MAGNETIC IMAGING OF CHROMIUM DEPLETION IN THERMALLY SENSITIZED NI-CR-FE ALLOYS

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Abstract: Magnetic imaging of chromium depletion in thermally sensitized Ni-Cr-Fe alloys, which is one of the origins for the stress corrosion cracking, was achieved. Magnetic force microscopy (MFM) observation was performed on Alloy600 as a function of heating time at 873K. After thermal treatment, precipitation of chromium carbides was confirmed at the grain boundary by SEM image and ferromagnetic contrast was observed along the grain boundary in MFM images. Magnetic properties of ternary model alloys suggested that the chromium depletion occurred in the vicinity of carbides leads to raise the Curie temperature of Alloy600 near the grain boundary. This study shows a possibility for the application of magnetic techniques to the evaluation of thermal sensitization of Ni-Cr-Fe alloys.

Introduction: Alloy600, austenitic Ni-Cr-Fe alloy, has a high corrosion resistance and has been used in steam generators in nuclear power plants. However, thermal treatment including welding during construction causes chromium carbide precipitations and chromium depletion at the grain boundary [1-3]. This phenomenon is called thermal sensitization, and it is a serious problem because it leads to lower the corrosion resistance. Alloy600 is normally non-ferromagnetic at room temperature. However, a change of chemical composition during the sensitization may cause a ferromagnetic transition of Alloy600. It means that we can non-destructively evaluate the sensitization by magnetic method. This paper presents the magnetic properties of thermally sensitized Alloy600 and shows a mechanism of the magnetic imaging of chromium depletion.

Experiments: Two types of specimens were prepared as presented in Table 1: Alloy600, and Ni-Cr-Fe ternary model alloy. Specimens of Alloy600 were heated at 823K from 1 hour to 100 hours following 1 hour solution anneal at 1273K. After the thermal treatment, all specimens were electrically polished. Surface microstructures were observed by using field emission SEM system equipped with EDS apparatus (JEOL, JSM-6500F), and surface magnetic images were obtained by using MFM (SII, SPA400) at room temperature. MFM is a powerful technique for magnetic imaging with high spatial resolution because it uses a magnetic interaction between a sharp ferromagnetic tip and a ferromagnetic specimen. As for ternary alloy, specimens with different Cr concentrations below 16wt.% were prepared for simulating the chromium depletion of Alloy 600. Magnetic properties of ternary alloys were investigated by using SQUID magnetometer (Quantum Design, MPMS-XL5) from 4.5K to room temperature, and the Curie temperature was determined. Combined with the results of ternary model alloys, the effects of thermal sensitization on the surface magnetic images of Alloy600 were discussed.

Table 1 Chemical composition of the specimens

Wt.%	Ni	Cr	Fe	Mn	Si	C
Alloy600	76.0	15.5	7.8	0.5	0.2	0.08
NiCrFe alloy (X = 9-12,16)	92-X	X	8	-	-	-

Results: Fig.1 shows a typical surface SEM image of Alloy600 after 1 hour heating and its chemical composition profiles across the grain boundary obtained by FE-SEM-EDS system. Fig. 1(a) shows an augmentation of concentration in both carbon and chromium composition, which implies the chromium carbide formation. Contrary to the chemical analysis previously obtained by destructive TEM-EDS experiments [2-3], the chromium depletion could not be confirmed by the present FE-SEM-EDS system as shown in Fig.1 (b). Although the field emission SEM has an excellent beam focusing, the dispersion of an electron beam inside the specimen lower the spatial resolution of chemical analysis. The chromium depletion region of several tens nm width might be too narrow to be detected by the FE-SEM-EDS system.

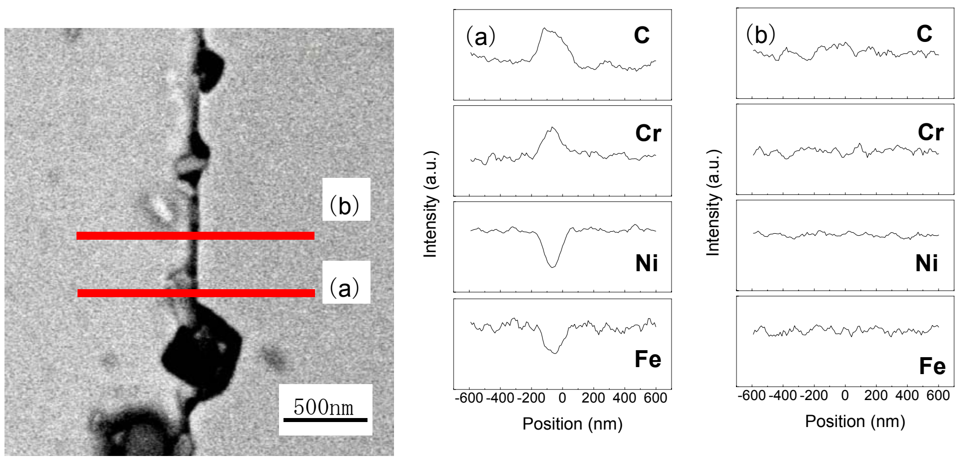

Fig.1. FE-SEM image and composition profiles of Alloy600 after 1hour heating at 873K.

Fig.2 shows MFM images of Alloy600, which have been thermally treated at 873K for various heating times. There was no image contrast in a solution annealed specimen without thermal heat treatment. After thermal treatment, ferromagnetic contrast started to appear in the MFM images, showing the maximum contrast after 10 hours. These phenomena may be attributable to the ferromagnetic phase formation induced by the chromium deletion with heat treatment, that is, sensitization. However the contrast became weaker with heating time longer than 10 hours, resulting in no noticeable contrast in a specimen with 100 hours treatment. Similar behaviour was also observed in Alloy 600 with slightly different chemical composition and thermal history. In order to clarify the mechanism of these phenomena, magnetic properties of Ni-Cr-Fe ternary model alloy were investigated.

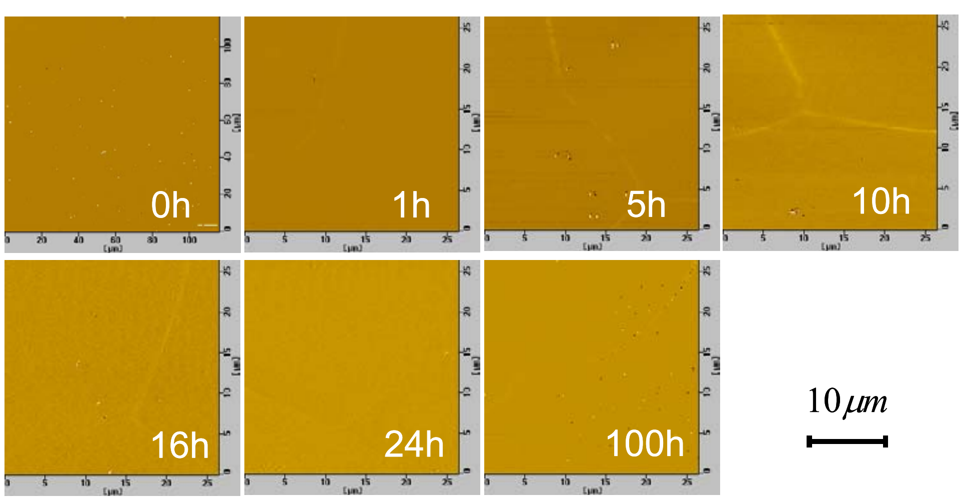

Fig.2. MFM images of Alloy600 before and after thermal treatment at 873K.

Fig.3 shows magnetization curves of $Ni_{92-x}Cr_xFe_8$ (x=16) ternary alloy measured at the temperature from 4.5K to 130K. The chromium concentration of 16wt.% is similar to that of a standard Alloy600. Magnetization reduces with increasing temperature, and at around 100K the shape of magnetization curve resembles the curve of paramagnetic one. It means that the Curie temperature of $Ni_{92-x}Cr_xFe_8$ (x=16) ternary alloy is around 100K.

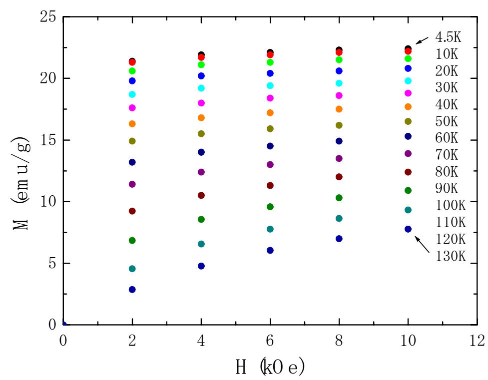

Fig.3. Magnetization curves of a $Ni_{92-x}Cr_xFe_8$ (x=16) ternary alloy.

For the precise determination of Curie temperature, spontaneous magnetization at each temperature, Ms(T) was estimated by Arrott plots [4]. Because of the itinerant electron nature of nickel-based ferromagnetic alloys, those magnetic properties are explained by self-consistent renormalization, SCR, theory of Moriya [5]. According to the SCR theory, the following relation is valid near the Curie temperature, Tc.

$$Ms(T)^2 = \zeta\left(T_c^{4/3} - T^{4/3}\right)$$

Considering this relation, Ms^2 vs. $T^{4/3}$ plots were made for each ternary alloys as shown in Fig.4. From the intersection at the horizontal axis, Curie temperature of each ternary alloys can be obtained. Fig.5 shows the chromium concentration dependence of Curie temperature. As for the specimen with 16wt.% chromium concentration, in which the chemical composition is similar to the Alloy600, the Curie temperature is 110K and hence it is non-ferromagnetic at room temperature. However, the Curie temperature increased rather linearly with decreasing the chromium concentration. When the chromium concentration arrives around 10%, the Curie temperature becomes higher than room temperature.

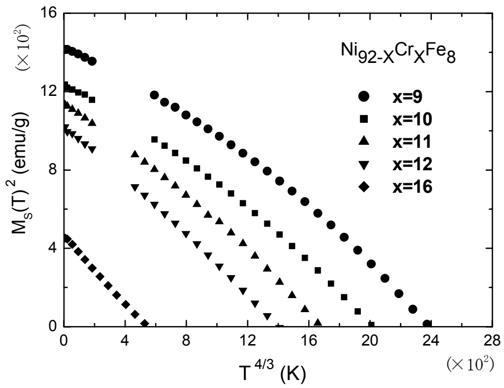

Fig.4. Ms^2 vs. $T^{4/3}$ plots of $Ni_{92-x}Cr_xFe_8$ ternary alloys.

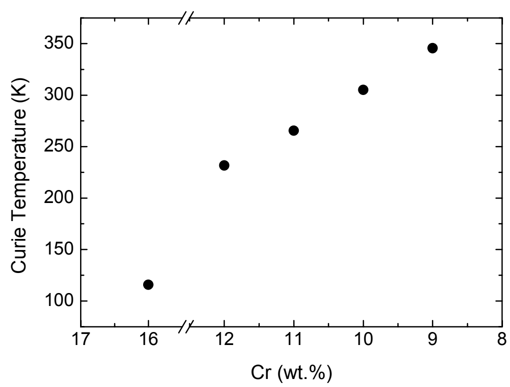

Fig.5. Curie temperature of $Ni_{92-x}Cr_xFe_8$ ternary alloys.

Discussion: The present results clearly show that a decrease of chromium concentration in Ni-Cr-Fe alloy causes an increase of Curie temperature. Considering this feature, MFM images of thermally sensitized Alloy600 can be simply explained through schematic representation of the microstructure and chromium concentration near grain boundary, as shown in Fig. 6. Before heat treatment, there were no carbides along the grain boundaries, and their chormium concentration was the same as that of the matrix, that is, 16wt.%Cr, as shown in Fig. 6(a). With thermal heat treatment, chromium carbides started to form with chromium depleted zones. When chromium concentration became lower than the critical amount of 10wt.%Cr, the chromium delpleted zones changed to ferromagnetic, since its Curie temperature is higher than room temperature. After 10 hour heat treatment, the chromium depleted zones grows to the maximum size, which is identified by the clearest MFM image, as shown in Fig. 6(b). With further heat treatment longer than 10 hours, there would be a sufficient time for chromium to diffuse to the depleted zone from the matrix. Then the ferromagnetic chromium depleted zones would change to the non-ferromagnetic phase, with more than 10wt.%Cr, as shown in Fig. 6(c). Therefore we can quantitatively evaluate the sensitization of Ni-Cr-Fe alloys with non-destructive magnetic techniques [6].

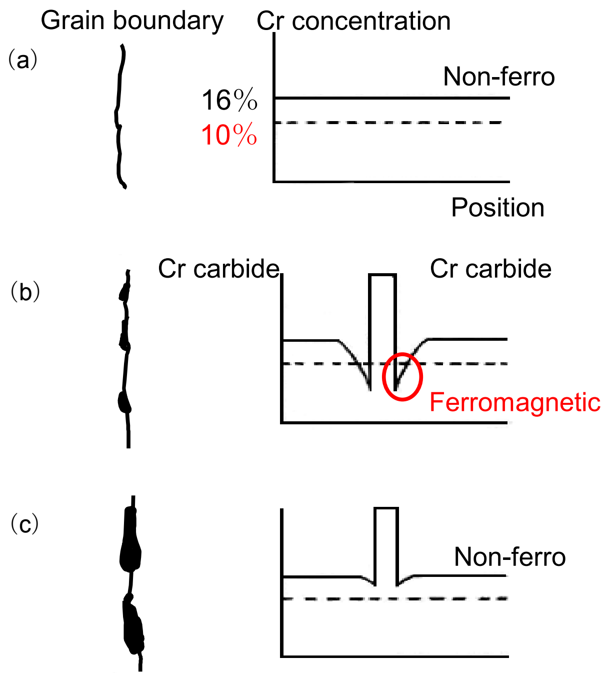

Fig.6. Schematic representations of microstructures and chromium profiles near the grain boundary.
Heating time is for (a) 0hour, (b) 10hours and (c) 100hours.

Conclusions: Magnetic imaging of chromium depletion in thermally sensitized Alloy600 was achieved by MFM observation. The origin of the ferromagnetic contrast is attributable to the increase of Curie temperature at the chromium depleted regions along the grain boundary. This study shows us a possibility for the application of magnetic techniques to the non-destructive evaluation of sensitization of Ni-Cr-Fe alloys.

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