

Does order–disorder transition exist in near-stoichiometric Ti–Ni shape memory alloys?

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Abstract

Previous work by Honma et al. suggested that there is an order–disorder transition around 1090 °C in Ti–Ni alloys, but its existence has not been confirmed by independent investigation. In the present work, various techniques including TG-DTA, resistance measurement and TEM were employed to detect the possible signs of such a transition. We found interestingly that when strong measures were taken to prevent sample oxidation, no sign for order–disorder transition was detected; but when the sample was allowed to be oxidized during measurement, we did find a clear DTA peak at 1118 °C. With SEM-EPMA analysis this peak was identified as originating from a eutectic reaction in the oxidation-affected layer, where selective oxidation of Ti causes significant enrichment of Ni and hence drives the oxidation-affected layer into the eutectic regime. Therefore, our results disprove the existence of “order–disorder transition” in the B2 portion of the Ti–Ni phase diagram.

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1. Introduction

Ti–Ni and Ti–Ni-based alloys have attracted significant attention over the past few decades [1,2], since they are the most important shape memory alloys with a combination of excellent functional properties (shape memory effect, superelasticity) and good mechanical properties. As a basis for understanding this alloy family, the phase diagram of the Ti–Ni system is of fundamental importance, especially the central B2 phase regime (with composition around Ti–50Ni), which undergoes a B2–B19' martensitic transformation and exhibits shape memory effect. The phase diagram of Ti–Ni binary alloys was essentially established by the

end of 1980s [3], but has undergone an important update recently [4,5]. It is the addition of an order–disorder transition line at 1090 °C in the B2 phase regime. The addition of this line of transition is due to the work of Honma et al. [6], who reported the existence of an order–disorder (B2–BCC) transition in the B2 regime. They found that there existed a clear peak around 1090 °C in their differential thermal analysis (DTA) curve; they also observed that there existed a “superlattice peak” in their neutron diffraction spectrum at low temperature. These pieces of evidence seem persuasive for the existence of the order–disorder transition, but there has been no independent study confirming their findings.

There are two surprising features associated with their suggested “order–disorder” transition in Ti–Ni. The first one is that their order–disorder transition temperature is independent of the composition (Fig. 1). This feature does not exist in any other order–disorder system, as it is normal

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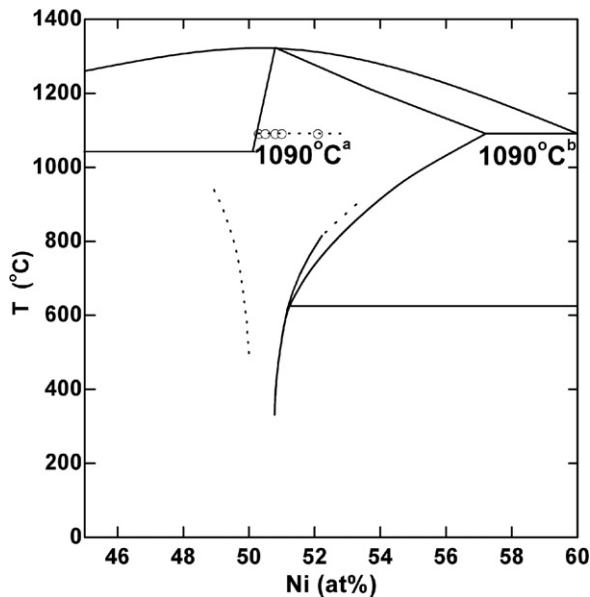


Fig. 1. Phase diagram of near-stoichiometric Ti–Ni (after Honma et al. [6]). 1090 °C^a: order–disorder transition temperature (bcc→B2); 1090 °C^b: eutectic reaction temperature (L→TiNi + TiNi₃).

that the order–disorder transition temperature is highest at the stoichiometric composition. It is hard to imagine a composition-independent order–disorder transition temperature from a thermodynamic point of view [7]. The second surprising feature is that the composition-independent critical temperature ($T_c = 1090$ °C) coincides with the temperature of a eutectic reaction, liquid (TiNi)→TiNi + TiNi₃ (also at 1090 °C, see Fig. 1), the latter existing only in a Ni-rich composition regime of Ni > 57 at.%. Although it is not inconceivable that the temperature for the order–disorder transition of a near-stoichiometric composition coincides with that for the eutectic reaction of a different composition, it seems too accidental that they are identical for all the compositions in the B2 regime.

In view of the importance of the order–disorder transition on the shape memory properties of Ti–Ni, and also because of the above-mentioned puzzles with the suggested order–disorder transition in this system, we carried out a systematic investigation with two objectives: (1) to reach a definite conclusion about whether or not there exists an order–disorder transition in Ti–Ni; (2) to provide a clear answer to the puzzles described above. We note that all of Honma’s experiments are performed in air, thus oxidation might have occurred during their high-temperature measurements like DTA and in situ neutron diffraction. Thus, there is a possibility that their results were affected by sample oxidation. Considering the possible influence of oxidation on the results, we did two types of experiments in the present study. The first type aims to find evidence for order–disorder transition in an essentially non-oxidation environment; the second type allows the samples to be oxidized, and aims to clarify the effect of oxidation on experimental results.

As will become evident in the following, we find striking results. When the samples are not allowed to be oxidized during high-temperature measurement, there exists no evidence for the existence of an order–disorder transition, despite the various techniques employed. On the other hand, if the samples are allowed to be oxidized during high-temperature measurement, we do reproduce the DTA peak reported by Honma et al., who apparently took it as evidence for the existence of order–disorder transition. However, our scanning electron microscopy/electron probe X-ray microanalysis (SEM-EPMA) analysis shows that this peak originates from a eutectic reaction in the oxidation-affected layer, where selective oxidation of Ti causes significant enrichment of Ni and hence drives the oxidation-affected layer into the eutectic composition regime. This eutectic reaction and the enrichment of Ni explain the possible “evidence” for the order–disorder transition in Ti–Ni.

Therefore, our findings disprove the existence of an order–disorder transition in near-stoichiometric Ti–Ni; thus the B2 phase persists up to the melting point. Our work settles the dispute about the B2 portion of the Ti–Ni phase diagram and it may have implications for the interpretation of the effect of heat treatment on martensitic transformation and shape memory behavior of the Ti–Ni alloys. Furthermore, the finding of the eutectic reaction due to oxidation reveals the importance of anti-oxidation measures in heat-treating this important but delicate alloy.

2. Experimental

2.1. Experimental procedure – two types of experiment

For the two purposes mentioned above, we divided our experiment into two groups. Group 1 was studied with an atmosphere of strongly reducing capability, that is, Ti-getter plus a mixture gas of Ar–1%H₂. This environment produces a negligible amount of oxidation during high-temperature experiments. Group 2 was studied with an atmosphere that can produce an appreciable amount of oxidation during high-temperature experiments. The experimental method for each group is described separately in the following. The chemical basis for the difference in oxidation between the two kinds of environment will be given in the next section.

2.1.1. Group 1: Detecting the possible order–disorder transition in an essentially non-oxidation environment

If an order–disorder transition exists, the materials under investigation will undergo a change in thermal or/and electrical properties at the transition temperature; thus one may observe a peak in the DTA curve and a slope change in the resistance vs. temperature curve [8]. Also one may observe a characteristic anti-phase domain boundary (APB) pattern in TEM when the sample is quenched through its transition temperature T_c ; this has been considered as a test of the existence of a high-temperature order–disorder transition [9].

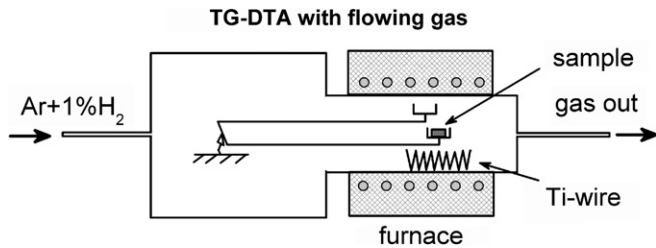


Fig. 2. Schematic illustration of TG-DTA setup with controlled oxygen partial pressure.

In Group 1 experiments, we employed the above three approaches to check the existence of the order–disorder transition. The experiments were performed in an essentially non-oxidation environment, i.e., with the Ti-getter and the Ar–1%H₂ mixture gas. In the present study, we used Ti–50Ni alloys for TG-DTA, and electrical resistance measurements, and Ti–51Ni alloy for TEM observations.

The sample with 3 mm diameter for TG-DTA was spark-cut into small pieces, and followed by mechanical polishing and chemical etching to obtain a clean and bright sample surface. High-temperature DTA experiments were performed with a commercial TG-DTA apparatus (Rigaku Thermo Plus TG 8120) with a heating/cooling rate of 3 K min^{−1}. During the TG-DTA experiment, the Ti–50Ni (97.3 mg) sample was protected by both Ti-getter and Ar–1%H₂ mixture gas (as shown in Fig. 2), and its oxygen partial pressure was monitored by a ZrO₂ cell. TG-DTA measures both the thermal peak of a phase transition and also the weight gain due to oxidation. The temperature dependence of electrical resistance of a Ti–50Ni wire was measured by a four-terminal method under the protection of Ti-getter and the Ar–1%H₂ mixture gas. The sample was also heated at a rate of 3 K min^{−1}.

TEM observation of a possible APB contrast was carried out with a Ti–51Ni sample. Using Ti–51Ni instead of 50Ni is to keep the B2 state down to room temperature; thus this facilitates the TEM observation of APB at room temperature. The sample was mechanically polished and chemically etched, followed by sealing it into a quartz tube with argon and Ti-getter. It was solution-treated at 1200 °C (above the claimed T_c) for 0.5 h and followed by quenching into ice salt water with the tube broken immediately by a hammer. After the above heat treatment, the samples were mechanically polished to about 0.1 mm thick and finally electropolished using a twin-jet apparatus operating at 250 K. The electrolytic solution consists of 5 vol.% HClO₄ and 95 vol.% CH₃CH₂OH. TEM observation was performed at room temperature with JEM-200CX operated at 200 kV.

2.1.2. Group 2: TG-DTA experiment in oxidizing environment

To understand the effect of sample oxidation on the TG-DTA result, the Group 2 experiment was done in a slightly oxidizing atmosphere: a mixture gas of Ar–1%H₂.

Although this mixture gas itself seems like a reducing atmosphere, it produces an oxygen partial pressure of about 10^{−15} atm at 1000 °C, which is still much higher than the critical oxygen partial pressure for Ti oxidation in TiNi (about 10^{−26} atm at 1000 °C); thus the mixture gas is actually an oxidizing gas for Ti–Ni alloy. The details of the chemical basis for the oxidation are given in Section 2.2. It should be mentioned that we did not simply use air as an oxidizing gas, because it is so strong that most of the sample became oxidized after heating it to high temperatures (1200 °C). In the Group 2 experiment with TG-DTA, one Ti–50Ni (128.3 mg) and one Ti–51Ni (40.1 mg) sample were oxidized by Ar–1%H₂ mixture gas with a flow rate of 50 ml min^{−1}.

Finally, for the above two groups of samples we did SEM-EPMA to analyze the oxidation and microstructure change due to oxidation after their TG-DTA measurement.

2.2. Chemical basis for controlling oxidation of Ti–Ni by the Ar–1%H₂ mixture gas and Ti-getter

To understand the difference in the environment between Group 1 and Group 2 experiments, we need to first calculate the critical oxygen partial pressure for the oxidation of TiNi. Firstly it is noted that the oxidation of Ti–Ni is actually a selective oxidation of Ti, because of the large difference in the formation energy of the two oxides (TiO₂: 709.5 kJ mol^{−1}; NiO: 121.3 kJ mol^{−1} at 1000 °C) [10]. From the thermodynamic data for the oxidation reaction TiNi + O₂ → TiO₂ + Ni in Ref. [10], one can easily calculate the critical oxygen partial pressure for Ti oxidation in TiNi to be 10^{−26} atm at 1000 °C, which is an extremely low value.

This result has an important consequence: Ti in TiNi alloy can be easily oxidized at high temperature, and it is very difficult to prevent the oxidation due to the extremely low oxygen partial pressure P_{O_2} required. Clearly, heating in air ($P_{O_2} = 0.2$ atm), in vacuum by pumping ($P_{O_2} = 10^{-6}$ – 10^{-8} atm) or in argon ($P_{O_2} = 10^{-8}$ atm) will result in severe oxidation. In fact, we found that after carrying out DTA measurement (heating up to 1300 °C) in low vacuum ($P_{O_2} = 10^{-6}$ atm), a Ti–Ni sample was covered with a thick layer of white oxide layer, which is basically TiO₂. The use of Ar–1%H₂ mixture gas can produce lower oxygen partial pressure, but still not sufficient to prevent the sample from oxidation. For the Ar–1%H₂ mixture gas environment, we measured its oxygen partial pressure at the entrance of our DTA chamber by a ZrO₂ cell kept at 735 °C. The cell read 10^{−20}–10^{−22} atm (which means that the H₂/H₂O ratio of the Ar–1%H₂ gas is as large as 1–0.1). From this ratio and the thermodynamic equilibrium (2H₂ + O₂ → 2H₂O), we can calculate the oxygen partial pressure in the DTA furnace (1000 °C) to be 10^{−15.1}–10^{−17.1} atm [10]. Clearly it is about 10 orders of magnitude higher than the critical oxygen partial pressure for oxidation of Ti in Ti–Ni; thus the mixture gas is actually an oxidizing gas for Ti–Ni. This is the environment for the Group 2 experiment.

On the other hand, in the Group 1 experiment, Ti-getter plus the Ar–1% H_2 mixture gas was employed. Pure Ti can in principle create an extremely low oxygen partial pressure of 10^{-30} atm at 1000 °C [10], and thus can prevent the sample from oxidizing. However, this cannot be achieved kinetically if Ti is placed in a high vacuum, as it would take a very long time to achieve equilibrium. Using a combination of Ti-getter and Ar–1% H_2 mixture gas can enhance the reaction rate and make the protecting atmosphere more efficient from a kinetic point of view, although at the expense of slightly increasing the oxygen partial pressure. For this reason, the sample may still be slightly oxidized, but to a negligible extent.

3. Results

3.1. The absence of DTA peak up to the melting point in Ti–Ni measured in a non-oxidizing atmosphere

As the first of the Group 1 experiments, we did a TG–DTA measurement for a Ti–50Ni sample in a non-oxidizing atmosphere, Ti-getter plus the mixture gas Ar–1% H_2 . Fig. 3 shows the result. Surprisingly there is no DTA peak up to the melting point at 1310 °C, where a DTA peak for the melting appears. The TG curve shows that the weight gain during the heating and cooling cycles is a very small value of about 1 mg cm^{-2} ; this suggests that the sample oxidation during the measurement is minimal. Note that our DTA result is in contrast with that obtained by Honma et al., who found a DTA peak at 1090 °C. We noticed that the difference between our experiment and their experiment seems to come from a difference in the environment: we used a strong reducing atmosphere to prevent oxidation, whereas they apparently did not take into account the sample oxidation. As will be seen below, such a difference in environment indeed makes a large difference in the sample.

3.2. The absence of resistance anomaly in Ti–Ni alloys in a non-oxidizing atmosphere

The second Group 1 experiment was to measure electrical resistance vs. temperature curve around the suggested T_c (1090 °C) to detect whether the order–disorder transition

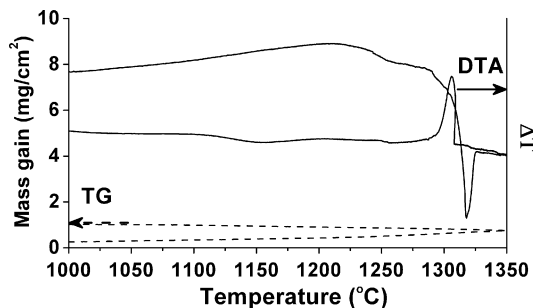


Fig. 3. DTA curves and corresponding TG curves (dashed lines) for a Ti–50Ni specimen protected by Ti-getter and Ar–1% H_2 mixture gas. The environment can also be changed into the mixture gas alone.

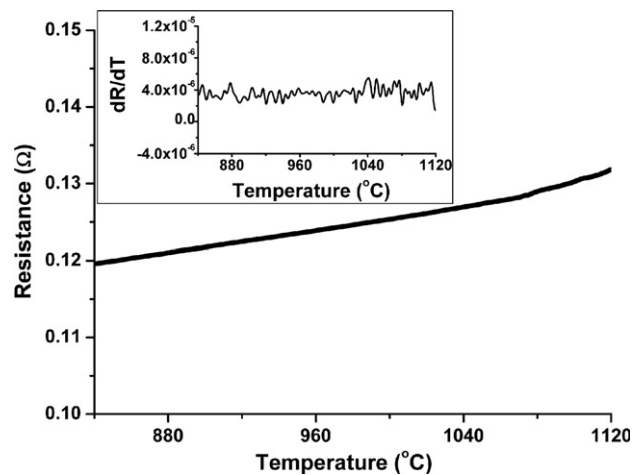


Fig. 4. Temperature dependence of electrical resistance of Ti–50Ni alloy measured under the protection of Ti-getter and Ar–1% H_2 mixture gas. The heating rate was 3 K min^{-1} (the inset shows a differential (dR/dT) curve as a function of temperature).

exists. Resistance measurement has the advantage of being able to detect an order–disorder transition that has too small a thermal effect to be detected by DTA, such as a second-order transition. It has been found that, at the order–disorder transition temperature, a drastic change appears in the electrical resistance or in its derivative with respect to temperature [8]. Our resistance measurement was done in a non-oxidizing environment with Ti-getter and the mixture gas Ar–1% H_2 in a tube furnace (being similar to the DTA setup shown in Fig. 2).

The result of such an experiment is shown in Fig. 4. It is clear that no change in resistance or in its derivative is observed. The electrical resistance of the sample increases smoothly with increasing the temperature and there is no drastic change over the whole temperature range measured (up to 1120 °C). The first derivative of electrical resistance with respect to temperature remains a constant (as shown in the inset of Fig. 4) over a wide temperature range spanning the supposed order–disorder transition temperature 1090 °C. Thus we do not find any evidence for the order–disorder transition in Ti–Ni with resistance measurement.

3.3. The absence of anti-phase boundaries (APB) in Ti–Ni quenched from 1200 °C (above the suggested $T_c = 1090$ °C)

The third Group 1 experiment was to observe APB in a Ti–51Ni alloy quenched from above the suggested order–disorder transition temperature (1090 °C). If an order–disorder transition exists, one should be able to observe anti-phase boundaries (APB) by TEM in a sample rapidly cooled from above T_c [9]. This is because the ordered phase nucleates at various places out of a disordered state, and the phase difference between different domains creates APBs, which may be retained by fast quenching. In this experiment we tried to observe APBs by TEM using a Ti–51Ni alloy, which was quenched from 1200 °C (above the reported order–disorder transition temperature), into ice–salt water

with the quartz tube broken immediately. Fig. 5 shows a dark field image of the sample by using (010)_{B2} superlattice reflection taken with [001]_{B2} zone axis. Clearly no APB is observed. We have made many TEM observations to search for APB, but none was found. This negative result is also consistent with the fact there has been no report on the presence of APB in Ti–Ni to our knowledge.

3.4. The appearance of a DTA peak at 1118 °C measured in an oxidizing atmosphere

We now show the experimental results of Group 2. For this group the TG-DTA experiment was performed in an oxidizing environment: the mixture gas Ar–1%H₂. Our aim is to find the effect of oxidation on the TG-DTA result. The TG-DTA curve for Ti–50Ni is shown in Fig. 6, and that for Ti–51Ni is shown in Fig. 7.

Fig. 6a shows the DTA curves in four heating–cooling cycles for a Ti–50Ni sample. Contrasting strikingly with the non-existence of the DTA peaks for samples measured in non-oxidizing environment (Fig. 3), all the DTA curves here show distinct peaks around 1124 °C upon heating and 1116 °C upon cooling except for the first heating run, and the peak temperatures keep essentially constant for each cycle. This seems to reproduce Honma et al.’s DTA evidence for an “order–disorder transition” (except for a slight difference in the peak temperature; they reported $T_c = 1090$ °C). It is also interesting to note that the peak is much larger upon cooling than that during heating for each cycle, and its intensity also increases with increasing heating–cooling cycles. This strange feature has not been found previously in any order–disorder transition.

Fig. 6b shows the corresponding TG curve of the four heating–cooling runs associated with Fig. 6a. It is clear that the mass gain increases steadily with more cycles. Clearly, the Ti–Ni sample is oxidized during the DTA measurement in an oxidizing environment. The effect of oxidation on the microstructure of the Ti–Ni samples will be shown in the next section.

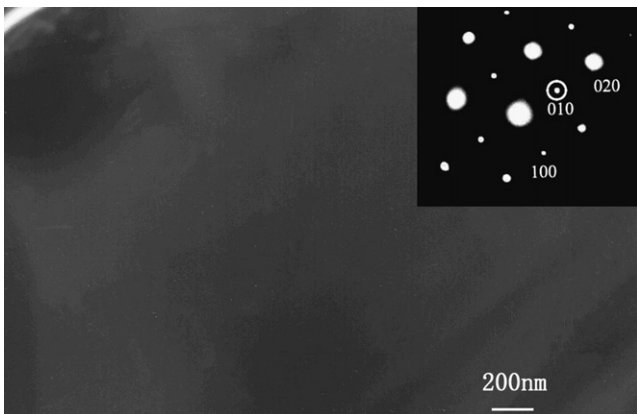


Fig. 5. Dark field image of Ti–51Ni by using (010)_{B2} superlattice reflection (encircled) in the inset diffraction pattern. Incident beam // [001] direction.

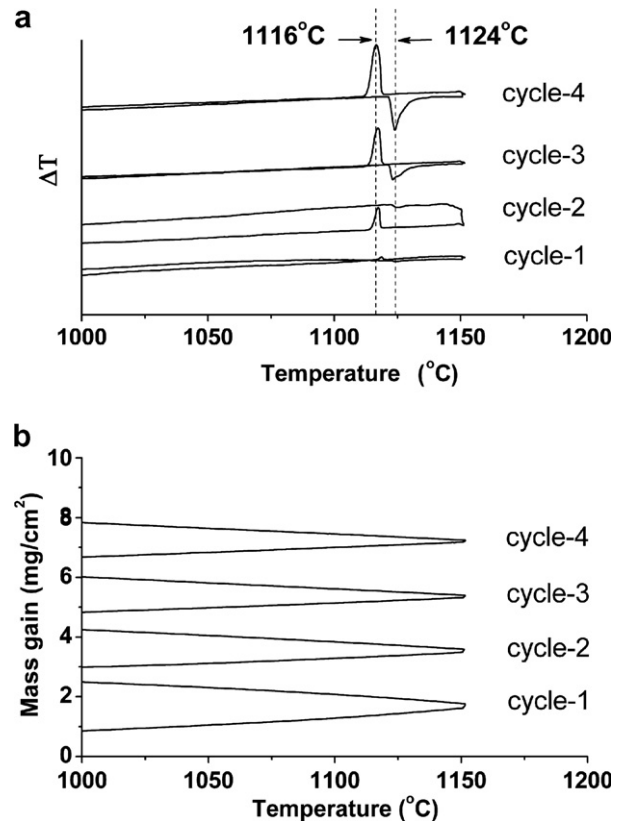


Fig. 6. (a) DTA curves for a Ti–50Ni specimen in Ar–1%H₂ environment (oxidizing); (b) the corresponding TG curves.

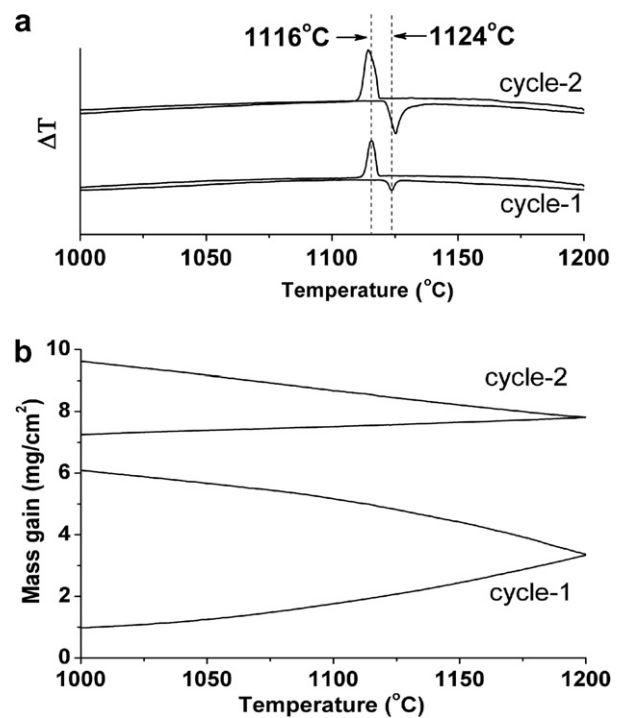


Fig. 7. (a) DTA curves for a Ti–51Ni specimen in Ar–1%H₂ environment (oxidizing); (b) the corresponding TG curves.

Fig. 7a and b shows the DTA and the corresponding TG curves for two heating–cooling runs for a Ti–51Ni sample, which were also measured in the same mixture gas. It is clear that there is also a pair of endothermic and exothermic peaks at 1116 and 1124 °C, respectively. Compared with the peak temperature of Ti–50Ni shown in Fig. 6a, we can see that the transition temperature is independent of composition. This again reproduces Honma et al.’s result about the composition independence of the DTA peaks.

It should be noted that the average of the measured DTA peak temperatures for the cooling and heating coincides well with the eutectic temperature (1118 °C) for the reaction: liquid (TiNi) → TiNi + TiNi₃, according to the most recent Ti–Ni binary phase diagram [3,4]. This reaction exists only in a higher Ni composition regime from 57Ni to 75Ni. Thus again we reproduce Honma et al.’s experimental result: the “order–disorder transition” temperature (if considering the peak as such a transition) always coincides with the temperature of the eutectic reaction. We notice that Honma et al.’s peak temperature (1090 °C) is slightly different from ours (1118 °C); such a difference is probably due to an error in their temperature measurement. Thus it seems reasonable to conclude that Honma et al.’s 1090 °C peak is the same as our 1118 °C peak in Figs. 6 and 7. For convenience, hereafter we call the DTA peaks around 1118 °C (shown as Figs. 6 and 7) as the 1118 °C DTA peak. The Group 2 experiment clearly shows that the “evidence” for order–disorder transition can be reproduced only when the sample is oxidized during the high temperature measurement. This seems to suggest a very different scenario for the proposed “order–disorder transition.”

3.5. Microstructure and composition analysis for the Group 1 and Group 2 samples by SEM-EPMA

In order to understand the difference in DTA results between the oxidizing and non-oxidizing atmospheres and to identify the origin of the 1118 °C DTA peak, the microstructure of the DTA samples in both oxidizing and non-oxidizing atmospheres was characterized by SEM-EPMA. The results are shown in the following.

Fig. 8 and Table 1 show the SEM and EPMA results of a Ti–50Ni sample after experiencing a high-temperature TG-DTA measurement in the oxidizing atmosphere (in the mixture gas Ar–1%H₂, Group 2). Fig. 8a is a low-magnification SEM micrograph of the cross-section, and b is a line scan of the elements O, Ti, and Ni from the surface to the interior. It is clear that there exists a thick oxidation-affected layer of 500 μm thick, whose microstructure is apparently very different from that expected for a single B2 phase. The composition image at a higher magnification is shown in Fig. 8c, where different phases show different brightness. The compositions of these different phases (marked with a, b, c, and d) are determined quantitatively with point analysis and the results are listed in Table 1, where the phases are identified according to Refs. [11–13].

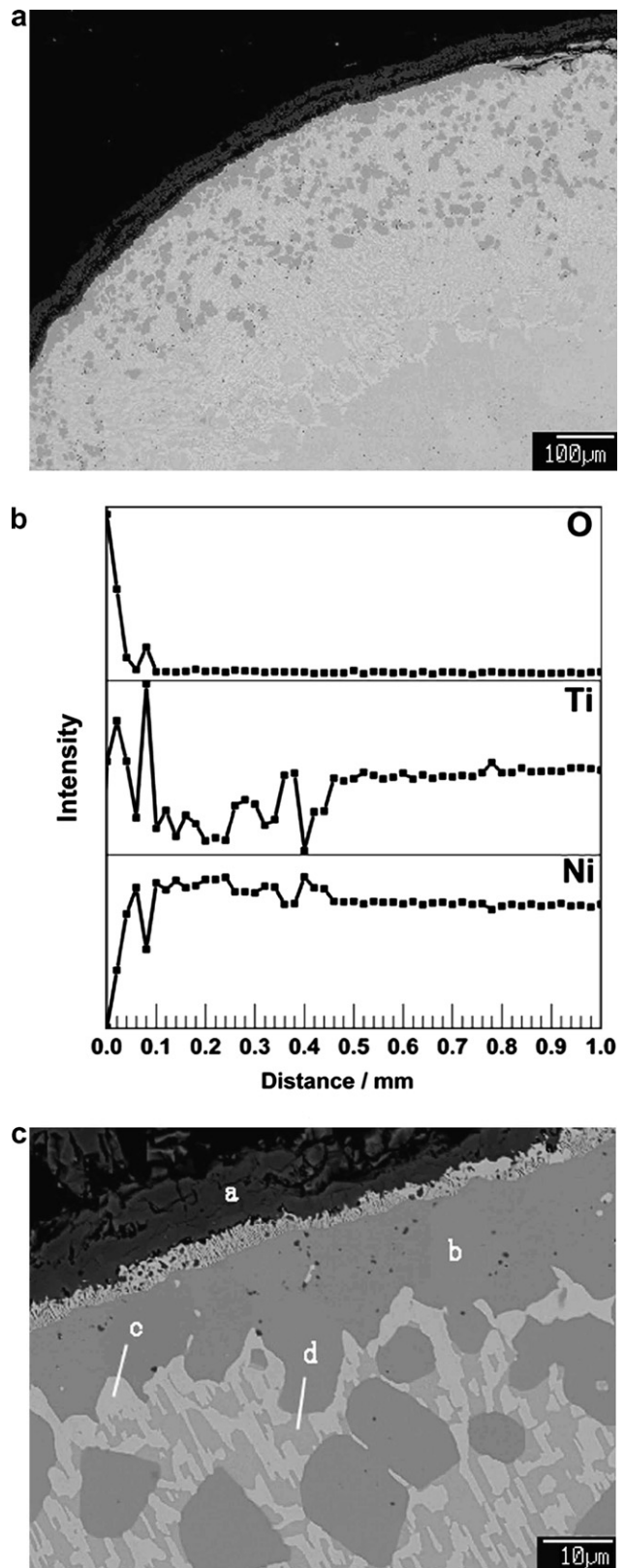


Fig. 8. SEM and EPMA results of the Ti–50Ni sample after the TG-DTA measurement in Ar–1%H₂ mixture environment (Fig. 6): (a) a low-magnification SEM micrograph of the cross-section; (b) EPMA line scan from the surface to the interior; (c) high magnification SEM micrograph of the oxidation-affected zone near surface. The composition at points a, b, c and d is listed in Table 1.

Table 1
Chemical composition and phase identification at different locations in Fig. 8c (unit: at.%)

	(a)	(b)	(c)	(d)	Near the oxidation layer	Center of the sample
O	65.0	16.4	1.3	2.2	1.6	1.5
Ti	34.9	55.3	26.9	47.7	46.4	47.6
Ni	0.1	28.3	71.8	50.1	52.0	50.9
Phase	TiO ₂	Ti ₄ Ni ₂ O	TiNi ₃	TiNi	TiNi	TiNi

For the sample treated in the oxidizing environment (Fig. 8a), the oxidation is severe and the affected layer is about 500 μm thick, which is consistent with line scan results in Fig. 8b. From the surface to interior, the sample can be divided into three zones. The first zone, the surface part, is TiO₂ ranging from the surface to around 50 μm deep, which is porous and nearly free of Ni; the second zone is about 260 μm thick, and contains three phases, Ti₄Ni₂O, TiNi₃ and TiNi; the third layer contains TiNi₃ and TiNi with a thickness of about 190 μm . As can be seen from Fig. 8a and c, in the majority of the oxidation affected zones (the second and the third), a characteristic intergrowth or lamellae microstructure of TiNi₃ and matrix (B2) is identified. Such a microstructure is normally seen in a eutectic alloy.

Fig. 9a–c shows the SEM and EPMA results of a Ti–50Ni sample after experiencing a high-temperature TG-DTA measurement in the non-oxidizing atmosphere (Ti-getter plus the mixture gas Ar–1% H₂, Group 1). As shown in Fig. 9a, the oxidation is much less than the above case, although oxidation is not completely eliminated. The thickness of oxidation affected layer is about 100 μm from the line scanning results in Fig. 9b. According to composition image of Fig. 9c and the point composition analysis for locations a, b, and c (Table 2), the oxidation affected layer can also be divided into three layers from the surface to the center: the first is TiO₂ layer about 17 μm ; the second layer contains Ti₄Ni₂O and TiNi₃, which is merely about 4 μm thick; the rest is the matrix TiNi with small amount of TiNi₃ precipitates. It is noted that no signature of a eutectic reaction is found. This is in sharp contrast with the case of oxidizing atmosphere. This corresponds to the disappearance of 1118 $^{\circ}\text{C}$ peak in the non-oxidizing environment. Therefore, it becomes clear that the difference in the degree of oxidation plays a key role in causing the conspicuous difference in the DTA curves. Such a difference reveals the origin of the 1118 $^{\circ}\text{C}$ DTA peak, the mechanism of which will be discussed later.

4. Discussions

4.1. Non-existence of order–disorder transition in Ti–Ni

From the Group 1 experiment (i.e., essentially free of oxidation during measurement), we do not find any sign of an order–disorder transition, such as a thermal peak in

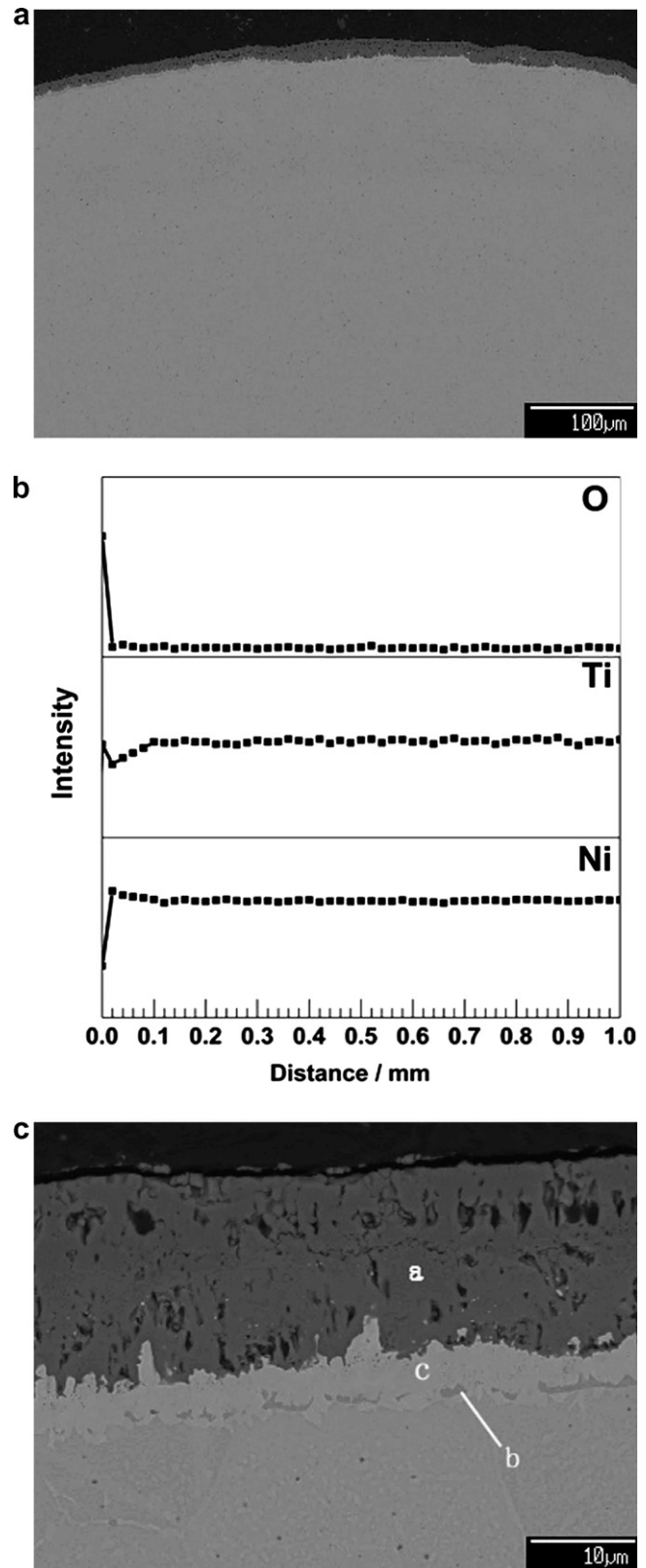


Fig. 9. SEM and EPMA results of Ti–50Ni sample after the TG-DTA measurement in Ar–1% H₂ mixture environment (Fig. 3): (a) a low-magnification SEM micrograph of the cross-section; (b) EPMA line scan from the surface to the interior; (c) high-magnification SEM micrograph of the oxidation-affected zone near surface. The composition at points a, b, c is listed in Table 2.

Table 2
Chemical composition and phase identification at different locations in Fig. 9c (unit: at.%)

	(a)	(b)	(c)	Near the oxidation layer	Center of the sample
O	63.9	16.0	1.5	2.3	1.9
Ti	35.8	55.9	28.1	46.7	50.0
Ni	0.3	28.1	70.4	51.0	48.1
Phase	TiO ₂	Ti ₄ Ni ₂ O	TiNi ₃	TiNi	TiNi

DTA curve, a resistance anomaly, or APB in the quenched samples. These negative results unambiguously indicate that there exists no order–disorder transition in the near-equi-atomic Ti–Ni alloys. We note that there is no chance for undetectability of these techniques to a possible second-order transition, because resistance and APB observation are sensitive methods to detect such type of transition. Therefore, the “order–disorder transition” suggested by Honma et al. seems to be due to something extrinsic to the system, which will be discussed in the next section.

Therefore, our findings disprove the existence of order–disorder transition in near-stoichiometric Ti–Ni; thus the B2 phase persists up to the melting point, as shown in the old phase diagram [3,4]. Our work thus clarifies the B2 portion of the Ti–Ni phase diagram and may have important implications for the heat treatment of Ti–Ni alloys, since the non-existence of an order–disorder transition means that solution-treatment temperature is no longer crucial for the transformation temperature and shape memory properties of the system, as long as the treatment is carried out in the single-phase B2 regime and oxidation is avoided.

4.2. Origin of the 1118 °C DTA peak in the oxidizing atmosphere

From the result of the Group 2 experiment (Figs. 6 and 7) and the contrasting result for the Group 1 experiment (Fig. 3), it is clear the 1118 °C DTA peak in the oxidizing atmosphere is related to severe oxidation. Now referring to Fig. 10, we reveal the origin of this peak, and also explain why it does not appear in a non-oxidizing environment.

In Fig. 10, we consider the surface composition change of two Ti–50Ni samples (a and b) during the DTA heating–cooling runs. Sample a is heated and cooled in an oxidizing atmosphere (i.e., a Group 2 sample, with the mixture gas Ar–1%H₂ alone), and sample b is heated and cooled in a much less oxidizing atmosphere (i.e., a Group 1 sample, with the Ti-getter and the mixture gas Ar–1%H₂).

From the SEM-EPMA results (Tables 1 and 2), all the oxidation products are Ti-rich ones like TiO₂ and Ti₄Ni₂O. This clearly shows that the oxidation of Ti–Ni is essentially a selective oxidation of Ti, and Ni is essentially intact. Then it is natural that the excessive Ni will enter into the matrix Ti–Ni and form a Ni-rich Ti–Ni. With further oxidation or

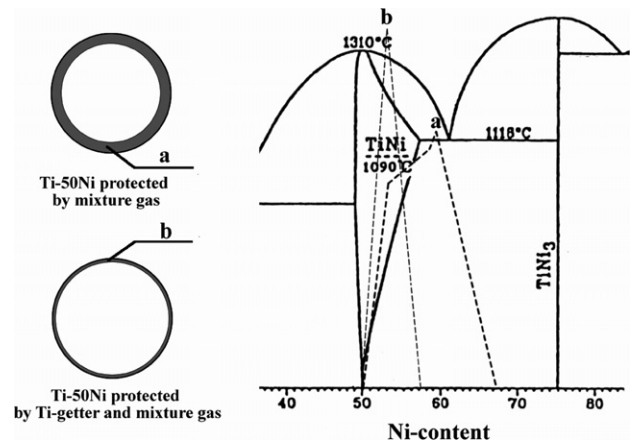


Fig. 10. Schematic evolution of the average surface Ni content of two Ti–50Ni samples (a and b) with heating/cooling cycles, indicated as a and b in the Ti–Ni phase diagram (right). (a) is the case for the Ti–50Ni protected by an oxidizing atmosphere; (b) is the case for the Ti–50Ni protected by a non-oxidizing atmosphere.

high-temperature cycles during DTA measurement, the surface layer becomes more and more Ni-rich. But the sample a and sample b have very different speed of Ni-enrichment. Sample a experiences severe oxidation and thus the Ni-enrichment at the surface occurs at a high speed during DTA high temperature cycles, as shown in curve a in the phase diagram. Within one high-temperature cycle, the surface Ni content of sample a reaches the eutectic regime (from 57Ni to 75Ni), and then a eutectic peak at 1118 °C can be detected with DTA. This explains the finding in Group 2 samples and Honma et al.’s DTA result. It also explains why Honma et al.’s “order–disorder transition” does not depend on the Ni content, because the eutectic reaction temperature is composition-independent within a certain composition range.

On the other hand, sample b experiences much less oxidation and thus the Ni-enrichment at the surface occurs at a low speed during DTA high temperature cycles, as shown in curve b in the phase diagram. Within the high-temperature cycle, the Ni content in the surface of sample b is yet to reach the eutectic regime, thus the eutectic peak at 1118 °C does not appear. This explains our results with Group 1 samples, i.e., no DTA peak appears when the sample is well-protected against oxidation.

4.3. Discussion on the neutron diffraction data by Honma et al.

As shown clearly above, Honma et al.’s evidence for the existence of order–disorder transition in Ti–Ni, i.e., the DTA peak at 1090 °C, has been shown to be due to an extrinsic effect caused by oxidation. Nevertheless, in their work they provided another piece of evidence for the existence of an order–disorder transition: the change of the intensities of superlattice reflections in neutron diffraction with temperature, which was carried out for a Ni-rich

(Ti–52Ni) polycrystal. As a diffraction study normally provides strong evidence for a structural transition, we cannot overlook this important fact. In the following we show that the change in superlattice intensity may be due to an indirect consequence of precipitation or oxidation.

Firstly we note an important fact. They did not demonstrate directly that the superlattice spots disappear above T_c (1090 °C). Thus they did not provide direct evidence for the order–disorder transition with the diffraction technique. Actually the change of the “superlattice intensity” may be explained alternatively by an artifact due to their Ni-rich sample (Ti–52Ni) selected and/or a sample oxidation effect, as their samples were oxidized during the measurement. Under such situations, from the metastable Ti–Ni phase diagram [4] and above discussions, it is evident that during the high-temperature neutron experiment there exist several precipitates like Ti_3Ni_4 , Ti_2Ni_3 and $TiNi_3$, and the amount of these precipitates changes with temperature. It is noted that some reflections of these precipitates ((211) reflection of Ti_3Ni_4 , (100) reflection of Ti_2Ni_3 and (102) reflection of $TiNi_3$ etc.) coincide with the superlattice reflection (100) of the B2 TiNi they measured [14–16]. Thus with increasing temperature, the amount of these precipitates decreases; thus it causes a decrease in the intensities of the reflections coinciding with that of the B2 (100) superlattice reflections. Then one may observe an apparent decrease in “B2 superlattice intensity.” It is clear that unless such an alternative interpretation of their neutron result can be excluded, their results remain inconclusive. If such neutron diffraction is to be carried out, it is advised that it should be done with Ti–50Ni alloy (to avoid precipitation) under well-protected atmosphere, so as to avoid the complexities due to oxidation and precipitates.

5. Conclusions

To critically check whether or not the order–disorder transition exists in near-stoichiometric TiNi system, we investigated the high-temperature characteristics of Ti–50Ni and Ti–51Ni alloys by using TG-DTA, electrical resistance measurement, TEM, SEM and EPMA under controlled atmospheres. As a result, the following conclusions were obtained:

- (1) When the samples are measured in an essentially non-oxidizing atmosphere created by Ti-getter and Ar–1% H_2 mixture gas, we do not find any evidence for an order–disorder transition, such as a thermal peak in DTA curve, a resistance anomaly, or APB in the quenched samples. These negative results imply that there exists no order–disorder transition in the near-equi-atomic Ti–Ni alloys.
- (2) In the oxidizing atmosphere, the 1118 °C DTA peak, which was taken as evidence for the order–disorder transition by Honma et al., is shown to be due to a eutectic reaction: liquid (TiNi) \rightarrow TiNi + $TiNi_3$, which is caused by the Ni-enrichment due to the selective oxidation of Ti at high temperatures.
- (3) Our work clarifies the B2 portion of the Ti–Ni phase diagram and may have important implications for the heat treatment of Ti–Ni alloys, since the non-existence of an order–disorder transition means that solution-treatment temperature is no longer crucial for the transformation temperature and shape memory properties of the system, as long as the treatment is carried out in the single-phase B2 regime and oxidation is avoided.

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