Improvement of Oxidation Resistance of an Fe–Mn–Si–Cr Shape Memory Alloy by Annealing under Vacuum

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Electron microprobe microanalysis (EPMA), secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) were used for charactering the surface composition of an Fe–Mn–Si–Cr shape memory alloy. The effect of annealing under vacuum on the surface composition of the alloy was studied. It was found that the amount of manganese decreased, while the amount of chromium increased in a surface layer by annealing. The thickness of the surface layer is of the order of ten micrometers, which is comparable to that obtained by conventional plating or coating. As a result, the surface of the Fe–Mn–Si shape memory alloy annealed under a vacuum exhibited better oxidation resistant than that of the as-lapped alloy.

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1. Introduction

Fe-Mn-Si austenitic alloys exhibit shape memory effect, of which originates from the reverse transformation of stressinduced martensite.¹⁻³⁾ The austenitic alloys do not contain precious elements, which is a significant advantage in industrial application. However, the Fe-Mn-Si shape memory alloys are easily corroded under humid atmospheric conditions. Therefore, the chemical composition of the allovs is modified by the addition of a small percentage of chromium in order to improve their oxidation and corrosion resistance.4) The effect of chromium addition on the oxidation and corrosion resistance should be fully exploited for improving surface properties since the chemical composition in the surface layer may be modified by further treatment. For example, chromium is enriched to the surface of iron-chromium alloys by annealing under ultra high vacuum and the chromium-enriched layer is known to suppress the native oxide layer formed at room temperature.5,6)

These observations prompt us to carry out a feasible study on the modification of the surface composition of an Fe–Mn– Si–Cr shape memory alloy. In this study, electron microprobe microanalysis (EPMA), secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) were used for charactering the surface composition of the Fe–Mn– Si–Cr shape memory alloy. The effect of annealing under vacuum on the surface composition of the alloy was investigated. Moreover, the surface layers of the alloys, which were initially as-lapped and subsequently annealed under vacuum, formed by oxidation in air were analyzed.

2. Experimental

A sheet of an Fe–28 mass%Mn–6 mass%Si–5 mass%Cr (Fe–27 at%Mn–11 at%Si–5 at%Cr) alloy, which is a typical

shape memory alloy,⁴⁾ was cut into pieces of approximate $5 \text{ mm} \times 10 \text{ mm}$. These were lapped to a mirror surface and will be referred to as LA hereafter. Some of the samples were subsequently annealed at 1173 K for 3600 s under vacuum of 10^{-2} Pa, and the samples are called AN.

In order to evaluate the oxidation resistance of LA and AN samples, they were oxidized in air at 673 and 873 K. These temperatures lie in a temperature range in which the shape recovery of the present shape memory alloy under consideration occurs.⁴⁾ The surface layers of the samples were characterized by EPMA, SIMS and XPS. The EPMA apparatus was used for analyzing the average chemical composition in the bulk and surface layer. The semiquantitative analysis for a bulk and surface layer of the alloy was carried out in order to compare their chemical composition. SIMS was used for analyzing the elemental depth profile in the surface layer, as oxygen penetrates and alloying elements are redistributed in the surface layer of the alloy. SIMS measurements were carried out using an apparatus with quadrupole-type mass spectrometer.7) An incident beam of 5.0 keV Cs⁺ ions was irradiated onto a sample, and positive secondary ions were counted. XPS measurement was carried out for analyzing the chemical composition of a few nanometers of the surface layer. Although the chemical composition obtained by XPS is not necessarily a representative value for the surface layer, it is useful in the discussion of the reaction process at the surface.⁶⁾ The XPS spectra were taken by monochromated incident Al-K α .⁷⁾ In addition, the structure and crystallographic orientation of the surface layer was analyzed by electron backscattering pattern (EBSP). The results were shown in the orientation image (OIM) of face centered cubic (fcc) or body centered cubic (bcc) phases.

3. Results and Discussion

3.1 Surface layer formed by annealing under vacuum

Figures 1(a), (b), (c) and (d) show a secondary electron image, Fe K image, Mn K image and Cr K image of a cross-

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Fig. 1 (a) Secondary electron image, (b) Fe K image, (c) Mn K image and (d) Cr image of a cross-section of the present Fe–Mn–Si–Cr alloy annealed under vacuum.

section of sample AN, respectively. A relative scale of the amount of elements is also given in Fig. 1. A surface layer of about $20 \,\mu$ m thickness was formed by annealing. This layer is possibly formed by the evaporation of manganese from the surface of the alloy due to its high vapor pressure.⁸⁾ This may result in an increase in the amounts of chromium and iron in the surface layer.

Since compositional change in an alloy may induce a phase transformation, the constituent phase of the surface layer of sample AN was examined by the OIM. The sample AN was electrochemically polished close to the interface between the surface layer and the substrate. Figure 2 show the OIM images from the top-view, as illustrated in Fig. 2(c). The black contrast in the images corresponds to an area, of which any structure could not be assigned in bcc or fcc image. The results show that a main phase of the surface layer is bcc, while the alloy substrate is fcc or austenite. This observation is consistent with the fact that manganese, which is one of the elements stabilizing austenite, is depleted on the surface layer. As a result, the amount of chromium, which is one of the elements stabilizing ferrite, increases in the surface layer.

3.2 Oxidation of surface layer by annealing in air

Figures 3 show diagrams of the chemical composition of samples LA and AN, which were oxidized at 673 and 873 K in air, by EPMA. The compositional information is obtained from a surface layer of approximately one µm thickness. The chemical composition of a surface layer of sample LA is the same as the bulk composition since its surface of sample LA is mechanically polished and the native oxide layer is very thin. On the other hand, the composition of sample AN annealed under vacuum by EPMA differs from that of sample LA: the amount of manganese decreases, while the amounts of chromium and iron increase. These results are consistent with the observation made shown in Fig. 1.

The oxidation in samples at 673 or 873 K depends on the chemical compositions of a surface layer, as shown in Fig. 3. The amount of oxygen in sample AN, as detected by EPMA,



Fig. 2 OIM images of (a) bcc and (b) fcc phases in a surface layer of AN, which are shown as orientations from the top-view, as shown in (c). The black contrast corresponds to an area, to which each phase cannot be assigned.



Fig. 3 Chemical compositions of samples LA and AN, and subsequently oxidized samples at 673 and 873 K in air (ox 673 K or ox 873 K), determined by EPMA.

is lower than that for sample LA, indicating that the surface of sample AN possesses good oxidation resistance. This can be attributed to the increase in the amount of chromium in the surface layer during annealing since the amount of chromium in iron-based alloys is directly related to their oxidation resistance.^{9,10)} The relative amounts of iron, manganese, silicon and chromium are marginally changed by oxidation, and this is likely to result from the elemental redistribution during oxidation.

Figures 4(a) and (b) show SIMS depth profiles for the samples, which were as-lapped (LA) and those that were as-lapped and subsequently annealed under vacuum (AN),



Fig. 4 SIMS depth profiles for samples that were as-lapped (LA) and those that were as-lapped and subsequently annealed under a vacuum (AN).

respectively. As the sample surface is covered by a native oxide layer, which is formed due to exposure to air, the oxygen-relevant ion, CsO^+ , was detected in the depth profiles. In the profiles, a significant change in the intensity of manganese-relevant ion, $CsMn^+$, was observed, which was found to decrease by annealing, although the quantitative amounts of elements are hardly discussed in SIMS profiles. This result agrees with the data obtained using EPMA, as shown in Figs. 1 and 3.

The SIMS depth profiles for samples LA and AN oxidized at 873 K in air are shown in Figs. 5(a) and (b), respectively. Depth profiling up to approximately 0.4 micrometers were measured. The oxide layer is formed on the outer side on the surface layer by oxidation, is thinner than that in the case of sample AN as compared to that in sample LA. This result corresponds to the EPMA results shown in Fig. 3, which include information pertaining to the layered structure comprising the oxide layer and the surface layer.

In order to obtain information on the very thin layer formed on the oxide layer, XPS measurements were carried out. Figure 6 summarizes the chemical composition of LA and AN, which were as-lapped and subsequently oxidized in air at 673 and 873 K, measured using XPS. As XPS data usually provide the chemical composition of elements in the surface layer of a few nanometers, the large amount of oxygen detected using XPS originates from the native oxide layer with a small amount of water. The chemical compo-



Fig. 5 SIMS depth profiles for samples LA and AN oxidized at 873 K in air.



Fig. 6 Chemical compositions of samples LA and AN, and subsequently oxidized samples at 673 and 873 K in air (ox 673 K or ox 873 K), determined by XPS.

sition of metallic elements in sample AN is almost the same as the bulk composition, although the native oxide covers the sample surface. On the other hand, the chemical composition of manganese and silicon on the surface of sample AN annealed under vacuum is higher than that for sample LA. This phenomena are considered to result from the characteristic behaviors of silicon and manganese occurring on the iron surface,^{10,11} although they may appear to be inconsistent with the results as shown in Fig. 2, which is concerned with the bulk properties.

3.3 Formation process surface layer and its oxidation resistance

In order to consider the formation mechanism of the surface layer with manganese depletion, the rate-controlled process of surface layer formation should be discussed on the basis of diffusion processes. At 1173 K, at which the surface layer was formed in this work, the diffusion coefficients D of manganese in ferritic iron and austenitic iron are estimated about 5.4×10^{-15} and 3.4×10^{-17} m²/s, respectively.¹²⁾ The diffusion distances $2\sqrt{Dt}$ after annealing for 3600 s are estimated to be about 0.7 and 10 µm, respectively. The latter diffusion distance is comparable to the thickness of the present surface layer, although diffusion coefficients of manganese in these phases were simply estimated based on the temperature dependence of the diffusion coefficients of manganese at high temperatures. Thus, the rate-controlled process is primary dominated by the diffusion of manganese in ferritic iron rather than austenitic iron.

Although the Fe-Mn-Si-Cr alloys in this work were oxidized below 873 K, main alloying elements were redistributed in the surface layer, as shown in Figs. 4, 5 and 6. Figure 7 illustrates the schematics of cross-sectional layered structure of sample LA and samples AN and the corresponding oxidized samples. It should be noted that the chemical composition in the surface layer of approximately 20 µm in thickness, which was formed by annealing under vacuum, improved the oxidation resistance of the alloy. It was also observed that manganese was enriched on the surface side during oxidation; however, a role of the manganese enrichment in the oxide layer should be further investigated using structural analysis.¹⁰⁾ Thus, precise surface analytical results provide information on the control of the surface properties and oxidation processes, which are strongly related to the chemical composition of the surface layers.



Fig. 7 Schematics of the cross-sectional layered structure of (a) sample aslapped and (b) sample annealed under vacuum, and oxidized sample (c) after being as-lapped and (d) after being annealed under vacuum.

4. Concluding Remarks

Electron microprobe analysis (EPMA), secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) were used for charactering the surface composition of an Fe–Mn–Si–Cr shape memory alloy. The oxidized layer formed on the surfaces of samples as-lapped and those annealed under vacuum were analyzed. The main results obtained in this study are as follows:

- (1) The amount of manganese decreases while the amount of chromium increases on a surface side of the alloy by annealing under vacuum, which leading to the formation of a characteristic surface layer.
- (2) The surface layer consists primary of ferritic phase due to the depletion of manganese. The formation of the surface layer is likely to be controlled by the diffusion of manganese in the ferritic phase.
- (3) As a result of an increase in the amount of chromium as well as a decrease in that of manganese in the surface layer, the oxidation resistance of the alloy was enhanced by annealing under vacuum. These results indicate that the compositional control of a surface layer by annealing is effective to improve the surface properties of steels.

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REFERENCES

- A. Sato, E. Chishima, K. Soma and T. Mori: Acta Metall. 30 (1982) 1177–1183.
- 2) A. Sato and T. Mori: Mater. Sci. Eng. A 146 (1991) 197–204.
- A. Sato, Y. Yamaji and T. Mori: Acta Metall. 34 (1986) 287–294.
 H. Ohtsuka, H. Yamada, T. Maruyama, H. Tanahashi, S. Matsuda and
- M. Murakami: ISIJ Inter. **30** (1990) 674–679.
- S. Suzuki, T. Kosaka, H. Inoue, M. Isshiki and Y. Waseda: Appl. Surf. Sci. 103 (1996) 495–502.
- S. Suzuki: Surfaces and Interfaces, Purification Processes and Characterization of Ultra High-Purity Metals, Ed. by Y. Waseda and M. Isshiki, (Springer-Verlag, Heidelberg, 2002) pp. 277–307.
- S. Suzuki, K. Yanagihara, S. Yamazaki and Y. Waseda: Surf. Interface Anal. 35 (2003) 276–281.
- Metal Data-book, Ed. by Japan Institute Metals, (Maruzen, Tokyo, 2004) p. 17.
- P. Kofstad: *High Temperature Corrosion*, (Elsevier Applied Science, London, 1988) pp. 389–408.
- 10) S. Suzuki and K. Suzuki: Surf. Interface Anal. 17 (1991) 551-555.
- S. Suzuki, T. Kosaka, M. Saito, Y. Waseda, E. Matsubara and M. Oku: Scripta Mater. 36 (1997) 841–845.
- Metal Data-book, Ed. by Japan Institute Metals, (Maruzen, Tokyo, 2004) pp. 20–25.