Role of Carbon and Nitrogen on the Transformation of the σ Phase in Highly Purified Fe–50 mass%Cr Alloys

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The role of carbon and nitrogen on the transformation of the σ phase was investigated using highly purified Fe–Cr alloys containing 50 mass% chromium. In highly purified Fe–50 mass%Cr alloy the σ phase transforms at grain boundaries across the surface of the specimen and then grows inward along grain boundaries. Extremely small amounts of the σ phase are transformed in Fe–50 mass%Cr alloys containing carbon. On the other hand, in Fe–50 mass%Cr alloys containing nitrogen aged for long periods, 3.6 Ms and more, the σ phase transforms on grain boundaries at the inside of the specimen and grows along grain boundaries. In these alloys it was observed that plate-like nitride Cr_2N precipitated along grain boundaries and resulted in a depleted zone of chromium around it. The σ phase preferentially transforms on the α grain boundaries. In Fe–50 mass%Cr alloy containing carbon and nitrogen aged for 18 Ms, the α phase consists of 49.1 mass% chromium and 50.9 mass% iron. On the other hand, the σ phase consists of 47.9 mass% chromium and 52.1 mass% iron. It was confirmed that chromium enrichment occurred in the α phase at the interface between the α and σ phases. Consequently, in annealed Fe–50 mass%Cr alloys, the transformation of the σ phase is suppressed by the presence of a small amount of carbon and by purification, especially the reduction of the nitrogen concentration and the absence of nitride.

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1. Introduction

High-chromium ferritic stainless steel possesses excellent strength at high temperature, high corrosion resistance, and high resistance to stress corrosion cracking. However, in Fe–Cr alloys with high chromium content, the transformation of the σ phase causes drastic deterioration in mechanical properties such as ductility and impact toughness, which is well-known as σ embrittlement.

There are many papers on the transformation of the σ phase in Fe–Cr alloys with high chromium content.^{1–7)} Chevenard,⁸⁾ Bain and Griffiths⁹⁾ reported an intermediate phase formed in Fe–Cr alloys. The phase was identified as σ phase by Jette and Foote.¹⁰⁾ In 1954, Bergman and Shoemaker¹¹⁾ determined the crystal structure of the σ phase in Fe–Cr alloys as a tetragonal crystal structure composed of 30 atoms with 5 inequivalent sites in an unit cell. The probability for the occupation of the substitutional sites by iron or chromium atoms were determined by X-ray diffraction, neutron diffraction, and Mössbauer spectroscopy.^{12–14)} Some researchers have investigated the transformation mechanism of the σ phase in the commercial alloys such as the ternary Fe–Cr–Ni alloys,^{15–18)} the ternary Fe–Ni–Mn alloys and the dual phase stainless steels.¹⁹⁾

Recently, Abiko and co-workers have found that the ductility of Fe–50 mass%Cr alloy is remarkably improved by purification.^{20,21)} There are significant differences in the results on the ductility of Fe–Cr alloys with high chromium content and on the transformation behavior of the σ phase from the α phase between earlier papers and their papers.^{21–23)} Yano and Abiko²³⁾ reported that the transformation of the σ phase in an-

nealed Fe–50 mass%Cr alloys is suppressed by the existence of a small amount of carbon and by purification, especially reduction of nitrogen.

The purpose of the present study is to investigate the role of carbon and nitrogen on the transformation of the σ phase by using highly purified Fe–50 mass%Cr alloys. Furthermore, the transformation mechanism of the σ phase is clarified in the binary Fe–50 mass%Cr alloys.

2. Experimental Procedure

Highly purified Fe–50 mass%Cr alloys were made from high-purity electrolytic iron²⁴⁾ and high-purity chromium. The ingots were melted in a cold crucible made of copper by high frequency induction heating. The amount of carbon and nitrogen in Fe–Cr alloys were controlled by the addition of Fe–4.7 mass%C mother alloy and Cr_2N , respectively. A LP50Cr–H(C+N) alloy²⁵⁾ containing impurities other than carbon and nitrogen was melted in a ceramic crucible with the addition of aluminum for deoxidizing. The chemical compositions of Fe–50 mass%Cr alloys are shown in Table 1.

The ingots were hot-forged to round rods of 20 mm in diameter after heating at 1323 K in an atmosphere of high-purity Ar, and then hot-rolled to round rods of 7.5 mm and 4 mm in diameter. In order to examine the transformation behavior of the σ phase, specimens of 7 mm in diameter and 10 mm in length were machined from the 7.5 mm round rods. Specimens of 3.6 mm in diameter and 32 mm in length for Auger electron spectroscopy (AES) were machined from the round rod of 4 mm. Every specimen was annealed for 3600 s at 1373 K under a high vacuum of better than 2.7×10^{-2} Pa, quenched into oil at 273 K and aged for various periods at 973 K under a high vacuum of better than 2.7×10^{-4} Pa. The aging heat treatments for 18 Ms at 973 K were performed in a quartz tube of high vacuum to protect the specimen against

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Table 1 Chemical composition of Fe–50 mass%Cr alloys investigated.

Alloy	mass%						mass ppm							
	Cr	C	S	N	O	P	Si	Mn	Al	Cu	Ni	Ti	B	
HP50Cr–LC	50.3	15	2	8	66	6	14	3	2	3	8	3	1.0	
HP50Cr–MC	48.9	166	3	7	50	7	15	3	3	3	8	3	0.7	
HP50Cr–HC	48.4	309	3	10	53	5	10	3	2	3	8	3	1.0	
HP50Cr–MN	49.2	10	3	136	85	6	11	3	6	3	8	3	1.0	
HP50Cr–H(C+N)	50.0	277	6	275	78	9	131	12	190	3	19	5	0.8	

oxidation. The handling and heat treatment of all specimens took place with special caution for contamination.

The existence of transformed σ phase was identified by X-ray diffraction. Every specimen was cut at the center of the original length and polished for microscopic observation. After electrolytic etching, the transformation behavior and the amount of the σ phase were examined by optical microscopy. The concentrations of chromium and iron in σ phase and in the matrix were determined by electron probe X-ray micro analyzer (EPMA) and Field emission Auger electron spectroscopy (FE-AES). FE-AES analysis was performed with a primary electron beam of 10 keV. The effective radius of Auger electron generation region caused by backscattered electron is less than 0.3 μm .²⁶⁾ Auger peak height ratios of the chromium peak at 529 eV to the iron peak at 703 eV were used to evaluate the degree of chromium concentration. Field emission transmission electron microscopy (FE-TEM) was performed to investigate microstructures. Thin foils for FE-TEM was mechanically polished to about 100 μm in thickness and then jet-polished at 273 K in a solution containing 10 vol% perchloric acid and 90 vol% acetic acid. Electron diffraction was used to identify the precipitates. The degree of grain boundary segregation of the solutes was measured using scanning AES on individual grain boundary facets revealed by fracturing specimens at 213 K under ultra-high vacuum of better than 1×10^{-8} Pa. AES analyses were performed with a primary electron beam of 3 keV and 0.1 μA , with a beam size of 3 μm . The degree of a segregated element was given by the ratio of the Auger peak height of the element to that of iron at 703 eV.

3. Results

3.1 Transformation rate of the σ phase in Fe–50 mass%Cr alloys

Figure 1 shows the effect of impurities on the transformation kinetics of the σ phase in Fe–50 mass%Cr alloys aged at 973 K. By X-ray diffractometry the newly observed phase was identified to be the σ phase. The data of the transformed σ phase for a low-purity Fe–50 mass%Cr alloy aged at 923 K after Tetsui *et al.*²²⁾ is also plotted in the same figure. The transformation rate of the σ phase in the present study is extremely smaller than that by Tetsui *et al.* The transformation rate in HP50Cr–LC alloy is equivalent to that in HP50Cr–MN alloy. The transformation rate in HP50Cr–LC alloy is smaller than that in LP50Cr–H(C+N) alloy, although it is larger than that in HP50Cr–MC and HP50Cr–HC alloys. The amount of the σ phase is extremely small in highly purified

Fig. 1 Effect of impurities on the transformation kinetics of the σ phase in Fe–50 mass%Cr alloys aged at 973 K.

Fe–50 mass%Cr alloys containing carbon.

Figure 2 shows the typical microstructures of the σ phase in Fe–50 mass%Cr alloys aged for 18 Ms at 973 K. It was observed that the σ phase nucleates at grain boundaries across the surface of the specimen and then grows inward along grain boundaries in HP50Cr–LC, HP50Cr–MC and HP50Cr–HC alloys. In these alloys, no σ phase was observed at the inside of the specimen. On the other hand, in HP50Cr–MN and LP50Cr–H(C+N) alloys the σ phase was observed on grain boundaries at the inside of the specimen. The transformation behavior of LP50Cr–H(C+N) alloys aged less than 3.6 Ms is similar to that of HP50Cr–MN alloys aged less than 18 Ms.

These results show that the transformation of the σ phase was suppressed by the presence of a small amount of carbon and by purification, especially the reduction of nitrogen. It is also found that the transformation of the σ phase is strongly affected by interfaces such as surface and grain boundary.

3.2 Grain boundary concentration of solute atoms

Figure 3 shows the area fraction of α grain boundaries covered by the σ phase in Fe–50 mass%Cr alloys aged at 973 K. The fraction is extremely small in the alloys containing carbon, namely HP50Cr–MC and HP50Cr–HC alloys. On the other hand, in LP50Cr–H(C+N) alloy aged for 18 Ms, the

400 μm

Fig. 2 Typical microstructures of the σ phase in (a) HP50Cr-LC, (b) HP50Cr-MC, (c) HP50Cr-HC, (d) HP50Cr-MN and (e) LP50Cr-H(C+N) alloys aged for 18 Ms at 973 K.

area fraction of α grain boundaries covered by the σ phase is 85%. Nevertheless the area fraction of the σ phase through the specimen is 16% in LP50Cr-H(C+N) alloy, as shown in Fig. 1. The fraction of the σ phase transformed in α grain is extremely smaller than that along α grain boundary. Therefore it is considered that the σ phase in Fe-50 mass%Cr alloys containing many impurities such as nitrogen nucleates at grain boundaries of the α phase.

Figure 4 shows typical Auger spectra taken from the intergranular facets of Fe-50 mass%Cr alloys without and with aging for 360 ks at 973 K. HP50Cr-LC alloy without aging was fractured by the transgranular manner. In HP50Cr-LC alloy with aging, the Auger peaks of carbon and nitro-

gen from the intergranular facets are found in addition to the peaks of iron and chromium. Auger peaks of carbon, iron and chromium are found in the spectrum from HP50Cr-MC alloy without aging. The Auger peak of nitrogen in HP50Cr-MC alloy becomes large by aging. The peak of nitrogen are also observed in the spectra from HP50Cr-MN and LP50Cr-H(C+N) alloys without aging. It should be emphasized that the peak heights of nitrogen and chromium in HP50Cr-MN and LP50Cr-H(C+N) alloys increase drastically by aging, although the peak height of carbon decreases.

Figure 5 shows the Auger peak height ratios of solute elements peak (carbon, nitrogen and chromium) to iron peak from the intergranular fractured facets of LP50Cr-H(C+N)

Fig. 3 Area fraction of the σ phase transformed at α grain boundaries in Fe–50 mass%Cr alloys aged at 973 K.

Fig. 4 Typical Auger spectra taken from the intergranular facets of Fe–50 mass%Cr alloys (a) without and (b) with aging.

Fig. 5 Auger peak height ratios of carbon, nitrogen and chromium peaks to iron peak at the intergranular fractured facets of LP50Cr–H(C+N) alloy.

alloy. These ratios are calculated by the Auger spectra taken from more than 10 individual intergranular facets for alloys without and with aging for 360 ks at 973 K. To indicate the amount of scatter in measured values, the difference between minimum and maximum values is shown by lines in Fig. 5. The ratios of N/Fe and Cr/Fe increases drastically by aging. The ratio of C/Fe, however, almost constant.

3.3 Concentration profile in and near precipitates

The precipitation behavior of carbides and nitrides was confirmed by TEM observation in Fe–50 mass%Cr alloys. Figure 6 shows typical electron micrographs of a nitride and a carbide in LP50Cr–H(C+N) alloy aged for 360 ks at 973 K. Many precipitates in LP50Cr–H(C+N) alloy aged for 360 ks at 973 K are morphologically classified into two types: polyhedral precipitates were observed at grain boundaries and in grains and plate-like precipitates along grain boundaries. Most of polyhedral precipitates are identified to be $M_{23}C_6$ containing chromium and iron atoms. Most of plate-like precipitates are identified to be Cr_2N .

Figure 7 shows the concentration profiles of chromium around the precipitates as shown in Fig. 6 by EPMA. The depleted zone of chromium is detected around the plate-like precipitate (Cr_2N) formed at a grain boundary, as shown in Figure 6(a). The zone of about 20 nm wide contains 45 mass% chromium. On the other hand, the depleted zone is not observed around the polyhedral precipitate ($M_{23}C_6$) as shown in Figure 6(b). Although the zone around the carbide could not observed in the present study, it is expected that a narrow depleted zone of chromium exists around the carbide. It is concluded that the transformation of the σ phase on grain boundaries at the inside of the specimens is related to the grain boundary precipitation of nitrides.

3.4 Concentration profile in and near the σ phase

Figure 8 shows the concentration of chromium and iron in the α and σ phases in LP50Cr–H(C+N) alloy aged for 18 Ms at 973 K. The α and σ phases consist of 49.1 mass% chromium and 50.9 mass% iron, of 47.9 mass% chromium

Fig. 6 Typical electron micrographs of (a) a nitride and (b) a carbide in LP50Cr–H(C+N) alloy aged for 360 ks at 973 K.

Fig. 7 Concentration profiles of chromium near the interface of precipitates in LP50Cr–H(C+N) alloy aged for 360 ks at 973 K.

and 52.1 mass% iron, respectively. The chromium concentration of the σ phase is smaller than that of the α phase. It is considered from this result that the transformation of the σ phase from the α phase is related to the diffusion of chromium atoms.

Figure 9 shows the secondary electron micrograph at the interface between the α and σ phases in a LP50Cr–H(C+N) alloy aged for 18 Ms by FE-AES. The Auger peak height ratios of the chromium peak to the iron peak as shown in Fig. 10 means the concentration profiles of chromium along the direction across the interface. The region at the peak of chromium

Fig. 8 Concentration of chromium and iron in α and σ phases in a LP50Cr–H(C+N) alloy aged for 18 Ms at 973 K.

is approximately $0.3\ \mu\text{m}$ in wide, which is nearly equal to the effective radius of the beams used for the detection in microprobe. It was confirmed that chromium enrichment results in the α phase at the interface between the α and σ phases.

4. Discussion

4.1 Nucleation mechanism of the σ phase in Fe–50 mass%Cr alloys

Duwez and Martens¹⁾ have reported that nitrogen in Fe–48 mass%Cr–3 mass%W alloys induces the high transformation rate of the σ phase and that the rate is affected by the actual amount of chromium in solution. In the present study,

Fig. 9 Electron micrograph by FE-AES at the interface between the σ phase and the α phase in LP50Cr-H(C+N) alloy aged for 18 Ms at 973 K.

nitrogen and chromium in solution segregate to grain boundaries of the α phase by aging at 973 K in HP50Cr-MN and LP50Cr-H(C+N) alloys, as shown in Fig. 4. During aging, segregated nitrogen and chromium precipitates as a chromium nitride, Cr_2N , at grain boundaries as shown in Fig. 6(a). Because the binding of nitrogen to chromium is stronger than that to iron at high temperature. The depleted zone of chromium forms around the nitrides as shown in Fig. 7. The growth of nitrides along grain boundaries enhances the development of the depleted zone. The concentration of chromium at the depleted zone becomes from the bulk concentration of chromium, 50 mass%, to 47.9 mass% as shown in Fig. 8. The σ phase nucleates at the zone of which concentration becomes near the stoichiometric composition (45 mass%Cr) of the σ phase, after Yano and Abiko.²³⁾ Namely, the depleted zone at the inside of specimen acts as the nucleation site of the σ phase due to aging of an Fe-50 mass%Cr alloy containing nitrogen such as HP50Cr-MN and LP50Cr-H(C+N) alloys at 973 K. This is the nucleation mechanism of the σ phase in an Fe-50 mass%Cr alloy containing nitrogen.

On the other hand, the binding of carbon to chromium is also stronger than that to iron at high temperature. The solubility of carbon is lower than that of nitrogen in Fe-30 mass%Cr alloy after Fukuda *et al.*²⁷⁾ However, the contribution of carbon to form the depleted zone is lower than that of nitrogen, because the depleted zone is hardly observed around carbide as shown in Fig. 7. Moreover, carbon segregated at grain boundaries by aging suppresses the segregation of nitrogen to grain boundaries in a HP50Cr-MC alloy as shown in Fig. 4. Due to this competition phenomenon, the precipitation of nitrides prohibited in an Fe-50 mass%Cr alloy containing a small amount of nitrogen during aging. Furthermore, the morphological effect of carbides on the depleted zone is smaller than that of nitrides with the continuous flat plate-like shape as shown in Fig. 6(a) and (b). Consequently, it is concluded that the σ phase at the inside of specimen containing carbon hardly nucleates around carbides

Fig. 10 Auger peak height ratios of chromium peak to iron peak at interface of the σ and α phases in a LP50Cr-H(C+N) alloy aged for 18 Ms at 973 K.

precipitated during aging.

The σ phase at the surface of specimen after aging for long period nucleates at some grain boundaries in Fe-50 mass%Cr alloys as shown in Fig. 2. It is considered that the surface of specimen is covered by the oxide layer during aging at 973 K under the atmosphere of high vacuum in quartz tubing. Under such an aging condition, chromium atoms diffuse to the surface through grain boundaries. It means that the depleted zone forms along grain boundaries across the surface of specimen and that the σ phase nucleates at the depleted zone. The role of oxide layer is a very importance for the nucleation of the σ phase. Oxygen easily affects the uniformity of chromium contents in the impure alloys. Especially, in Fe-high Cr alloys made by conventional powder metallurgy, a lot of oxygen is localized through the specimen. This is one of the reasons why the transformation rate of the σ phase is so large in the impure alloys, in comparison with high-purity alloys as shown in Fig. 1.²²⁾

4.2 Growth of the σ phase in Fe-50 mass%Cr alloy

In the actual transformation of the σ phase, the σ phase will appear after incubation period, as shown in Fig. 1. As discussed in 4.1, the transformation of the σ phase is suppressed by purification, especially the reduction of nitrogen and the absence of nitride, in annealed Fe-50 mass%Cr alloys. Purification of the Fe-50 mass%Cr alloy may greatly influence on the number of the σ nucleus and the incubation period. However, after the σ phase nucleates even in highly purified Fe-Cr alloys, the σ phase will grow due to the chromium diffusion at the interface.

The grain boundary diffusion is faster than the volume diffusion. The grain boundary diffusion of chromium enhances the growth of the σ phase along grain boundaries of α phase. Moreover the specific volume of the σ phase is smaller than that of the α phase.²⁹⁾ The difference of specific volume between the α phase and the σ phase induces the stress around

their interface. It is expected that the stress affects the diffusion rate of solute atoms and then the growth rate of the σ phase. In other words, the stress caused by the nucleation of the σ phase consequently enhances the transformation of the σ phase.

Wakai *et al.*²⁸⁾ have reported that the chromium concentration in a Fe–50 mass%Cr–8 mass%W alloy irradiated at 943 K for 1.2 ks decreases in the σ phase, as compared with the α phase. In the present study, the chromium concentration of the σ phase is different from that of the α phase in a LP50Cr–H(C+N) alloy aged for 18 Ms at 973 K, as shown in Fig. 8. Furthermore it was confirmed that chromium enrichment occurs in the α phase at the interface between the α and σ phases in the alloy. Consequently, it is found that the growth of the σ phase is responsible for the diffusion of chromium atoms.

Finally, in the present study, the effect of impurities such as carbon and nitrogen on the nucleation and growth of the σ phase is clarified in a highly purified Fe–50 mass%Cr alloy. It is necessary to study the nucleation and growth of the σ phase from the α phase by using highly purified Fe–Cr alloys containing wider compositions of chromium in order to establish the transformation kinetics of the σ phase.

5. Conclusion

The role of carbon and nitrogen on the transformation of the σ phase in highly purified Fe–50 mass%Cr alloys has been investigated and the nucleation and growth of the σ phase has been discussed. The experimental results are as follows;

(1) In annealed Fe–50 mass%Cr alloys, a small amount of carbon up to 300 mass ppm suppresses the transformation of the σ phase. Purification, especially the reduction of nitrogen and the absence of nitride, also suppresses the transformation.

(2) In the Fe–50 mass%Cr alloy containing carbon and nitrogen, it was observed that the depleted zones of chromium around plate-like nitrides (Cr_2N) precipitate at the grain boundaries of the α phase. The σ phase preferentially transforms at such α grain boundaries.

(3) Chromium enrichment occurs in the α phase at the interface between the α and σ phases in the Fe–50 mass%Cr alloy containing carbon and nitrogen. The growth of the σ phase is responsible for the diffusion of chromium atoms.

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