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Materials Transactions

47

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2381-2386

2006

http://hdl.handle.net/10097/51934

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Effect of Alloying Elements on fcc/hcp Martensitic Transformation and Shape Memory Properties in Co-Al Alloys

Keisuke Ando1,*, Toshihiro Omori2, Jun Sato1,*, Yuji Sutou2, Katsunari Oikawa1, Ryosuke Kainuma3 and Kiyohito Ishida1

1Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
2Tohoku University Biomedical Engineering Research Organization, Sendai 980-8579, Japan
3Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Effects of alloying elements (Si, Ti, V, Cr, Mn, Fe, Ni, Nb, Mo, Ta and W) on γ (fcc)/ε (hcp) martensitic transformation, ductility and shape memory (SM) properties of Co0.5Al0.5 alloy were investigated by means of differential scanning calorimetry, X-ray diffraction method, cold-rolling and an SM test. The addition of Ti, V, Mn, Fe, Ni, Nb, Mo, Ta or W decreased the volume fraction of the ε martensite phase (Vm), resulting in improvement of the ductility due to the stabilization of the γ phase, and the addition of Si or Cr, known as hcp stabilizing elements, slightly decreased Vm. The relationship between the martensitic transformation temperatures and Vm was determined in Co-Al and Co-Al-Fe alloys. Co-Al alloys showed behavior different from that of other alloys. The SM effect decreased with decreasing Vm and the Co-Al binary alloys showed the highest SM effect in this study, whereas the transformation temperatures and the ductility could be controlled by the alloying element. [doi:10.2320/matertrans.47.2381]

(Received May 17, 2006; Accepted July 19, 2006; Published September 15, 2006)

Keywords: cobalt-aluminum, martensitic transformation, high-temperature shape memory alloy, ferromagnetic shape memory alloy, alloying element

1. Introduction

Unique properties of the shape memory (SM) effect and pseudoelasticity have been studied in various alloy systems for several decades and SM alloys have been practically used as functional materials. In particular, Ti-Ni alloys are the most attractive system due to their excellent SM properties and good bio-compatibility, which enable their wide use in the field of industry and medicine.1,2)

Since Ti-Ni alloys are limited to use at temperatures lower than 100 °C, the development of SM alloys which can operate at higher temperatures is required. Several types of high-temperature SM alloys have been reported, for example, Ti-Ni-(Zr, Hf, Pd or Pt), Ni-Al, Zr-Cu-based alloys and so on.3) Ferromagnetic SM alloys, the strain of which is controlled by an external magnetic field, are of great interest because of the possibility of a quick response as opposed to the slow response of conventional SM alloys controlled by heat. Moreover, the magnetic-field-induced strain of ferromagnetic SM alloys is greater than that of magnetostrictive materials. This type of SM alloys, such as Ni-Mn-(Ga or Al),4,5) Ni-Mn-(In, Sn or Sb),6,7) Co-Ni-(Al or Ga),8–10) Ni-Fe-Ga11,12) and Fe-(Pd or Pt),13,14) have been extensively studied.

Recently, the present authors have reported that ductile Co-Al alloys containing Al over 10 at% exhibit an SM effect associated with γ (fcc)/ε (hcp) martensitic transformation and that the reverse transformation temperatures are located between 200 and 300 °C.5,15) One of the characteristic features of Co-Al SM alloys is their ferromagnetism, where the Curie temperature and the saturation magnetization at 25 °C are 689 °C and 120 emu/g, respectively, in Co60Al40.16) Therefore, the Co-Al alloys can be classified as ferromagnetic high-temperature SM alloys.

Since microstructural control is useful for improvement of the SM properties of Co-Al binary alloys,17) the effect of the addition of alloying elements is also of interest. In the present paper, the effects of third elements on the martensitic transformation temperatures, the volume fraction of the ε martensite phase, the ductility and the SM properties of Co-Al SM alloys are reported.

2. Experimental Procedure

(Co0.5Al0.5)(100−X)X (X = Si, Ti, V, Cr, Mn, Fe, Ni, Nb, Mo, Ta or W) ternary alloy ingots with different X contents in each alloy system were prepared by induction melting under an Ar atmosphere, the X elements being added to a master reference alloy in stages and the alloys being cast in partial quantities at every stage, as previously described in details.18) The advantage of this technique is that ternary alloys with different X contents but exactly the same composition ratio of Co and Al as in the base reference alloy can be obtained. Co100−yAl y binary alloys (y = 0–16) were also obtained by induction melting. Sheet specimens were fabricated by hot-rolling at 1200 °C followed by cold-rolling. Specimens were solution-treated at 1200 °C for 1 h and were subsequently quenched in water of about 10 °C. The chemical compositions of the ternary alloys were measured by energy dispersion X-ray spectrometry (EDX), and the results are listed in Table 1. The microstructures were observed by optical microscopy (OM). The martensitic and reverse transformation temperatures (Mf, Ms, Arf and A1f) were determined by differential scanning calorimetry (DSC), and the volume fraction of the ε martensite phase Vm was estimated by the following equation:19) Vm = I(10,1ε) / [I(10,1ε) + 1.5I(200ε)], where I is the integrated intensity of the indicated peak measured using an X-ray diffraction (XRD) method with Cu-Kα radiation at room temperature. The ductility was evaluated by the
maximum reduction in thickness defined as \( W = \left( t_1 - t_{\text{min}} \right) / t_1 \times 100 \% \), where \( t_1 \) is the initial thickness and \( t_{\text{min}} \) is the minimum thickness before cracks appear on the surface of the samples during cold-rolling. The SM effect was evaluated by bending followed by heating. Namely, a rectangular specimen with dimensions of thickness \( \times \) width \( \times \) length was deformed into a round shape with a surface strain \( \varepsilon_s = 1.2\% \) at room temperature and the residual surface strain \( \varepsilon_b \) was evaluated from curvature of the specimen after it was heated up to 1000°C. The surface strain is defined as \( \varepsilon = t/2r \times 100 \% \), where \( t \) is the thickness of the specimen and \( r \) is the radius of curvature. The SM effect, \( R_{\text{SME}} \), was evaluated by
\[
R_{\text{SME}} = \left( \varepsilon_1 - \varepsilon_b \right) / \varepsilon_1 \times 100 \%.
\]

3. Results and Discussion

3.1 Microstructure

Figures 1(a) and (b) show optical micrographs of \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{1}\) and \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{4}\) alloys, where the microstructure is the typical \( \varepsilon \) martensite and \( \gamma \) single-phase structure, respectively, which indicates that the addition of Fe decreases the martensitic transformation temperatures. The morphology of \( \varepsilon \) martensite in other Co-Al-X alloys is similar to that shown in Fig. 1(a), and neither a noticeable difference in the grain size nor any precipitations were observed. It was confirmed by XRD examination that the \( \gamma \) parent phase was retained in the \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{1}\) alloy below the \( M_t \) temperature detected by DSC. This microstructural feature has been reported in other alloys, such as Co and Fe alloys, undergoing a non-thermoelastic martensitic transformation.\(^{15-17,20-23}\)

3.2 Martensitic transformation and fraction of martensite

XRD examinations at 10°C were employed to determine the volume fraction of the \( \varepsilon \) martensite phase and the retained \( \gamma \) parent phase. An XRD profile of \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{2}\) alloy indicating the \( \gamma \) and \( \varepsilon \) two-phase structure is shown in Fig. 2. The volume fraction of the \( \varepsilon \) martensite phase, \( V_m \), determined by the specific peaks in the XRD profiles is shown as a function of the content of the alloying element \( X \) (\( X = \text{Si}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Ni}, \text{Nb}, \text{Mo}, \text{Ta} \) and \( \text{W} \)) in Table 1 and Fig. 3. The \( V_m \) of the \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\) master alloy is 99%, and the addition of every element decreases the \( V_m \). The elements can be classified into three types based on the degree of the decrement:

| Table 1 Compositions (at%) of Co-Al-X ternary alloys for \( X = \text{Si}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Ni}, \text{Nb}, \text{Mo}, \text{Ta} \) and \( \text{W} \), and volume fraction (%) of martensite phase \( V_m \) after quenching in water at 10°C. |
|---|---|---|---|---|---|---|---|---|
| | Co | Al | X | \( V_m \) | Co | Al | X | \( V_m \) |
| Si | 88.5 | 9.1 | 2.4 | 97 | 85.6 | 8.4 | 6.0 | 55 |
| Ti | 89.4 | 8.7 | 1.9 | 59 | 90.0 | 9.0 | 1.0 | 68 |
| V | 87.4 | 8.8 | 3.8 | 0 | 89.0 | 9.0 | 2.0 | 40 |
| Cr | 85.3 | 9.1 | 5.6 | 94 | 89.4 | 9.5 | 1.1 | 44 |
| Mn | 85.8 | 8.7 | 5.5 | 90 | 88.7 | 9.1 | 2.2 | 72 |
| Fe | 85.1 | 9.0 | 1.2 | 92 | 87.4 | 8.6 | 4.0 | 17 |
| Ni | 88.7 | 9.0 | 2.3 | 55 | 86.3 | 7.5 | 6.2 | 0 |
| Nb | 87.1 | 8.6 | 4.3 | 0 |

Fig. 1 Optical micrograph of (a) \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{1}\) alloy with \( \varepsilon + \gamma \) two-phase structure and (b) \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{4}\) alloy with \( \gamma \) single-phase structure.

Fig. 2 X-ray diffraction pattern of \((\text{Co}_{90}\text{Al}_{10})_{\text{x}}\text{Fe}_{2}\) alloy with \( \varepsilon + \gamma \) two-phase structure.
A) Elements which greatly decrease $V_m$: Ti, V, Fe, Nb, Mo, Ta and W.

B) Elements which gradually decrease $V_m$: Mn and Ni.

C) Elements which hardly decrease $V_m$: of Cr and Si, known as hcp stabilizers in cobalt.

Figure 4 shows $C_{V_m=0}$ for type A and B elements, where the $C_{V_m=0}$ is the content of element X at $V_m = 0$ in Fig. 3, i.e., at $M_s = 10^\circ C$. One can see that the elements in groups 4, 5 and 6, which are far from Co in group 9 in the periodic table, belong to type A, while elements in groups 7 and 10, which are close to Co in the periodic table, are in type B. The group 8 element Fe is next to Co, but belongs to type A. The $C_{V_m=0}$ is plotted as a function of solubility of the $\gamma$ phase $24)$ in Fig. 5. It was empirically found that $C_{V_m=0}$ is proportional to the solubility except for Fe, i.e., the elements which tend to form an intermediate phase with a limited solubility in Co greatly decrease the $V_m$, and the slope is 0.19. This result indicates that the degree of the decrement in $V_m$ can be roughly estimated from the solubility, although it depends on the grain size and cooling rate. Origin of the anomaly of Fe shown in Figs. 4 and 5 is not clear, but the magnetic contribution, which strongly affects phase stability, $25)$ may be one of the reasons.

The martensitic transformation temperatures of ($Co_{90}$-$Al_{10}$)$_{100-x}$Fe$_{x}$ alloys are shown in Fig. 6, where they almost linearly decrease with increasing Fe content. Figure 7 shows the volume fraction of the parent phase $V_p$ (i.e., $1 - V_m$) against $M_s - T_q$ for Co-Al binary alloys and Co-Al-Fe ternary alloys with various $M_s$ temperatures, where $T_q$ is the lowest temperature reached during quenching and is fixed at $10^\circ C$ in this study. The $V_p$ decreases with increasing $M_s$ temperature in Co-Al-Fe alloys. Other Co-Al-X alloys with alloying elements in Type A and Type B showed the same tendency, although the martensitic transformation temperatures were not detected in all the specimens by DSC, probably due to the low fraction of transformed martensite. However, the $V_p$ decreased by increasing Al content leading to a decrease in $M_s - T_q$ in Co-Al binary alloys, a result...
opposite that of other alloys. Further investigations are required to clarify this unusual behavior. The relationship between $V_m$ and temperature has been discussed mainly in steel, and the following formula has been derived:

$$
\frac{1}{C_{0}} V_m = \exp \left( \frac{\Delta G}{kT} \right) \left( \frac{M_s}{C_{0} T_q} \right) \quad (1)
$$

where $V$ is the average volume of the newly formed martensite plate, $\varphi$ is the proportionality constant and $\Delta G$ is the difference in free energy per unit volume between the parent phase and the martensite phase. It has also been proposed that the relationship is empirically expressed in the following form:

$$
\frac{1}{C_{0}} V_m = \exp \left( \alpha (M_s - T_q) \right) \quad (2)
$$

where $\alpha$ is a proportionality constant depending on the alloy system. This equation means that the $V_m$ in an alloy is dependent only on the temperature interval ($M_s - T_q$), while comparing eq. (2) with eq. (1), $\alpha$ corresponds to $\bar{V}\varphi(\Delta G/dT)$ and $\Delta G/dT$ is a function of $M_s$ temperature.

$$
\alpha = -0.039
$$

Hence, $\alpha$ is not a constant in a strict sense, but an almost linear relationship is obtained between $\ln V_m$ and $M_s - T_q$ in Fig. 7. In the Co-Al-Fe alloys, $\alpha$ is determined to be $-0.0309$, larger than $\alpha = -0.011^{21}$ in the Fe-C alloys and $\alpha = -0.00526$ in the Co-Ni alloys, which means that a higher percentage of martensite can transform for the same degree of undercooling below the $M_s$ temperature in the Co-Al-Fe alloys.

### 3.3 Ductility

Figures 8(a) and (b) show the ductility evaluated by cold-rolling in the ($Co_{90}Al_{10})_{100-y}Fe_y (X = Si, Ti, V, Cr, Mn, Fe, Ni, Nb, Mo, Ta or W)$ ternary alloys. The ductility declines with the addition of Cr and Si, while it is improved by the addition of other elements. This result is obviously related to the fact that the hcp structure has a high work-hardening rate and the high volume fraction of the $\epsilon$ martensite phase, as shown in Fig. 3, causes the deterioration of ductility in the Co-Al-Cr and Co-Al-Si alloys. The ductility in specimens with other alloying elements is enhanced due to the increase in the stability of the $\gamma$ phase. It was found that the addition of

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**Fig. 6** Martensitic transformation temperatures of ($Co_{90}Al_{10})_{100-y}Fe_y$ alloys.

**Fig. 7** Relationship between volume fraction of the $\gamma$ parent phase at $10^\circ{C}$ and $M_s - T_q$ in Co-Al and ($Co_{90}Al_{10})_{100-y}Fe_y$ alloys.

**Fig. 8** Ductility of Co-Al-X alloys evaluated by cold-rolling.
Fe, Ti, W, Nb or W is particularly effective to improve the ductility of Co-based alloys unless no precipitates are formed.

3.4 Shape memory properties

Shown in Figs. 9(a) and (b) are the SM effect in \((\text{Co}_{90}\text{Al}_{10})_{100-x}X_x\) (X = Si, Ti, V, Cr, Mn, Fe, Ni, Nb, Mo, Ta or W) alloys. \(\text{Co}_{90}\text{Al}_{10}\) binary alloys show the highest shape recovery, and the SM effect decreased with the addition of the third elements. Figure 10 shows the SM effect as a function of \(V_m\), which indicates that the specimens with the \(/C13 /C13\) single-phase state show shape recovery at a rate of less than 20% suggesting that a high volume fraction of the "martensite phase tends to result in a good SM effect, although the volume fraction is not the only factor involved in the SM effect, the martensitic transformation temperatures also being considered to affect it. The existence of a high fraction of the martensite in Co-Al binary alloys with low \(M_s\) temperatures is probably one of the reasons for the excellent SM effect.

It is concluded that an alloying element cannot improve the SM effect in the Co-Al alloys. Nevertheless, it is effective to control the martensitic transformation temperatures and to improve the ductility.

4. Conclusions

The effect of Si, Ti, V, Cr, Mn, Fe, Ni, Nb, Mo, Ta and W alloying elements on \(\gamma/\varepsilon\) martensitic transformation, ductility and SM properties was investigated in Co-Al-X ternary alloys.

(1) No noticeable differences in the microstructures were observed in the range of X content in this study.

(2) The volume fraction of the \(\varepsilon\) martensite in Co-Al-X alloys greatly decreased by the addition of Ti, V, Fe, Nb, Mo, Ta and W, gradually decreased by the addition of Mn and Ni, and slightly decreased by the addition of Cr and Si.

(3) The volume fraction of the parent phase, \(V_p\), decreased with increasing \(M_s - T_q\), and the relationship between \(V_p\) and \(M_s - T_q\) was almost linear, the proportionality constant \(\alpha\) being determined to be \(-0.039\) in Co-Al-Fe alloys, while the tendency in Co-Al binary alloys was opposite that in Co-Al-Fe alloys.

(4) The ductility was improved by the addition of alloying...
elements, such addition increasing the stability of the γ phase.

(5) It was suggested that a high volume fraction of the ε martensite phase tends to cause a good SM effect and a high fraction of the martensite phase is probably one of the reasons for excellent SM properties in Co-Al binary alloys.

Acknowledgement

The support from CREST, Japan Science and Technology Agency, is acknowledged.

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