The nonexistence of an order–disorder transition in near-stoichiometric TiNi alloy

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Abstract

It is usually believed that there is an order–disorder transition at 1090 °C in binary Ti–Ni alloys, as Honma et al. reported previously. The presence or absence of such transition is very important, because the result may greatly affect the martensitic transformation behavior, and the associated shape memory characteristics. In the present paper, we question whether such transition really exists or not. One of the difficulties in such experiments, including the work of Honma et al., lies in the fact that Ti can be easily oxidized at such high temperatures, which complicates the alloy behavior greatly and may lead to erroneous interpretation of experimental data. After doing carefully designed experiments on this point, we did not find any differential thermal analysis peak up to the melting temperature, or any drastic change in electrical resistance in a wide temperature region including 1090 °C, which is the characteristic of order–disorder transition. These observations lead to the conclusion that such order–disorder transition does not exist in Ti–Ni binary shape memory alloys.

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1. Introduction

Recently, Ti–Ni and Ti–Ni-based alloys have attracted keen attention [1–6], since they are the most important shape memory alloys (SMAs) with excellent mechanical properties. As a basis to understand such an alloy, the phase diagram of Ti–Ni system is extremely important, especially the portion for near-stoichiometric TiNi with B2 phase undergoing martensitic transition, since heat-treatments are quite useful to improve shape memory characteristics. The phase diagram of Ti–Ni binary alloys had been controversial until the end of 1980s [7], and the most recent phase diagram being shown in ref. [8], was based on Massalski et al. [9] and Zhang [10] works. In the phase diagram, it can be seen clearly that there is a ‘so-called’ order–disorder transition at 1090 °C in near-stoichiometric TiNi system, which was reported in 1979 by Honma et al. [11] and has not been confirmed by independent works. Furthermore, their result suggests the \( T_c \) (order–disorder transition temperature) to be independent of composition (Fig. 1), which is thermodynamically unreasonable [12]. According to the Bragg–Williams approximation, the stoichiometric alloy has a highest degree of order at a specific temperature and pressure, compared to off-stoichiometric ones. Therefore, the stoichiometric alloy has the highest \( T_c \). In the case of TiNi, \( T_c \) of Ti–50% Ni should be highest and \( T_c \) will gradually decrease with the increase of Ni-content in the Ni-rich side and Ti-content in the Ti-rich side.

In the present investigation, we focused attention on the alleged order–disorder transition from B2 to BCC at 1090 °C indicated by a dotted line in the phase diagram of Ti–Ni. In order to confirm whether the order–disorder transition exists at 1090 °C in near-stoichiometric TiNi system, we carried out experiments including high temperature differential thermal analysis (DTA) and electrical resistance measurement carefully, to avoid the oxidation and evaporation of Ti-atoms during the measurement. Thus, the purpose of the present paper is to report the results under controlled atmosphere.

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2. Experimental procedure

Stoichiometric Ti–50 at.% Ni polycrystals were used in the present investigation. The composition of the samples was estimated from their transformation temperatures and confirmed by electron probe microanalysis.

2.1. Procedure of DTA measurement

A Ti–50 at.% Ni wire of 3 mm diameter was spark cut into small pieces with thickness of 2 mm. In order to remove the affected surfaces, the samples were mechanically polished and chemically etched. High temperature DTA experiments were performed on Rigaku Thermo plus TG 8120 with a sample mass around 100 mg. The samples were heated up and then cooled down at a rate of 3 K/min. One set of the samples were protected by Ar and H₂ mixture gas with flow rate of 50 ml/min without Ti-getter, while the other set were protected by both Ti-getter and mixture gas (we use the term “mixture gas” for short in the following).

2.2. Procedure of high temperature electrical resistance measurement

The Ti–50 at.% Ni wire with 1 mm diameter was cut into segments of 100 mm, which were mechanically polished to clean the surface. The temperature dependence of electrical resistance was measured by four-terminal method with the protection of Ti-getter and mixture gas. The sample was heated at a rate of 3 K/min.

3. Results and discussion

We report the high temperature DTA curves for Ti–50 at.% Ni samples. Figs. 2 and 3 show the DTA results of samples with and without the protection of Ti-getter, respectively. For the sample only protected by mixture gas, the DTA curve does show distinct peaks at 1114.5 °C upon cooling and at 1122.5 °C upon heating, which are very close to the order–disorder transition temperature at 1090 °C reported by Honma et al. However, these peaks disappear, if the samples are protected by both Ti-getter and mixture gas, and no peak appears before melting upon heating, as will be described soon below.

Fig. 4 shows the electrical resistance versus temperature curve for the temperature interval from 840 to 1120 °C, under the atmosphere of no oxidation by the protection of both Ti-getter and mixture gas. The electrical resistance increased slowly with the increase of temperature, which should be due to aggravating of the thermal vibration of atoms. And we did not see any abrupt change in electrical resistance throughout our measurement. Furthermore, by taking a derivative of the curve with
with the protection of mixture gas and Ti-getter.

respect to temperature, we see that the slope of the curve is constant (see Fig. 5).

As mentioned above, one of the difficulties in such experiments, including the work of Honma et al., is that Ti-atoms are very easily to be oxidized (above 600 °C) [13] and also easily to evaporate at high temperatures, while Ni-atoms have high oxidation resistance even at high temperatures. Thus, the Ni-content of the alloy will increase as a result of the oxidation and evaporation of Ti at such high temperatures. In addition, it also complicates the alloys’ behavior, which may lead to erroneous interpretation. So, only the results without the influence of oxidation are reliable to reveal the high temperature characteristics of TiNi.

As shown in Fig. 3, the melting point of the sample is equilibrium to 1311 °C, which is close to the melting point of Ti–50 at.% Ni (1310 °C). This important result indicates that the composition of the sample does not change, and thus the oxidation and evaporation of Ti-atoms was essentially eliminated in our experiment by the co-protection of Ti-getter and mixture gas.

Therefore, when the sample was only protected with mixture gas, the oxidation and evaporation of Ti-atoms is inevitable and the Ni-content will increase. From the results shown in preceding sections, the peak around 1118 °C disappeared when the sample was co-protected by Ti-getter and mixture gas during measurement, and this suggests that the peaks shown in Fig. 2 correspond to a transformation other than the order–disorder transition. From Fig. 2, we find that the equilibrium temperature of the peaks is equal to 1118.25 °C, which is equal to the eutectic reaction temperature exhibiting among the range from Ti–57 at.% Ni to Ti–75 at.% Ni, according to the most recent phase diagram. Actually, it is easy to satisfy the condition for existence of such eutectic reaction in even Ti–50 at.% Ni. For instance, when the sample was not sufficiently protected against oxidation, the surfaces of the specimen and the grain boundaries will be oxidized firstly compared with the grain interior, and thus Ni-content of the surfaces and the grain boundaries became much higher than that in grain interior, which leads to the eutectic reaction. Actually, there are some distinct differences between the phase diagram used in Honma’s paper (shown as Fig. 1, in present paper) and the recent phase diagram, since the existence of order–disorder transition at 1090 °C in TiNi was reported by Honma et al. before the phase diagram of TiNi was established at the end of 1980s. One of great differences between the two phase diagrams is that the eutectic reaction temperature in the old one (shown as Fig. 1) was 1090 °C, which is equal to alleged $T_c$. Therefore, it is quite likely that the endothermic peaks, which are the key evidence for the existence of order–disorder transition in Honma’s paper, are also corresponding to the eutectic reaction as shown in Fig. 2.

The results of the samples protected by Ti-getter and mixture gas are shown in Figs. 3 and 4, which clearly give the high temperature characteristics of near-stoichiometric TiNi. As shown in Fig. 3, there is no peak in the high temperature DTA curve till melting point. However, the absence of the DTA peak is not sufficient to conclude the nonexistence of order–disorder transition in near-stoichiometric TiNi at 1090, for an order–disorder transition can take place discontinuously as a first-order transition or continuously as a higher-order cooperative transition that may be undetectable by DTA. On the contrary, the electrical resistance results shown in Figs. 4 and 5 indeed supports the absence of such order–disorder transition, because electrical resistivity is very sensitive to point defects such as vacancies and anti-structure defects (ASD), which will be introduced abundantly if order–disorder transition really occurs.

Therefore, our results suggest that the order–disorder transition at 1090 °C reported by Honma et al. is likely the eutectic reaction shown in lately phase diagram, and thus there is no order–disorder transition in near-stoichiometric TiNi system.

4. Conclusion

In order to critically test whether or not the order–disorder transition actually exists in near-stoichiometric TiNi system, we investigated the high temperature characteristics of Ti–50 at. %
Ni alloy by using DTA and electrical resistance measurement under carefully controlled environment. As a result, we obtained the following conclusions:

(1) No peak was observed in the high temperature DTA curve before the sample melts at 1310°C, when oxidation of the sample was eliminated by the protection of Ti-getter and mixture gas.

(2) The endothermic peaks existing around 1090°C in Honma’s paper most likely corresponds to the eutectic reaction due to the oxidation at such high temperatures, when the sample was not sufficiently protected against oxidation.

(3) No significant change was observed on the slope of the electrical resistance versus temperature curve in a wide temperature region including 1090°C, when the oxidation of the sample was eliminated by the protection of Ti-getter and mixture gas.

(4) From both the DTA and electrical resistance measurement results with the protection of Ti-getter and mixture gas, it is concluded that the order–disorder transition does not exist in near-stoichiometric TiNi system.

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