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FCC/HCP Martensitic Transformation and High-Temperature Shape Memory Properties in Co-Si Alloys

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The microstructure, martensitic transformation temperatures and shape memory properties of Co-Si binary alloys were investigated by means of optical and transmission electron microscopy, differential scanning calorimetry and a shape memory test. The ε martensite phase with a hexagonal close-packed (hcp) structure was observed to coexist with the face-centered cubic (fcc) γ parent phase at room temperature. The γ/ε martensitic transformation temperatures linearly increased with Si content up to 4 mol%, but the trend flattened beyond 4 mol%Si while the transformation hysteresis and intervals monotonously increased. The Co-Si alloys exhibited shape recovery at high temperatures up to 900°C and a relatively high thermal stability up to 600°C. These results suggest that Co-Si alloy system has a possibility for high-temperature shape memory alloys. [doi:10.2320/matertrans.47.2377]

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1. Introduction

Since AuCd alloys were revealed to exhibit a shape memory phenomenon,[1,2] many sorts of shape memory alloys (SMAs) have been reported.[3] Although TiNi alloys, which are located as the most important alloy system for practical applications, have been utilized for pipe couplings, sensors, medical uses, *etc.*, TiNi-based commercial SMAs are limited for the use at temperatures below 100°C. High-temperature shape memory alloys (HTSMAs), which can operate at temperatures higher than 100°C, are currently receiving much attention due to their potential applications in the automotive industry and other fields. To date, many HTSMAs, such as TiNi(Hf, Zr, Pd, Pt), NiAl, NiMnGa, Zr-based, NbRu and Co-based alloys, have been reported.[4]

It is known that the γ phase with a face-centered cubic (fcc) structure at high temperatures transforms to the ε martensite phase with a hexagonal close-packed (hcp) structure during cooling by the movement of $1/6\langle 112\rangle$ partial dislocations on every alternate $\{111\}$ planes at about 400°C in pure Co, and several reports on the shape memory effect (SME) in Co, Co-Ni and other Co alloys have been published.[5–8] Recently, the present authors have found that ferromagnetic Co-Al alloys exhibit a good SME at temperatures higher than 200°C associated with the γ/ε martensitic transformation,[9,10] which means that Co-based alloys are promising candidates for HTSMAs. Although an addition of Al is effective to enhance the SME in Co alloys,[9] the martensitic transformation temperatures decrease by the addition of Al. On the other hand, Si addition is a suitable choice for development of HTSMAs operating at higher temperatures because the γ/ε transformation temperatures increase with Si content in the Co-Si alloys.[11] However, the shape memory properties in Co-Si alloys have not been reported. In this study, the martensitic transformation and the shape memory properties of Co-Si alloys were investigated.

2. Experimental

Pure Co and Co-Si alloys with nominal compositions of $Co_{96}Si_4$, $Co_{92}Si_8$ and $Co_{86}Si_{14}$ were prepared by an induction furnace under an argon atmosphere from pure cobalt (99.9%) and silicon (99.999%). Sheet specimens were obtained by hot-rolling at 1200°C and subsequent cold-rolling. Pieces of the specimens were solution treated at 1200°C for 1 hour in a vacuum followed by quenching in water. The microstructure was observed using optical microscopy (OM) and transmission electron microscopy (TEM). A thin foil specimen for TEM observations was prepared by jet polishing in a solution of 20% perchloric acid and 80% ethanol.

The martensitic transformation temperatures (M_s, M_f, A_s and A_f) were measured by differential scanning calorimetry (DSC) at heating and cooling rates of 10°C/min, where the transformation temperatures were defined as the point of intersection of the base line and the tangent line with the maximum or minimum inclination of transformation peaks in the DSC curves.

The SME was evaluated by bending a rectangular specimen of $0.24 \times 4 \times 50\,mm^3$ a round shape to a surface strain of 1.2% at room temperature. The reason why the applied strain is relatively small is the limited ability of shape recovery in Co and Co-Si alloys. The shape with a surface strain, ε_c, after unloading was recorded. The specimen was then heated by putting it into a furnace at a constant temperature of 1000°C in the air, and keeping it for about 5 seconds. The shape was recorded immediately after taking out the specimen from the furnace and the residual surface strain, ε_h, was evaluated from the curvature. It was confirmed by comparing a shape recovery in the air with that in a vacuum that it is hardly influenced by thin scale formed

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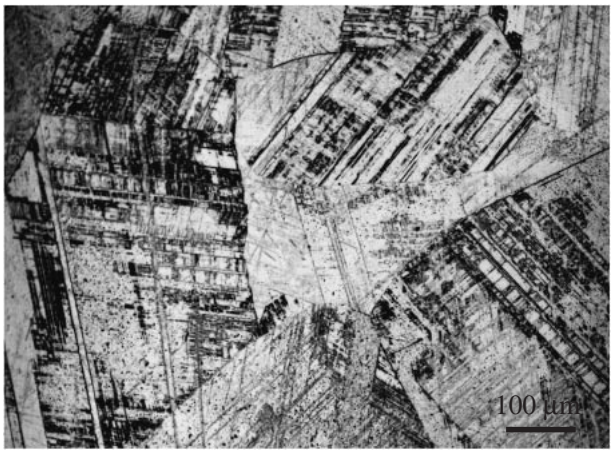

Fig. 1 Optical micrograph of $Co_{92}Si_8$ quenched from 1200°C.

during heating in the air in this SME test. The shape change due to gravity at the high temperature was not detected in other Co-based alloy with the same dimension and no SME ability; therefore, the effect is though to be negligible. The surface strain is defined as $\varepsilon = t/2r \times 100$ (%), where t is the thickness of a specimen and r is the radius of curvature. The shape recovery rate, R_{SME}, and recovery strain, ε_{SME}, were evaluated by $R_{SME} = (\varepsilon_c - \varepsilon_h)/\ \varepsilon_c \times 100$ (%) and $\varepsilon_{SME} = \varepsilon_c - \varepsilon_h$, respectively.

3. Results and Discussion

3.1 Martensitic Transformation and Microstructure

An optical micrograph taken from the $Co_{92}Si_8$ alloy at room temperature is shown in Fig. 1, where the typical microstructure of the ε martensite is observed. Figure 2 shows (a) a bright field image (BFI) taken from the same $Co_{92}Si_8$ alloy and selected area diffraction patterns (SADPs) from (b) the γ parent and (c) the ε martensite phases, where the incident beam directions are $[0\bar{1}1]_\gamma$ and $[\bar{1}2\bar{1}0]_\varepsilon$, respectively. The ε martensite phase with an hcp structure has a high density of stacking faults due to lattice invariant deformation accompanied by a streak in the c-axis direction in the corresponding SADP of Fig. 2(c). Although the martensitic transformation finish temperature M_f detected by DSC was 523°C in the $Co_{92}Si_8$ alloy as mentioned later, the γ parent phase coexists even at room temperature. The residual parent phase has been reported in many alloys, such as Co and Fe alloys, undergoing a non-thermoelastic martensitic transformation.[7,9,10,12,13] The correlation between the fraction of the γ phase and the martensitic transformation temperature in Co alloys will be presented elsewhere. Figures 2(b) and (c) indicate that the crystal orientation relationship between the γ and the ε phases is of the Shoji-Nishiyama relationship, that is, $(111)_\gamma\ //\ (0001)_\varepsilon$ and $[1\bar{1}0]_\gamma\ //\ [11\bar{2}0]_\varepsilon$. These microstructural features are similar to those observed in Co-Al SMAs.[9,10] Although these γ and martensitic ε phases are metastable and the α (Co_2Si) and ε phases are stable at low temperatures,[11] no precipitates were observed in any as-quenched specimens.

The martensitic transformation temperatures of $Co_{100-x}Si_x$ (x = 0–8) alloys are plotted in Fig. 3 together with some

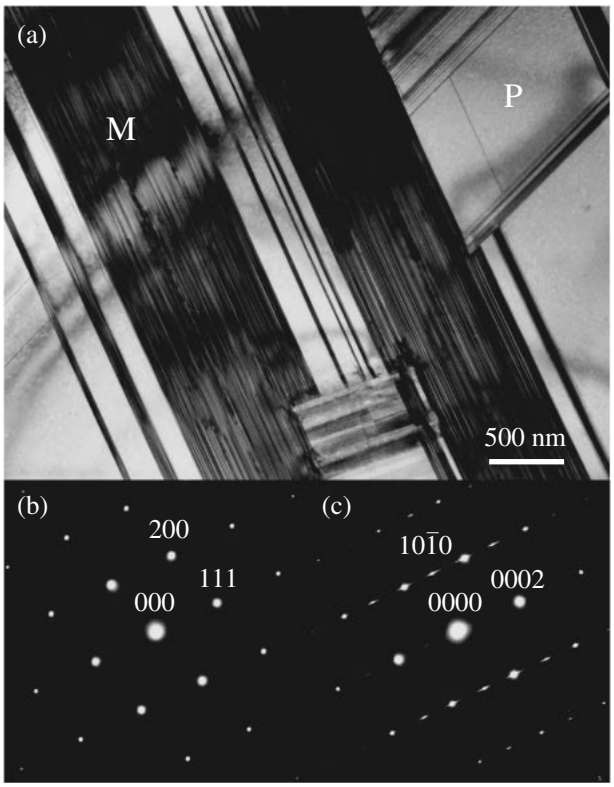

Fig. 2 (a) Bright field image of $Co_{92}Si_8$, (b) selected area diffraction patterns from γ phase and (c) ε phase. Incident beam directions are $[0\bar{1}1]_\gamma$ in (b) and $[\bar{1}2\bar{1}0]_\varepsilon$ in (c).

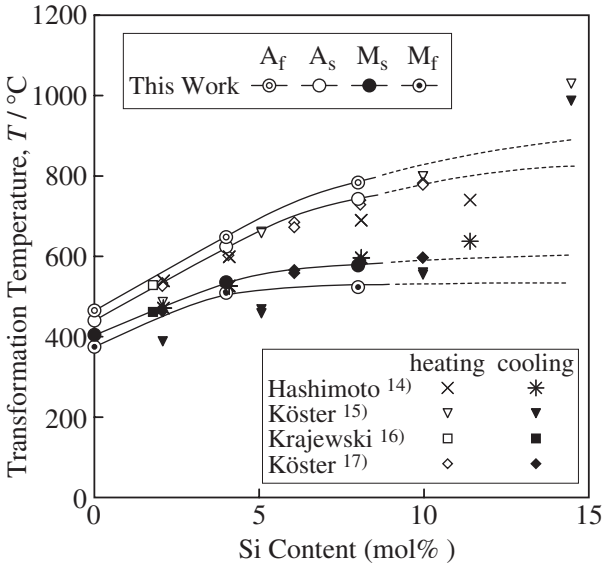

Fig. 3 Martensitic transformation temperatures of Co and Co-Si alloys, including the previous data.[14–17]

previous experimental data.[14–17] The present study indicates that the martensitic transformation temperatures linearly increase with Si content up to 4 mol% and that the inclination gradually becomes smaller in the range of Si over 4 mol%. Increasing with Si content, the transformation temperature hysteresis is over 100°C in the high Si region over 4 mol% in which the transformation intervals are also large. In the

$Co_{86}Si_{14}$ alloy, some diffusional transformations such as decomposition of the γ phase occurred before the martensitic and reverse transformations during cooling and heating in the DSC examination, which was not suppressed even at higher heating and cooling rates of 40°C/min. Therefore, the martensitic transformation temperatures could not be determined. However, it can be deduced that the reverse martensitic transformation temperatures are located at temperatures between 800 and 900°C because the $Co_{86}Si_{14}$ sheet specimen showed a shape recovery due to the SME in the temperature range from 800 to 900°C during rapid heating. It is known that the martensitic transformation temperatures depend on experimental conditions, such as purity, grain size and heating and cooling rates. The transformation temperatures determined from some specimens in the same condition showed only small scattering within 15°C, and no significant correlation between the scattering of transformation temperatures and the Si content was found. Comparing the data taken from the present study with those of previous reports, the results in this study are in good agreement with the report by Köster,[17] and the tendency is the same as that in reports by Hashimoto[14] and Köster,[15] except for the characteristic temperatures at about 1000°C in $Co_{85.5}Si_{14.5}$ alloy obtained by Köster,[15] which are probably due to equilibrating reactions.

3.2 Shape Memory Properties

The change of surface strain, ε_h, in the $Co_{92}Si_8$ alloy in relation to the elevated temperatures is shown in Fig. 4, where a surface strain, ε_c, of 0.84% was initially introduced by bending at room temperature. Here, appearances of the specimen bent at room temperature and of that heated up to 1000°C after bending followed by cooling to room temperature are also shown in Fig. 4. Slightly decreasing by heating up to 700°C, the surface strain drastically changes at around 800°C, which corresponds to the reverse martensitic transformation temperatures as shown in Table 1 and Fig. 3. The reason why the strain changes at temperatures below the martensitic reverse transformation temperatures is not yet clear, but this result means that an SME occurs at a very high temperature in the Co-Si alloy.

The initial surface strain, ε_{SME}, the surface strain induced by the shape recovery strain, ε_{SME}, and the recovery rate, R_{SME}, by heating to 1000°C are plotted as a function of Si content in Fig. 5. It was found that the shape memory properties are hardly enhanced by the addition of Si and that the shape recovery strain is about 0.3% with a recovery rate of around 40% in Co and in all Co-Si alloys. It should be emphasized that although the shape memory property of Co-Si alloys is inferior to that of the Co-Al alloys,[9,10] the shape recovery temperatures are much higher than those of the other Co-based SMAs. From Fig. 3, the shape recovery temperature can be expected to increase with increasing Si content, whereas the thermal stability decreases. As men-

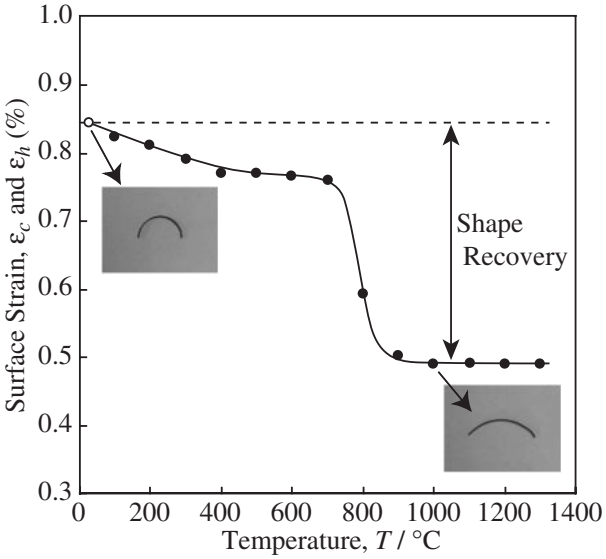

Fig. 4 Shape change of $Co_{92}Si_8$ sheet specimen by heating, where a surface strain, ε_c, of 0.84% was initially introduced at room temperature. The surface strain, ε_h, was measured at each heating cycle, the heating temperature being increased at intervals of 100°C from 100°C to 1300°C.

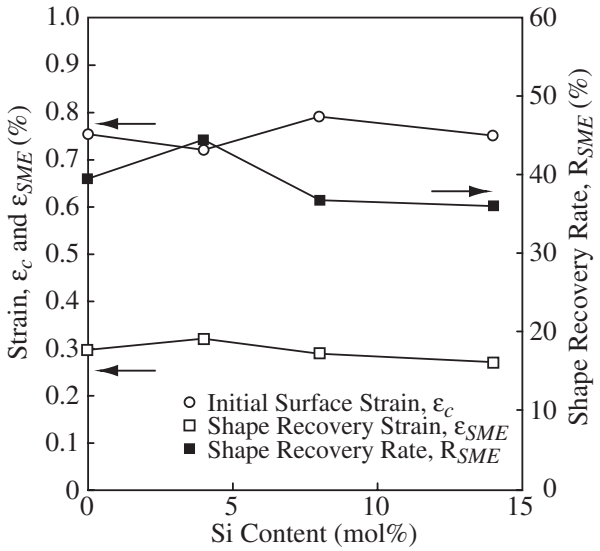

Fig. 5 Initial surface strain, ε_c, shape recovery strain, ε_{SME}, and recovery rate, R_{SME}, of Co and Co-Si alloys by heating to 1000°C as a function of Si content.

Table 1 Martensitic transformation temperatures, hystereses and intervals of Co and Co-Si alloys.

Si (mol%)	Martensitic Trans. Temp.				Hysteresis		Interval	
	M_s	M_f	A_s	A_f	A_f-M_s	A_s-M_f	M_s-M_f	A_f-A_s
0	404	372	439	461	57	67	32	22
4	536	508	624	649	113	116	28	25
8	578	523	743	785	207	220	55	42

tioned in the previous section, the $Co_{86}Si_{14}$ alloy exhibits shape recovery at temperatures between 800 and 900°C, but decomposition can easily occur at temperatures over 600°C. Considering their thermal stability, the Co-Si alloys with lower Si content can be used as high-temperature SMAs operating at temperatures up to 600°C.

4. Summary

The microstructures of Co-Si alloys were examined using OM and TEM, and the typical ε martensite in the γ parent phase was observed at room temperature. The γ/ε martensitic transformation temperatures were determined, and found to be in good agreement with those in the previous reports. The transformation temperatures increased with increasing Si content up to 4 mol% and the slope became smaller and the transformation hysteresis and intervals were larger in the range of Si content over 4 mol%. The Co-Si alloys exhibited a shape recovery at an elevated temperature corresponding to the reverse martensitic transformation temperature. The addition of Si hardly enhanced the shape memory properties, and a shape strain of 0.3% was obtained by heating to 1000°C with a recovery rate of 40%, which is comparable to values in pure Co. However, the shape recovery temperatures of Co-Si alloys were found to be higher than those of other Co-base alloys and, therefore, the Co-Si alloys have a possibility for HTSMAs operating at temperatures up to 600°C.

Acknowledgment

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