Shape Memory Effect Associated with FCC–HCP Martensitic Transformation in Co-Al Alloys

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The martensitic transformation and shape memory (SM) effect in Co-Al alloys containing 0–16 at%Al were investigated by differential scanning calorimetry (DSC) and bending tests. It was found that the martensitic transformation temperatures decrease and the thermal hystereses increase with increasing Al content. It was also found that an incomplete SM effect occurring in pure Co can be enhanced by the addition of Al over 4 at% and that Co-Al alloys containing Al over 10 at% show an excellent SM effect. Co-Al SM alloys possessing high reverse transformation temperatures over 200 °C and martensitic transformation in the ferromagnetic state show promise as a new type of SM alloys.

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1. Introduction

Since shape memory (SM) effect was first reported in an Au–47.5 at%Cd alloy, many sorts of SM alloy systems have been studied. Among them, extensive work has been devoted to ordered β Hume-Rothery alloys and Ni-Ti based alloys accompanied by thermoelastic martensite transformation such as Cu-Al-Ni, Cu-Zn-Al, Cu-Al-Mn, Ni-Al-based β and Ni-Ti-Cu alloys. In particular, Ni-Ti based alloys have been put to various practical uses such as pipe couplings, medical materials, etc., due to their excellent SM properties.

The maximum 419 temperature of conventional Ni-Ti alloys is limited to about 120 °C, although high-temperature SM alloys are required in a lot of fields. Some attempts to develop high-temperature SM alloys have been performed for Ti-Ni-Pd, Ti-Ni-(Hf or Zr), Cu-Al-Ni-Ti-Mn, Ni-Al, Cu-Zr, Zr-Cu-Co and Ni-Mn-Ga alloys, with limited success due to poor SM and mechanical properties, poor thermal stability or high cost.1

The martensitic transformation takes place in pure Co from the γ phase (fcc) to the ε phase (hcp) and that it proceeds by the movement of a/6{[112]}fcc Shockley partial dislocations. The martensitic transformation starting temperature (Ms = 400–419 °C) and the reverse transformation starting temperature (As = 429–445 °C) of pure Co depend on the purity, the cooling/heating rates and the grain size. It has been reported that polycrystalline Co and Co-Ni alloys show no or only slight SM effects,9–11 while the SM effect can be obtained in Co-32 mass%Ni single crystal only in the [001]fcc compressive direction with As = 156 °C.9 Although Koval has reported the SM effect of Co-Al, Ge, Mo, Zr alloys where the shape recovery is less than 40%,12 there have been no systematic studies on the SM effect in Co-based alloys except Co-Ni. It has been widely accepted that an ordered structure of the parent phase is one of the essential conditions for a perfect SM effect, and the addition of Al is thus supposed to be favorable for the improvement of the SM effect of Co due to the promotion of L12 ordering. Moreover, the solubility (about 16 at%) of Al in Co is relatively high and the addition of Al does not reduce the ductility. Recently, the present authors have found that polycrystalline Co-Al alloys exhibit an excellent SM effect due to martensitic transformation from fcc to hcp. The Co-Al alloys, therefore, show promise as high-temperature SM alloys due to their high transformation temperatures and high thermal stability. The purpose of this paper is to report the martensitic transformation and SM effect in a polycrystalline Co-Al alloy system in the range of Co-(0–16) at%Al.

2. Experimental

Pure Co and Co-X at%Al (X = 4, 8, 10, 14 and 16) binary alloys ingots were prepared in an induction furnace under an argon atmosphere from pure cobalt (99.9%) and aluminum (99.7%). Sheet specimens were obtained from the ingots by hot-rolling at 1200 °C followed by cold-rolling. Co-(0–14) at%Al and Co-16 at%Al specimens were solution treated at 1200 °C for 1 hour and 1300 °C for 15 minutes in the γ single-phase region, respectively, and then quenched in water. The microstructures were observed using an optical microscope (OM), a solution of 75% hydrochloric acid and 25% nitric acid being used as an etchant.

The martensitic transformation temperatures (Ms, Mt, A1 and A3) were measured by differential scanning calorimetry (DSC) at heating and cooling rates of 10 °C/min. These temperatures were defined as points of intersection between the base line and the tangent of maximum or minimum inclination in the DSC curves.

The SM effect was evaluated by bending a rectangular specimen of 0.24 × 4 × 50 mm3 into a round shape at room temperature, unloading it (surface strain εc) and then heating it up to 800 °C (surface strain εh). The surface strain is defined as ε = t/2r × 100, where t is the thickness of the specimen and r is the radius of curvature. The shape recovery RSM and recoverable strain εSM were evaluated by RSM = (εc − εh)/εc × 100 and εSM = εc − εh, respectively. SM testing was also carried out for a Co-10 at%Al specimen subjected to...
a thermomechanical treatment (TMT) which consists of 10% cold-rolling and subsequent annealing at 900°C for 3 minutes after solution treatment at 1200°C.

3. Results and Discussion

3.1 Martensitic transformation and microstructure

Figure 1 shows the microstructure of Co-14 at%Al alloy at room temperature. The typical ε martensite structure is observed.

Formed martensites are observed, which are considered to be formed by the motion of $(a/6)\langle 112 \rangle_{\text{fcc}}$ Shockley partial dislocations. It seems that the morphologies of the ε martensites are similar to those observed in Co and Co-Ni alloys. A small amount of γ phase was also detected by X-ray diffraction and TEM observation. All the specimens in this study included some residual γ phase at room temperature, although the $M_f$ temperatures of all the specimens were located above room temperature. It is well known that the residual austenite phase exists in hcp martensite phase of Fe-Mn-based alloys, Co-based alloys and so on. $^{11,15-17}$

Figure 2 shows (a) the phase diagram in Co-Al system $^{18}$ and (b) martensitic transformation temperatures. The martensitic transformation temperatures are high compared with those of conventional SM alloys. The martensitic transformation temperatures, the transformation temperature hystereses $TTH$ ($A_f - M_s$ and $A_s - M_f$) and the transformation temperature intervals $TTI$ ($M_s - M_f$ and $A_s - A_f$) are listed in Table 1. The $TTH$ of pure Co is quite small ($A_f - M_s = 57°C$ and $A_s - M_f = 67°C$) compared with that of other non-thermoelastic martensite transformations. While the $TTI$ does not strongly depend on Al content, the $TTH$ drastically increases with increasing Al content. The DSC heating and cooling curves of Co-8 at%Al water-quenched (WQ) and air-cooled (AC) from 1200°C are shown in Fig. 3. The AC specimen shows a single peak of the reverse transformation in heating, while the WQ specimen shows a reverse transformation peak at around 300°C and an additional small peak.

<table>
<thead>
<tr>
<th>Al (at%)</th>
<th>Martensitic transformation temperature/°C</th>
<th>Hysteresis/°C</th>
<th>Interval/°C</th>
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<tr>
<td></td>
<td>$M_s$</td>
<td>$M_f$</td>
<td>$A_s$</td>
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</table>
at around 430°C. In cooling, only one peak of forward transformation appears in both specimens. The sum of the latent heat of the two peaks during heating in the WQ specimen is almost equal to that in AC specimen, and the smaller peak was not seen in subsequent heating cycles. From the X-ray diffraction analysis at high temperatures, it is considered that a part of martensite is stabilized by quenching and that the small peak corresponds to a reverse transformation of the stabilized martensite. A small peak at higher temperature was also detected in Co-10 at%Al. Although affecting the transformation behavior, the cooling process hardly influences the SM properties of the specimens.

3.2 Shape memory effect

Figure 4 shows the shape recovery $R_{SME}$ of a Co-14 at%Al sheet as a function of heating temperature. It is seen that the deformed shape drastically recovers in the temperature range of 200°C to 300°C, which corresponds to the reverse transformation temperatures, $A_s = 236°C$ and $A_f = 260°C$, as listed in Table 1. This result means that the shape recovery is due to the martensitic reverse transformation and that Co-Al is a high-temperature SM alloy. The shape recovery and the recovered strain $\varepsilon_{SME}$ evaluated by the bending test are plotted against the Al content in Fig. 5. For an applied surface strain (ASS) of 1.2%, pure Co exhibits a poor SM effect of $R_{SME} = 40\%$, while the addition of Al drastically improves the SM effect. The SM effect is almost independent of the Al content up to 4 at%Al, but is considerably improved by the addition of Al over 4 to 10 at%. Over 10 at%Al, the SM effect reaches about 80% and becomes steady again. The tendency of the $R_{SME}$ for ASS = 2.0% is the same as that for ASS = 1.2%, while the $R_{SME}$ is always lower than that of the ASS = 1.2% specimens. In the case of SM strain $\varepsilon_{SME}$, the $\varepsilon_{SME}$ for ASS = 1.2% and 2.0%, which are almost the same in pure Co, increase with increasing Al content and the $\varepsilon_{SME}$ of ASS = 2.0% becomes larger than that of ASS = 1.2%. These results suggest that the maximal recoverable strain, namely, the maximum of the SM ability in the materials, is limited to about 0.3% in pure Co, while it increases with increasing Al content. An $\varepsilon_{SME}$ of 1.1% was obtained in Co-16 at%Al for ASS = 2.0%. It is known that TMT is effective to improve the SM effect in Fe-Mn-Si alloys. 19) As shown in Fig. 5, the TMT also improves the SM effect in the Co-Al alloys.

It has been proposed that alloys satisfying the following requirements exhibit shape memory effects with a perfect reversibility:20,21)

i) The martensitic transformation is thermoelastic.

ii) The structure of the parent phase is ordered or the lattice deformation associated with the transformation is small.

iii) The lattice invariant strains are caused not by dislocations but by twins.

It is known, however, that the perfect shape memory effect can be obtained in Fe-Mn-Si alloys, which have a disordered structure with non-thermoelastic martensite transformation under certain conditions. 19,22) When discussing the SM effect in the Co-Al alloys, it is helpful to compare these alloys with
Fe-Mn-Si alloys since these SM alloys are similar in the nonthermoelastic martensite transformation from disordered fcc to hcp with low stacking fault energy. Several explanations have been proposed for the origin of the SM effect in the Fe-Mn-Si alloys. One of them is that the existence of internal stress causes backward stress on the reversible movement of Shockley partial dislocations upon reverse transformation, and another is that the SM effect is due to the short range ordered structure or small coherent ordered particles. Although both explanations might be applied to Co-Al alloys, the report by Bradley and Seager and Edwards, in which there is a metastable phase thought to be a Co$_3$Al L2$_1$ ordered structure, supports the latter. It should be noted that even though they are deformed at a temperature below $M_f$ with only a slight amount of retained fcc phase, the Co-Al alloys show a good SM effect, while Fe-Mn-Si alloys exhibit an excellent SM effect associated only with stress-induced martensite. This fact suggests that there is an essential difference in the mechanism of the SM effect between the Co-Al and the Fe-Mn-Si alloys. The deformation in the martensite state may be important to obtain the excellent SM effect and further investigations such as the observation of the microstructural change by deformation are necessary to understand the mechanism.

From the results obtained in the present study, the Co-Al SM alloys show promise as high-temperature SM alloys. Other characteristic features of Co-Al SM alloys are that the martensitic transformation occurs in a ferromagnetic state and the Co-Al can be easily cold-worked in contrast to other ordered ferromagnetic SM alloys such as Ni$_2$MnGa. Thus, the Co-Al SM alloys also have potential as ferromagnetic SM alloys with high Curie temperatures above 600°C and high $A_s$ temperatures above 200°C.

### 4. Conclusion

$\gamma$(fcc)/$\delta$(hcp) transformations of Co-Al alloys in the range of 0-16 at%Al were investigated. The martensitic transformation temperatures of these alloys were found to decrease with increasing Al content, whereas the transformation temperature hysteresis was observed to increases. With regard to stabilized martensite, an additional peak was observed in the DSC heating curves of as-quenched Co$_8$ at%Al and Co$_{10}$ at%Al specimens, although it hardly affects the recoverable strain due to the SM effect. The SM effect is enhanced by the addition of Al over 4 at% and Co-Al alloys over 10 at% exhibit an excellent SM effect. The shape recovery of $\varepsilon_{\text{SME}} = 1.1\%$ and $R_{\text{SME}} = 80\%$ was obtained in Co-16 at%Al. The TMT is also effective for improving the SM effect. Since the SM effect can be obtained at over 200°C, Co-Al SM alloys show promise as high-temperature SM alloys.

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### REFERENCES