Effect of Electroslag Remelting Parameters on Primary Carbides in Stainless Steel 8Cr13MoV

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The solidification microstructure and primary carbides in stainless steel 8Cr13MoV produced by electroslag remelting (ESR) were studied. The microstructure is finer when ESR using lower current intensity or higher cooling intensity. The amount of carbides is larger but the fraction is lower when using lower current intensity in ESR. The current intensity has no effect on the morphology and type of primary carbides. Under the condition of higher cooling intensity, distribution of primary carbides is more even, the size and alloy elements content of primary carbides is smaller. With increasing cooling intensity, the primary carbides change from skeleton-like shape composed of many fine clusters to skeleton-like shape composed of regular and short bar-like crystals, and the internal structure of primary carbides become more compact.

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1. Introduction

Martensitic stainless steels have been widely used in steam engines, high pressure vessels,^{1,2)} knife and scissor products due to their excellent performance, such as high hardness, strength, good wear resistance and corrosion resistance. Among martensitic stainless steels, Cr13 stainless steel is the main material used in knife and scissor industry. In recent years, 8Cr13MoV is developed for high-grade knives and scissors. However, compared with conventional Cr13 stainless steel, many primary carbides were generated in 8Cr13MoV steel due to the increase of carbon to 0.8 mass%, Mo and V contents.

The size and distribution of primary carbides have great influence on the mechanical property of tool steel.^{3–5)} These carbides can easily fall off from steel matrix, causing the edge collapsing of knives and scissors.⁶⁾ It is very important to control the size and distribution of primary carbides in steel used as knife and scissor raw materials. So far, reports about carbides mainly focused on the heat treatment stage.^{7–9)} However, during heat treatment stage, it was difficult to eliminate defects caused by primary carbides.¹⁰⁾ Primary carbides can also precipitate during ESR process. So, it was the fundamental way to control the carbides in this process.

In this study, effects of current intensity and cooling intensity on microstructure and primary carbides during ESR process were studied by optical microscope, SEM with energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). Moreover, the mechanism of the effect of current intensity and cooling intensity on primary carbides distribution and morphology was discussed.

2. Experimental

8Cr13MoV steel produced by vacuum induction furnace was used as consumable electrode. The chemical composition is shown in Table 1. The diameter of electrode is 25 mm. The diameter of mold is 40 mm. The experiment was divided

Table 1 Chemical composition of 8Cr13MoV steel (mass%).

C	Cr	Mo	Mn	Si	V	Ni	P	S	Fe
0.775	14.68	0.213	0.458	0.333	0.182	0.157	0.031	0.004	Bal.

Table 2 Operation parameters used in ESR experiments.

Group No.	Sample	Current intensity (A)	Voltage (V)	Cooling water flow (L/h)
1	S1-1	700	24	800
	S1-2	800	24	800
	S1-3	1000	24	800
2	S2-1	1000	24	600
	S2-2 (S1-3)	1000	24	800
	S2-3	1000	24	1000

into two groups, as shown in Table 2. The cooling water flow around crystallizer was steady, while the input current was changed in the first group. In the second group, the input current was fixed, while the cooling water flow rate varied according to a certain rule. Five ESR ingots were obtained in this experiment. Metallographic specimens of 12 mm × 12 mm were taken from middle of the ingot. For microstructural observation, the specimens were etched with Kalling agentia (1.5 g cupric chloride, 33 ml hydrochloric acid, 33 ml alcohol and 33 ml water) and another agentia containing 5 g ferric chloride, 25 ml hydrochloric acid and 25 ml alcohol, respectively. For the statistics of carbides area, the etchant was alkaline supersaturated potassium permanganate solution. For three-dimensional morphology observation of carbide, the etchant was mixed solution of HF and H₂O₂. Carbides were extracted from a round rod sampled from the middle of the ESR ingot. The size of round rod is 40 mm in diameter and 70 mm in length. The electrolyte is a kind of non-aqueous organic solution. The extracted carbides were analyzed by SEM-EDS and XRD to determine their morphology, composition and type.

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3. Results

Figure 1 shows the microstructure of as-cast ESR ingot. The microstructure was composed of ferrite, retained austenite, martensite, primary carbides and secondary carbides. During the solidification of liquid steel in the mold, the martensitic transformation happened due to the high chromium content in steel. However, the martensitic transformation was not complete, there were still much retained austenite. As shown in Fig. 1(a), the white parts are retained austenite which are not eroded. The dark-colored parts with needle shape in austenite are martensite. The dark parts are dyed ferrite. In samples etched by ferric chloride, secondary carbides can be observed on the grain boundary, as shown in Fig. 1(b).

3.1 Effect of current intensity on the microstructure of ESR ingot

As shown in Fig. 2 (a) and (b), the white area was retained austenite, while the dark area was ferrite which was eroded. The dark-colored martensite and austenite were coexisting. Three images showed obvious isometric dendrite, while the isometric dendrite in sample S1-1 and S1-2 was finer. This is because the input power to molten pool is lower under low

Fig. 1 Microstructure of as-cast 8Cr13MoV steel: (a) etched by Kalling agentia, (b) etched by ferric chloride, hydrochloric acid and alcohol.

Fig. 2 The microstructure and distribution of carbides of ESR ingots produced under different cooling intensity: (a) microstructure of sample S1-1, (b) microstructure of sample S1-2, (c) microstructure of sample S1-3, (d) carbides in sample S1-1, (e) carbides in sample S1-2, (f) carbides in sample S1-3.

current. The temperature of slag pool was low, and the metal molten pool is shallow. The local solidification time is shorter, so interdendritic spacing can be shortened and dendrites are too late to grow up.¹¹⁾ In ERS process, the growth of secondary dendrites was suppressed due to the effect of current,¹²⁾ so the growth of secondary dendrites is not obvious in three samples.

3.2 Effect of current intensity on the primary carbides in ESR ingot

Figure 2(d)–(f) show the primary carbides in ESR ingot produced at different current. The carbides in sample S1-1 and sample S1-2 precipitated more uniformly, and they are granules distributed discontinuously. The size was smaller than that in sample S1-3. Therefore, these carbides were more easily to dissolve into the matrix during the subsequent hot working.¹³⁾ In sample S1-3, the carbides were polygonal. Some carbides even connected with each other. The basic parameters and characteristic parameters of primary carbides were analyzed by image analysis. The characteristic parameters include: volume fraction V_V , the number of carbides per unit volume N_V , the average diameter of carbides $\bar{D}$ and the spacing of carbides t_0 .¹⁴⁾ The relationship between them is shown in Table 3. The following parameters can be obtained by the software: length (L) and width (W) of the metallographs, the number (N) of carbides, the area (A) of carbides, the average diameter ($\bar{D}$) of carbides, as shown in Table 3. According to Table 3 and a part of Table 4, characteristic parameters of carbides can be calculated, as shown in Table 4. Comparing characteristic parameters of carbides, it was found that the amount of carbides per volume decreased with increasing current intensity, while the total volume fraction of carbides increased. This illustrated that the total volume of carbides was lower under the lower current intensity. Carbides were smaller and its distribution was more dispersed.

The SEM images of carbides are shown in Fig. 3. There was no obvious difference in the morphology of carbides in these three samples. These carbides presented eutectic structure consisting of short rods. There were big carbides distributed along grain boundaries and small carbides inset in the ferritic matrix.

The carbides extracted from samples under different cur-

Table 3 Characteristic parameters of carbides.

Relation	Unit	The meaning of space characteristic parameters
$V_V = A_A$	%	volume fraction of carbides
$N_V = N_A / \bar{D}$	--	the number of carbides per unit volume
$t_0 = \sqrt[3]{1/N_V}$	μm	spacing of carbides

Table 4 Basic parameters and Characteristic parameters of carbides.

Sample No.	The basic parameters of quantitative metallography					Characteristic parameters of carbides		
	N	$A/\mu\text{m}^2$	$\bar{D}/\mu\text{m}$	$L/\mu\text{m}$	$W/\mu\text{m}$	$V_V/\%$	N_V	$t_0/\mu\text{m}$
S1-1	628	6373.36	10.15	1103.21	815.09	0.71	6.88e^{-5}	24.40
S1-2	532	6257.19	11.50	979.55	734.47	0.87	6.43e^{-5}	24.96
S1-3	567	9945.95	14.95	1103.21	815.09	1.11	4.22e^{-5}	28.72

Table 5 Basic parameters parameters and Characteristic parameters of carbides.

Sample No.	The basic parameters of quantitative metallography					Characteristic parameters of carbides		
	N	$A/\mu\text{m}^2$	$\bar{D}/\mu\text{m}$	$L/\mu\text{m}$	$W/\mu\text{m}$	$V_V/\%$	N_V	$t_0/\mu\text{m}$
S2-1	814	14786.10	18.17	1103.21	815.09	1.64	4.98e^{-5}	27.18
S1-3	567	9945.95	14.95	1103.21	815.09	1.11	4.22e^{-5}	28.72
S2-2	665	8153.58	14.38	1103.21	815.09	0.91	5.06e^{-5}	27.02

Fig. 3 The morphology of carbides under different current intensity: (a) sample S1-1, (b) sample S1-2, (b) sample S1-3.

Fig. 4 XRD pattern of carbides extracted from ESR ingots produced under different current intensity.

rent intensity were analyzed by XRD as shown in Fig. 4. The carbides were confirmed to be Cr_7C_3 and $(\text{Cr}_{11.9}\text{Fe}_{4.3}\text{Mo}_{0.1})\text{C}_3$ and $(\text{Cr}_{18.93}\text{Fe}_{4.07})\text{C}_6$ in both samples, which belonged to M_7C_3 type. This indicated that the change of current intensity had no effect on the type of carbides. In fact, in the Fe based alloy, there is no pure Cr_7C_3 , and the dissolution of Fe in Cr_7C_3 fluctuates within a certain range. However, the PDF database of XRD program does not contain all types of M_7C_3 .

3.3 Effect of cooling intensity on the microstructure of electroslag ingot

As shown in Fig. 5 (a) and (b), cooling intensity had a significant effect on the solidified microstructure of the steel. The dendrite is coarsened under lower cooling intensity. The secondary dendrite grew obviously. The overall growth had certain direction. There were many isometric crystals existed in the samples under high cooling intensity. These isometric crystals distributed uniformly, and the secondary dendrite is smaller with a petal shape.

3.4 Effect of cooling intensity on the carbides

As shown in Fig. 5 (d)–(f), the distribution of carbides in steel produced under low cooling intensity was extremely uneven, and primary carbides were highly concentrated in some places. In addition, network structure was formed between some primary carbides. With increasing cooling intensity in

Fig. 5 The microstructure and distribution of carbides of ESR ingots produced under different cooling intensity: (a) microstructure of sample S2-1, (b) microstructure of sample S2-2, (c) microstructure of sample S2-3; (d) carbides in sample S2-1, (e) carbides in sample S2-2, (f) carbides in sample S2-3.

Fig. 6 The morphology of carbides under different cooling intensity: (a) carbide in matrix of sample S2-1, (b) carbide in matrix of sample S2-3, (c) carbides extracted from S2-1, carbides extracted from S2-3.

ESR process, the distribution of carbides was more uniform.

As shown in Table 5, the metallographic parameters and microstructural characteristic parameters were calculated. Under lower cooling intensity, the carbides volume fraction V_V is larger. The average diameter $\bar{D}$ was larger, and the spacing of carbides was smaller when the number of carbides per unit volume was equal. With decreasing the cooling intensity, not only the amount but also the size of carbides increased obviously, and the crowding intensity of carbides increased.

The morphology of primary carbides changed obviously under different cooling intensity. Under low cooling intensity, the primary carbides were thick. As can be seen from Fig. 6(a)–(c), the volume of carbides in sample S2-1 was larger than that in other two samples. The typical morphology of carbides extracted from the ESR ingots using anode electrolysis is shown in Fig. 6 (d)–(f). The internal structure of carbides can be seen clearly after electrolysis. The carbides in

sample S2-1 show cluster-like, which connected with many long rod-like carbides. Carbides in sample S2-2 was smaller than that in sample S2-1, and the structure of carbides in sample S2-2 was mostly same with that in sample S2-3, while a small fraction is similar with the structure of carbides in sample S2-1. The carbides in sample S2-3 were skeleton-like, and connected by many granular or short-bar-shaped carbides.

4. Discussions

4.1 The effect of current intensity on the solidification structure and carbides

In ESR operation, the remelting rate is determined by current intensity. With increasing the current intensity, remelting rate is accelerated.^{11,15} According to research, remelting rate has a certain relationship with the local solidification time. With the increase of remelting rate, the local solidification time is shorten first and then increased.^{15,16} Local solidification time can be reflected by the dendritic spacing. Flemings¹⁷ indicated that, local solidification time and dendrital axial spacing have the following relation:

$$\log d = k_1 + k_2 \log T$$

where d is the dendrital axial spacing, μm , k_1 and k_2 are constant and determined by the content of alloy element; T is the local solidification time, min. According to above formula, with increasing the local solidification time, the dendrital axial spacing increases. The interdendritic spacing was measured using image analysis software, which is shown in Fig. 7. Twenty data points were randomly obtained in each sample, and the distribution of interdendritic spacing was revealed. In Fig. 7, the upper and lower endpoint of vertical line represented the maximum and minimum value of interdendritic spacing, respectively. The black point the vertical line represented the average value. The interdendritic spacing of S1-1 is much smaller than that of other two samples, which demonstrated that the local solidification time of ESR ingot using lower current is shorter than that using higher current. A homogeneous microstructure with less composition segregation can be obtained by shortening interdendritic spacing. The formation of primary carbides is closely related to the composition segregation¹⁸. The segregation degree of S1-1 is smaller, which leads to smaller amount of carbides. In addition, because of most carbides are likely to precipitate at grain boundary, carbides can distribute more diffusely when the grain size is more smaller.

Fig. 7 Statistical chart of the interdendritic spacing.

4.2 Effect of cooling intensity on the solidification structure and carbides

The local solidification time was directly influenced by cooling intensity. As shown in Fig. 7, with the increase of cooling intensity, the dendritic spacing shortened, which leads to less segregation. Therefore, increasing cooling intensity and decreasing current intensity have consistent effect on the microstructure.

It is accepted that the solid/liquid interface structure changes from faceted plates to non-faceted dendrites with the increase of undercooling. This view was verified in Al-Si alloy.¹⁹ Zhou¹⁴ has put forward the same assumption in the research of carbides in M2 high speed steel, and he confirmed that the diffraction intensity of carbides under different cooling intensity had large difference. Improving cooling intensity can result in the increasing of undercooling directly. The sample S2-1 and S2-3 were chosen to study the effect of cooling intensity on carbides for the largest difference in cooling intensity between these two samples. The carbides extracted from steel samples were analyzed by XRD. As shown in Fig. 8, the intensity of main diffraction peak did not change significantly. This proved that the crystallography surface did not change significantly.

According to metal solidification principle, the preliminary analysis suggests that the morphology of carbides is affected by cooling intensity, grain size and segregation degree. Thermo-calc was employed to calculate the equilibrium and non-equilibrium phase diagram for 8Cr13MoV steel. As shown in Fig. 9, 8Cr13MoV belongs to hypereutectoid steel. The primary austenite precipitates from liquid steel first. Whereafter, because of composition segregation, the composition of liquid phase meets the characteristic of hypolitectic alloy when the carbon content at solidification front reaches about 1%. As the austenite continues to precipitate from liquid steel, carbon content at solidification front keeps increasing, and eutectic reaction ($L \rightarrow M_7C_3 + \gamma$) can take place. M_7C_3 carbides precipitated from liquid steel directly in non-equilibrium condition, as shown in Fig. 9(b).

As shown in Fig. 10, the shadow area around dendritic crystal represents solute enrichment area. As for S2-1, the cooling intensity is low. The grain size is large and the dendrite spacing is wide. When the composition of residual liquid steel reaches eutectic point, primary carbides will precipitate along pre-existing austenite. Because of the concentration gradient of carbon content, the premier carbides may grow up from one grain boundary to other grain boundaries.

Fig. 8 The XRD pattern of carbides under different cooling intensity.

Fig. 9 Phase transformation in 8Cr13MoV steel calculated by Thermo-calc: (a) equilibrium phase diagram, (b) non-equilibrium phase diagram.

Fig. 10 Schematic diagram for the growth of primary carbides: (a) S2-1, (b) S2-2; λ : the distance between eutectic structure of carbides.

This is the reason for the directional growth of carbides, which is shown by arrows in Fig. 10(a). However, the concentration gradient of element content is low in some area, the growth of carbides has no directivity, which is shown by circle in Fig. 10. The cooling intensity of S2-2 is large. The grain size is small and the dendrite spacing is narrow. The growth of carbides will lose its directivity due to more areas with lower concentration gradient and more grain boundaries.

In addition to the overall appearance of carbides, the compact degree of eutectic structure was different in ESR ingots produced under different cooling intensity. When the eutectic reaction proceeded, solute atoms (C, Cr and Mo) were discharged from liquid steel and formed another phase, *i.e.*, M_7C_3 carbides. Therefore, the radial diffusion along solid-fluid interface perpendicular to the primary carbides will become dominant and effectively decrease the solute concentration on the solidification front. This radial diffusion caused the decrease in the distance (λ) between eutectic structures of carbides.²⁰ Lu *et al.*²¹ studied the microstructure of directionally solidified Fe-Cr-C eutectic alloy. According to the result $\lambda = 7.94 \times R^{-0.19}$, obtained by Lu (where R is cooling rate), λ decreased with increasing cooling intensity obviously. Trivedi *et al.*²⁰ obtained a similar trend based on experimental work. With increasing cooling intensity, the segregation of solute atoms was decreased, consequently the solute concentration in remaining liquid steel decreased. This effect was similar with radial diffusion of solute atoms. Therefore, with increasing cooling intensity, λ decreases and the eutectic structure of carbides becomes more compact.

5. Conclusions

(1) The solidification microstructure of stainless steel 8Cr13MoV produced by ESR is composed of ferrite, retained austenite, martensite, M_7C_3 primary carbides and $M_{23}C_6$. The M_7C_3 primary carbides locate around grain boundary and in ferrite matrix.

(2) The decrease in current intensity or increasing cooling

intensity in ESR process gave many advantages, such as homogenization and refinement of microstructure, homogenization of carbides distribution, and decrease in the fraction of carbides.

(3) The change of current intensity and cooling intensity cannot change the types of carbides, while the eutectic structure of carbides can become more compact with increasing cooling intensity. The carbides transform from skeleton-like shape composed of many fine rod-like to skeleton-like shape composed of many granular or short-bar-shaped carbides with the increase of cooling intensity because of the decrease of segregation degree.

(4) Increasing the cooling intensity is practicable for improving the primary carbides, which will be favorable for the crush and dissolution of primary carbides during hot rolling of steel, as well as for obtaining better microstructure of steel.

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