Structure of the Passive Film formed on Fe–Mn–Si–Cr–Ni Shape Memory Alloy after Wet and Dry Corrosion Test

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The corrosion resistance of an Fe–Mn–Si–Cr–Ni shape memory (16 Mn) alloy was estimated by the wet and dry corrosion tests, and the structure of the passive film formed on the alloy was examined by primary EELS (Electron Energy Loss Spectroscopy) using TEM (Transmission Electron Microscopy) analysis. The electrochemical behavior of 16 Mn alloy was investigated by EIS (Electrochemical Impedance Spectroscopy). 16 Mn alloy showed much higher corrosion resistance than the carbon steel (SM) in wet and dry corrosion tests. In EIS measurement following corrosion test, 16 Mn alloy had much larger value of corrosion resistance (Z_{ImHz}) by forming the passive film as compared to SM. In AES (Auger Electron Spectroscopy) and XPS (X-ray Photoelectron Spectroscopy) analysis, the passive film of 16 Mn alloy was shown to contain Fe, Mn, Cr, Si and Ni. From TEM-EELS, the passive film was found to consist of 2 layers of a Cr–Si-rich in inner and an Mn-rich outer layer of Fe oxide. It was found that 16 Mn alloy could maintain the passive film which composed of effective elements in the wet and dry environment. [doi:10.2320/matertrans.M2014029]

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1. Introduction

The shape memory effect has been found in Au–Cd, Ti–Ni, Cu–Zn–Al and several other alloy systems.^{1–3)} Among them, Iron base alloys have attentions because of reduced material cost. Recently, an Fe–Mn–Si base shape memory alloy has been reported by A. Sato *et al.*, and showed the excellent mechanical property.^{4,5)} However, there are few papers which deal with corrosion resistance of this type of the iron-base shape memory alloy.⁶⁾ H. Fukai *et al.* investigated the oxidation resistance of an Fe–Mn–Si–Cr base shape memory alloy using primarily EPMA (Electron Probe Micro Analyzer) and XPS, and found high effect of Cr on the oxidation resistance.⁷⁾

In order to identify the atmospheric corrosion resistance of this alloy, it is important to conduct the wet and dry corrosion test containing chloride solution.⁸⁾ Generally, this type of alloy makes the passive film in the atmospheric environment. As the passive film was very thin ($\sim$ nm), nano structure of the film was investigated by using TEM in this study. The passive film formed in the wet and dry test was cut using FIB (Focused Ion Beam), and the chemical state of each element was investigated by EELS.⁹⁾ EIS was employed for the samples following the wet and dry test to investigate the electrochemical behavior of an Fe–Mn–Si–Cr base shape memory alloy.⁸⁾

2. Experimental Procedure

2.1 Wet and dry cyclic corrosion test and samples

The corrosion test consisted of (1) wetting sample surfaces with 0.4 L of a 0.5 mass% NaCl solution in 1 m², and (2) drying the sample in a chamber maintained at 25 degree C, 60% RH for 12 h.⁸⁾ Immediately before dropping a solution, the sample was washed in distilled water and dried to prevent progressive salt accumulation. The sample material (16 Mn alloy) was an Fe-16%Mn-12%Cr-5%Si-5%Ni (mass%) shape memory alloy. As a basis for comparison, the carbon steel (SM) was used in this study.

2.2 Physical analysis of the passive film on 16 Mn shape memory alloy

AES (Auger Electron Spectroscopy) and XPS (X-ray Photo electron Spectroscopy) were employed for the surface analysis of the sample of 16 Mn alloy. AES was performed with an accelerate voltage of 5 kV, a sample current of 0.1 μ A, an experimental region of $10 \times 10 \mu\text{m}$, a slope angle of 30 degree for the sample. In the case of the depth profile acquired by ASE, Argon spatter was used with a voltage of 2 kV, and a rate of 1 nm/min. XPS spectra were acquired by Al K α of 600 $\mu\text{m}\phi$ for the sample of 16 Mn alloy with a take-off angle of 30, 60 and 90 degrees.

In order to investigate the surface (passive) film at the nano level, TEM was employed for the sample of 16 Mn alloy. After the sample was mounted in resin, it was mirror-polished using emery paper and diamond paste. The passive film of 16 Mn alloy was cut by FIB (focused ion beam) from the above sample using SEM. A depth profile of elements for the passive film of the sample was examined by EDXS (Energy dispersing X-ray)-TEM analysis with a beam of 0.2 nm in the area of $5 \times 8 \text{ nm}$. The concentrations of Fe, Mn, Cr, Si and Ni in the passive film were measured for the 16 Mn alloy. EELS-TEM analysis was carried out to examine the chemical state of Fe, Mn, Cr, Si, Ni and Oxygen in the passive film of 16 Mn alloy.

2.3 EIS measurement

After the corrosion test, electrodes were fabricated out of 16 Mn alloy. Then, EIS measurements were performed in 0.1 M Na₂SO₄ solution using a 2-electrode system with a measurement frequency range of 20 kHz to 1.0 mHz and an applied voltage of 10 mV.

3. Results and Considerations

3.1 Corrosion resistance of 16 Mn shape memory alloy

The corrosion resistance of the Fe–Mn–Si–Cr–Ni shape memory alloy (16Mn alloy) was estimated by the wet and dry corrosion test for 4 weeks. Figure 1 shows the corrosion test results for 16Mn alloy and carbon steel (SM). The extent of

Fig. 1 Corrosion of 16Mn alloy and carbon steel (SM) after wet and dry corrosion test using 0.5 mass% NaCl.

Fig. 2 Impedance spectra of 16Mn alloys after corrosion test.

corrosion was determined by the weight loss of samples following removal of the rust. The amount of corrosion of SM increases with time, and it is not saturated at 4 weeks. On the other hand, the amount of corrosion of 16 Mn alloy is much less than that of SM after 4 weeks. In fact, 16Mn alloy could maintain a passive film on the surface after the corrosion test (like a stainless steel). Thus, 16 Mn alloy exhibits excellent corrosion resistance in the corrosion test as compared to SM.

Figure 2 shows the results of EIS of 16Mn alloy after 4 weeks of the corrosion test. The two resistance components and one capacitance can be recognised in the spectrum. The impedance at higher frequency region (Z_h) is considered to be related to the resistance of the solution. On the other hand, as the impedance at lower frequency region (R_l) is very high, it is considered to be the passive film resistance. Thus, the capacitance in the spectrum is considered the film capacitance. In this way, 16Mn alloy can maintain a passive film after a corrosion test, and shows high corrosion resistance.

Figure 3 displays the results of EIS of samples after the corrosion test, showing $Z_{1\text{mHz}}$ measured at 1 mHz in Fig. 2.

Fig. 3 Impedance values ($Z_{1\text{mHz}}$) at 1 mHz for 16Mn alloy and carbon steel (SM) after corrosion test.

Fig. 4 Depth profile of elements by AES analysis for the passive film on 16 Mn alloy.

The 16Mn alloy shows much higher value of $Z_{1\text{mHz}}$ than that of SM each week. Since $Z_{1\text{mHz}}$ is assumed to be the corrosion resistance, this fact shows that 16 Mn alloy has a higher resistance against corrosion than that of SM. In fact, because 16Mn alloy can maintain a passive film, a much higher resistance against corrosion (as compared to SM) is imparted to it.

3.2 Surface analysis of the passive film on 16 Mn shape memory alloy

In order to identify the corrosion-preventing mechanism of 16Mn alloy, the passive film was estimated by surface analysis. Figure 4 shows a depth profile of the elements in the passive film of 16Mn alloy obtained by AES after 4 weeks of the corrosion test. The concentrations (at%) of Fe, Mn, Si, Cr, Ni and Oxygen are shown. From the profile of Oxygen, the oxide film thickness is estimated almost 3 nm due to 5 min sputtering time. In this film, the concentrations of Cr and Ni are low at the surface, and they increase with the sputter time. Thus, Cr and Ni exist in inner of the film as much as that of the base metal. On the other hand, Mn and Si exist in the film, however, there is no special enrichment of these elements.

Figure 5 shows the results of XPS analysis of the elements in the passive film on 16 Mn alloy.¹⁰⁾ The XPS spectra were acquired for the sample of 16Mn alloy with the take-off angle of 30, 60 and 90 degree. In the case of Fe 2p, the peak at 712 and 707 eV are shown, which indicates that Fe is detected

Fig. 5 XPS analysis for the elements in the passive film on 16 Mn alloy; (1) Fe2p, (2) Mn2p, (3) Cr2p, (4) Si2p, (5) Ni2p.

both as the oxide and metal state. The peak of metal of Fe at 707 eV is higher at the angle of 90 degree, indicating that Fe is detected as a metal in the inner of the film. In other word, Fe oxide exists mainly at the surface of the film of the alloy. For Mn 2p, there is a sharp peak at 640 eV and a very small peak at 636 eV, which indicates that Mn exists mainly as an oxide state. This is almost the same as the case of Fe. For Cr 2p, there is a sharp peak at 577 eV and a very small peak at 573 eV, which indicates that Cr exists mainly as an oxide state. This is very similar to Si 2p, which has a sharp peak at 101 eV and a very small peak at 99 eV. On the other hand, in the case of Ni 2p, only the peak at 853 eV is sharp, which indicates that Ni exists primarily as the metal state. Moreover, this metallic peak of Ni at 853 eV is the highest at the angle of 90 degree, showing that Ni is enriched at the interface of the film and metal. From these results of XPS, it is found that the passive film contains Fe, Mn, Cr and Si, and that Ni is enriched at the interface of the film and metal. However, it is not possible to verify the chemical state of each element in the film in this study using the peak shift of XPS spectrum.

In order to investigate the nano structure of the passive film on 16Mn alloy, an FIB-TEM analysis was conducted after the corrosion test. Figure 6 shows the FIB-TEM result for the passive film on 16 Mn alloys. The spot numbers for the EDXS analysis are shown in the figure. From the contrast of the figure, it is possible to distinguish the position of the metal (1–5), the passive film (6–13) and the polymer (14). Thus the thickness of the passive film is estimated almost 2.5 nm from spot number 6 to 13.

Figure 7 shows TEM-EDXS profiles for the elements in the passive film of 16 Mn alloy. From the profile of Oxygen, the oxide film exists almost in spot number 7 to 14. In the

Fig. 6 FIB-TEM analysis for the passive film on 16 Mn alloy.

Fig. 7 TEM-EDXS results for the elements of the passive film of 16 Mn alloy. Spot No is according to the point in Fig. 6.

passive film, Mn is enriched at the surface of the passive film. On the other hand, Cr and Si are enriched in the inner of the film. Ni is strongly enriched at the interface of the metal and

Fig. 8 TEM-EELS spectra of oxygen and Mn for the passive film of 16 Mn alloy.

Fig. 9 TEM-EELS spectra of Cr and Si for the passive film of 16 Mn alloy.

film. In this way, it is found that each element is enriched at the particular position in the passive film of 16 Mn alloy. These results correlate well with those of XPS measurements in Fig. 5.

The chemical state in each element in the passive film was identified by using EELS, as shown in Figs. 8 to 10. The positions in EELS observation are the same as those in Fig. 6.

In Fig. 8, *O-k* EELS spectra in the passive film of 16 Mn alloy are shown in the spot of 7, 9, 11 and 13. Peaks at 532 and 538 eV are shown in the spot of 7, 9 and 11. However, there is no peak in the spot 2 and 6. Thus alloy is thought as the metal state in spot 2 and 6. The peak at 532 eV is a pre-peak in the shape of the spectrum of *O-k*, which expresses the existence of the Oxygen that combines with the transient metals.¹¹⁾ Thus, in spots 7, 9 and 11, the amount of Oxygen is thought high, which results in the passive film of alloy.

Mn-L EELS spectra are shown in Fig. 8, and can be placed into in two separate groups of (2, 6) and (7, 9, 11) in terms of spot number. Peaks are observed at 640 and 650 eV for spots 2 and 6. On the other hand, Peaks at 639 and 651 are shown for spots 7, 9 and 11. Thus, in the spectra of spots 7, 9 and 11, the top peak of Mn-L₃ are shifted 1 eV lower, and that of Mn-L₂ are shifted 1 eV higher. The shapes of Mn-L₃ are very

sharply reduced from the top peak to higher energy direction for spots 7, 9 and 11, which is different from spots 2 and 6. Moreover, the peak ratios of (Mn-L₂/Mn-L₃) are lower for spots 7, 9 and 11 as compared to spots 2 and 6. From these results, Mn is thought to exist in different state between spot (2, 6) and (7, 9, 11). In the case of spot 2, Mn exists in the metal state, per the result of Oxygen in Fig. 8. L. Laffont examined EELS spectra of MnO and Mn₂O₃.¹²⁾ The spectrum of spot 6 is similar to Mn₂O₃ and those of spots 7, 9 and 11 are similar to MnO in his work. Besides, the chemical shift of the peak and peak ratios are able to explain by his work. Thus, Mn is thought to exist as Mn³⁺ oxide state in inner film of spot 6, and Mn²⁺ oxide state in outer film of spots 7, 9 and 11.

Cr-L EELS spectra in the passive film of 16 Mn alloy are shown in Fig. 9. Cr-L EELS spectra are similarly classified into two groups of (2, 6) and (7, 9, 11) by spot number. The peaks at 576 and 585 eV are shown for spots 2 and 6. On the other hand, peaks at 578 and 586 are shown for spots 7, 9 and 11. Thus, for the spectra of spots 7, 9 and 11, the top peaks of Cr-L₃ are shifted 2 eV higher, and those of Cr-L₂ are shifted 1 eV higher. Moreover, the peak ratios of (Cr-L₂/Cr-L₃) are lower for spots 7, 9 and 11 as compared to spots 2 and 6. From these results, Cr exists in different states in two groups.

Fig. 10 TEM-EELS spectra of Ni and Fe for the passive film of 16 Mn alloy.

In spot 2, Cr exists as a metal state from the result of Oxygen in Fig. 8. T. L. Daulton *et al.* summarized EELS spectra of Chromium oxides including Cr(II) O and Cr_2O_3 .^{13,14} The spectrum of spot 6 is similar to Cr(II) O and those of spots 7, 9 and 11 are similar to Cr_2O_3 in their papers. Besides, the chemical shift of the peak and peak ratios are able to explain by his work. Thus, Cr is thought to exist as Cr^{2+} oxide state in inner film of spot 6, and Cr^{3+} oxide state in outer film of spot 7, 9 and 11.

Si-L EELS spectra are shown in Fig. 9. These spectra are grouped in three by spot number of (2), (6) and (7, 9, 11). From the results of Oxygen in Fig. 8, the spectrum of the spot 2 is thought to demonstrate Si in the metal state. The spectrum of spot 6 has the absorbing edge at 101 eV, however, the spectra of spots 7, 9 and 11 have it at 106 eV. In addition, the spectra of the spots 7, 9 and 11 have sharp peaks at 110 and 118 eV. From these results, Si exists in a different state for 6 and (7, 9, 11). In the previous paper,^{9,15} EELS spectra of Si oxides were detected including standard chemicals of Si and SiO_2 . The spectra of spot 7, 9 and 11 are similar to that of SiO_2 . Thus, Si is thought to exist in Si^{4+} oxide state in outer film of spot 7, 9 and 11. The spectrum of spot 6 is shown as the middle style between that of SiO_2 and metal Si. As the shape of the spectra is reflected by the valence of Si, the valence of Si of spot 6 is thought as 2 which is the middle of 0 and 4. Thus, Si is thought to exist in Si^{2+} oxide state in inner film of spot 6.

Ni-L EELS spectra of 16 Mn alloy are shown in spots 2, 6 and 7 in Fig. 10. From results of Oxygen in Fig. 8, the spectrum of the spot 2 is thought to show that Ni is present in the metal state. Peaks at 854 and 872 eV are shown for spots 6 and 7. However, there is no peak detected for spots 9 and 11. Thus Ni is enriched only at the interface of the film and metal, and there is no Ni in outer region of the passive film.

Fe-L EELS spectra are shown in the two groups of (2, 6) and (7, 9, 11) by spot number. Peaks at 708 and 721 eV are present for spots 2 and 6, while peaks at 707 and 720 are shown for spots 7, 9 and 11. Thus, the top peak of Fe-L₃ and Fe-L₂ are shifted 1 eV lower for the latter group. Moreover, the peak ratio (Fe-L₂/Fe-L₃) is lower for spots 7, 9 and 11 as compared to spots 2 and 6. From these results, Fe also exists

in a different state in spots (2, 6) and (7, 9, 11). For spot 2, Fe exists in a metal state from the result of Oxygen in Fig. 8. H. Tan *et al.* examined the EELS spectra of Iron oxides including Fe(II) O and Fe_2O_3 .¹⁴ The spectrum of spot 6 is similar to that of Fe(II) O. Thus, Fe is thought to exist mainly as Fe^{2+} oxide state in inner film of spot 6. On the other hand, the spectra of spot (7, 9, 11) are similar to that of Fe_2O_3 . Thus Fe is thought to exist mainly as Fe^{3+} oxide state in outer film of spot (7, 9, 11).

In this way, although it needs more work to identify precisely, the chemical state of each element in the passive film of 16 Mn alloy are examined in this study.

3.3 Nano structure of the passive film of 16 Mn shape memory alloy

In the wet and dry corrosion test, 16 Mn alloy showed much higher corrosion resistance than SM. Moreover, in EIS measurements, 16 Mn alloy had much larger value of Z_{lmHz} than that of SM after corrosion test. The primary reason for these was considered that the passive film of 16 Mn alloy was maintained during the corrosion test, and could show high corrosion resistance.

TEM-EELS measurements were conducted to identify the nano structure of the passive film on 16 Mn alloy. Figure 11 is a schematic diagram which shows the results of the TEM measurements. The passive film consists of 2 layers of a Cr-Si rich in inner and Mn-rich outer layer. Besides, the interface between the metal and film is enriched by Ni. The chemical state of each element is changing from the inner to outer layer. The chemical states are supposed as Mn^{3+} , Cr^{2+} , Si^{2+} and Fe^{2+} in inner layer, and Mn^{2+} , Cr^{3+} , Si^{4+} and Fe^{3+} in outer layer. Only Mn shows higher valence in inner layer than outer one. Maybe the inner or outer layer has another crystal structure, and each structure contains the suitable valence of Mn. However, it needs more investigation to demonstrate this matter.

Thus, for the inner layer, the film is thought to contain mainly Cr^{2+} and Si^{2+} in Fe oxides. On the other hand, for the outer layer, the film is thought to contain mainly Mn^{2+} in Fe oxides. As the corrosion resistance of 16 Mn alloy is thought to depend on the inner layer of the passive film, Cr and Si are

Fig. 11 Schematic diagram for the passive film of 16 Mn alloy.

identified as the effective elements. Moreover, Ni and Mn are thought to support the passive film by forming an enrichment in the interface and outer layer, respectively. In this way, 16 Mn alloy can maintain the passive film composed of effective elements in the wet and dry environment. Thus, 16 Mn alloy is able to have high corrosion resistance in the atmosphere containing Chloride ions.

4. Conclusions

A Fe–Mn–Si–Cr–Ni shape memory (16 Mn) alloy showed much higher corrosion resistance than carbon steel (SM) in the wet and dry corrosion test. Moreover, in EIS measurement, 16 Mn alloy had a much larger value of corrosion resistance ($Z_{1\text{mHz}}$) by forming the passive film as compared to SM after corrosion test. In AES and XPS analysis, the passive film of 16 Mn alloy was shown to contain Fe, Mn, Cr, Si and Ni. Based on TEM-EELS, the passive film consisted of 2 layers of Cr–Si (Cr^{2+} and Si^{2+}) enriched in inner and Mn (Mn^{2+}) enriched outer layer of Fe oxide. In addition, the interface between the metal and film was enriched with Ni. It was found that 16 Mn alloy could maintain the passive

film composed of effective elements in the wet and dry environment.

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