Effects of Aging and Co Addition on Martensitic and Magnetic Transitions in Ni–Al–Fe β-based Shape Memory Alloys

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Effects of low temperature aging and the addition of Co on the martensitic and magnetic transitions in the Ni–Al–Fe β (B2-type structure) alloy system were investigated using differential scanning calorimetry, transmission electron microscopy and vibrating sample magnetometry. The martensitic transition temperatures of a Ni57Al25Fe18 specimen homogenized at 1473 K for 1 h were decreased by aging after homogenization, the maximum decrease by aging being observed at 573 K. On the other hand, the substitution of Co or Fe for Ni induced a decrease of the martensitic transition temperatures and an increase of the Curie temperature, while the substitution of Co for Fe resulted in an increase of the martensitic transition and Curie temperatures. Co was thus shown to be an effective element by which both the martensitic and magnetic transition temperatures can be controlled.

KEY WORDS: phase transformation; martensite; shape memory; Curie temperature; aging effect.

1. Introduction

Shape memory alloys (SMAs) possessing ferromagnetic properties have received attention as new solid-state actuator materials since a large magnetic-field-induced strain due to rearrangement of twin variants was reported in the Ni–Mn–Ga system.1) To date several candidates for ferromagnetic shape memory alloys (FSMAs), including Fe–Pd,2) Fe–Pt3) and Co–Ni–Ga4,5) alloy systems, have been reported. The present authors have also conducted systematic studies on martensitic and magnetic transitions in several ordered bcc alloy systems and found Ni–Mn–Al,6) Co–Ni–Al,7) Co–Ni–Ga,5) Ni–Fe–Ga,8,9) Cu–Mn–Ga10) and Ni–Mn–(In, Sn, Sb)11,12) to be promising ferromagnetic shape memory alloy systems.

The β phase with a B2-type (ordered bcc) structure in the Ni–Al–Fe ternary system is known to undergo a thermoelastic martensitic transition to a L10 structure and to exhibit a shape memory effect (SME).13) It has been reported that the introduction of several percents of the γ phase with a disordered fcc structure in the β matrix drastically improves the ductility13) whose alloys are potential high temperature SMAs.14) Recently, systematic study of the martensitic and magnetic transition temperatures of Ni35Al25Fe β single-phase alloys5) has indicated that the martensitic transition temperature decreases and the Curie temperature increases with increasing Fe content. Although β phase alloys with a Fe composition of over 22.3 at% undergo martensitic transition in the ferromagnetic state, the martensitic and magnetic transition temperatures are lower than room temperature, which is not very attractive from a practical point of view. On the other hand, it has recently been reported that low temperature aging16,17) and/or the addition of Co are effective means to control the martensitic and magnetic transition temperatures of Ni–Ga–Fe alloys.18–20) In the present work, influences of low temperature aging and the addition of Co on the martensitic and magnetic transitions in the Ni–Al–Fe alloy system were examined.

2. Experimental Procedures

Ingots of Ni–Al–Fe ternary and Ni–Al–Fe–Co quaternary alloys, weighing about 300 g each, were prepared by melting pure iron (99.9%), nickel (99.9%), cobalt (99.5%) and aluminium (99.7%) in an induction furnace under an argon gas atmosphere, the melt being cast into a steel mold. Small specimens were taken from the ingots and sealed in quartz capsules filled with argon gas. The specimens were homogenized in a temperature range of 1473 to 1623 K and quenched in ice water. The quenched Ni–Al–Fe samples were aged from 473 to 873 K for several hours and then quenched in ice water again. The magnetic properties were measured by vibrating sample magnetometry (VSM), and the characteristic transition temperature, the martensitic transition starting temperature (M_s), the martensitic transition finishing temperature (M_f), the reverse transition starting temperature (A_s) and the reverse transition finishing temperature (A_f) were measured.
temperature \( (A_f) \) were determined by differential scanning calorimetry (DSC) at a cooling and heating 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 magnetic field strength \( H \) of 39.8 kA/m. Phase identification and characterization were carried out by transmission electron microscopy with energy dispersive X-ray (TEM-EDX) microanalysis. The chemical composition of several equilibrated samples was determined by scanning electron microscopy with energy dispersive X-ray (SEM-EDX) microanalysis.

3. Results and Discussion

3.1. Aging Effect on Phase Transition Temperature

The martensitic transition temperatures of the Ni\(_{57}\)Al\(_{25}\)Fe\(_{18}\) alloy aged at 473 to 873 K for 1 h after homogenization at 1 473 K for 1 h are shown in Fig. 1. The martensitic characterized temperatures \( (M_s, M_f, A_s, \) and \( A_f) \) decreased with increasing aging temperature and reached a minimum after aging at 573 K. Further elevation of the aging temperature increased the characteristic martensitic temperatures. This behavior is very similar to the result in the Ni\(_{57.7}\)Al\(_{24.1}\)Fe\(_{18.2}\) alloy reported by Xie and Wu,\(^{21}\) although their result showed a minimum after aging at 673 K.

The thermomagnetization curves obtained from the Ni\(_{50}\)Al\(_{25}\)Fe\(_{25}\) specimen homogenized at 1 623 K for 1 d and aged at 573 K for 5 d are shown in Fig. 2. Both of the magnetization curves show a gradual decrease of magnetization due to the ferro/paramagnetic transition with increasing temperature. It can be seen that the decrease in the magnetization of the aged alloy is smaller than that of the as-quenched alloy in the vicinity of the transition temperature and that the magnetization still remains at temperatures over 300 K.

These effects of aging on the martensitic and magnetic transitions would be connected with the B2/L2\(_1\) order–disorder transition as reported in Ni–Ga–Fe alloys\(^{16,17}\) or with the microstructural changes. TEM micrographs of the Ni\(_{57}\)Al\(_{25}\)Fe\(_{18}\) alloy aged at 673 K for 7 d after homogenization at 1 473 K for 1 h are shown in Fig. 3. As shown in Fig. 3(a), besides the fundamental spots, only the ordered spots, such as the \( \{100\}_B2 \) reflections, characterizing the B2-type structure were observed in the selected area diffraction (SAD) patterns taken from the \( \beta \) parent phase, and there was no other phase with a structure different from the B2. On the other hand, the dark field image (DFI) taken from the \( \{100\}_B2 \) ordered spots showed a dark contrast from very fine spherical particles with a mean diameter of several nm as exhibited in Fig. 3(b). These characteristic features showed by the TEM examination suggest that the fine spherical particles with a dark contrast can be considered as a disordered bcc phase. Compositional analysis of some precipitates and the matrix was performed by TEM-EDX. The obtained data are listed in Table 1. It was confirmed that the Fe and Al contents of the dark area are higher and lower, respectively than those of the bright area, although this measurement is not quantitative due to the small size of the precipitates. Figure 3(c) shows the SAD pattern of the martensite phase obtained at 83 K, where the crystal structure of the martensite phase of the aged sample can be identified as an 8M structure, although the crystal structure of the martensite phase before aging in the Ni\(_{57}\)Al\(_{25}\)Fe\(_{18}\) alloy is different.
annealed at 1 473 K has been reported to be a 2M structure.\textsuperscript{13)} The effect of the aging on the microstructure on the Ni\textsubscript{50}Al\textsubscript{25}Fe\textsubscript{25} alloy is expected to be analogous to those of the Ni\textsubscript{57}Al\textsubscript{25}Fe\textsubscript{18} alloy, because the chemical composition of these alloys is close each other.

According to the Ni–Al–Fe ternary phase diagram, there is a wide miscibility gap between the \(\alpha\)-Fe phase (with a disorder bcc structure) and the NiAl \(\beta\) phase in the middle region of the isothermal section.\textsuperscript{22,23)} Both Ni\textsubscript{57}Al\textsubscript{25}Fe\textsubscript{18} and Ni\textsubscript{50}Al\textsubscript{25}Fe\textsubscript{25} alloys are presumed to be located in the \(\alpha\)-Fe and \(\beta\) two-phase region at lower temperature from the Ni–Al–Fe ternary phase diagrams.\textsuperscript{22)} By TEM analysis, Guha et al. also confirmed the precipitation of the Fe-rich bcc phase in the NiAl \(\beta\) phase in Ni–Al–Fe alloys aged at 573 K.\textsuperscript{24)} Furthermore, with regard to Ni–Al–Fe \(\beta\) based alloy, Ko et al. reported that the Fe-rich bcc phase precipitates by aging at low temperature, which brings about superparamagnetism.\textsuperscript{25,26)} Therefore, it is concluded that the very fine dark contrast in the NiAl \(\beta\) matrix shown in Fig. 3(b) resulted from the Fe-rich bcc particles, which had a strong effect on the martensitic transition temperature, the crystal structure of the martensite phase and the thermomagnetization curve shown in Fig. 2.

3.2. Effect of the addition of Co

Optical micrographs of Ni\textsubscript{55.5}Al\textsubscript{25}Fe\textsubscript{19.5} and Ni\textsubscript{47}Al\textsubscript{25}Fe\textsubscript{11}Co\textsubscript{17} alloys homogenized at 1 623 K for 1 d are shown in Fig. 4. The Ni\textsubscript{55.5}Al\textsubscript{25}Fe\textsubscript{19.5} ternary alloy has showed a \(\beta\) single phase structure as shown in Fig. 4(a). A similar microstructure was observed in Ni\textsubscript{56}Al\textsubscript{13}Fe\textsubscript{11} \((x: 18.5–25\text{ at\%})\) homogenized at 1 623 K. On the other hand, the Ni\textsubscript{47}Al\textsubscript{25}Fe\textsubscript{11}Co\textsubscript{17} alloy showed the precipitation of the second phase in the \(\beta\) matrix. The precipitate is considered to be the \(\gamma\) phase from the phase diagrams of the Ni–Al–Fe\textsuperscript{27)} and Ni–Al–Co\textsuperscript{28)} ternary systems. A similar microstructure was observed in the Ni\textsubscript{62}–Al\textsubscript{12}Fe\textsubscript{11}Co\textsubscript{17} and Ni\textsubscript{64}–Al\textsubscript{12}Fe\textsubscript{11}Co\textsubscript{17} \((x: 12–17\text{ at\%})\) series homogenized at 1 623 K. The isothermal phase diagrams at 1 573 K of the Ni–Al–Fe\textsuperscript{29)} and Ni–Al–Co\textsuperscript{28,29)} systems are shown in Fig. 5. The phase equilibrium compositions between the \(\beta\) and \(\gamma\) phases in the Ni–Al–Fe ternary system were determined in the present work as listed in Table 2. The present results are consistent with the phase diagrams reported by Bradley,\textsuperscript{27)} although his work did not include the isothermal section at 1 573 K. As shown in the phase diagrams, the Al contents of the \(\beta\) phase boundary equilibrating with the \(\gamma\) phase in the Ni–Al–Co system are higher than those in the Ni–Al–Fe system.

It has been reported that such precipitation of small amount of \(\gamma\) phase improves ductility of the Ni–Al-based shape memory alloys.\textsuperscript{13)} Therefore, it would be useful to determine the martensitic and magnetic transformation temperatures of these \(\beta + \gamma\) quaternary alloys. The character-

\begin{table}[h]
\centering
\caption{Chemical composition of \(\beta\) and \(\gamma\) phases in the Ni–Al–Fe system at 1 573 K.}
\begin{tabular}{|c|c|c|c|}
\hline
Chemical compositions [at %] & & & \\
\hline
\(\gamma\) & \(\beta\) & \\
\hline
Temp. [K] & Al & Fe & Al & Fe \\
\hline
13.0 & 49.8 & 23.6 & 34.2 \\
14.6 & 37.1 & 25.2 & 25.7 \\
1573 & 15.9 & 26.1 & 17.9 \\
16.9 & 22.1 & 26.8 & 14.8 \\
19.3 & 13.2 & 26.9 & 10.0 \\
1623 & 16.5 & 25.5 & 24.8 & 19.2 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Chemical composition of \(\beta\) and \(\gamma\) phases in the Ni–Al–Fe–Co system at 1 623 K.}
\begin{tabular}{|c|c|c|c|c|}
\hline
Chemical compositions [at %] & & & & \\
\hline
\(\gamma\) & \(\beta\) & & & \\
\hline
sample & Al & Fe & Co & Al & Fe & Co \\
\hline
Ni\textsubscript{62}Al\textsubscript{12}Fe\textsubscript{11}Co\textsubscript{17} & 15.4 & 15.7 & 21.6 & 25.8 & 10.7 & 17.4 \\
Ni\textsubscript{64}Al\textsubscript{12}Fe\textsubscript{11}Co\textsubscript{17} & 14.5 & 18.6 & 19.5 & 25.3 & 12.4 & 14.7 \\
Ni\textsubscript{66}Al\textsubscript{12}Fe\textsubscript{11}Co\textsubscript{17} & 15.3 & 19.0 & 20.0 & 25.7 & 12.1 & 15.7 \\
\hline
\end{tabular}
\end{table}
Table 4. Characteristic martensitic temperature, Curie temperature and microstructure of Ni–Al–Fe–Co alloys annealed at 1 623 K for 1 d.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_s ) [K]</th>
<th>( A_f ) [K]</th>
<th>( T_C ) [K]</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{56.5}Al_{25}Fe_{18.5}</td>
<td>410*</td>
<td>438*</td>
<td>220*</td>
<td>single-phase</td>
</tr>
<tr>
<td>Ni_{53.5}Al_{25}Fe_{17.5}</td>
<td>172*</td>
<td>236*</td>
<td>-</td>
<td>single-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{25}</td>
<td>-</td>
<td>-</td>
<td>202*</td>
<td>single-phase</td>
</tr>
<tr>
<td>Ni_{51.5}Al_{25}Fe_{18.5}Co</td>
<td>304</td>
<td>323</td>
<td>-</td>
<td>single-phase</td>
</tr>
<tr>
<td>Ni_{52.5}Al_{25}Fe_{18.5}Co</td>
<td>181</td>
<td>204</td>
<td>-</td>
<td>single-phase</td>
</tr>
<tr>
<td>Ni_{51.5}Al_{25}Fe_{18.5}Co</td>
<td>363</td>
<td>-</td>
<td>-</td>
<td>single-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{18.5}Co</td>
<td>372.8</td>
<td>396.9</td>
<td>291.9</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{51}Al_{25}Fe_{18.5}Co</td>
<td>347.9</td>
<td>348.7</td>
<td>-</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{25}Co</td>
<td>269.4</td>
<td>322.2</td>
<td>334.3</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{25}Co</td>
<td>220.4</td>
<td>254.1</td>
<td>372.2</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{25}Co</td>
<td>177.3</td>
<td>205.7</td>
<td>394</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{18.5}Co</td>
<td>472.7</td>
<td>492.3</td>
<td>284</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{18.5}Co</td>
<td>451.6</td>
<td>478.4</td>
<td>302.4</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{18.5}Co</td>
<td>416.8</td>
<td>443.3</td>
<td>320.3</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{18.5}Co</td>
<td>380.2</td>
<td>409.5</td>
<td>322.3</td>
<td>two-phase</td>
</tr>
<tr>
<td>Ni_{50}Al_{25}Fe_{18.5}Co</td>
<td>315.8</td>
<td>349.8</td>
<td>-</td>
<td>two-phase</td>
</tr>
</tbody>
</table>

* The data reported in the previous paper.

Fig. 6. Composition dependence of \( M_s \), \( A_f \), and \( T_C \) of \( \text{Ni}_{56.5}\text{Al}_{25}\text{Fe}_{18.5}\text{Co} \), \( \text{Ni}_{50}\text{Al}_{25}\text{Fe}_{25}\text{Co} \), and \( \text{Ni}_{50}\text{Al}_{25}\text{Fe}_{18.5}\text{Co} \) quenched after equilibration treatment at 1 623 K for 1 d. \( T_C^M \) and \( T_C^A \) denote the Curie temperature of the martensite and austenite phases, respectively.

Fig. 7. Composition dependence of \( T_C^M \) and \( T_C^A \) of \( \text{Ni}_{53.5}\text{Al}_{25}\text{Fe}_{18.5}\text{Co} \) and \( \text{Ni}_{50}\text{Al}_{25}\text{Fe}_{25}\text{Co} \) alloys quenched after equilibration treatment at 1 623 K for 1 d.

4. Conclusions

Influences of low temperature aging and addition of Co on the martensitic and magnetic transitions in the Ni–Al–Fe \( \beta \) alloy system were investigated and the following findings were obtained:

1) The martensitic transition temperatures of the \( \text{Ni}_{50}\text{Al}_{25}\text{Fe}_{18} \) alloy homogenized at 1 473 K for 1 h decreased by aging, and the maximum decrease by aging being detected at 573 K.

2) TEM analysis revealed that the precipitation of the Fe-rich bcc phase occurs in the \( \beta \) matrix due to aging, which affects the martensitic and magnetic transitions and the crystal structure of martensite phase.

3) The substitution of Co for Ni decreases the \( M_s \) and \( A_f \), and increases the Curie temperature \( T_C \), while the substitution of Co for Fe increases all the transition temperatures. Therefore, Co is an effective element which can be used to control both the martensitic and magnetic transition temperatures.

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