Morphology of Sulfide Formed in the Fe–Cr–S Ternary Alloys

Hajime MITSUI, Katsunari OIKAWA, Ikuo OHNUMA, Ryosuke KAINUMA and Kiyohito ISHIDA

Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama, Aoba-ku, Sendai 980-8579 Japan. 1) National Institute of Advanced Industrial Science and Technology (AIST) Tohoku Center, Nigatake, Miyagino-ku, Sendai 983-8551 Japan.

(Received on March 11, 2002; accepted in final form on July 15, 2002)

The evolution of sulfide morphology in the Fe–(0.3–18)mass%Cr–(0.05–0.3)mass%S alloys during solidification and heat treatment was investigated by means of optical microscopy, scanning electron microscopy, analytical electron microscopy and X-ray diffraction. In situ observation of the formation of the fine particle sulfide was also conducted at elevated temperatures by confocal scanning laser microscopy. The morphology of sulfide in the Fe–Cr–S ternary alloys was found to change from a cell wall type to a globular type with increasing Cr content. Accompanying the phase transformation of the matrix from the δ phase to the γ phase, two types of transgranular fine particle sulfide were formed. One is a fine spherical sulfide formed from the FeS-rich liquid phase through the remelting reaction of δ → γ + Liq. in less than 5 mass% Cr alloys, and the other is a fine rod-like sulfide formed through the eutectoid reaction of δ → γ + sulfide in 5 to 13 mass% Cr alloys. The formation mechanism of various types of sulfide morphology was examined based on phase diagram information.

KEY WORDS: sulfide morphology; in situ observation; mechanism of sulfide formation; phase diagram; stainless steel.

1. Introduction

Non-metallic inclusions such as oxide and sulfide in steels are generally detrimental and considerable efforts have been made to reduce such impurities. On the other hand, the introduction and modification of inclusions have also received a great deal of attention as a new technique for improving the mechanical properties of steel.1–9) For instance, since manganese sulfide acts as a heterogeneous nucleation site of intragranular ferrite, it is used for refining the ferritic structure3,4) and for improving the toughness in the heat-affected zone (HAZ) of the weld metal.5) Furthermore, it is well-known that MnS inclusion improves the machinability of steels.6) Although there have been extensive studies on the formation and morphology of MnS in steel,7,8,10–15) few studies on the microstructural features of CrS have been performed. There have also been reports on the improvement of corrosion resistance resulting from the decreasing Mn/S ratio in stainless steel consequent with increasing Cr content in sulfide.7–9)

The present work is one of a series of systematic studies9–11,16–22) on the phase equilibria and the morphology of various sulfides in metals, which focuses on the microstructural features of CrS in the Fe–Cr–S ternary system. In particular, a confocal scanning laser microscope (CSLM) with infrared image furnace was utilized for direct investigation of the microstructure at high temperature.12,23,24) The advantage of the in situ observation method using CSLM is that, because of strong, deep-focusing laser light, it is possible to observe a high temperature phenomenon with steep surface change that is difficult to achieve by conventional optical microscopy. In the present study, therefore, in situ observation of the formation of sulfide in the Fe–Cr–S ternary alloys was conducted at elevated temperatures with CSLM to reveal the formation mechanism of the sulfide.

2. Experimental

Alloy ingots weighing about 300 g each, with composition ranges of 0.3–18 mass% Cr and 0.05–0.3 mass% S, were prepared from electrolytic iron, electrolytic chromium and iron sulfide by induction melting in magnesia crucibles under an argon atmosphere. The mixture of iron and chromium was melted first and then iron sulfide was added to the molten alloy. After the addition of iron sulfide, the bath was kept in the molten state for 5 min and then allowed to solidify in the crucible. The cooling rate in the solidification range was about 30 K/min.

Microstructure examination was carried out using an optical microscope (OM) and a field emission scanning electron microscope (FE-SEM). In situ video camera observation of the sulfide was performed using a CSLM with an infrared image furnace, the details of which have been described by Chikama et al.23) The surfaces of mirror-polished disk specimens (4 mm in diameter and 2 mm in thickness) in a high purity alumina crucible (5.5 mm outer diameter and 4.5 mm inner diameter) were observed by CSLM under a highly purified argon atmosphere; the heating rate was 20 K/min from 1373 to 1673 K. The sections of the specimens to be examined by FE-SEM were etched elec-
trolytically in a 1% tetra-methyl-ammonium chloride–10% acetyl-acetone-methanol solution.

The composition of sulfide was determined by a scanning electron microscope equipped with an energy dispersive X-ray micro-analyzer (SEM-EDS) and an analytical electron microscope (AEM) for fine particles below 1 μm. The crystal structure of sulfide was determined by X-ray diffraction (XRD).

3. Results

3.1. Morphology of Sulfide

Typical micrographs of sulfide in the Fe–Cr–S as-cast alloys are shown in Fig. 1. The morphology of sulfide can be classified into three types, i.e., cell wall, globular and fine particle, as previously reported. The morphology of sulfide observed in the present study is summarized in Fig. 2. It can be seen that the cell wall sulfide formed along the grain boundary is observed in Fe–(0.3–1)mass%Cr–0.3mass%S alloys, while the globular sulfide more than 2 μm in diameter is observed at the grain boundary in the Fe–1mass%Cr–(0.05–0.1)mass%S and Fe–(3–18)mass%Cr–(0.05–0.3)mass%S alloys. Figure 3 shows the composition of sulfide determined by EDS analysis in Fe–Cr–0.3mass%S as-cast alloys, by which it is confirmed that the sulfide can be designated as (Fe,Cr)S. The Cr content in (Fe,Cr)S increases with increasing Cr content in alloys and Cr becomes the major metal element in sulfide above 5 mass% Cr. The morphology of sulfide changes from cell wall to globular with the increase in Cr content in the sulfide, which can be explained by the phase diagrams as discussed later. Very fine particle sulfide, less than 1 μm in diameter, is observed in the alloys with Cr content below 8 mass%, and such sulfides are uniformly dispersed in the grains.

3.2. In Situ Observation of Remelting Reaction

The in situ observation of fine particle sulfide in the Fe–1mass%Cr–0.05mass%S alloy by CSLM with heating from 1100 to 1400°C is shown in Figs. 4(a) to 4(f), enlarged photos of sulfide at each temperature being shown at the bottom left of Figs. 4(a) to 4(c). Figure 4(a) shows the existence of many fine particles of sulfide less than 1 μm in diameter in the γ phase matrix at about 1100°C. When the sample is heated above 1200°C, the sulfide begins to coalesce into a closer particle and grows larger as shown in Figs. 4(b) and 4(c). With further heating over 1300°C, the δ phase precipitates at the grain boundary of the γ phase, and simultaneously the sulfide dissolves as shown by the circles in Figs. 4(d) and 4(e). Finally, the sulfide completely dissolves and a single δ phase is formed over 1400°C as shown in Fig. 4(f).

Fig. 1. Typical micrographs of sulfides in the Fe–Cr–S ternary as-cast alloys. (a) Cell wall (Fe–1Cr–0.3S), (b) globular (Fe–13Cr–0.3S) and (c) fine particle (Fe–1Cr–0.05S).

Fig. 2. Morphology of sulfide in the Fe–Cr–S as-cast alloys.
3.3. Morphology of Fine Particle Sulfide

Figure 5 shows the typical morphology of fine particle sulfide, where two types of spherical and rod-like sulfides can be observed. In the Fe–1mass%Cr–0.05mass%S as-cast alloy, fine spherical sulfide is observed (Fig. 5(a)), while not only fine spherical sulfide but also fine rod-like type sulfide can be seen in the Fe–8mass%Cr–0.05mass%S as-cast alloy, as shown in Fig. 5(b). Figure 6 shows the variation of mean size of fine spherical sulfide with Cr content in the Fe–Cr–S as-cast alloys. It is seen that the size of sulfide decreases with increasing Cr content, which is related to the partition of Cr in the sulfide. As shown in Fig. 3, Cr in (Fe,Cr)S increases with increasing Cr content of alloys. Since the diffusivity of Cr in α-Fe or γ-Fe is remarkably less than that of S, the finer particles of sulfide with high Cr content are formed due to the effect of partition and the low diffusivity of Cr.

In order to examine the sequence of rod-like sulfide formation, the Fe–1mass%Cr–0.05mass%S and Fe–8mass%Cr–0.05mass%S alloys are solution treated for 30 min at 1400°C where the δ single phase is formed in both alloys. After that, they are heat treated for 10 min at 1200°C. The morphology of sulfide of the Fe–1mass%Cr–0.05mass%S and Fe–8mass%Cr–0.05mass%S alloys, as shown in Figs. 5(c) and 5(d), respectively, indicates that the mean size of spherical sulfide with a diameter of 410 nm is formed in the Fe–1mass%Cr–0.05mass%S alloy, while fine rod-like sulfide whose mean size of major axis is 390 nm is observed in the Fe–8mass%Cr–0.05mass%S alloy. Figure 7 shows the change of the mean size of the rod-like sulfide in the Fe–8mass%Cr–0.05mass%S alloy with heating time at 1200°C. The aspect ratio increases to 4.5 for the first
20 min and then decreases to 1.7 for 60 min, i.e., the rod-like sulfide grows for the first 20 min and then begins to spheroidize. As shown in Fig. 5(b), the major morphology of sulfide in the Fe–8mass%Cr–0.05mass%S as-cast alloy shows the fine spherical sulfide, which can be explained as being due to the fact that the sulfide precipitated as a rod-like structure has spheroidized on cooling because the cooling rate in the solidification range is relatively low (about 30 K/min). It should be noted that two types of fine spherical and rod-like sulfides were uniformly observed in the matrix in cases of both as-cast and heat treated specimens at 1200°C.

4. Discussion

4.1. Formation of Cell Wall and Globular Sulfides

The morphological change of sulfide from cell wall type to globular type accompanied by increasing Cr content during solidification of Fe–Cr–0.3mass%S alloys as shown in Fig. 2 can be explained on the basis of phase diagrams as follows. Figure 8 shows the calculated vertical section diagrams of Fe–1mass%Cr–S and Fe–13mass%Cr–S alloys based on thermodynamic assessment. The Fe–Cr–S phase diagram at 1 mass% Cr is similar to that of the Fe–FeS binary system. Therefore, the expected solidification path and the microstructural development of the Fe–1mass%Cr–0.3mass%S alloy is as follows: (i) primary δ phase crystallization and sulfur enrichment of the liquid phase, and (ii) solidification of the sulfur-rich liquid phase around the primary Fe phase through the eutectic reaction (Liq. → Fe + sul-
fide) and the formation of the cell wall type sulfide.

The Cr content in the sulfide phase increases with increasing Cr content of the alloy, which leads to the formation of two liquids, a Fe-rich liquid (Liq. 1) and a CrS liquid (Liq. 2) in high Cr alloys as shown in Fig. 8(b). In the case of the Fe–13mass%Cr–0.3mass%S alloy melt, therefore, the expected solidification path would be one that leads first to the precipitation of the primary Fe phase and then to the formation of Cr-rich sulfide through the monotectic reaction (Liq. 1 → Fe + Liq. 2) in the liquid state. This solidification sequence gives rise to the globular sulfide morphology.

4.2. Formation of Fine Particle Sulfide

As shown in the previous section, the characteristic feature of the morphology of fine spherical and rod-like sulfides was observed. The formation of these sulfides can also be explained by the phase diagram. Figure 9 shows the calculated vertical section diagram of Fe–Cr–0.05mass%S alloy, which shows the remelting reaction (δ → γ + Liq. 2) below 5 mass% Cr and the eutectoid reaction (δ → γ + sulfide) in 5–13 mass% Cr. These two reactions are directly related to the formation mechanism of the two types of fine particle sulfide during the solidification as discussed below.

4.2.1. Remelting Reaction

Figure 10 shows the calculated mole fraction changes of the δ, γ, sulfide and liquid phases in the Fe–1mass%Cr–0.05mass%S alloy. During cooling from the δ single-phase, the liquid phase (Liq. 2) appears in the γ phase matrix at 1370°C through the remelting reaction. The mole fraction of Liq. 2 increases with a decrease in temperature, and the liquid phase transforms to the sulfide phase at 1188°C. The amount of sulfide phase increases with decreasing temperature and is about 0.174 mol% at 600°C. Calculated transformation temperatures from Liq. 2 to sulfide and the remelting point agree well with the in situ observation by CSLM.

Figure 11 shows the calculated phase boundaries of Liq. 2 and sulfide equilibrated in the three-phase regions of Fe + Liq. 2 + sulfide or the two-phase regions of Fe + Liq. 2 and Fe + sulfide. As shown in Table 1, the fine spherical sulfide in the Fe–1Cr–0.05S alloy contains 11.8 mass% Cr and 12.7 mass% Cr at 1200°C and 1250°C, respectively, and these compositions correspond to the two-phase region of γ + Liq. 2 in Fig. 11, which shows good agreement with the calculated phase boundaries. Therefore, the sulfide in the Fe–1mass%Cr–0.05mass%S alloy is formed from the liquid phase through the remelting reaction (δ → γ + Liq. 2).

4.2.2. Eutectoid Reaction

The Cr composition in the fine rod-like sulfide in the Fe–8mass%Cr–0.05mass%S alloy is 53.8 mass% Cr and 53.1 mass% Cr at 1250°C and 1200°C, respectively, as listed in Table 1, and these compositions correspond to the

| Temp. / °C | Fe-1Cr-0.05S | Fe-8Cr-0.05S |
|------------------|------------------|------------------|
| 1200             | 51.0 (39.5)      | 51.8 (43.1)      |
| 1250             | 48.7 (37.6)      | 53.1 (42.7)      |

The value in parentheses shows at.%
two-phase region of $\gamma +$ sulfide in Fig. 11. Since the melting point of CrS is 1565°C as reported by Vogel et al.,\(^{26}\) that of Cr-rich sulfide in Table 1 should be higher than 1250°C. Therefore, the sulfide in Fe–8mass%Cr–0.05mass%S alloy is not formed from the liquid phase but rather from the solid phase through the eutectoid reaction ($d \rightarrow \gamma +$ sulfide) as shown in Fig. 9. The crystallographic feature between the rod-like sulfide and matrix could not be confirmed by the TEM observation.

5. Summary

The morphology of three types of sulfide formed during the solidification and the heat treatment in the Fe–Cr–S ternary alloys was investigated and the formation mechanisms of these sulfides were examined in relation to the phase diagrams. The results obtained are as follows:

1. Three types of sulfides with morphologies defined as the cell wall, globular and fine particle type are formed.

2. The Cr content in sulfide increases with increasing Cr content in alloys, and the morphology of sulfide changes from cell wall to globular. This is attributed to the change in the nature of the phase diagram from the eutectic type to the monotectic type with increasing Cr content.

3. Two types of fine particle sulfide are formed through the remelting reaction ($d \rightarrow \gamma +$ Liq. 2) in less than 5 mass% Cr alloys and through the eutectoid reaction ($d \rightarrow \gamma +$ sulfide) in 5 to 13 mass% Cr alloys.

4. The in situ observation by the confocal scanning laser microscope reveals that the fine spherical sulfide is formed through the remelting reaction in the Fe–Cr–S ternary alloy with less than 5 mass% Cr.

5. The fine rod-like sulfide formed through the eutectoid reaction changes to the spherical type with keeping time at elevated temperatures.

6. The morphological changes of sulfide can be explained by the phase diagrams.

REFERENCES

1) C. E. Sims and F. B. Dahle: Trans. Am. Foundrymen’s Ass., 46 (1938), 65.
2) H. Kaneko, T. Nishizawa and K. Tamaki: J. Jpn. Inst. Met., 25 (1961), 560.
3) I. Takamura and S. Mizoguchi: Proc. 6th Int. Iron and Steel Cong., Vol. 1, ISIJ, Tokyo, (1990), 591.
4) H. Takechi: Materia Jpn., 30 (1991), 677.
5) K. Yamamoto, T. Hasegawa and J. Takamura: Tetsu-to-Hagané, 79 (1993), 1169.
6) K. Isobe, Y. Kusano and H. Maede: Tetsu-to-Hagané, 80 (1994), 890.
7) K. Ono and T. Kawano: Denki Seiko, 51 (1980), 122.
8) T. Koga, T. Shimizu and M. Okabe: Denki Seiko, 67 (1996), 75.
9) H. Kaneko, T. Nishizawa and K. Tamaki: J. Jpn. Inst. Met., 27 (1963), 299.
10) K. Okikawa, H. Ohtani, K. Ishida and T. Nishizawa: ISIJ Int., 35 (1995), 402.
11) K. Okikawa, K. Ishida and T. Nishizawa: ISIJ Int., 37 (1997), 332.
12) H. Hasegawa, K. Nakajima and S. Mizoguchi: Tetsu-to-Hagané, 87 (2001), 433.
13) N. Sano, M. Iwata, H. Hosoda and Y. Matsushita: Tetsu-to-Hagané, 13 (1971), 124.
14) T. J. Baker and J. A. Charles: J. Iron Steel Inst., 209 (1972), 702.
15) H. Fredriksson and M. Hillert: Scand. J. Metall., 2 (1973), 125.
16) K. Okikawa, Y. Kawashita, H. Ohtani, K. Ishida and T. Nishizawa: J. Jpn. Inst. Met., 59 (1995), 1207.
17) Y. Ohuchii, K. Okikawa, I. Ohnuma and K. Ishida: Mater. Sci. Forum, 284–286 (1998), 509.
18) K. Okikawa, S.-I. Sumi and K. Ishida: Z. Metallkd., 90 (1999), 215.
19) K. Okikawa, S.-I. Sumi and K. Ishida: J. Phase Equilibria, 20 (1999), 215.
20) K. Okikawa, T. Ikeshoji, H. Mitsui and K. Ishida: Mater. Res. Soc. Symp. Proc., 580 (2000), 369.
21) K. Okikawa, H. Mitsui, H. Ohtani and K. Ishida: ISIJ Int., 40 (2000), 182.
22) H. Ohtani, K. Okikawa and K. Ishida: High Temp. Mater. Process., 19 (2000), 197.
23) H. Chikama, H. Shibata, T. Eki and M. Suzuki: Mater. Trans. JIM, 37 (1996), 620.
24) T. Hanamura, H. Shibata, Y. Waseda, H. Nakajima, S. Torizuka, T. Takanashi and K. Nagai: ISIJ Int., 39 (1999), 1188.
25) H. Okikawa: Technology Report, Tohoku Univ., 48 (1983), No. 1, 7.
26) R. Vogel and R. Reinbach: Arch. Eisenhüttenwes., 11 (1938), 457.