Magnetic and martensitic phase transitions in the Ni-Al-Fe shape memory alloys

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The martensitic and magnetic phase transformations of $Ni_{75-X}Al_{25}Fe_X$ β phase alloys (X: 10 - 25 at.%) were investigated. The Curie temperature (T_C) and the magnetization curve were measured by vibration sample magnetometer (VSM) and the martensitic characterized temperatures (Ms, Mf, As and Af) were measured by differential scanning calorimetry (DSC). The martensite temperatures decrease and the Tc increases with increasing Fe content. The Tc curve intersects the equilibrium temperature T_0 (=(Af+Ms)/2) curve at around 22 at.% Fe. Thus, possessing the ferromagnetic martensite phase, the β phase alloys including Fe more than 20.5 at% become a ferromagnetic shape memory alloy (FSMA), while the Tc of the FSMAs is limited below 250 K.
Key wards: shape memory alloy, ferromagnetic, martensite, phase diagram,

1. INTRODUCTION

Ferromagnetic shape memory alloys (FSMAs) have received attention as high performance magnetically controlled actuator materials, because some of them show a large magnetically induced strain by a rearrangement of twin variants in a martensitic phase and a magnetically induced shape memory effect (SME) by a thermoelastic martensitic transformation. Up to now, several FSMAs candidate systems have been proposed including Ni_2MnGa,[1,2] Fe—Pd,[3,4] Fe—Pt,[5,6] Ni_2MnAl[7,8] and Co_2NiGa [9] systems.

Recently, the present authors have proposed new FSMAs in Co—Ni—Al,[10-13] Co—Ni—Ga[13] and Ni—Fe—Ga[14,15] ternary alloys with bcc ordered structure. The crystal structures of the austenite phase β and the martensite phase β' are B2 and $L1_0$ structure in the Co—Ni—Al[10] and Co—Ni—Ga[13] FSMAs, respectively. On the other hand, the β and β' phases in the Fe—Ni—Ga FSMAs are $L2_1$ and 10M or 14M modulated structures, respectively.[14,15] The order-disorder transition temperature from the B2 to $L2_1$ structure was confirmed about 700 °C in the β phase of the Ni—Fe—Ga system.[15] One of the common characteristics of these FSMAs are the ductility which can be improved by introduction of several percent of γ phase (A1 disordered fcc structure) in the β matrix using the same manner as that previously reported in the Ni—Al—Fe β (B2 structure) based alloys.[16]

The β phase (B2 structure) in the Ni—Al—Fe ternary system exists over a wide range of composition.[17] The Ni-rich β phase has been known to undergo a thermoelastic martensitic transformation from B2 to $L1_0$ structure and to exhibit SME.[18,19] It is expected that the Ni—Fe—Al β alloys replacing Al for Ga of the Ni—Fe—Ga FSMAs show ferromagnetism on the analogy with relation between the Co—Ni—Al and Co—Ni—Ga FSMAs. Although the effects of Fe addition on the martensitic transformation in the Ni-Al base alloys have been reported,[18-20] the magnetic properties are still unknown. The present study undertakes to investigate the details of the magnetic and martensitic transformations of the β phase in the Ni—Al—Fe ternary system.

2. EXPERIMENT

Ni_{75-X} Al_{25} Fe_X alloy ingots (X: 10-25 at.%), weighing about 300 g each, were prepared by melting pure iron (99.9%), nickel (99.9%) and aluminum (99.7%) in an induction furnace under argon gas atmosphere and cast into the steel mold. Small pieces were cut out of the ingots and sealed in the quartz capsule filled with argon gas and heat-treated at 1623 K for 3 hours to prepare β single phase alloys. After the heat treatment, the samples were quenched into ice water. The magnetic properties were measured using a vibrating sample magnetometer (VSM), and the martenstitic transformation temperatures (Ms, Mf, As and Af) were determined by differential scanning calorimetry (DSC) with scanning rate of 10 K/min. The Curie temperature (T_C) was defined as the minimum point of the temperature derivative of magnetization (dM/dT) vs temperature at a field strength H of 500 Oe, where such the method for determining T_C was performed because no straight parallel lines of Arrot plots could be obtained. It was

Table 1 The Composition, martensitic characterized temperature and the Curie temperature of $Ni_{75-X}Fe_XAl_{25}$ alloys.

Alloy	M_s(K)	M_f(K)	A_s(K)	A_f(K)	T_C(K)	T_h(K)	T_0(K)
$Ni_{56.5}Fe_{18.5}Al_{25}$	410	379	409	438	220	28	424
$Ni_{55.5}Fe_{19.5}Al_{25}$	330	312	337	354	241	24	342
$Ni_{55}Fe_{20}Al_{25}$	290	272	297	312	247	22	301
$Ni_{54.5}Fe_{20.5}Al_{25}$	252	238	258	276	—	24	264
$Ni_{54}Fe_{21}Al_{25}$	219	203	221	236	—	17	227.5
$Ni_{53.5}Fe_{21.5}Al_{25}$	172	149	172	195	—	23	183.5
$Ni_{53}Fe_{22}Al_{25}$	—	—	152*	175*	—	—	—
$Ni_{52.7}Fe_{22.3}Al_{25}$	—	—	125*	155*	157	—	—
$Ni_{52}Fe_{23}Al_{25}$	—	—	—	—	166	—	—
$Ni_{51}Fe_{24}Al_{25}$	—	—	—	—	184	—	—
$Ni_{50}Fe_{25}Al_{25}$	—	—	—	—	202	—	—

M_s, M_f, A_s, A_f and T_C: martesite start, martensite finish, austenite start, austenite finish and Curie temepratures.
$T_h = A_f - M_s$: martensite transformation hysterisis and $T_0 = (A_f + M_s)/2$: equilibrium temperature.
* A_s and A_f were determined from the M-T curve.

previously reported for this method to yield reliable T_C.[21]

3. RESULTS AND DISCUSSION

The Tc and the martensitic transformation characterized temperatures are listed in Table 1 and those data are plotted in Fig. 1 as a function of Fe content. It is seen in Fig. 1 that the T_C temperatures increase with increasing Fe content, while the M_s and A_f temperatures decrease, and that the Tc in the martensite phase is about 60K higher than that in the austenite phase. The T_C and equilibrium temperature T_0 ($=(M_s+A_f)/2$) curves cross at around 20.6 and 22.1 at.% Fe, and the T_C is higher than the T_0 temperature in the composition region (Region I) over 22.3 at.% Fe. This result means that the alloys in Region I exhibit the

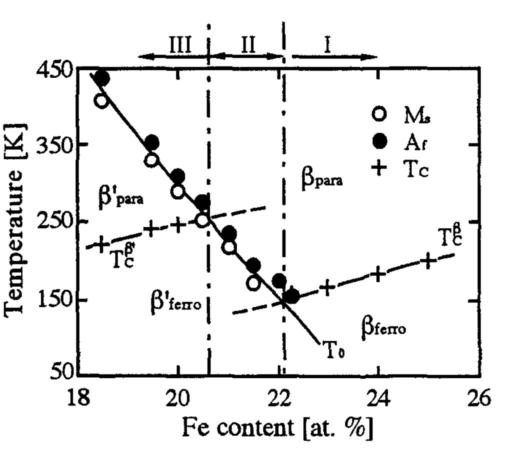

Fig. 1 Composition dependence of the Curie temperature T_C, the martensitic start M_s and the austenitic finish A_f temperatures, and the equilibrium temperature $T_0=(M_s+A_f)/2$ in $Ni_{75-X}Fe_XAl_{25}$ alloys.

martensitic transformation in the ferromagnetic state. Since the M_s temperatures are very low in the high Fe region, no alloy exhibiting the martensitc transformation in ferromagnetic state could be confirmed in this study. Reducing Al content is expected to lead to increase of the T_C and the martensite temperatures as reported in the Co—Ni—Al [10] and Ni-Al-Fe SMAs [18]. However, since the β /γ+β solubility boundary which restricts composition of the β single-phase alloys is located along just about 25 at.% Al in the isothermal phase diagram of 1623 K, it is difficult to obtain the β single-phase bulk samples with Al content less than 25 at.% by conventional treatments. Some novel processes such as the rapid solidification may be useful to fabricate a FSMA with high transition temperatures in Ni-Fe-Al system. The $T_C^{\beta'}$ curve extrapolated from the martensite to austenite phase is not continuous with the T_C^{β} of the austenite β phase and these curves show a temperature step around the cross point of the T_0 and the T_C curves, because the Tc of martensite phase is different from that of austenite. This feature of the phase diagram is very similar to that of the Co—Ni—Al,[11,13] Co—Ni—Ga[13] and Ni—Fe—Ga[15] ternary FSMA s. Based on the behavior of the T_C and T_0 curves, the phase diagram is divided into three regions as shown in Fig. 1 following the previous study of the Co—Ni—Al[11] and Co—Ni—Ga[13] systems. Region I: $T_0 < T_C^{\beta}$. Region II: $T_C^{\beta'} > T_0 > T_C^{\beta}$. Region III: $T_C^{\beta'} < T_0$.

Figure 2 shows a typical thermomagnetization curve on heating of the $Ni_{53.5}Fe_{21.5}Al_{25}$ alloy in Region II. The magnetization drastically decreases with increasing temperature in the region from A_s to A_f. The minimum point of dM/dT is located at the middle point between A_s

and A_f, and the spontaneous magnetization disappears above A_f temperature, namely the magnetic transition from the ferromagnetism to the paramagnetism occurs together with the reverse martensitic transformation as well as in the $Co_{35}Ni_{35}Al_{30}$ (B2),[11] the $Ni_{54}Fe_{19}Ga_{27}$ ($L2_1$)[14] and the $Ni_{54.75}Mn_{20.25}Ga_{25}$ ($L2_1$)[22] alloys.

Both Al and Ga belong to column IIIb in the periodic table. The FSMAs replaced by Al or Ga each other have many similarities on the configuration of phase diagram as well as that between the Co—Ni—Al[11] and Co—Ni–Ga[13] systems or between the Ni_2MnAl[17,23] and Ni_2MnGa[24] systems. In the case of Ni—Fe—Al systems, however, the order-disorder transition from B2 to $L2_1$ structure has not been confirmed so far, whereas confirmed at around 973 K in the Ni—Fe—Ga systems. Although the $Ni_{55}Fe_{20}Al_{25}$ alloy was tried to anneal at 573 K for three hours, the β phase still kept the B2 structure.

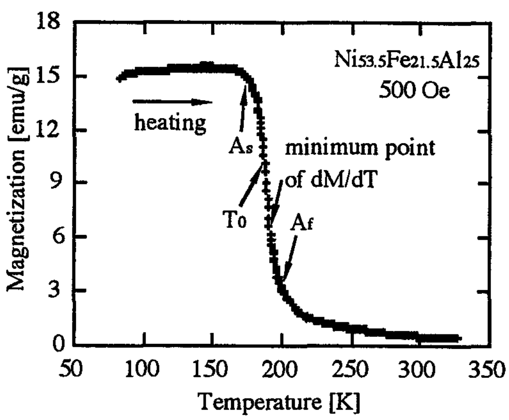

Fig. 2 Thermomagnetization curve on heating in a magnetic field of 500 Oe for Type II $Ni_{53.5}Fe_{21.5}Al_{25}$ alloy.

4. CONCLUSIONS

The martensitic and magnetic phase transformations of the $Ni_{75-X}Fe_XAl_{25}$ (X: 10 - 25 at.%) β phase alloys were investigated and the following results were obtained. The martensitic characterized temperatures decrease with increasing Fe content, while the Curie temperature increases. The Tc temperatures of the martensite phase are relatively higher than those in the austenite, and the Tc curves in the martensite and austenite phases intersect the T_0 curve around 20.6 and 22.1 at.% Fe, respectively. The β phase alloys including Fe more than 22.3 at% undergo the martensitic transformation in the ferromagnetic state. Thus, the Ni—Fe—Al alloys have a potential as the ferromagnetic shape memory alloys (FSMAs). Further investigations for raising the Tc of them may be required.

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