Influence of Co Addition on Martensitic and Magnetic Transitions in Ni-Fe-Ga $\beta$ Based Shape Memory Alloys

Katsunari Oikawa1,5, Yousuke Imano2,*, Volodymyr A. Chernenko3, Fenghua Luo4, Toshihiro Omori2,*, Yuji Sutou2,5, Ryosuke Kainuma2,5, Takeshi Kanomata6 and Kiyohito Ishida2,5

1National Institute of Advanced Industrial Science and Technology, Tohoku Center, Sendai 983-8551, Japan
2Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
3Institute of Magnetism, Vernadsky str. 36-b, Kyiv 03142, Ukraine
4National Institute of Advanced Industrial Science and Technology, Now Powder Metallurgy Research Institute Central South University, Changsha 410083, P.R. China
5CREST, Japan Science and Technology Agency, Tokyo 105-6218, Japan
6Department of Applied Physics, Faculty of Engineering, Tohoku Gakuin University, Tagajo 985-8537, Japan

The effect of Co addition on the martensitic transition and magnetic properties of the Ni-Fe-Ga $\beta$ alloys is investigated. The values of both the Curie temperature $T_c$ and martensitic transition starting temperature $T_m$ increase, while the saturation magnetization $I_s$ decreases with increasing Co content in the series of Ni$_{51}$Fe$_{22}$-xCo$_x$Ga$_{27}$ alloys. On the other hand, the values of both $T_c$ and $I_s$ increase and $T_m$ decrease with increasing Co content in the series of Ni$_{54}$-xFe$_{16}$Co$_x$Ga$_{27}$ alloys. $T_c$ and $I_s$ show a strong dependence on the average magnetic valence number $Z_m$. Consequently, Co is an effective element to control both the martensitic and the magnetic transition temperatures.

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1. Introduction

Ferromagnetic shape memory alloys have received much attention as new solid-state actuator materials since a large strain produced by a magnetic field induced rearrangement of twin variants in the Ni-Mn-Ga system have been reported.1) Since then, many ferromagnetic shape memory candidates have been investigated, such as Fe-Pd,2) Fe-Pt3) Ni-Mn-(Al, Sn, Sb, In),4,5) Co-Ni-(Al, Ga),6–10) Ni-Fe-(Al, Ga)11–13) and Cu-Mn-Ga14) alloy systems.

The present authors proposed the Ni-Fe-Ga $\beta$ alloy system as promising ferromagnetic shape memory materials.1,2,13) One of the practically attractive characteristics of this system is a good ductility in hot- and/or cold-working due to the presence of disordered fcc precipitates in $\beta$ phase matrix. The martensitic transition in the Ni-Fe-Ga $\beta$ phase alloy system involves a spontaneous change from either B2-ordered or L2$_1$ Heusler structure to 10 M or 14 M martensitic structure,1,2,13) although the formation of the L2$_1$ ordered stoichiometric Ni$_3$Fe$_2$Ga compound is hindered by the stable $\beta$ + $\gamma$ two-phase region.15) In recent studies, a low compressive stress of less than 3 MPa16) and a large magneto-crystalline anisotropy energy were measured in a Ni-Fe-Ga single crystal.17) Since these characteristics are very similar to those of Ni$_2$MnGa alloys, a large magnetic field induced strain is expected to be obtained in the Ni-Ga-Fe ferromagnetic martensites, although the magnetic field induced strain of only 0.02% was measured in a single crystal of Ni-Fe-Ga alloy so far.18) Liu et al. succeeded in a synthesis of the stoichiometric compound Ni$_2$FeGa by a melt-spinning technique19) and found 12 M together with the 14 M and 10 M martensitic structures.20) A first principle calculation was performed to clarify the electronic structure of Ni$_2$FeGa.21) The calculation provided that the Fe atoms tend to hold the localized magnetic moments like Mn atoms as suggested in Ni$_2$MnGa alloys. The DOS(electron density of states) of orthorhombic martensite showed a split of Ni peak near the Fermi level, suggesting that a band Jahn-Teller effect is expected for the martensitic transition in the Ni$_2$FeGa compound likewise in Ni$_2$MnGa.

The martensitic and magnetic transition temperatures of the ternary Ni-Fe-Ga $\beta$ phase alloys depend on the off-stoichiometry as well as the degree of order of the L2$_1$ structure.22) However in those alloys, the martensitic transition temperature is lower than room temperature when the Curie temperature of parent phase is above the room temperature, which is a disadvantage for a practical use. In the present work, an influence of partial substitution of either Ni or Fe for Co on the martensitic and magnetic transitions in Ni-Fe-Ga alloy system has been examined. Generally, it was shown that Co is an effective element to control the transition temperatures of Ni-Fe-Ga $\beta$ phase alloys.

2. Experimental

Ni-Fe-Co-Ga alloy buttons, weighing about 20 g each, with different compositions were prepared by arc melting or induction melting using high purity iron, nickel, cobalt and gallium. The small samples of each alloy were sealed in a quartz capsule filled with an argon gas. In order to prepare a homogeneous $\beta$ single-phase alloy, the solution heat treatment was conducted at 1160°C for 1 day and then the samples were quenched into ice water. The quenched samples were sealed in the quartz capsule again and aged at 500°C for 1 day followed by quenching into ice water. The microstructure of the aged-samples was observed by an optical microscope. It was confirmed that the samples were the $\beta$ single-phase alloys. Transmission electron microscopy...
TEM observation was conducted at room temperature to identify the crystal structure. The thin foils for TEM studies were prepared by jet-electropolishing with a solution of ethanol and 20 vol% perchloric acid. The characteristic martensitic transition temperatures, $M_s$: martensitic transition starting temperature and $A_f$: reverse transition finishing temperature were determined by differential scanning calorimetry (DSC) with cooling and heating rates of 10°C/min. The Curie temperature $T_C$ and magnetization $I$ were measured using a vibrating sample magnetometer (VSM). The $T_C$ was defined as the minimum point of the temperature derivative of magnetization measured in a field of 40 KAm$^{-1}$ with heating rates of 2°C/min.

3. Results

3.1 Crystal structures

The TEM observations have been performed at a room temperature evidencing either cubic parent phase or martensitic phase. Figure 1 shows a typical bright-field image of the parent phase of Ni$_{50}$Fe$_{18}$Co$_5$Ga$_{27}$ alloy with $M_s=16$°C and $A_f=40$°C and its corresponding selected area diffraction (SAD) pattern. The bright-field image shows a mottled contrast as seen in Fig. 1(a). The (111)$_B$ spots in the SAD pattern shown in Fig. 1(b) characterize the L2$_1$-ordered structure. These characteristics of the parent phase are the same as in the Ni-Fe-Ga ternary alloys.$^{13,23}$ Figures 2(a) and (b) show a bright-field image of the martensite phase of Ni$_{50}$Fe$_{17}$Co$_6$Ga$_{27}$ with $M_s=106$°C and $A_f=140$°C and its corresponding SAD pattern, respectively. A typical morphology of martensite phase including a lot of micro-twins is observed as shown in Fig. 2(a). From the SAD pattern, the crystal structure was identified as the tetragonal L1$_0$ (2M) structure, although 14M and/or 10M modulated structures are more common to occur in the Ni-Fe-Ga ternary alloys annealed at the same temperature.$^{13,14}$ However, these modulated structures were also observed in the several Ni-Fe-Co-Ga alloys aged at some temperatures lower than 450°C. Details of the effect of annealing temperature on the crystal structure of the Ni-Fe-Co-Ga alloys will be reported elsewhere.$^{24}$

3.2 Martensitic and magnetic transition temperatures

The characteristic temperatures $M_s$, $A_f$ and $T_C$ of $\beta$ single-phase alloys plotted as a function of Co content are shown in Fig. 3. In the series of Ni$_{54-x}$Fe$_{15}$Co$_x$Ga$_{27}$ alloys by the substitution of Ni for Co, the temperature $T_C$ increases while temperatures $M_s$ and $A_f$ decrease with increasing Co content as shown in Fig. 3(a). On the other hand, the values of $M_s$ and $A_f$ increase with increasing Co content in the series of Ni$_{51}$Fe$_{22-x}$Co$_x$Ga$_{27}$ alloys in which Fe is substituted by Co, as shown in Fig. 3(b). In the latter case, the change of $T_C$ as a function of Co content is non-monotonous. The value of $T_C$ increases with increasing of Co content in a composition range between 3 and 5 at% of Co. However, the $T_C$ of Ni$_{51}$Fe$_{22}$Ga$_{27}$ ternary alloy is higher than that of the Ni$_{51}$Fe$_{22-x}$Co$_x$Ga$_{27}$ quaternary alloys. This fact suggests that the $T_C$ decreases with increasing of Co content in a Co-poor region and reaches a minimum.

Figure 4 shows the saturation magnetization $I_s$ of the
The martensitic transition temperature and magnetic properties of the Ni-Mn-Ga alloys were plotted as a function of the average electron concentration \( \varepsilon/\alpha \). Figure 5 shows a plot of the equilibrium temperature \( T_0 = (M_s + A_f)/2 \) as a function of \( \varepsilon/\alpha \). Both Ni\(_{51}\)Fe\(_{22-x}\)Co\(_x\)Ga\(_{27}\) and Ni\(_{54-x}\)Fe\(_x\)Co\(_x\)Ga\(_{27}\) alloys show the tendency of the linear increase of \( T_0 \) with increasing \( \varepsilon/\alpha \). However, the slopes of lines are quite different, for instance, the same value of \( \varepsilon/\alpha \) is 7.67 in the Ni\(_{48}\)Fe\(_{19}\)Co\(_9\)Ga\(_{27}\) and Ni\(_{51}\)Fe\(_{22}\)Ga\(_{27}\) alloys is correspondent to quite different values of \( T_0 \). Therefore, it is rather difficult to explain the variation of the martensitic transition temperature of this system by the \( \varepsilon/\alpha \) ratio.

The values of \( I_s \) and \( T_C \) do not show a good correlation with the \( \varepsilon/\alpha \) ratio either. Recently, we found the good correlation between \( I_s \) and \( T_C \), and the average magnetic valence number \( Z_m \) which was introduced in the generalized Slater-Pauling curve.\(^{28,29}\) These quantities are plotted as a function of \( Z_m \) in Fig. 6. In accordance to the Ref. 28, the values of \( Z_m \) equal to 2, 1, 0 and \(-3\) for pure Fe, Co, Ni and Ga were taken, respectively. In ternary and Co-doped Ni-Fe-Ga alloys, both the \( T_C \) and \( I_s \) increases with an increase of \( Z_m \) demonstrating almost linear dependence as shown in Figs. 6(a) and (b), respectively. It is worth noting that the \( T_C \) curves of the parent phase and martensite do not fall on the same line. Moreover, the \( T_C \) values of martensite are systematically higher than that for parent phase which is observed in other ferromagnetic shape memory alloys.\(^{6,7,11,27,30}\) The value of \( I_s \) is normalized by the Bohr magneton and plotted as a function of \( Z_m \) in Fig. 6(c). The best fitted line of the data is obtained as \( I_s = 1.25Z_m + 1.1 \) and the extrapolation of the line to the stoichiometric compound Ni\(_2\)FeGa (\( Z_m = -0.25 \)) yields \( I_s = 0.7875 \mu_B/\)atom, in agreement with the theoretically calculated value.\(^{21}\)

**5. Conclusion**

An influence of either Ni or Fe substitution for Co in composition range of 3–6 at\%Co on the martensitic transition temperatures and magnetic properties of the Ni-Fe-Ga \( \beta \) alloys was clarified and following conclusions can be made.

(1) The crystal structure of the parent and martensite phase
of Co added ternary Ni-Fe-Ga alloys annealed at 500 °C is identified as a cubic L21- and tetragonal L10-ordered structure, respectively.

(2) The Curie temperature $T_C$ and martensitic transition temperatures $M_t$ and $A_t$ increase and the saturation magnetization $I_s$ decrease with increasing Co content in the series of Ni$_{54-x}$Fe$_{22}$Co$_x$Ga$_{27}$ alloys. On the other hand, the $T_C$ and $I_s$ increase and the $M_t$ and $A_t$ decrease with increasing Co content in the series of Ni$_{54-x}$Fe$_{19}$Co$_x$Ga$_{27}$ alloys. Thus, Co is one of the effective elements to control both the martensitic and magnetic transition temperatures.

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