 1962), and is referred as "Zener ordering".

Similarly, we can expect that some diffusional rearrangement occurs in some inorganic crystals (such as ferroelectric or ferroelastic ceramics) after a diffusionless transition, if diffusion is possible during aging.

4. SUMMARY

We have critically reviewed available models for martensite aging phenomena (stabilization and RLB) in terms of generality criterion. These models include pseudotwin-type model, LRO model, SRO model, dislocation model, domain boundary pinning model, and symmetry-conforming short-range ordering (SC-SRO) model. It turned out that the SC-SRO model is the only one that satisfies the criterion, and thus is able to explain all known experimental facts on martensite aging in both ordered and disordered alloys. This model is a natural application of a general principle (symmetry-conforming principle) that the symmetry of SRO configuration of lattice defects in equilibrium conforms to the symmetry of the crystal lattice. Therefore, we have reason to believe that we are approaching the final solution to the 65 year old problem of martensite aging.

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