Note

Formation of Monotectic Sulfide in Free-Machining Ferritic Stainless Steels during Solidification

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The sulfide morphology in free-machining ferritic stainless steel was investigated and the mechanism of monotectic sulfide formation was evaluated. Metastable monotectic sulfide containing oxygen was mainly observed. The decrease in sulfide activity by dissolved oxygen can be considered to contribute to the formation of monotectic sulfide. It is considered that the oxygen content greatly affected the formation of monotectic sulfide because of the generation of oxide inclusions ($\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO--Cr}_2\text{O}_3$), which became the nucleation sites for liquid sulfide in the monotectic reaction. Microsegregation of sulfur and oxygen during solidification reduces the interfacial energy between liquid and monotectic sulfide. Nucleation plays an important role in the selection of sulfide morphology.

KEY WORDS: ferritic stainless steel; sulfide; eutectic; monotectic; solidification; microsegregation.

1. Introduction

SUS303 and SUS430F stainless steels contain more than 0.15% sulfur, which improves their machinability. The machinability of stainless steels is basically enhanced by an increase in the amount of sulfide.^{1–3)} It is also affected by the distribution and composition of inclusions.^{4–9)} For instance, larger spherical sulfides with a low aspect ratio are favorable for chip disposability and tool life.^{10,11)}

Oikawa *et al.*^{12,13)} showed that manganese sulfide (MnS) in steel formed during solidification can be classified into stable eutectic ($\text{L} \rightarrow \text{Fe(s)} + \text{MnS(s)}$) and metastable monotectic ($\text{L} \rightarrow \text{Fe(s)} + \text{MnS(l)}$), and non-metallic inclusions, which become nucleation sites for sulfides, influence the selection of sulfide type. However, there are few studies on the sulfide morphology in free-machining ferritic stainless steel with the single-phase ferrite solidification mode. Oikawa *et al.*¹⁴⁾ investigated the effect of chromium and manganese content on the sulfide type. Monotectic sulfides formed at a lower manganese content ($\text{Mn/S} < 3.5$). However, observation using a confocal scanning laser microscope revealed that granular sulfides, which seemed to be monotectic, were formed in Fe-30%Cr-0.3%S-1.5%Mn-0.7%Si alloy.¹⁵⁾ The effect of manganese content on sulfide morphology has not been clarified.

Moreover, the effects of addition of deoxidation elements

(C, Si, Ti, Al) on the sulfide morphology in ferritic stainless steel have been studied by Oikawa *et al.*¹⁶⁾ However, the effect of oxygen content on sulfide morphology has not been elucidated. It is very important to clarify how the selection between monotectic and eutectic occurs during solidification, which forms the basis of sulfide shape control. We investigated the effect of alloying elements on sulfide morphology using cast SUS430F and examined the factors causing sulfide morphology selection.

2. Experimental Procedure

Table 1 shows the chemical composition of the specimens used in this study. Manganese content was varied according to Ref. 14). Aluminum was added for deoxidation in several specimens (F2 and F4). Each sample was obtained from the middle part of the ingot (100 mm square and 170 mm height) cast in a 16 kg vacuum induction-melting furnace. MgO crucible was used for melting. The target tapping temperature was determined in order to obtain 100 K superheating, and then each casting was performed within plus or minus 10 K of that.

First, the sulfide morphology was observed from the surface layer to the inside of the ingot, mainly 30 mm from the surface, using an optical microscope. Next, the morphology and composition of the inclusions (sulfides and oxides) were examined by scanning electron microscopy equipped with an energy-dispersive X-ray spectrometer (SEM-EDS).

3. Results and Discussion

3.1. Sulfide Morphology in Cast Ingots

Similar to previous studies,^{12–17)} two types of (Mn,Cr) S sulfides were observed: (i) eutectic (consisting of fine rod-like sulfides) and (ii) monotectic (globular sulfides). Figure 1 shows the distribution of sulfides in the ingots. In the entire region, from the surface layer to the inside, monotectic sulfides were observed at the interdendritic part for F1, F2 and F3. It is supposed that engulfment of monotectic sulfides at the solidifying interface caused by the interface tension gradient¹⁸⁾ does not occur in high-sulfur steel. However, eutectic sulfides were present in every part of the ingot for F4. In addition, fine sulfides, which seemed to be eutectic, were found in a small portion for F2. It is considered that F2 is near the critical condition of sulfide morphology selection.

Figure 2 shows examples of the inclusions observed by SEM. $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO--Cr}_2\text{O}_3$ oxides surrounded by monotectic sulfides were found in F1 and F3. Liquid-phase oxides can act as a nucleation site of monotectic liquid sulfide. Oxygen was also present in the sulfide (0.5–7 mass%, mainly 1–2 mass%). On the other hand, the oxide inclusion formed in F4, with added aluminum, was Al_2O_3 . Al_2O_3 was also observed in F2 with aluminum deoxidation. It is suggested that solid inclusions act as a nucleation site for stable eutectic MnS (s).^{12,13,19)} However, eutectic sulfide was not

Table 1. Chemical composition of materials.

	(mass%)									
	C	Si	Mn	P	S	Ni	Cr	Al	T.O	N Mn/S
F1	0.027	0.33	0.48	0.021	0.30	0.27	16.0	0.001	0.015	0.012 1.6
F2	0.027	0.35	0.51	0.019	0.29	0.27	16.1	0.009	0.006	0.011 1.8
F3	0.028	0.36	0.98	0.021	0.31	0.27	16.1	0.001	0.015	0.012 3.1
F4	0.026	0.36	0.95	0.021	0.33	0.27	16.1	0.015	0.008	0.011 2.9

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Fig. 1. Typical sulfide morphologies observed in this study (30 mm from the surface).

Fig. 2. SEM images of sulfides in ingots (30 mm from the surface).

observed in F2. $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO--Cr}_2\text{O}_3$ oxide, nucleation site of monotectic sulfide, could not be found in F2.

Oxide composition at liquidus temperature (T_L) for samples F1 and F2 was estimated using Thermo-Calc software.²⁰⁾ Calculation was carried out for the Fe–Cr–Ni–C–Si–Mn–S–Al–N–O system, and Fe-*DATA* Ver. 6²¹⁾ and *SLAG3* were used as the thermodynamic databases. It was analyzed that SiO_2 and $2\text{SiO}_2\cdot 3\text{Al}_2\text{O}_3$ could form in F1 and that Al_2O_3 could form in F2.

The chemical composition of the monotectic sulfides (F1 and F3) is shown in **Table 2**. The composition of eight sulfides was measured to obtain the average value. The sulfide composition in ferritic stainless steels can be predicted by equilibrium calculation. The calculation at 1 323 K was performed by the computational thermodynamics software *PANDAT*.²²⁾ 1 323 K was chosen in consideration of a composition change of (Mn,Cr)S in the solid state. Components for calculation were the Fe–Cr–Ni–C–Mn–S–N system and the components not described above were disregarded in this calculation. It should be noted that although oxygen

Table 2. Chemical composition of monotectic sulfides.

	(mass%)			
	experiment		calculation*	
	(Cr)	(Mn)	(Cr)	(Mn)
F1	27.3	38.5	23.4	37.3
F3	10.1	56.4	10.5	51.6

* (Mn,Cr,Fe)S calculated at 1 323 K

(0.5–7 mass%) was detected in the monotectic sulfides by SEM-EDS analysis, it was disregarded in this table for comparing the measured data with the calculated values. The chemical composition of monotectic sulfides in F2 (Mn/S=1.8) was similar to that of F1 (Mn/S=1.6).

Oikawa *et al.*¹⁴⁾ showed that monotectic sulfides form in lower manganese content ($\text{Mn} \leq 0.7\%$ in Fe–15%Cr–0.2%S–0.1%Ti alloy, under N_2 atmosphere) and in higher chromium content. In their work, TiN, solid inclusion was formed as an inoculant. They considered the selection of sulfide morphology to be due to thermodynamic equilibrium (Fe–CrS type).^{16,23,24)} Similar experimental results were obtained in the present study. However, the formation of monotectic sulfides could not be explained by thermodynamic calculation in the present study. CrS was not observed as shown in Fig. 2 and Table 2. Therefore, other factors were examined.

3.2. Sulfide Formation during Solidification

Figure 3 shows the relationship between the solid fraction (f_s) and the concentration of sulfur in molten steel for F2 and F4 calculated using *PANDAT* software and the Scheil solidification model. The solid line and broken line in the figure correspond to stable eutectic and metastable monotectic sulfide, respectively. The concentration of sulfur with a small partition coefficient (*e.g.* $k_s=0.07$) increases by microsegregation even after sulfide formation. Stable eutectic sulfides are expected to form in both cases. The difference in the sulfide formation temperature between the eutectic and monotectic phase is small, about 8.1 K in F2 and about 6.6 K in F4, respectively. Although metastable monotectic sulfide formed only in F2, the required undercooling for metastable sulfide formation does not differ in both cases. Sulfide precipitation in F4, which has a higher manganese content, acting as sulfide stabilizing elements, is earlier (smaller f_s , $f_s \geq 0.7$) than that in F2. The location of monotectic sulfides in F2 is estimated to be the final solidification part between the primary dendrite arms ($f_s \geq 0.8$).

Figure 4 shows the microsegregation of elements in liquid phase. Microsegregation was estimated using Thermo-Calc software²⁰⁾ and the Scheil solidification model in the Fe–Cr–Ni–C–Si–Mn–S–Al–N–O system. Liquid composition at T_L was applied for this calculation ignoring inclusion formation. As shown in Fig. 4(a), enriched oxygen content at $f_s = 0.8$ was about 0.062 mass% in F1 and about 0.0038 mass% in F2 (aluminum deoxidation), respectively. Microsegregation of alloying elements (Si, Mn, Cr) in F1 is also indicated in Fig. 4(b). The concentrations of Mn and Cr in molten steel increased remarkably during solidification. It was also calculated that SiO_2 and liquid $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO--Cr}_2\text{O}_3$ inclusions could form in F1, and Al_2O_3 could form in F2 at $f_s = 0.8$, according to the thermodynamic equilibrium calculation for the enriched composition. These results are corresponding to the observed inclusions in Fig. 2. It is suggested that the microsegregation during solidification influences the sulfide morphology selection.

Fig. 3. Microsegregation of sulfur calculated using PANDAT and the Scheil solidification model. (Online version in color.)

Fig. 4. Microsegregation of elements calculated using ThermoCalc and the Scheil solidification model. (Online version in color.)

3.3. Mechanism of Metastable Monotectic Sulfide Formation

The transition from eutectic to monotectic sulfide occurred by decreasing the manganese content ($\text{Mn/S} < 3.5$).¹⁴⁾ Monotectic sulfides were formed at a higher fraction of the solid phase (ferrite) in this work, as shown in Fig. 3. When an increase in the sulfur and oxygen content in the remaining melt reached a certain level by microsegregation, liquid sulfide or oxy-sulfide could be formed by monotectic reaction: $\text{L} \rightarrow \text{Fe(s)} + \text{MnS(l)}$. Oxygen also has a small partition coefficient (e.g. $k_{\text{O}} = 0.02$) and reduces the sulfur activity in molten steel. Stable eutectic reaction could be inhibited by the increase in oxygen content.

It has been reported that globular liquid sulfide forms in the molten steel with high oxygen content.^{25–29)} Complex inclusions and oxy-sulfides were observed in previous works. It is thought that oxygen dissolved in liquid sulfide reduces the sulfide activity and promotes the formation of metastable monotectic sulfides. Oxygen could dissolve in liquid sulfide (monotectic), but not in solid sulfide (eutectic). It is expected that the development of a thermodynamic databank for sulfide and oxy-sulfide in multicomponent systems permit accurate prediction of sulfide morphology control in ferritic stainless steels.

Nucleation plays an important role in the selection between eutectic and monotectic sulfides. Main factor for nucleation is thought to be interfacial energy, which is related to the degree of undercooling. If $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO--Cr}_2\text{O}_3$ inclusions form during solidification, they become the nucleation sites for liquid monotectic sulfide (F1, F3) due to lower interfacial energy.³⁰⁾ Al_2O_3 acts as a nucleation site for eutectic sulfide (F4). However, Al_2O_3 did not work for F2 with aluminum deoxidation. It is not clear if oxides are involved in the formation of all monotectic sulfides. Estimated interfacial energy between liquid iron and MnS(l) was small.^{12,31)} Furthermore, microsegregation of sulfur at

the final stage of solidification could reduce the surface tension of liquid steel, and the interfacial energy between liquid and MnS(l) . It is thought that monotectic sulfide in F2 is preferred to form in a supersaturated liquid because of smaller nucleation undercooling than that of eutectic sulfide. Three types of nucleation behavior were considered in this work.

4. Conclusion

The formation mechanism of metastable monotectic sulfide in free-machining ferritic stainless steels was examined. Microsegregation of oxygen and sulfur during solidification contributes to monotectic sulfide formation. Oxide ($\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MnO--Cr}_2\text{O}_3$) formed during solidification can become the nucleation site for liquid sulfide due to lower interfacial energy. The decrease in the interfacial energy between liquid and monotectic sulfide, which is caused by enriched sulfur during solidification, can also promote the nucleation of monotectic sulfide.

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