

Manufacturing of 9CrMoCoB Steel of Large Ingot with Homogeneity by ESR Process

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Abstract. In case of 9CrMoCoB (COST FB2) steel, equilibrium relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio is very important to control $[Si]$ and $[B]$ in optimum range. Therefore, in this work, to investigate the thermodynamic equilibrium relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio, pilot ESR experiments of 9CrMoCoB steel were carried out using the CaF_2 - CaO - Al_2O_3 - SiO_2 - B_2O_3 slag system according to change of Si content in electrode and B_2O_3 content in the slag. Furthermore, through the test melting of the 20ton-class ESR ingot, the merits and demerits of soft arcing were investigated. From these results, it is concluded that oxygen content in the ESR ingot decrease with decreasing SiO_2 content in the slag, relation function between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio derived by Pilot ESR test shows a good agreement as compared to the calculated line with a same slope and soft arcing makes interior and surface quality of ingot worse. With the optimized ESR conditions obtained from the present study, a 1000mm diameter (20 tons) and 2200mm diameter (120ton) 9CrMoCoB steel of the ESR ingot were successfully manufactured with good homogeneity by the ESR process.

1. Introduction

For the USC(Ultra Super Critical) HIP(High and Intermediate Pressure) rotor, the high cleanliness and homogeneous ingots without interior defects such as non-metallic inclusion, porosity and segregation are required. For these demands, most turbine manufacturers have developed and applied an ESR (Electro Slag Re-melting) process to produce 9~12% Cr heat resistance steels.

Among ESR conditions, slag composition and melt rate are the important factors because slag composition gives the remarkable influence on the content of major elements and cleanliness and melt rate also has a great effect on segregation. Therefore it needs to decide carefully slag compositions and melt rate [1].

For the 9CrMoCoB steel(COST FB2) used up to as 630°C class USC power plant materials, it is very important to control the solute element such as Si, Nb and B in homogeneous and optimum range because the exchange reaction of the solutes between slag and molten metal occurs due to their thermodynamic equilibrium during ESR process.

Furthermore, for high cleanliness in the ESR ingot, especially to minimize $[Al]$, they have applied argon gas to prevent slag from oxidizing not to use Al deoxidation during ESR. However, recently, the effect of soft arcing created by ionization of argon gas on the quality of the ESR ingot also has been discussed particularly in the case of large ESR ingot manufacturing. Therefore, in this paper, relation function between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio derived by Pilot ESR test is introduced and



verified by 20~120 ton ESR melting. Furthermore, the effect of soft arcing on the surface and the inner quality of the ingot is discussed.

1.1. Pilot ESR experiments

The re-melting conditions of Pilot ESR experiments and the composition of the ESR electrode are shown in Tables 1 and 2, respectively. The experiments were carried out using the $\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ slag system with varying B_2O_3 and SiO_2 content to investigate the effect of SiO_2 and B_2O_3 content on cleanliness, behavior of major element content. The metal samples were taken from the axial center of the ESR ingot and the molten metal and slag samples were taken just before hot-topping stage.

Table 1. Re-melting conditions of Pilot ESR experiments

Classifications	Detailed Conditions	
Electrode	Composition	9CrMoCoB steel
	Size/Weight	$\phi 130\text{mm}/100\text{kg}$
Slag	System	$\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$
	Weight	5kg
ESR melting	Starting type	Cold start
	Mold dia.	$\phi 180\text{mm}$
	Fill ratio	0.72
	Atmosphere	Argon gas

Table 2. Chemical composition of Pilot ESR electrode (mass %)

C	Si	Mn	Ni	Cr	Nb	B
0.12	0.04~0.27	0.67	0.16	9.2	0.07	0.010

1.2. 20 Ton ESR Ingot Productions

To manufacture a 20 ton of 9%CrMoCoB of the ESR ingot, the ESR electrode was manufactured in a 30ton EAF and ladle refining furnace.

Detailed ESR conditions are listed in Table 3. ESR slag composition was selected based on the Pilot ESR experiment to obtain the optimum Si, Nb, B content and a low Al content. The melt rate was kept low and stable as much as possible. Table 4 shows the electrode chemical composition target for the 20 ton of 9%CrMoCo steel of the ESR ingot.

Table 3. Re-melting conditions of 20ton ESR operation

Classifications	Detailed Conditions	
Electrode	Size/Weight	800mm D, 20 tons
Slag	System	$\text{CaF}_2\text{-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$
ESR melting	Starting method	Hot start
	Voltage swing	4~6V
	Electrode surface	Shot blast
	Atmosphere	Argon gas
	Fill ratio	0.6~0.8

Table 4. Chemical composition of 20ton electrode (mass %)

	C	Si	Mn	Ni	Cr	Mo	Al	Co	Nb	B(ppm)
Min.	0.12	-	0.65	0.12	9.0	1.40	-	1.15	0.05	80
Max.	0.14	0.10	0.75	0.20	9.6	1.60	0.010	1.35	0.07	120

The metal samples were taken from the axial surface, middle and center of the product to check the behavior of main elements such as Si, B and Nb content. Molten slag and metal samples for chemical

analysis were taken at the end of hot topping to verify relation function between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio derived by Pilot ESR experiment.

1.3. 120 Ton ESR Ingot Productions

To manufacture the 120 ton-class 9%CrMoCoB of the ESR ingot, the ESR electrode was manufactured in a 100ton EAF and ladle refining furnace. Detailed ESR conditions are listed in Table 5. Among these conditions, especially, voltage swing set-point and control values for voltage swing control were optimized to keep the immersion depth as shallow as possible and prevent the soft arcing. Chemical composition of electrode is shown in table 6.

Table 5. Re-melting conditions of 120ton ESR operation

Classifications	Detailed Conditions	
Electrode	Size/Weight	2200mm D, 120 tons
Slag	System	CaF ₂ -CaO-Al ₂ O ₃ -SiO ₂ -B ₂ O ₃
ESR melting	Starting method	Cold start
	Voltage swing	8~10V
	Electrode surface	Shot blast
	Atmosphere	Argon gas
	Fill ratio	0.6~0.8

Table 6. Chemical composition of 120ton electrode (mass %)

	C	Si	Mn	Ni	Cr	Mo	Al	Co	Nb	B(ppm)
Min.	0.12	-	0.30	0.10	9.0	1.40	-	1.10	0.04	80
Max.	0.15	0.10	0.45	0.20	9.5	1.60	0.010	1.30	0.06	110

As the same as the method with re-melting process of the 20ton-class ingot, molten slag and metal samples were also taken at the end of hot topping to verify the relation function between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio derived by Pilot ESR experiment.

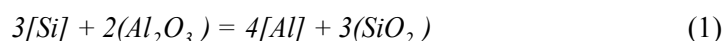
2. Results and Discussion

2.1. Pilot ESR experiments

In the case of 9%CrMoCoB steel containing Si, Mn, Nb and B, B is ought to oxidize first, followed Si, Mn and Nb. These elements have different chemical affinities for oxygen and their oxides have dissociation pressures. Because of this, during ESR, there may exist some chance of redox reaction taking place [2].

2.1.1 Effect of Si content in electrode on the behaviour Al, Nb content in ingot

First of all, the effect of Si content in electrode on Al content in the ingot was investigated. The equilibrium Si between slag and liquid metal pool can be represented as the following reaction (1). In the reaction (1), it can be seen that Al content can be controlled by using SiO₂ containing slag system [3].



The behavior of Al content according to Si content (0.08~0.27%) is shown in figure 1. Al content decreases with decreasing Si content and it can be suggested that Al content can be controlled below 0.005% when Si content is less than 0.1%.

In sequence, change of Nb recovery with Si content is also shown in figure 2. During ESR, equilibrium relation between Si and Nb can be represented as following reaction (2). Recovery of Nb

decreases with the decrease in Si content and it can be seen that recovery of Nb becomes below 80% when Si content is less than 0.06%.

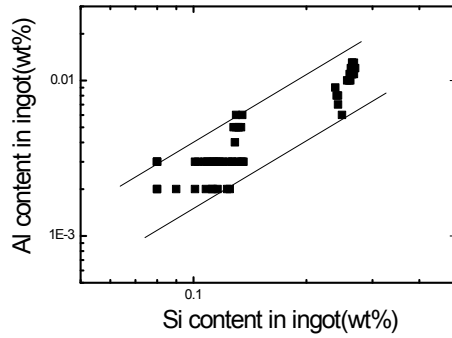
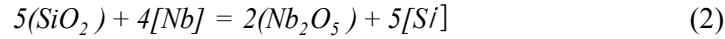


Figure 1. The effect of Si content on Al content

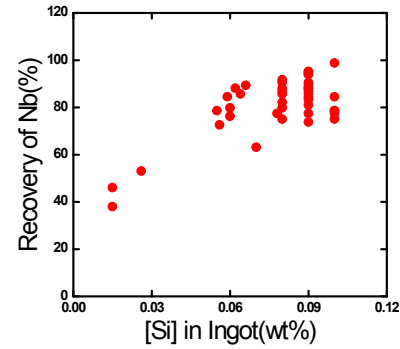


Figure 2. The effect of Si content in electrode on Nb recovery in the ingot

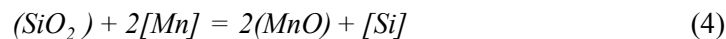
2.1.2 Effect of SiO_2 content in slag on ESR Ingot quality

The effect of SiO_2 content in slag on oxygen content in the ingot was investigated and the result is shown in figure 3. With increasing SiO_2 content in slag, oxygen content in the ingot increases because equilibrium oxygen content increases with an increase in SiO_2 activity as shown in equilibrium reaction (3) and the calculated line shown in figure 3 [4].

Change of cleanliness in the ingot according to slag basicity (CaO/SiO_2) is also shown in figure 4. In this figure, cleanliness means area ratio of non-metallic inclusion per unit area. As shown in figure 4, cleanliness improves with an increase in slag basicity. The reason seems to be attributed that equilibrium oxygen content decrease with increasing slag basicity.

$$\begin{aligned} \text{SiO}_2 &= \underline{\text{Si}} + 2\underline{\text{O}} \\ \log K_3 &= \frac{30110}{T} + 11.40 \\ \log [\% \text{O}] &= \frac{1}{2} (\log a_{\text{SiO}_2} - \log f_{\text{Si}} [\% \text{Si}] - 2 \log f_{\text{O}} + \log K_3) \end{aligned} \quad (3)$$

The recovery of major element such as Si, Mn and Nb according to slag basicity was evaluated and the result is shown in figure 5. The equilibrium of the Si, Nb and Mn between slag and liquid metal pool can be represented respectively as reaction (2) ~ (4).



First of all, in the case of Si, it can be seen that the recovery of Si increases with a decrease of slag basicity (increase SiO_2 content) in slag and Si pick-up occurs and then the recovery of Si becomes over 100% when the SiO_2 content in slag higher than that equilibrated with the Si content in electrode. On the other hand, in contrast to Si recovery, it can be seen that the recovery of Mn and Nb decrease with a decrease of slag basicity in slag and oxidation loss of Mn, Nb occurs and then the recovery of Mn and Nb greatly decreases when the SiO_2 content in slag higher than that equilibrated with the Si content in electrode.

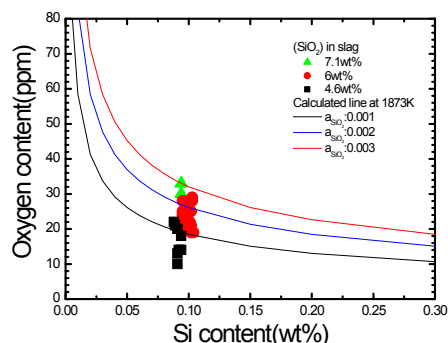


Figure 3. Effect of SiO₂ content in slag on oxygen content in the ingot

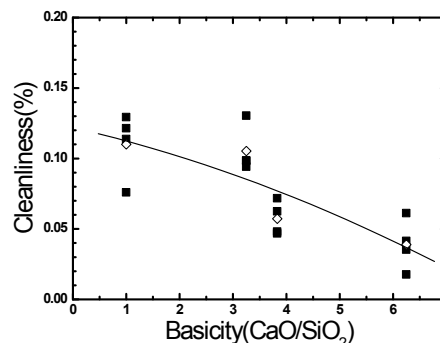


Figure 4. Effect of slag basicity on the ingot cleanliness

(Cleanliness(%)= (Total area of inclusion/Unit area) x 100)

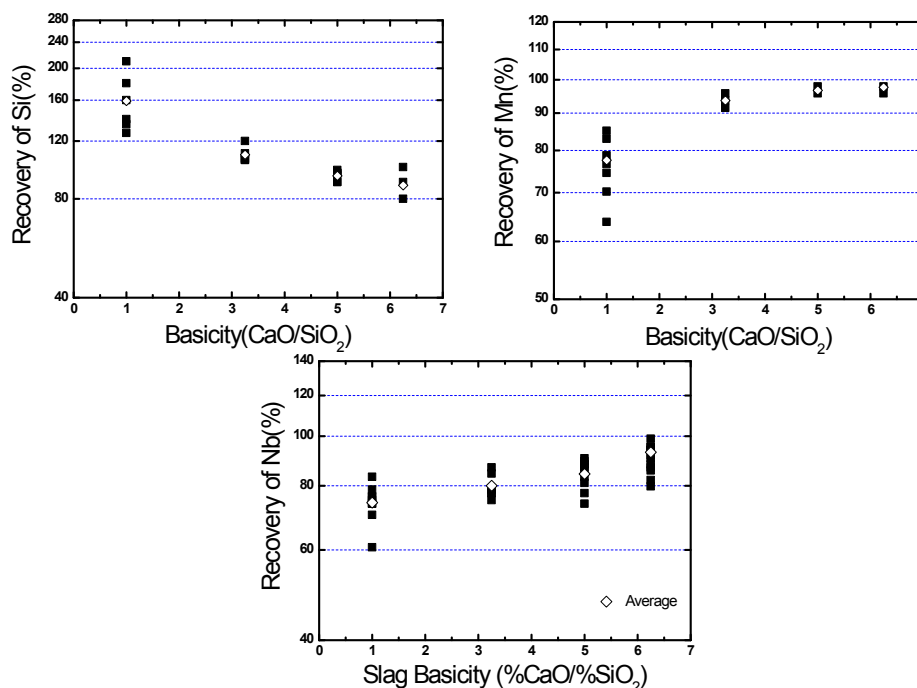


Figure 5. Effect of slag basicity on Si, Mn and Nb recovery during ESR

2.1.3 Equilibrium relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio during ESR

The equilibrium B between slag and liquid metal pool can be represented as reaction (5) [2]. In reaction (5), it can be seen that equilibrium B content in molten metal depends on B_2O_3 content in slag and Si content in electrode at the constant SiO_2 content in slag. Therefore, in order to control B content, the addition of B_2O_3 in to the slag is required to establish a thermodynamic equilibrium between the slag and molten metal. At the different Si content (0.08~0.27%) in electrode, the influence of B_2O_3 content in the slag on B content in the ingot is represented in figure 6. Equilibrium B content increases with an increase in B_2O_3 content in the slag and Si content in electrode.

Reaction (5) can be represented to relation between $\log([B]^4/[Si]^3)$ and $\log((B_2O_3)^2/(SiO_2)^2)$ as following equation (6).

$$4[B] + 3(\text{SiO}_2) = 2(\text{B}_2\text{O}_3) + 3[\text{Si}]$$

$$\log K_5 = \frac{5113.9}{T} + 4.763 \quad (5)$$

$$\log \frac{[\%B]^4}{[\%Si]^3} = \log \frac{(\%B_2O_3)^2}{(\%SiO_2)^3} - \log \frac{f_B^4 \gamma_{SiO_2}^3}{f_{Si}^3 \gamma_{B_2O_3}^2} - \log K_5 \quad (6)$$

Experimental results of Pilot ESR and calculation result using the equation (6) for relation between $\log([\text{B}]^4/[\text{Si}]^3)$ and $\log((\text{B}_2\text{O}_3)^2/(\text{SiO}_2)^2)$ are shown in figure 7. As shown in figure 7, experimental result shows a good linearization tendency according to calculated line with a same slope and relation function between $\log([\text{B}]^4/[\text{Si}]^3)$ and $\log((\text{B}_2\text{O}_3)^2/(\text{SiO}_2)^2)$ of experimental data can be represented as following equation (7).

$$\log \left(\frac{[\%B]^4}{[\%Si]^3} \right) = 1.06 \log \left(\frac{(\text{B}_2\text{O}_3)^2}{(\text{SiO}_2)^3} \right) - 2.04 \quad (7)$$

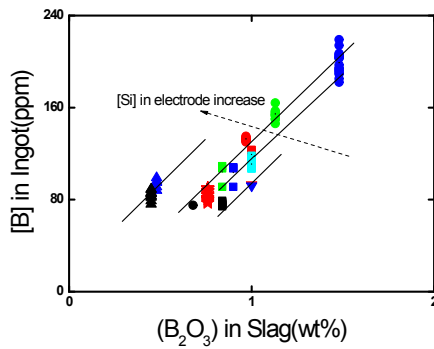


Figure 6. Effect of Si content in electrode on B content in ingot with B_2O_3 content in slag

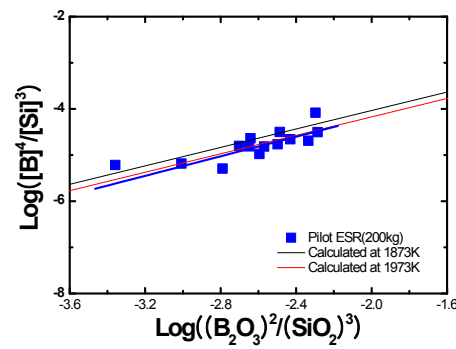


Figure 7. Equilibrium relation between $[\text{B}]/[\text{Si}]$ ratio and $(\text{B}_2\text{O}_3)/(\text{SiO}_2)$ ratio in the experimental and calculated data

From these results obtained by Pilot ESR experiments, Si content in electrode and SiO_2 , B_2O_3 content in the slag are optimized to control major alloy element such as Al, Mn, Nb, B in target range and improve ingot cleanliness.

2.2. 20 Ton ESR Ingot Productions

The ESR operation with the conditions shown in Table 3 was conducted. Two electrodes were re-melted but ESR operation results and surface quality were very different. Surface shape of one ingot was relatively smooth but in the other ingot soft arcing was occurred during ESR and deep ripple was generated on the whole surface. It is commonly known that soft arcing is generated between the electrode and the slag under argon gas atmosphere during ESR. The replacement of an air atmosphere with argon gas renders the ESR process more susceptible to instabilities caused soft arcing between the electrode and the slag due to ionization of the argon. During re-melting, ionization of the argon is indicated by the presence of a soft arcing between the electrode and the slag and a dramatic increase in noise from both the arcing and the power supply due to large voltage fluctuations [5].

Therefore, ESR operation results for each melts were compared and interior/exterior quality of the ingot was investigated according to the generation of soft arcing.

Firstly, ESR operation results such as melting current, voltage and melt rate were compared as shown in figure 8 and 9. As shown in figure 8, started melting after 10 minutes later, in the melt generated deep ripple on the ingot surface, melting voltage was abruptly increased, melting current was decreased simultaneously and then melt rate was increased greatly. Furthermore, melting voltage is higher but current is lower than that in other melt even though melt rate is almost same. This abnormal behavior of melting current and voltage was caused by soft arcing due to ionization of the argon between the electrode and the slag. The reason why soft arcing generates is attributed to the high voltage swing set-point in this work.

In additions, melting pattern on the soft arcing appears to resemble the Arc Slag Remelting process developed by the Paton institute [6]. Interestingly, as shown in figure 9, melting power(energy consumption) in melt with soft arcing is about 30% less than that in melt without soft arcing and this is in approximate agreement with results quoted by Paton et al [6].

In sequence, the effect of soft arcing on interior/exterior quality of the ingot was also investigated and the results are shown in figure10~12 respectively. In the case of surface quality of the ingot as shown in figure 10, it can be seen that slag skin becomes thicker and deep ripple is formed on the ingot surface when soft arcing is occurred. Cleanliness in middle part of the ingot height was compared according to generation of soft arcing and the result is shown in figure 11. It can be seen that cleanliness in the ingot without soft arcing is better than that in the ingot with soft arcing.

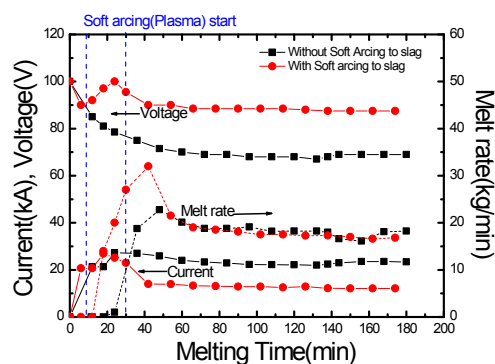


Figure 8. Behavior of melting current and voltage according to generation of soft arcing at same melt rate

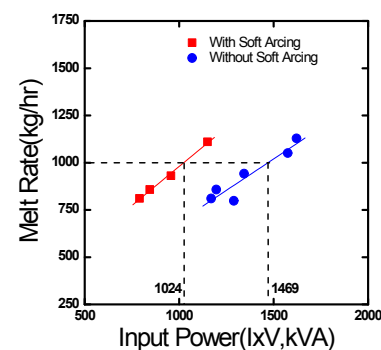


Figure 9. Comparison of melting power according to generation of soft arcing

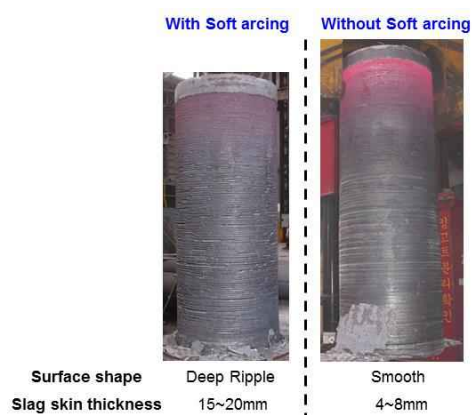


Figure 10. Comparison of ingot appearance with the generation of soft arcing

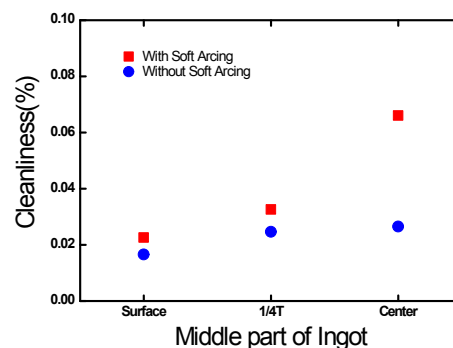


Figure 11. Comparison of ingot cleanliness with the generation of soft arcing

To verify the reason that cleanliness of the ingot with soft arcing is worse, specimen taken from the center in middle part of the ingot height with soft arcing was analysed by optical microscope and SEM-EDAX. As shown in figure 12, the reason why cleanliness of the ingot with soft arcing becomes worse seems to be attributed to the non-metallic inclusion and inclusion type is identified as Al_2O_3 rich inclusion. Accordingly, it can be estimated that when soft arcing generates, thickness of slag skin becomes thicker and depth of molten metal becomes deeper and then non-metallic inclusion could be caught more at the center part of the ingot.

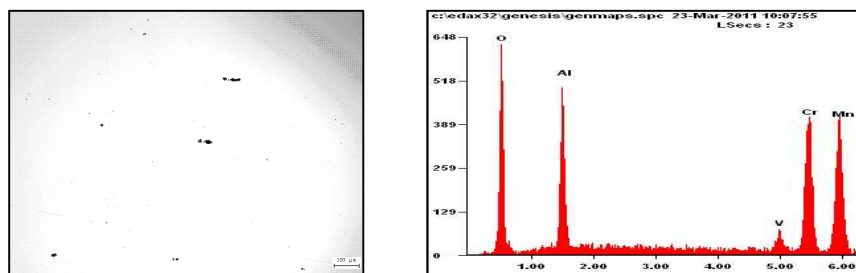


Figure 12. Analysis result of specimen taken from the ingot with soft arcing by OM, SEM-EDAX

As mentioned above, it can be conclude that soft arcing has a bad effect on both interior and exterior ingot quality even though melting power can be saved about 30%. Consequently, in order to get a satisfactory ingot quality, it is very important to design the optimum conditions of ESR operation to prevent soft arcing under argon gas atmosphere.

Finally, behavior of major elements in the ingot without soft arcing was analysed and analysis results are shown in figure 13. As shown in figure 13, it can be seen that the content of major elements in the ingot is uniform and nearly similar to alloy content in the electrode. Therefore, it can be concluded that slag composition was nearly close to the equilibrated composition with that of the electrode and very suitable for obtaining the optimum Si, Nb, Mn, B content and a low Al content less than 0.005%.

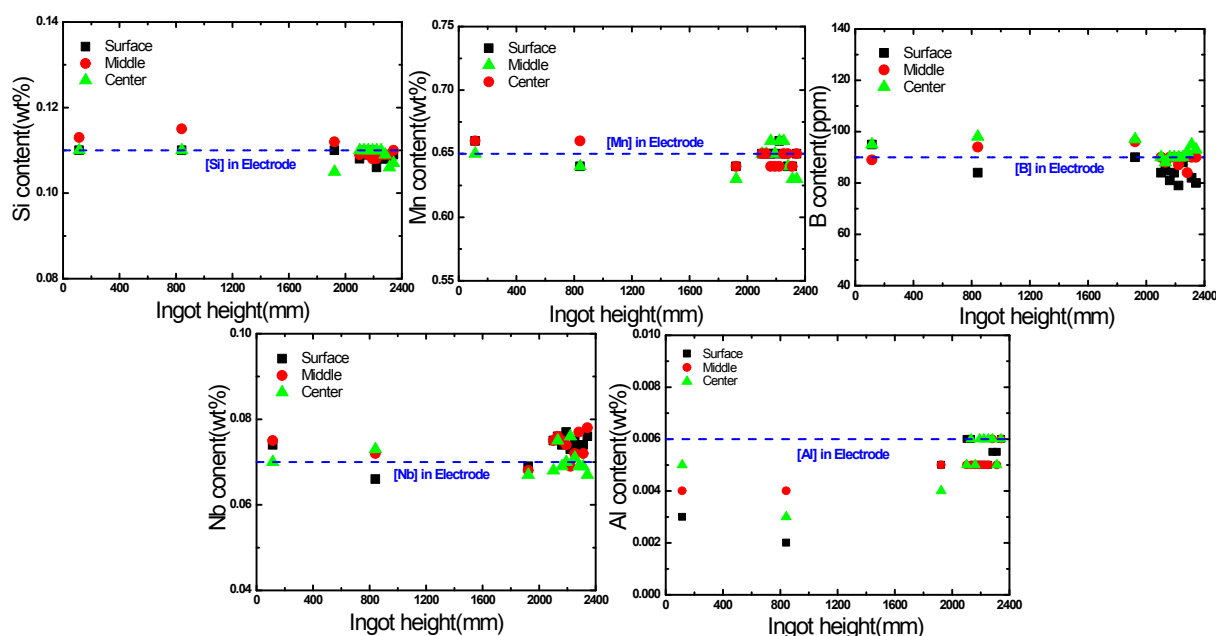


Figure 13. Analysis results of chemical compositions with axial surface, middle and center of the 20ton 9CrMoCoB Steel ESR ingot

2.3. 120 Ton ESR Ingot Productions

The ESR operation with the conditions shown in Table 5 was conducted. Especially, voltage swing set-point was optimized and voltage swing was controlled as target value to prevent soft arcing and obtain a smooth ingot surface. As shown in figure 14, 120ton 9CrMoCoB Steel ingot was successfully re-melted with very smooth surface and flat hot top. Metal samples for analysis of chemical composition were also taken from the ingot as shown in figure 15.



Figure 14. Appearance of 120ton-class 9CrMoCoB Steel of ESR ingot

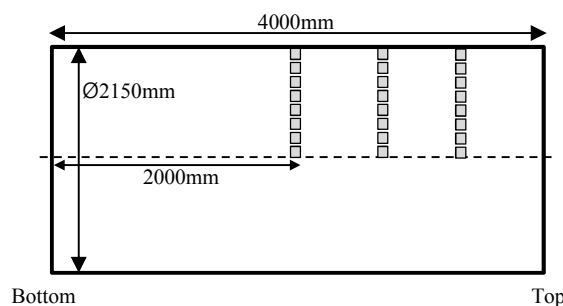


Figure 15. Point of chemical analysis of the 120ton-class 9CrMoCoB Steel of ESR ingot

Behaviors of chemical composition of major elements in the ingot are shown in figure 16. As shown in figure 16, it can be seen that the content of Si, Mn, Nb and B is nearly constant and similar to the content of elements in the electrode. Therefore, it can be concluded that slag composition was nearly close to the equilibrated composition with that of the electrode and very suitable for obtaining the optimum Si, Nb, Mn, B content. Furthermore, C, Mn and B having a low distribution coefficient are not segregated and show homogeneity in axis and thickness direction.

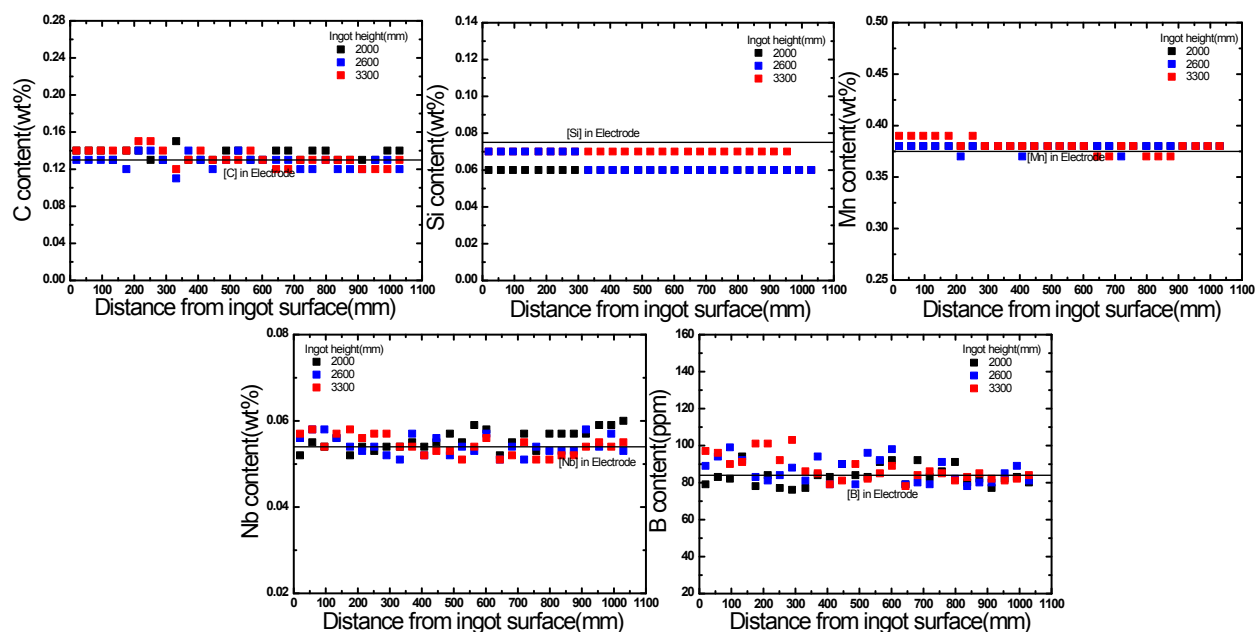


Figure 16. Analysis results of chemical compositions of the 120 ton-class 9CrMoCoB Steel of ESR ingot

Finally, content of B, Si and B_2O_3 , SiO_2 in each molten metal and slag taken at the end of hot topping was analysed and the result are plotted on the graph of relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio derived by Pilot ESR experiment as shown in figure 7 and represented with results of 10ton,

20ton and 70ton re-melting in figure 17. As shown in figure 17, relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio of 10~120ton re-melting shows a good agreement with relation function derived by Pilot ESR experiment irrespective of ingot weight. Accordingly, it can be suggested that relation function between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio as represented in equation (7) is very suitable to control B content in target under inert gas atmosphere during ESR.

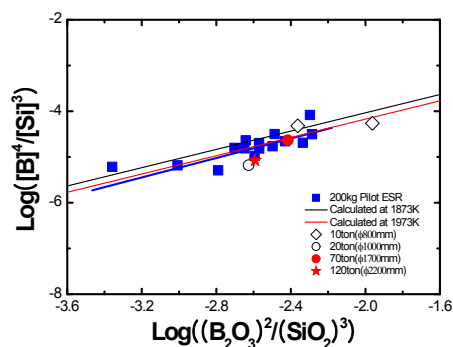


Figure 17. Result of 20~120ton re-melting plotted on the graph of relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio derived by Pilot ESR experiment

3. Conclusions

Through the pilot ESR experiments, the effect of Si content in electrode and SiO_2 content (slag basicity) in slag on the behavior of major element compositions and cleanliness in 9CrMoCoB Steel ESR ingot were investigated. In addition, equilibrium relation between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio was also investigated. Furthermore, in re-melting of 20ton-class ingot, the effect of soft arcing on ingot quality was also discussed.

In the results of Pilot ESR experiments, slag having a high basicity (low SiO_2 content) is advantageous to decrease the equilibrium oxygen content and get a good recovery of all oxidative elements such as Si, Mn and Nb simultaneously. Optimizing Si content in electrode enables the Al and Nb content to control in target value. Lastly, relation function between $[B]/[Si]$ ratio and $(B_2O_3)/(SiO_2)$ ratio is also derived from experiments and is verified by re-melting of 10~120ton-class ingot.

In the re-melting of 20ton-class ingot, operation results are compared according to generation of soft arcing. Soft arcing could deteriorate the ingot quality to generate deep ripple on the ingot surface and make an internal cleanliness worse. Accordingly, when ESR is carried out under an argon gas atmosphere, it is extremely necessary to determine optimum conditions of voltage swing control to prevent the soft arcing.

With the optimized ESR conditions obtained from these studies, a 2200mm diameter (120 ton) 9CrMoCoB Steel of ESR ingot was successfully manufactured with good homogeneity in Si, Mn, Nb, B content and no segregation by the ESR process.

4. References

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