

The Effect of Slag Types and Melting Rate on Electro-Slag Remelting (ESR) Processing

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Abstract

In this research, the influence of chemical composition of slags and the melting rate on the impurity of commercial grade iron in ESR processing has been investigated.

The chemical composition and microstructure studies were evaluated, using spectrophotometer, OM and EDX analyses attached to SEM.

The results show that ESR process has successfully reduced the amount and size of inclusions. In some cases, sulfide inclusions were not observed and the size of other inclusions was reduced down to 10 μm , whereas in primary electrodes the size of inclusion was up to 100 μm . An increase in the slag basicity up to a critical point and a decrease in the melting rate caused better desulfurization ability of the slags. However, the increase in the time of process was governed by the melt temperature and fluidity.

Keywords: Electro slag remelting (ESR), Pure iron, Desulfurization, Inclusion

Introduction

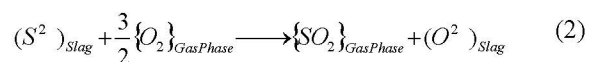
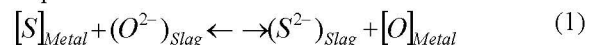
Electro Slag Remelting (ESR) is one of the remelting processes in the field of metal refinery. In this process, slag plays various roles such as heat generation, protection of melt, and chemical refining. The use of slags in this work consisted of $\text{CaF}_2/\text{CaO}/\text{Al}_2\text{O}_3/\text{MgO}/\text{SiO}_2$ where the composition of slag affects the composition, amount, size of inclusions, and alloying elements¹.

In clean alloy production, the amount of impurities such as sulfur, metallic, and nonmetallic oxide must be very low. These impurities affect mechanical behaviors in alloys. As a result, removal of these impurities is very important. Sulfur content in iron ingots can be reduced to 0.02 wt% by using traditional methods such as VIM, VOD and VD. In production of maraging steel, the sulfur concentration must be less than 0.004 wt%. This is achievable by using an ESR process, which is a well-known method in this field.

Less sensibility to primary ingot quality, desired and specified reactions, and economical aspects are some of the benefits of this process².

In the ESR process, desired reactions and floatation of various inclusions in the melting slags take place to decrease impurities like sulfides in the alloys, and subsequently this will lead to improve properties of the alloy. It is clear that sulfide inclusions are doughy in hot working temperature. Furthermore, their elongation in the direction of the applied force decreases mechanical properties and lifespan of samples.

Desulfurization could occur with a chemical reaction between the melt and slag. The following reaction can be proposed for the desulfurization sequence³.



As indicated in equation (1), by decreasing the amount of oxygen in the melt and increasing the slag, the desulfurization efficiency will be improved. In the end, sulfur content in the slag reacts with the oxygen in the environment and produces sulfur dioxide gas, equation (2). Therefore, oxygen plays an important role in this process⁴.

Other important factors are basification and melting rate. According to Bonneviante, basification factor can be considered as:

$$B = \frac{\text{CaO} + \frac{2}{3}\text{MgO}}{\text{SiO}_2 + \text{P}_2\text{O}_5 + \frac{1}{2}(\text{Al}_2\text{O}_3 + \text{FeO} + \text{MnO})} \quad (3)$$

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Where B is the basification factor⁵⁾. Reducing the melting rate and increasing the reaction time between metal and slag causes desulfurization to be carried out more efficiently. Parameter B also is limited by a decrease in temperature and fluidity⁶⁾.

CaO has excellent properties of sulfur absorption, but due to its high melting point it can't use more than 30 percent in remelting process. Traditional slags presently used in ESR have relatively high melting points. Using these slags will result in a low reaction rate and low lime utilization efficiency. Addition of CaF₂ to CaO-based slags can significantly reduce the slag melting point and hence improve the kinetics of the reactions. Al₂O₃ and SiO₂ improve electrical resistance and MgO increases the slag basisification⁷⁾.

In this work the suitable slags containing the various percent age of CaO, CaF₂, Al₂O₃, SiO₂ and MgO were prepared to identify the effect of the chemical composition of slags on desulfurization.

Experimental Procedures

First, primary electrodes were cast. Then they were forged to reach 80 mm diameter and cut in 50 cm lengths. The chemical compositions of these electrodes are given in Table 1.

The ESR device has the chromia-magnesia brick-made crucible, which is 250 mm in width and length, and 500 mm in depth, and has a steel plate in the bottom for electric conduction. During the process, molten drips were collected in the bottom up to 50 kg of weight. Finally, movable crucible was rotated and molten metal was cast into the permanent mould having the dimensions of $\Phi 200 \times 100$ mm; hence this device is also named ESC. Its model is YW159A, which was designed by Ukrainian company (Paton Co.).

Eight different slags, which have different properties, were prepared to determine the role of chemical compositions in slags. The slag

compositions should have a proper combination of desulfurization effect, good conduction, opportune density and low cost so that triplet system of CaO-CaF₂-Al₂O₃ can be selected. It is evident that the melting point of slags shouldn't be higher than that of primary electrodes (~1500°C). Otherwise, primary slag melting, that has high electric resistance and is a purifying layer, won't be produced. Therefore, concerning this matter and other research results, some multi-system slags were chosen, which are illustrated in Table 2.

Raw materials were milled completely before mixing to uniform the slags. This act, due to faster formation of eutectic zone, helps easier slag melting⁸⁾. Before melting, 5 kgs of the prepared slags were heated in a resistance furnace at 700°C for two hours to dry completely.

For studying the melting time effect (10 minute to 60 minute performed), the chemical composition of the used slag was invariable (i.e. No. 5). Different melting times were controlled with a change of voltage and current intensity. In 60 minutes melting process, low fluidity and cast defects were observed. Hence, after a long process, the graphite electrodes were used continuously without temperature and/or time limits. In addition, during all of the melting processes, small pieces of aluminum were added to the melt for deoxygenation.

The SEM (scanning electron microscope, model Cambridge stereo scan 360) equipped with EDX, was used for microstructure studies. Also, shape, size and distribution of inclusions were determined with an image analyser, BUEHLER model OMNIMET with Featurscan softener according to ASTM E1122. Furthermore, for chemical analysis, a quantometer model ARL 3465 was used. The results have been taken from three different areas (edge, center, intermediate) of the specimens and the average of these three points was reported.

Table 1. Chemical composition of iron primary electrode for remelting process (wt.%).

C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu	Co	Al	Fe
0.01185	0.00325	0.02019	0.01052	0.15493	0.08067	0.11603	0.01846	0.00096	0.11595	0.01008	0.01112	Rem.

Table 2. Chemical composition of slags (wt.%).

Slags No.	CaO	CaF ₂	Al ₂ O ₃	SiO ₂	MgO
1	30±1.5	70±2.5	0	0	0
2	30±2.5	50±2.5	15±1.5	3±0.5	2±0.1
3	30±1.5	40±1.5	30±1.5	0	0
4	30±2.5	30±2.5	33.5±2.5	1.5±0.1	3±0.1
5	30±2.5	15±2.5	50±2.5	1.5±0.1	2±0.1
6	20±1.5	70±1.5	0	10±1.5	≤0.08
7	20±1.5	60±2.5	10±1.5	10±1.5	0
8	15±1.5	70±2.5	15±1.5	0	0

Table 3. Chemical composition of remelted samples with different slags in 20 minutes time (wt.%).

Comp.	C	Si	S	P	Mn	Ni	Cr	Al	Fe	Slag type	Basicity
Sample 1	0.01690	0.00041	0.00349	0.00177	0.01420	0.09054	0.02524	0.00701	99.6062	70F/30/0/0/0	B ₁ = ∞
Sample 2	0.01226	0.00142	0.00264	0.00198	0.02288	0.08860	0.03619	0.00416	99.5595	50F/30/2/15/3	B ₂ = 3
Sample 3	0.02199	0.00337	0.00553	0.00152	0.04530	0.08116	0.06765	0.01883	99.5298	40F/30/0/30/0	B ₃ = 2
Sample 4	0.01324	0.00671	0.00657	0.00138	0.00974	0.08132	0.02329	0.00655	99.6823	30F/30/3/33/2	B ₄ = 1.75
Sample 5	0.01494	0.00843	0.00769	0.00174	0.02398	0.08942	0.08288	0.02537	99.3602	15F/30/2/50/2	B ₅ = 1.18
Sample 6	0.01003	0.00538	0.00393	0.00238	0.05761	0.07974	0.06619	0.00326	99.6246	70F/20/0/0/10	B ₆ = 2.15
Sample 7	0.02110	0.00831	0.00579	0.00167	0.01232	0.08735	0.02605	0.00199	99.6563	60F/20/0/10/10	B ₇ = 1.33
Sample 8	0.00817	0.00526	0.00513	0.00041	0.01209	0.08762	0.02576	0.00188	99.6595	70/15/0/15/0	B ₈ = 1.9

Table 4. Chemical composition of samples in different melting rate with 15F/30/2/50/2 slag (wt.%).

Comp.	C	Si	S	P	Mn	Ni	Cr	Al	Fe	Time (Min)	Desulfurization (%)
Sample 1	0.01416	0.00729	0.01775	0.00133	0.01917	0.08151	0.06263	0.00768	99.6243	10	12.08
Sample 2	0.01494	0.00843	0.00769	0.00174	0.02398	0.08942	0.08288	0.02537	99.3602	20	61.91
Sample 3	0.01076	0.00919	0.00545	0.00199	0.03050	0.07907	0.08425	0.05866	99.6288	30	73.00
Sample 4	0.01488	0.01660	0.00049	0.00701	0.04766	0.09108	0.08329	0.08723	99.3641	40	97.57
Sample 5	0.14474	0.02875	0.00018	0.00571	0.06261	0.08522	0.07666	0.02606	99.3736	60	99.10

Results and discussion

a) The effect of different slag types:

Chemical compositions of molten samples with different slag types and constant time (20 minutes) have been given in Table 3. The amounts of sulfur have been decreased considerably in all of the samples. But the maximum decrease was observed in sample 2 (86.7 wt %).

It is clear that ESR process is very suitable for desulfurization but its efficiency depended on conditions such as the amount of basicity of the selected slags. The slag basicity-sulfur wt% curve has been shown in Figure 1. As shown, the sulfur amount decreased when the basicity increased until a specific point due to addition of Ca⁺ cation in molten slag.

After a critical point, the amount of sulfur increased due to the increase in the solubility of sulfur, and therefore the formation of SO₂ reduced. Also, amounts of other elements such as Silicon, Aluminum and Magnesium varied in the samples, as shown in Table 3.

Generally, in proper desulfurization conditions, active elements like Si, Al react with oxygen within the slag and decrease in the molten state. As indicated in equations (1) and (2), an increment in desulfurization increases oxygen content in the slag. Therefore, the active elements react with this excessive oxygen. Total variations of the element depend on slags composition.

For example, as shown in Figure 2, Si content decreases as basicity increases except for sample No.7 that has a very high SiO₂ level. Also, high

Alumina slag (slag No.5) causes increase in the Al content in samples.

b) The effect of melting time:

In this stage, samples with the same slag compositions were melted in different times that were controlled with voltage and current intensity of ESR device.

The amount of alloy elements in the melts have changed due to temperature and melt fluidity variations as shown in Table 4 and Figures 3 and 4.

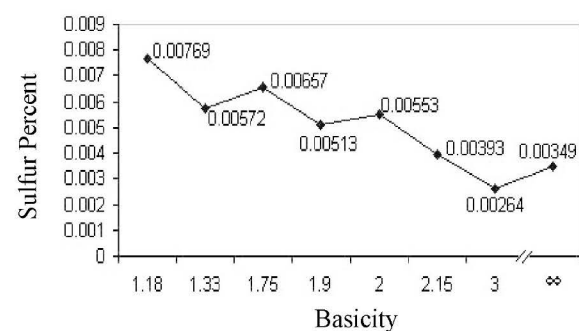


Fig. 1. The effect of slag basicity on sulfur content.

Having a long melting process, due to a need for more time for reaction between slag layer and melted drops of electrode, caused higher solving of inclusions in the slag melt. In sample 5, by increasing the melting time from 20 minutes to 60 minutes, the amount of desulfurization increased from 61.91 wt.% to about 99.1 wt.%. As indicated in Figure 3, an increment in melting time decreased the sulfur content although some problems such as: the

temperature and fluidity reduction, and subsequently deoxygenation decreased, and an increase in the number of voids resulted. In some cases, slags are locked up in the melt during casting. Thus, after 1 hour of melting, graphite electrodes with 100 mm in diameter were used before casting. As a result, carbon contents increased up to 10 times.

The effect of the melting time on Silicon content is the opposite of its effect on sulfur content. As shown in Figure 4, with constant basicity, Si content increased with an increase in the melting time so that Al can have less Gibbs Free Energy (ΔG) and more reduction power than Si. Longer melting times caused better reaction between Silica and the remaining aluminum which didn't participate in deoxygenation due to increase in melt viscosity. Hence, in a long melting process, reduced Silicon dissolves in molten metal and its amounts slightly increase.

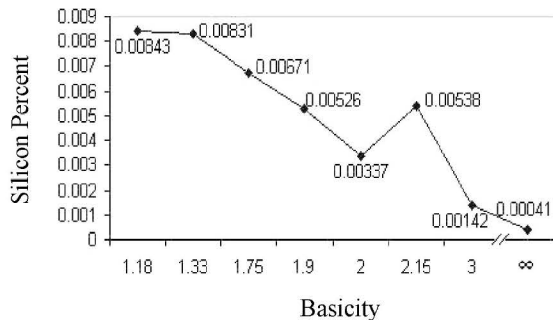
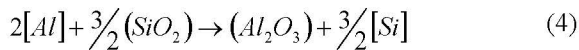


Fig. 2. The effect of slag basicity on silicon content.

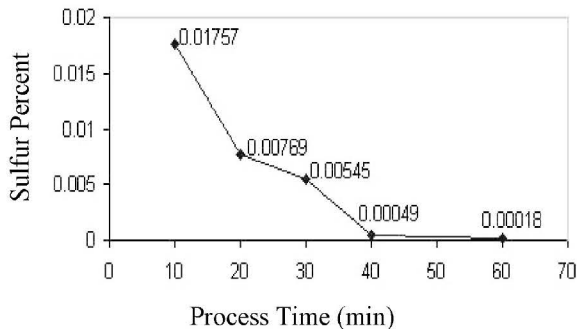


Fig. 3. The effect of process time on sulfur content.

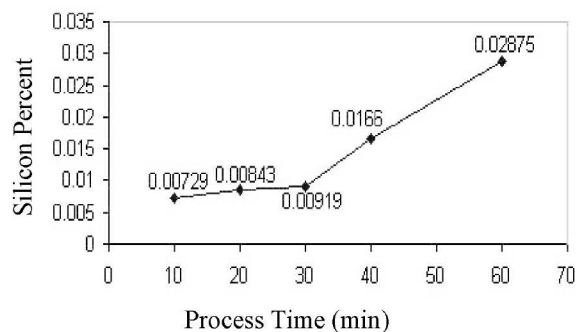


Fig. 4. The effect of process time on silicon content.

c) Microscopical studies:

Figures 5 and 6 show SEM images of samples before and after the ESR process. As is seen, the number of inclusions decreased and were uniformly distributed. The iron grain of initial samples is smaller than remelted samples due to forging processes which are applied on primary electrodes. Also, Figures 7, 9 and 11 show SEM images of some samples that most inclusions contain spherical and polyhedron spherical shapes clustered together. EDX analysis of inclusion corresponded with Figures 8, 10 and 12.

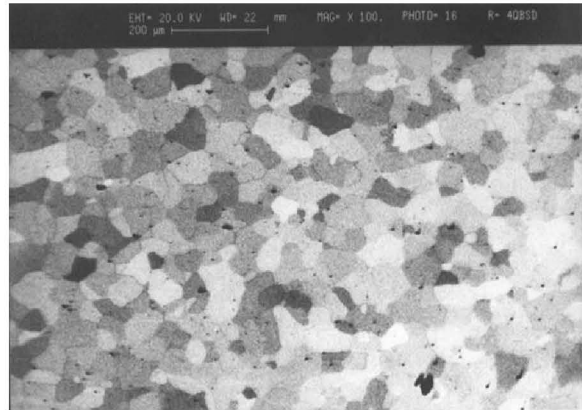


Fig. 5. The SEM image of the initial sample before ESR process.

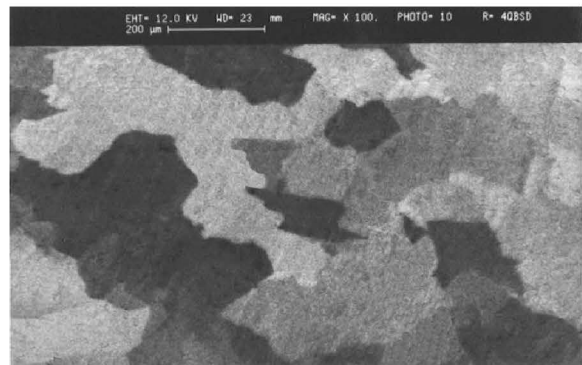


Fig. 6. The SEM image of the samples after ESR process.

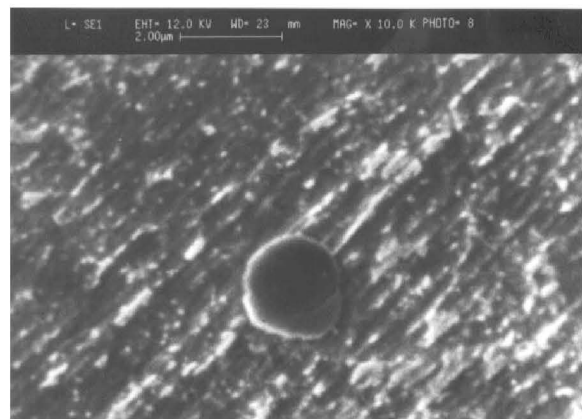


Fig. 7. SEM micrograph of complex Iron-Manganese Sulfide inclusion in sample No. 5.

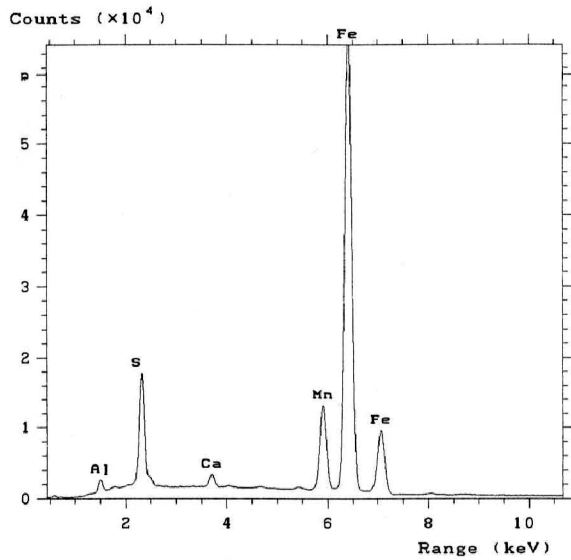


Fig. 8. EDX analysis curve of complex iron-manganese sulfide inclusion.

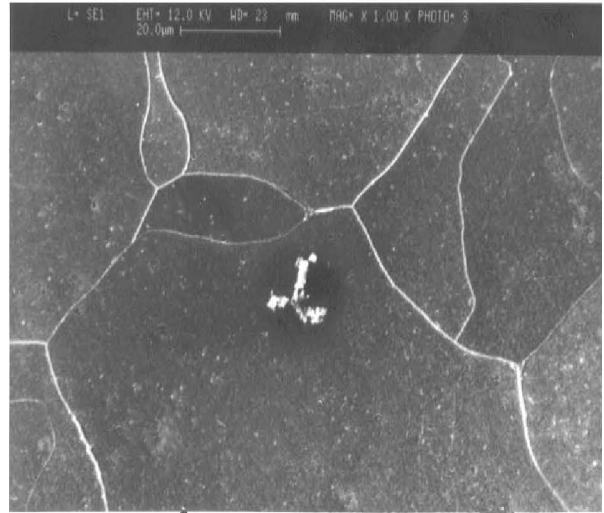


Fig. 11. SEM micrograph of silica inclusion in sample No. 7.

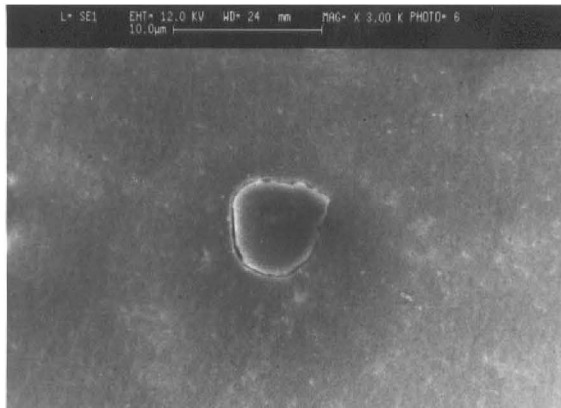


Fig. 9. SEM micrograph of alumina inclusion in sample No. 3.

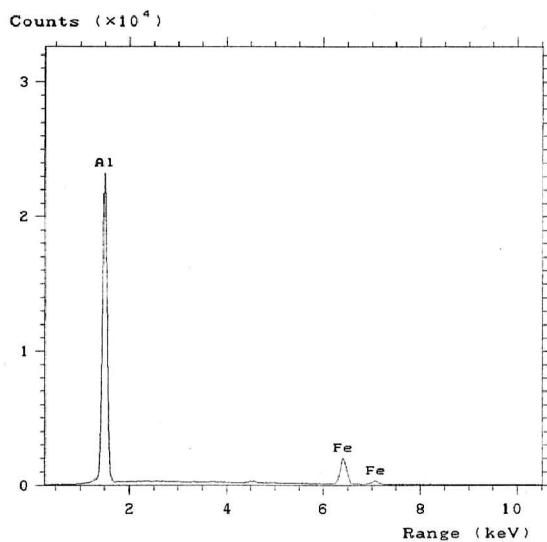


Fig. 10. EDX analysis curve of alumina inclusion.

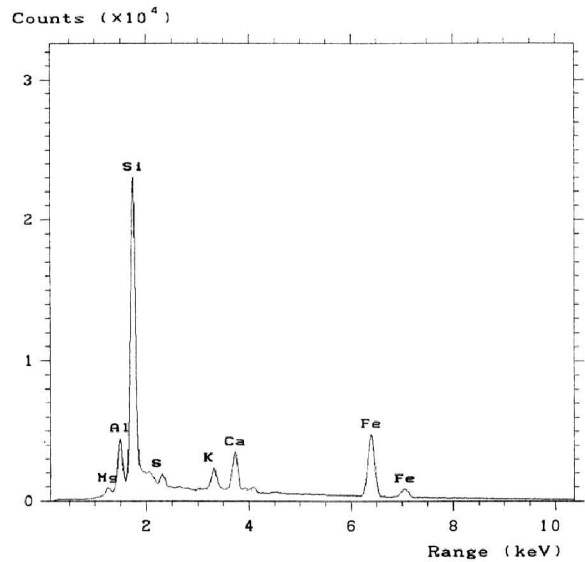


Fig. 12. EDX analysis spectra of silica inclusion.

SEM observation and EDX analysis showed that inclusion types are usually sulfide, alumina and silica. Sulfide inclusions decreased sharply and were omitted in some slag compositions.

Also, the amounts of other inclusions were changed by slag compositions and the condition of the process. For example, in some cases, alumina inclusions slightly increased due to addition of Al to the slag for more deoxygenation.

The image analyser results, before and after ESR processes, are given in the same order in Table 5. As is shown, average inclusion diameters sharply decreased from 14 μm to 5 μm in a 0.005 mm² area.

Table 5. The result of image analyser studies (wt.%).

Sample No.	Slag type	Number of inclusion (in 0.005 mm ²)	Average diameters (μ)	Average ratio (Length/Wide)	Inclusion surface fraction (%)
Initial	Without slag	11	14	1.68	33.86
1	70F/30/0/0/0	4	3.67	1.42	0.84
2	50F/30/2/15/3	6	4.91	1.40	2.27
3	40F/30/0/30/0	8	3.35	1.58	1.41
4	30F/30/3/33/2	6	2.87	1.28	0.77
5	15F/30/2/50/2	3	5.31	1.66	1.32
6	70F/20/0/0/10	7	3.72	1.40	1.52
7	60F/20/0/10/10	4	4.22	1.51	1.11
8	70F/15/0/15/0	6	4.16	1.31	1.63

Conclusions

- 1- Optimum condition (i.e. high desulfurization, low number and size of inclusion, good distribution) was observed in sample 2 (50F/30/2/15/3).
- 2- An increase in melting time increased desulfurization, but a reduction in temperature resulted in fluidity and deoxygenation.
- 3- Longer melting times resulted in numerous voids in as-cast specimens due to imperfect deoxygenation.
- 4- In addition to reduction of inclusion numbers, low size and uniform distribution of remained inclusions were observed in refined specimens.

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