Change in Magnetic Susceptibility of Ti–Ni Shape Memory Alloys Associated with Martensitic Transformations

Takashi Fukuda

Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The main phases (B2, R, B19, B19' and Ti₃Ni₄) appearing in Ti–Ni-based shape memory alloys are band paramagnetism with magnetic susceptibility in the order of 10^{-8} m³/kg. All martensitic transformations in the cooling process (B2 → B19', B2 → R, B2 → B19, R → B19' and B19 → B19') are associated with the decrease in magnetic susceptibility. This implies that all martensitic transformations in Ti–Ni-based shape memory alloys are associated with decrease in electronic density of states at Fermi energy. The change in magnetic susceptibility from the B2-phase is largest for the B2-B19' transformation and smallest for the B2-R transformation. [doi:10.2320/matertrans.MT-MJ2019003]

(Received June 24, 2019; Accepted August 6, 2019; Published September 24, 2019)

Keywords: martensitic transformation, shape memory alloys, electronic structure, density of states, magnetic susceptibility

1. Introduction

Titanium–nickel based shape memory alloys (Ti–Ni SMAs) exhibit various martensitic transformations. The parent phase takes a cubic structure (B2-phase), and the martensite phases take three different structures. The first one is a monoclinic structure (B19'-phase^{1,2)}), which appears in most Ti–Ni SMAs. The second one is a trigonal structure (R-phase^{3,4)}), which appears in thermo-mechanically treated alloys, aged Ni-rich Ti–Ni alloys, and those including an adequate amount of third elements such as Fe, Co and Al. The third one is an orthorhombic structure (B19-phase^{5,6)}), which appears in alloys including an adequate amount of third elements such as Cu and Pd. Representative martensitic transformation sequences are B2 → B19', B2 → R, B2 → R → B19', B2 → B19 and B2 → B19 → B19'. Another sequence B2 → R → B19 → B19' was reported only in an iron-doped Ti–Ni–Cu alloy,⁷⁾ and there is no report of B2 → B19 → R → B19' transformation.

The crystal structure and transformation behavior of metals and alloys are essentially governed by electronic structure, especially that near Fermi energy. This means that in order to understand the reason for the appearance of the three types of martensite phases and their transformation sequence described above, information of the electronic structure is particularly important. A part of such information can be obtained experimentally from some physical properties which are directly related to it. Magnetic susceptibility is one of such physical properties. It provides us information of magnetism and electronic density of state at Fermi energy, and helps us understand the martensitic transformation from the view point of electronic structure.

Although abundant papers have been published concerning the martensitic transformations of Ti–Ni alloys,^{8–10)} magnetic susceptibility of Ti–Ni alloys have been reported only in a few papers.^{11–13)} Furthermore, there are no systematic work which examines martensitic transformations of Ti–Ni alloys from a view point of magnetic susceptibility.

The purpose of the present paper, therefore, is to examine representative martensitic transformations described above through magnetic susceptibility measurements. By using the obtained results, we discuss the magnetic state of the parent

phase and the three martensite phases. Moreover, we discuss the change in electronic structure associated with the martensitic transformations.

2. Experimental Procedure

Alloys used in the present study are Ti–50Ni, Ti–51Ni, Ti–52Ni, Ti–48Ni–2Fe, Ti–46Ni–4Fe, Ti–45Ni–5Cu, Ti–37.5Ni–12.5Cu and Ti–30Ni–20Cu (at%). Ingots of the former five alloys were prepared by arc melting, and those of the latter three alloys by vacuum induction melting. One or two specimens of approximately 100 mg were cut from each ingot, and solution-treated for 3.6 ks at 1273 K followed by quenching into iced water. One specimen of the Ti–51Ni alloy was then aged at 773 K for 6 ks in order to change transformation sequence.¹⁴⁾ After the heat treatments, the surface of the specimens was electropolished by using an electrolyte composed of acetic acid and perchloric acid. Magnetic susceptibility measurements were made by using a superconducting quantum interference device (SQUID) magnetometer. The strength of applied magnetic field was 0.4 MA/m. *M*-*H* curves was also measured for Ti–48Ni–2Fe alloy using a vibrating sample magnetometer (VSM).

3. Results

3.1 B2 → B19' transformation

Temperature dependence of magnetic susceptibility χ of solution treated equiatomic Ti–50Ni alloy is shown in Fig. 1. In the cooling process, a large decrease of χ starting at about 350 K and finishing at about 300 K appears. There is a hysteresis between cooling and heating processes. This behavior agrees with previously reported result,¹³⁾ and is due to the martensitic transformation from the B2-phase to the B19'-phase.

In Fig. 1, χ -*T* relation of the solution treated Ti–51Ni and Ti–52Ni alloys are also shown. Similar to the Ti–50Ni alloy, the Ti–51Ni alloy exhibits the B2 → B19' transformation; in association with this transformation, χ exhibits a drastic decrease. In χ -*T* relation of the Ti–52 alloy, there is neither a drastic decrease nor hysteresis between cooling and heating processes, meaning that the martensitic transformation does

Fig. 1 Temperature dependence of magnetic susceptibility of solution treated Ti-50Ni, Ti-51Ni and Ti-52Ni alloys. Ti-50Ni and Ti-51Ni exhibit the B2 $\rightarrow$ B19' transformation, while Ti-52Ni does not exhibit martensitic transformation.

not occur. This agrees well with previous results obtained by electrical resistivity.¹⁵⁾ However, we notice a gradual decrease of χ around 150 K, which will be related to some electronic structure change. One possibility is formation of domain-like microstructure which is referred to strain glass.¹⁶⁾

3.2 B2 $\rightarrow$ R $\rightarrow$ B19' and B2 $\rightarrow$ R transformations

When a solution treated Ti-51Ni alloy is aged at intermediate temperatures, fine coherent precipitate of Ti_3Ni_4 forms,¹⁷⁾ and the aged alloy exhibits a two-step transformation from the B2-phase to the R-phase followed by the transformation to the B19'-phase.¹⁸⁾ The χ - T relation of the Ti-51Ni alloy aged at 773 K for 6 ks is shown in Fig. 2. In the cooling process, χ decreases in two steps starting at 325 K and at 285 K, respectively. The first decrease is due to the B2 $\rightarrow$ R transformation, and the second decrease is due to the R $\rightarrow$ B19' transformation. In the heating process, χ increases in one step starting at 320 K, which corresponds to the direct B19' $\rightarrow$ B2 transformation. The disappearance of the B19' $\rightarrow$

Fig. 2 Temperature dependence of magnetic susceptibility of an aged Ti-51Ni alloy, solution treated Ti-48Ni-2Fe and Ti-46Ni-4Fe alloys. The aged Ti-51Ni alloy and solution treated Ti-48Ni-2Fe alloy exhibits two-step B2 $\rightarrow$ R $\rightarrow$ B19' transformation, while the Ti-46Ni-4Fe alloy exhibits the B2 $\rightarrow$ R transformation.

R transformation is due to large transformation hysteresis. Similar behavior was reported in a cold rolled wire of Ti-49.8Ni (at%) alloy subjected to heat-treatment at 743 K.¹⁹⁾ When the specimen is heated before the R $\rightarrow$ B19' transformation initiates, the R-phase returns back to the B2-phase with small hysteresis as indicated by "A" in Fig. 2.

The B2 $\rightarrow$ R transformation is known to occur in Ti-Ni-Fe alloys as well as in aged Ni-rich Ti-Ni alloys. In Fig. 2, the χ - T relation of solution treated Ti-48Ni-2Fe and Ti-46Ni-4Fe alloys are also shown. Similar to the aged Ti-51Ni alloy, χ of the Ti-48Ni-2Fe alloy decreases in two steps due to the two-step B2 $\rightarrow$ R $\rightarrow$ B19' transformation. However, the heating process of this alloy is different from that of aged Ti-52Ni alloy, i.e., the reverse transformation also proceeds in two steps. Concerning the Ti-46Ni-4Fe alloy, χ decreases in one step. This decrease is due to the B2 $\rightarrow$ R transformation, whose temperature hysteresis between cooling and heating processes is small. This alloy does not transform to the B19'-phase.

3.3 B2 $\rightarrow$ B19 and B2 $\rightarrow$ B19 $\rightarrow$ B19' transformations

In Ti-(50-x)Ni-xCu ternary system, the martensitic transformation behavior changes as the copper content increases. Alloys containing 5 at% or less Cu exhibit B2 $\rightarrow$ B19' transformation, containing 20 at% or more Cu exhibit B2 $\rightarrow$ B19 transformation, and alloys with Cu content between 7.5 at% and 15 at% exhibit a two-step B2 $\rightarrow$ B19 $\rightarrow$ B19' transformation.⁵⁾

The χ - T relation of the Ti-45Ni-5Cu exhibiting the B2 $\rightarrow$ B19' transformation is shown in Fig. 3. This relation resembles that of the solution treated Ti-50Ni and Ti-51Ni alloys (Fig. 1). In Fig. 3, the χ - T relation of the Ti-30Ni-20Cu alloy and that of the Ti-37.5Ni-12.5Cu alloy are also shown. In the cooling process of Ti-30Ni-20Cu alloy, a decrease in χ starting at 330 K is observed. This is due to the B2 $\rightarrow$ B19 transformation. In the cooling process of the Ti-37.5Ni-12.5Cu alloy, χ decreases in two steps: the first one starting at 325 K is due to the B2 $\rightarrow$ B19 transformation and the second one starting at 270 K is due to the B19 $\rightarrow$ B19' transformation. The gradual decrease in χ below 270 K will

Fig. 3 Temperature dependence of magnetic susceptibility of Ti-45Ni-5Cu, Ti-37.5Ni-12.5Cu and Ti-30Ni-20Cu alloys. The Ti-45Ni-5Cu alloy exhibits B2 $\rightarrow$ B19' transformation, the Ti-37.5Ni-12.5Cu exhibits two-step B2 $\rightarrow$ B19 $\rightarrow$ B19' transformation, and the Ti-30Ni-20Cu alloy exhibit B2 $\rightarrow$ B19 transformation.

Fig. 4 M - H curves of Ti-48Ni-2Fe alloy measured at fixed temperatures of 300 K, 250 K and 150 K measured in the successive cooling process.

be related to the gradual increase in the fraction of the B19'-phase.

3.4 M - H curves

In order to confirm the paramagnetic property of each phase, we measured M - H curve of the Ti-48Ni-2Fe alloy. Figure 4 shows the M - H curves measured at fixed temperatures of 300 K (B2-phase), 250 K (R-phase) and 150 K (B19'-phase) in the successive cooling process. At all temperatures, the magnetization increases linearly up to the maximum field of 4 MA/m. This implies all the phases are paramagnetism. The slope is consistent with magnetic susceptibility of this alloy shown in Fig. 2.

4. Discussion

4.1 Magnetism of B2-, R-, B19 and B19'-phases

The change in magnetic susceptibility at martensitic transformation temperature is very clearly seen for every martensitic transformation, and the temperature at which the susceptibility starts to decrease agrees quite well with the temperature of martensitic transformation determined from other experiments such as electrical resistivity and differential scanning calorimetry. Furthermore, we can estimate the volume fraction of the transformed region at any temperature between transformation start and finish temperatures by using the lever rule. Accordingly, we believe that the magnetic susceptibility measurement is an effective method for examining all martensitic transformations in Ti-Ni SMAs.

As observed in Figs. 1, 2, and 3, the value of χ is in the order of $2\sim 4 \times 10^{-8} \text{ m}^3/\text{kg}$ ($1 \text{ m}^3/\text{kg}$ corresponds to 79.6 emu/gOe or $8480 \text{ cm}^3/\text{mol}$ in cgs unit for Ti-50Ni) for all phases, and is nearly temperature independent except in the vicinity of the transformation temperatures. Therefore, all the B2-, R-, B19- and B19'-phases can be regarded as band paramagnetism.

The aged Ti-51Ni includes fine precipitate of Ti_3Ni_4 , and its volume fraction is about 9%,¹⁷⁾ so the contribution of Ti_3Ni_4 for χ seen in Fig. 2 is not negligible. By comparing χ

of the solution treated Ti-51Ni alloy (Fig. 1) and that of aged Ti-51Ni (Fig. 2) for both B2- and B19'-phases, we notice that χ - T behavior of each phase does not change significantly by the existence of Ti_3Ni_4 . This result suggests that the Ti_3Ni_4 is also band paramagnetism and its magnetic susceptibility is the same order as that of the matrix.

In Figs. 1, 2 and 3, we notice a small increase of χ below $\sim 20 \text{ K}$. This behavior is especially significant in the Ti-52Ni and Ti-51Ni alloys including excess Ni atoms, but insignificant in the Ti-50Ni and Ti-Ni-Cu alloys, whose Ni content is 50 at% or less. It is likely that the increase of χ below about 20 K is due to magnetic impurities. Presumably, Ni clusters formed by excess Ni atoms act as magnetic impurities.

4.2 Change in magnetic susceptibility during martensitic transformations

As seen in Figs. 1, 2 and 3, the amount of decrease in χ during a martensitic transformation depends significantly on the structure of the parent and the martensite phases. It is the largest for the B2 $\rightarrow$ B19' transformation; intermediate for the R $\rightarrow$ B19' and the B2 $\rightarrow$ B19 transformations; small for the B2 $\rightarrow$ R and B19 $\rightarrow$ B19' transformations. These results imply that change in electronic structure is significant for the B2 $\rightarrow$ B19' transformation and less significant for the B2 $\rightarrow$ R and B19 $\rightarrow$ B19' transformations. In the following we briefly discuss the magnetic state of equiatomic TiNi semi-quantitatively by using the Stoner model.²⁰⁾ According to this model, magnetic susceptibility χ of band paramagnetism is given as,

$$\chi = \frac{\chi_P}{1 - \alpha\chi_P} + \chi_{\text{orb}} + \chi_{\text{dia}} \quad (1)$$

where χ_P , χ_{orb} and χ_{dia} are magnetic susceptibility of Pauli paramagnetism, orbital paramagnetism and diamagnetism, respectively. The parameter α is the Stoner exchange integral and $1/(1 - \alpha\chi_P)$ is Stoner enhancement parameter. From Fig. 1, χ of the B2- and B19'-phases of the Ti-50Ni alloy is obtained to be about 40.2 and $25.1 \times 10^{-9} \text{ m}^3/\text{kg}$, respectively. It is well known that χ_P is given as

$$\chi_P = 2n(\epsilon_F)\mu_B^2 \quad (2)$$

where $n(\epsilon_F)$ is the density of states at Fermi energy and μ_B is Bohr magneton. In the present evaluation for χ_P of the B2- and B19'-phases in TiNi, we used $n(\epsilon_F)$ of TiNi obtained by a band calculation²¹⁾ ($10.4 \text{ Ry}^{-1}\text{atom}^{-1}\text{spin}^{-1}$ for the B2-phase and 6.7 for the B19'-phase). Then χ_P of TiNi is calculated to be 11.7 and $7.5 \times 10^{-9} \text{ m}^3/\text{kg}$ for B2- and B19'-phases, respectively. For simplicity, we assume that α and $\chi_{\text{orb}} + \chi_{\text{dia}}$ in both phases take individually same constant values, although this is a rough approximation. Then we can obtain α and $\chi_{\text{orb}} + \chi_{\text{dia}}$ by substituting experimentally obtained value of χ and calculated χ_P for B2- and B19'-phases in eq. (1). As a result, α is obtained to be $4.86 \times 10^7 \text{ kg/m}^3$ (which corresponds to 54.5 mRy when χ is divided by μ_B^2), this value lies between α of pure Ti with A2-type structure (50 mRy) and α of pure Ni with A1-type structure (74 mRy).²⁰⁾ Furthermore, $\chi_{\text{orb}} + \chi_{\text{dia}}$ is obtained to be $13.3 \times 10^{-9} \text{ m}^3/\text{kg}$ ($0.56 \times 10^{-4} \text{ emu/mol}$), being the same order as that of the pure Ti ($0.73 \times 10^{-4} \text{ emu/mol}$) and/or that of pure

Ni (0.59×10^{-4} emu/mol).²²⁾ By using the calculated value of α and χ_B , the Stoner enhancement parameter is obtained to be 2.3 for the B2-phase and 1.6 for the B19'-phase. These values are also the same order as that of paramagnetic 3d-transition metals, being between 1.36 and 2.48.²³⁾

We can derive χ of the R-phase of the Ti-50Ni by using above results and $n(\epsilon_F)$ of the R-phase, although R-phase does not appear in solution treated Ti-50Ni. According to a band calculation,²¹⁾ $n(\epsilon_F)$ of the R-phase is 9.3 per Ry per atom in one spin direction. Then χ_P is calculated to be 10.4×10^{-9} m³/kg. If we use above value of α , the Stoner enhancement parameter becomes 2.0. By using the same value for $\chi_{orb} + \chi_{dia}$ described above, χ of the R-phase is derived to be 34.4×10^{-9} m³/kg. Then $\chi(B2) - \chi(R)$ of the Ti-50Ni is expected to be 5.8×10^{-9} m³/kg, which is roughly the same as that of the Ti-48Ni-2Fe alloy and/or that of the aged Ti-51Ni alloy.

Concerning the magnetic susceptibility of the B19-phase, it is hard to apply the above discussion because alloys exhibiting the B2 $\rightarrow$ B19 transformation contain a large amount of copper so that the enhancement factor α and $\chi_{orb} + \chi_{dia}$ of these alloys will be significantly different from that of the Ti-50Ni alloy. Nevertheless, it is probable from Fig. 3 that the $n(\epsilon_F)$ of the B19-phase is smaller than that of the B2-phase and is larger than that of the B19'-phase.

5. Conclusions

We have examined martensitic transformations (B2 $\rightarrow$ B19', B2 $\rightarrow$ R $\rightarrow$ B19', B2 $\rightarrow$ R, B2 $\rightarrow$ B19 $\rightarrow$ B19' and B2 $\rightarrow$ B19) in Ti-Ni alloys by magnetic susceptibility measurements. Using the experimental result and calculated density of states at Fermi energy, we discussed the magnetism of each phase and electronic structure change during the transformation.

- (1) Magnetic susceptibility decreases in association with all the martensitic transformations. The value of magnetic susceptibility is almost temperature independent for each phase, and is in the order of 10^{-8} m³/kg, which is typical value for band paramagnetism. The Ti₃Ni₄ precipitate appearing in aged Ti-51Ni alloy is also band paramagnetism. The change in magnetic susceptibility from the B2-phase is largest for the B2-B19' transformation and smallest for the B2-R transformation.
- (2) By using the measured χ and calculated density of states at Fermi energy, Stoner enhancement factor for the Pauli paramagnetic susceptibility is estimated to be

about 2.3, 2.0 and 1.6 for the B2-, R- and B19'-phases, respectively.

Acknowledgement

The present study was partly supported by JSPS KAKENHI Grand Number JP19H02460. The author appreciate discussion with Prof. Kakeshita on magnetic state of Ti-Ni alloys.

REFERENCES

- 1) Y. Kudoh, M. Tokonami, S. Miyazaki and K. Otsuka: *Acta Metall.* **33** (1985) 2049–2056.
- 2) M. Nishida, H. Ohgi, I. Itai, A. Chiba and K. Yamauchi: *Acta Metall. Mater.* **43** (1995) 1219–1227.
- 3) T. Hara, T. Ohba, E. Okunishi and K. Otsuka: *Mater. Trans., JIM* **38** (1997) 11–17.
- 4) E. Goo and R. Sinclair: *Acta Metall.* **33** (1985) 1717–1723.
- 5) T.-H. Nam, T. Saburi and K. Shimizu: *Mater. Trans., JIM* **31** (1990) 959–967.
- 6) L.C. Lo, S.K. Wu and H.E. Hong: *Acta Metall. Mater.* **41** (1993) 747–759.
- 7) C.-A. Yu, G.-B. Cho, T.-Y. Kim, Y.-J. Lee and T.-H. Nam: *Mater. Sci. Eng. A* **438–440** (2006) 500–503.
- 8) T. Saburi: *Shape Memory Alloys*, ed. by K. Otsuka and C.M. Wayman, (Cambridge University Press, Cambridge, 1998) Chap. 3.
- 9) C. Llexcellent: *Shape-Memory Alloys Handbook*, (Wiley, Hoboken, 2013).
- 10) D.C. Lagoudas: *Shape Memory Alloys*, (Springer, New York, 2008).
- 11) S. Mankovsky, I. Bakonyi and H. Ebert: *Phys. Rev. B* **76** (2007) 184405.
- 12) S.A. Shabalovskaja, A.I. Lotkov, I.I. Sasovskaja, A.G. Narmonev and A.I. Zakharov: *Solid State Commun.* **32** (1979) 735–738.
- 13) M. Matsumoto and T. Honma: Proc. 1st Japan Institute of Metals International Symposium. Supplement to Trans. JIM **17**, (1976) pp. 199–204.
- 14) M. Nishida and T. Honma: *Scr. Metall.* **18** (1984) 1299–1302.
- 15) T. Kakeshita, T. Fukuda, H. Tetsukawa, T. Saburi, K. Kindo, T. Takeuchi, M. Honda, S. Endo, T. Taniguchi and Y. Miyako: *Jpn. J. Appl. Phys.* **37** (1998) 2535–2539.
- 16) S. Sarkar, X. Ren and K. Otuka: *Phys. Rev. Lett.* **95** (2005) 205702.
- 17) T. Saburi, S. Nenno and T. Fukuda: *J. Less-Common Met.* **125** (1986) 157–166.
- 18) T. Fukuda, M. Takahata, T. Kakeshita and T. Saburi: *Mater. Trans.* **42** (2001) 323–328.
- 19) T. Todoroki and H. Tamura: *J. Japan Inst. Metals* **50** (1986) 546.
- 20) P. Mohn: *Magnetism in the Solid State*, (Springer, Berlin, 2002) Chap. 8.
- 21) T. Fukuda, T. Kakeshita, H. Houjoh, S. Shiraishi and T. Saburi: *Mater. Sci. Eng. A* **273–275** (1999) 166–169.
- 22) M. Shimizu: *Kinzoku Denshiron II*, ed. by K. Adachi, (Maruzen, Tokyo, 1973) p. 162.
- 23) J.F. Janak: *Phys. Rev. B* **16** (1977) 255–262.