

Composition Variation in Incoloy 800H Alloy Ingot during ESR Process

CHIN-YUAN CHEN*, GUO-WEI WANG** and YAN-MEI HU**

**Iron and Steel Research & Development Department
China Steel Corporation*

***Steelmaking Department, Metallurgical Department
Changzhou China Steel Precision Materials Co.,Ltd*

Easily oxidated elements are lost through burning and react with liquid slag causing a non-uniform composition along the height of the Incoloy 800H ingot, with a resulting ingot rejection. The factors on the mechanism of element losses are investigated. The results show that not only is the slag composition critical, but also the removal of electrode scale and atmospheric control are important as well. At the beginning of the remelting, the lower TiO₂ content in slag and the higher amount of oxygen in the atmosphere cause Ti, Al losses and Si enrichment by an exchange reaction between the molten pool and the liquid slag, as well as the burning loss by oxidation. By the addition of a small amount of TiO₂ into the slag and a lower oxygen level of the electrode, the losses of Al and Ti can be suppressed and slag-metal equilibrium is reached faster. Using a slag mixture containing 30% amount of returned slag can improve the homogeneity of the whole ESR ingot. Finally, the composition variations along the ingot in Al, Ti, and Si have been significantly improved from -0.39% to -0.07%, -0.468% to -0.04%, and 0.39% to 0.05%, respectively.

Keywords:Core loss, Indusion, RH refining process

1. INTRODUCTION

The advantage of Electro-Slag Refining (ESR) process is that ESR is known to obtain a low inclusion content, a low macro- and micro-segregation, and low micro-porosity of steel due to its near-directional solidification. However, the easily oxidated elements burn off during the lengthy process resulting in a non-homogeneous composition along the top of the ingot. In a typical ESR process, there exist a number of reaction sites involving solid/gas, solid/liquid, liquid/liquid and gas/liquid interfaces. The probability of chemical interactions suggests the desirability of the possible contributing factors. Precise control of the chemical composition and a uniform distribution of alloying elements are necessary to obtain high quality final products. The loss through burning of easily oxidated elements and the reaction with liquid slag can cause a non-uniform composition along the top surface of the ingot in the electroslag remelting practice. It is necessary to quickly identify the origins of the appearance of Al, Ti, Si fluctuations along the cast direction which occurred in Incoloy 800H ingots at China Steel Precision Materials Co. (CSPM).

The objectives of this paper are to study the influence of process parameters on the formation of Al, Ti

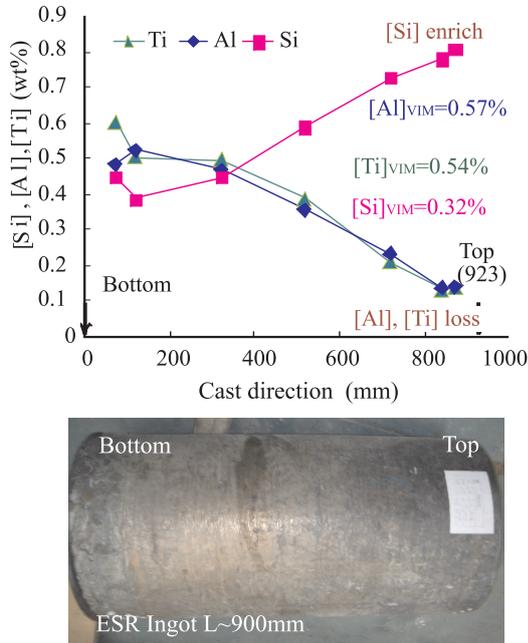
loss along the axial direction in ESR ingots, to investigate the mechanisms and operation procedure for this steel grade, and to identify possible ways by which defect-free ESR products can be produced.

2. EXPERIMENTAL METHOD

The chemical composition of Incoloy 800H is shown in Table 1. The steel grade contains high Ni, Cr with some Ti, Al content for high temperature application. The fluctuation of Ti, Al and Si along the top surface of the ingots can be observed in Fig.1. To reduce this composition fluctuation and to identify the key factors involved, a number of investigations were performed to analyze the formation mechanism and to resolve the problem. First, the plant data and procedure were statistically analyzed to reveal the tendency and the key process factors. The ESR ingots were tracked and sampled for metallographic analysis. The slag was also sampled at the top, middle and bottom part of the remelted ingot for analysis. The mechanism of Ti, Al burning loss during ESR was analyzed by the thermodynamic reaction equilibrium. After all the investigations, a suitable process was proposed and employed, and the results tracked to optimize the process again.

Table 1 Chemical composition of Incoloy 800H

Elements	C	Si	Mn	Cr	Al	Ti	Ni	Fe
%	0.05-0.08	≤1.00	0.50-1	19-23	0.15-0.6	0.15-0.6	30-35	≥39.5

**Fig.1.** [Ti], [Al], [Si] fluctuated along axial direction of ESR ingot.

3. RESULTS AND DISCUSSION

3.1 Mechanism of Ti, Al burning loss

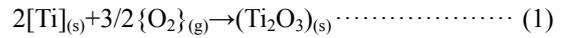
Many examples of composition changes in ESR processed alloys have been reported in the literature⁽¹⁻³⁾. These studies involved equilibrium reaction models and mass transfer analysis. An equilibrium relationship between the atmosphere, the liquid slag and the molten metal was applied to investigate the phenomenon during the ESR process. From some reports, the elements of [Ti], [Al] vary according to the oxidation behavior and the slag-metal equilibrium. The oxidation of the active elements due to scale on the electrode surfaces and the atmospheric conditions can result in a higher burning loss at the beginning stage, in which unsteady state between the slag and the metal deteriorated the atmospheric condition. The kinetic behavior of electroactive interfaces in the ESR-process has been attributed to the activities of reacting species on both sides⁽⁴⁻⁷⁾.

Oxidation by easily oxidated elements was due to many oxidizers: scale on the electrode surface; by the atmospheric condions; by relatively unstable oxidants in the slag; and by the presence of $[O]_{\text{free}}$ in the elec-

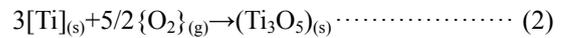
trodes. The chemical reaction of those oxidation and exchange reactions are the major factor in the Al, Ti losses.

Equations (1 to 10) express the loss of [Al], [Ti] by oxidation:

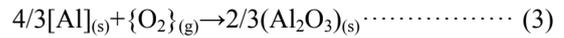
During the early stages of the ESR process, [Ti] reacted with $[O]_{\text{free}}$ in the electrode and with $\{O_2\}_{(g)}$ in the air according to the following formula:



$$G^0 = -1520900 + 291.85T$$

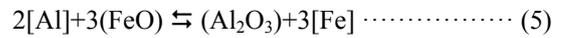
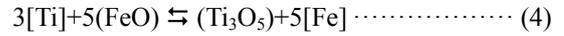


$$G^0 = -2459100 + 475.45T$$

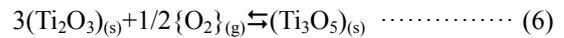


$$G^0 = -1131800 + 257.2T$$

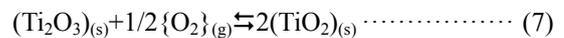
$(Ti_2O_3)_{(s)}$, $(Ti_3O_5)_{(s)}$ and $(Al_2O_3)_{(s)}$ were formed and entered into the molten slag during the early stage of ESR. Oxidation by scale on the surface of the electrodes may deteriorate.



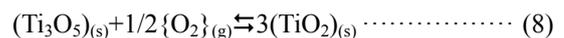
If there is a poor atmosphere in ESR, the Titanium oxides, $(Ti_2O_3)_{(s)}$ and $(Ti_3O_5)_{(s)}$, may oxidize more and then form the more stable $(TiO_2)_{(s)}$ in the liquid slag, which promotes [Al], [Ti] to oxidize further before a steady state of the reaction equilibrium is reached. Then b[Al], [Ti] loss will keep going.



$$G^0 = -355500 + 75.35T$$

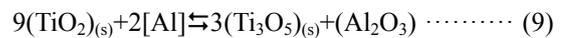


$$G^0 = -367100 + 78.55T$$



$$G^0 = -372900 + 80.15T$$

Further, the reactions of Al, Ti are coupled to each other by the following equations:



$$\Delta G = -579000 + 145.35T < 0$$

$$\begin{aligned}
 &= -RT\ln K = -19.14\text{Log}K \\
 \Rightarrow \log K &= \frac{30250.8}{T} - 7.6 \\
 \log K &= \log \frac{(\text{Ti}_3\text{O}_5)_3 \times (\text{Al}_2\text{O}_3)}{[\% \text{Al}]^2 \times (\text{TiO}_2)^9} > 0 \\
 6(\text{TiO}_2)_{(s)} + 2[\text{Al}] &\rightleftharpoons 3(\text{Ti}_2\text{O}_3)_{(s)} + 2(\text{Al}_2\text{O}_3) \cdots \cdots (10) \\
 \Delta G &= -596400 + 150.15T < 0 \\
 &= -RT\ln K = -19.14\text{Log}K \\
 \Rightarrow \log K &= \frac{31160}{T} - 7.8 \\
 \log K &= \log \frac{(\text{Ti}_2\text{O}_3)_3 \times (\text{Al}_2\text{O}_3)^2}{[\% \text{Al}]^2 \times (\text{TiO}_2)^6} > 0
 \end{aligned}$$

For the thermodynamic equilibriums between metal and liquid slag, the amount of Ti in Ti free slag increased by the metallic Ti oxidation at the initial period of ESR. It is assumed that the Ti in slag appears essentially as $(\text{Ti}_2\text{O}_3)_{(s)}$, $(\text{Ti}_3\text{O}_5)_{(s)}$ and the more stable $(\text{TiO}_2)_{(s)}$. The burning loss of Ti will continue until the equilibrium is reached between the liquid slag and the metal pool^(7,8).

The other major factor to affect the Ti, Al oxidation is the reaction of Al, Ti with the elements in ESR slags. The composition fluctuations of remelted ingot can be avoided by adjusting the compositions of the ESR slags. The SiO_2 , TiO_2 and Al_2O_3 contents of the slags show a great influence on this phenomenon of the exchange reaction between the slag and the metal.

$$\begin{aligned}
 3/2(\text{TiO}_2)_{(s)} + 2[\text{Al}] &\rightleftharpoons 3/2[\text{Ti}]_{(s)} + (\text{Al}_2\text{O}_3) \cdots \cdots (11) \\
 \Delta G &= -281700 + 108T < 0 \\
 &= -RT\ln K = -19.14\text{Log}K \\
 \Rightarrow \log K &= \frac{14718}{T} - 5.6 > 0 \\
 \log K &= \log \frac{[\% \text{Ti}]^{3/2} \times (\text{Al}_2\text{O}_3)}{[\text{Al}]^2 \times (\text{TiO}_2)^{3/2}} > 0
 \end{aligned}$$

$$3(\text{SiO}_2)_{(s)} + 4[\text{Al}] \rightleftharpoons 3[\text{Si}] + 4(\text{Al}_2\text{O}_3)_{(s)} \cdots \cdots (12)$$

$$\log K = \log \frac{[\% \text{Ti}]^{3/2} \times (\text{Al}_2\text{O}_3)}{[\text{Al}]^2 \times (\text{TiO}_2)^{3/2}} > 0$$

The above analysis of the composition changes during the ESR process can be described in using simplified reaction schemes, such as base of air, liquid slag, and the metal pool for the modeling systems, where many separate reactions may be required to reach simultaneous equilibrium solution, as shown in Fig.2. The phenomenon is the key factor to suppress the composition change in practice.

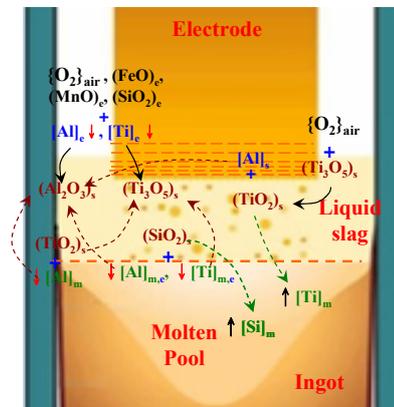


Fig.2. Schematic of the Al, Ti, burning loss and Si enrichment behavior during ESR process.

3.2 Procedural analysis and countermeasures

The major factors which affect Al, Ti losses were analyzed and confirmed, as shown in Table 2. Detailed examination showed that the appearance of Al, Ti burning loss may be connected to:

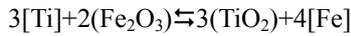
- (1) Scale on the surface of the electrode not being fully removed;
- (2) Insufficient atmosphere control; and/or
- (3) An unsuitable slag composition.

Some control methods to suppress elements losses are applied^(2,4). Oxidation by air or scale (FeO_x) caused an increase of oxygen content in the liquid slag and

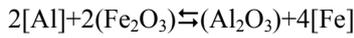
Table 2 Before and after process modification of ESR process

Process	Before	After
VIM electrode	Scale on the surface	Scale removed by polishing
Slag	Type:50F/17/3/25/5	Type:4Ti, mixed slag Moisture removed by heating to 600°C/2hr
Atmosphere	Slag addition by human being inefficient atmosphere control	Automatic Slag addition Ar purging for the whole process
Remelting	Al flake addition for liquid slag degassing	Same

metal pool, which enhances the oxidization of Al and Ti, according to the following formula:



$$K = \frac{\alpha_{\text{Fe}}^4 \cdot \alpha_{\text{TiO}_2}^3}{\alpha_{\text{Ti}}^3 \cdot \alpha_{\text{Fe}_2\text{O}_3}^4}$$



$$K = \frac{\alpha_{\text{Fe}}^4 \cdot \alpha_{\text{Al}_2\text{O}_3}}{\alpha_{\text{Al}}^2 \cdot \alpha_{\text{FeO}}^2}$$

Some operation, like surface polishing, could be adapted to clean the electrode surface before remelting. Blowing Ar gas into the mold chamber throughout the whole process was also applied to decrease oxygen content above the liquid slag and metal pool to suppress the oxidization by air or scale. During the investigation, an unstable Ar gas supply or an uncleaned electrode surface were observed in some tests, which resulted in a higher oxygen level suitable for Al, Ti oxidation. Such phenomena are more obvious at the beginning and final stages and need to be further modified.

An exchange reaction with other active oxides is the major factor that results in a high burning loss rate of Al, Ti. In a prior investigation, some active oxides like SiO_2 , Fe_2O_3 were found to be the source of Al, Ti oxidation, these could be avoided by adjusting the composition of the slag and the electrodes to reach the slag-metal equilibrium. For the practical remelting operation, a suitable amount of TiO_x should be added into the slag to ensure that a more close to steady-state would be achieved at the early stage of remelting⁽⁷⁾.

The basic slag types applied in CSMP are: general slag; 4Ti slag; and mixed slag. The chemical composition of these different slags is shown in Table 3. The [Al], [Ti] and [Si] that fluctuate along the axial direction have been analyzed, and slag from the top, middle and bottom parts were also sampled for analysis.

The extent of exchange reaction strongly depends

on the composition of the slag. Figure 3 shows the influence of different slag compositions on Ti, Al, Si fluctuation under the addition of different slags. The first ingot was remelted with a Ti-free slag (without TiO_2 addition in slag). At the beginning stage of remelting, the burning loss of Al, Ti can be observed, whereas Si is enriched. The situation goes on continuously with the remelting. At the height of 800 mm, a loss of Ti, Al content of 0.45 and 0.44 wt% (the loss rates are 75.5%, and 74 wt%, respectively) have been achieved. Perhaps due to oxidation by air and scale, as well as the exchange reaction with slag, the remelting process is always in the unsteady state. Consequently the ingot composition is out of specification. The second ingot was remelted with a 4 wt% TiO_2 addition into slag (4Ti slag). The analysis shows that the Ti content is nearly constant along the total length, although the Al burning loss and Si enrichment are slighter higher. After the remelting of 150 mm, an average increase of 0.21 wt% Ti is already achieved. The Al content is scattered with lower loss rates. A mixed slag of 30% general slag and 70% 4Ti slag was used in the third ingot. Compared with second ingot remelted using 4Ti slag, a lower Ti enrichment can be observed due to the smaller amount of TiO_2 for reaction, which also results a slightly lower loss at the beginning stage.

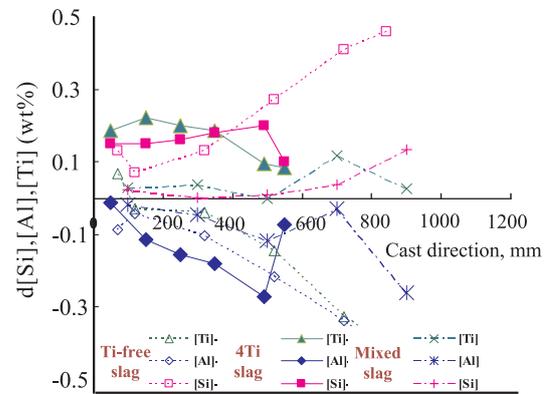


Fig.3. Effect of slag on [Al], [Ti] losses using: Ti-free slag 4Ti slag and mixed slag.

Table 3 Chemical composition of different slags applied in CSMP

Percentage (%)	CaF ₂	CaO	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	P	S
General slag (50F/17/3/25/5)	54.007	15.51	3.594	23.091	5.055	0.051	0.007	0.029
4Ti slag (53F/20/3/20/4Ti)	52.357	15.58	3.626	22.843	0.996	6.197	0.012	0.012
Mixed slag (2/3 4Ti slag+1/3 general slag)	52.907	15.56	3.615	22.926	2.349	4.148	0.01	0.018
Returned slag mixture (30% returned 4Ti slag)	42.387	20.12	3.912	30.102	0.397	3.925	0.012	0.016

Figure 4 shows a comparison of the fluctuation of $C_{\max}-C_{\min}$ for the three ingots. Only small fluctuations of Ti, Al, Si can be achieved. The activity of TiO_2 increased with the addition of TiO_2 in slag. Thus, the higher Ti loss at the ingot bottom can now be explained because at the beginning of the remelting the TiO_2 activity of the starting slag is nearly zero. Poor atmosphere control deteriorates this phenomenon. This reveals that a suitable amount of TiO_2 addition into slag is beneficial for Ti loss, and that good atmospheric monitoring is also important for Al control.

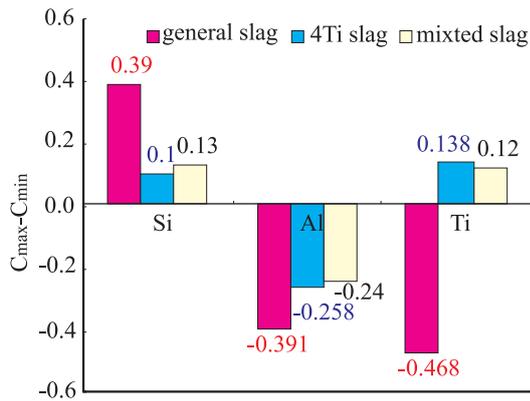


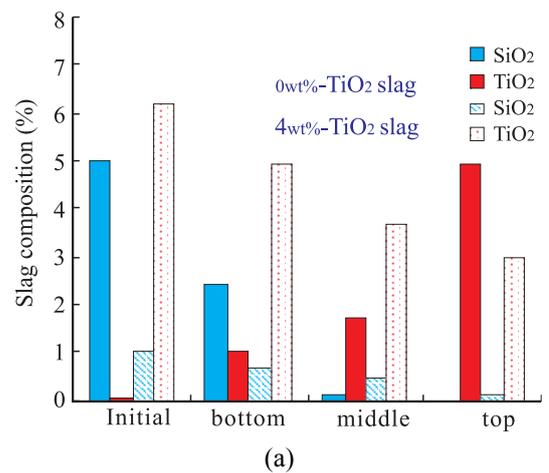
Fig.4. [Al], [Ti], [Si] variations for different slags.

Figure 5 shows the effect of TiO_2 content in slag on the variations of slag composition during the ESR process. One ingot was remelted with TiO_2 -free slag with 15.3 wt% CaO, 22.01 wt% Al_2O_3 , 2.2 wt% MgO, 4% SiO_2 and 52.6 wt% CaF_2 . The analysis result reveals that the TiO_2 content increases with the process for TiO_2 free slag, which implies that a higher Ti loss in the complete process can be observed. In comparison to that, the content of TiO_2 at 4Ti slag decreases slightly, in which the equilibrium is kept between the liquid slag and the metal pool. The chemical reaction reaches a relatively steady state at the initial period of remelting, so that TiO_2 enriches further. Due to the better atmospheric control over the full process, oxidation by air can be suppressed, resulting in a slight increase of SiO_2 and Al_2O_3 in the slag. On the contrary, without SiO_2 addition in 4Ti slag, the slag would deteriorate the loss of Al, Ti and enrich the Si due to the exchange reaction with TiO_2 and Al_2O_3 .

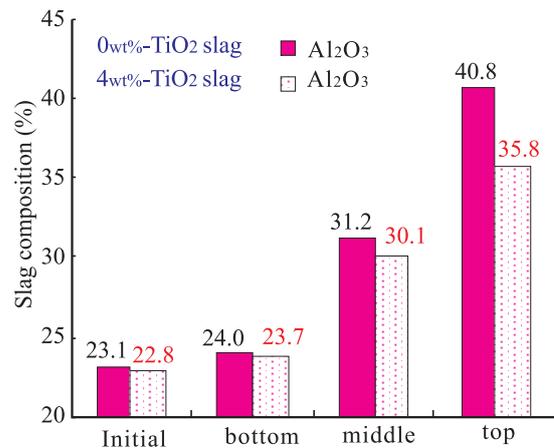
In operational practice, a slag formed by the addition of a suitable amount of returned slag into fresh slag (~30%) is a reasonable approach to reducing the usage of expensive special commercial slags. The advantage is not only in decreasing the remelting cost, but also the lower moisture and water of crystallization content in slag would be beneficial to [H] reduction. Moreover, the returned slag is closer to the steady state of metal-slag equilibrium. Figure 6 shows the com-

parison between general slag and the mixed slag in different [Si], [Al], [Ti] variations. A better control of losses can be seen at the initial stage of remelting. For whole ESR process, a higher homogeneity can be achieved. As a matter of the fact, the effect of the returned slag is similar to that of a mixed slag containing 30% general slag and 70% 4Ti slag. However, a smaller SiO_2 content will be helpful for Si control. Some practice has shown that more than 50% returned slag can be successfully reused to produce high quality ingot.

The experimental results of the test showed that the Ti Al, which fluctuated along the casting direction was essentially constant during the remelting process, except for the initial period of remelting. Corresponding to a Ti, Al loss up to about 0.39, 0.47, respectively, before modification, the results indicated that the Ti content at middle and final positions is closer to the stable condition of low oxygen level, and giving a slighter loss, as shown in Fig.7. For the practical



(a)



(b)

Fig.5. Variations of (a) SiO_2 , TiO_2 and (b) Al_2O_3 in slag for different slags.

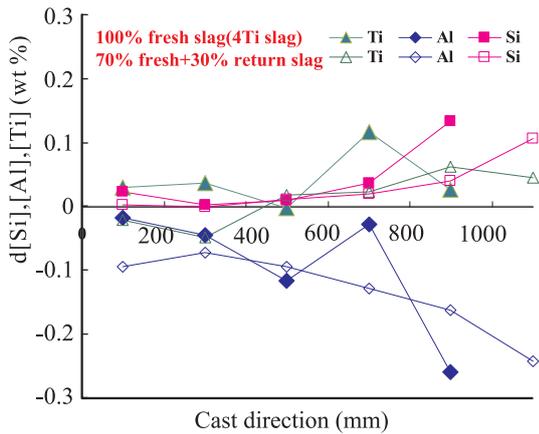


Fig.6. Returned slag shows a better control over [Al], [Ti], [Si].

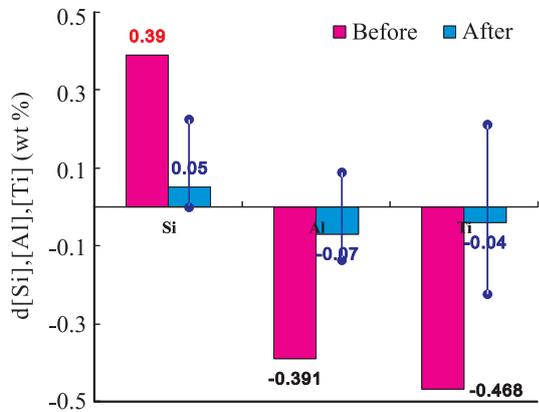


Fig.7. [Al], [Ti], [Si] fluctuations reduced after countermeasures.

remelting process, a suitable TiO_2 should be added into slag in order to ensure that the condition at the early stage of remelting is controlled to be close to the steady state of equilibrium and to obtain an ingot with adequate axial homogeneity. In this case, for the reductive unsteady state process, the axial non-homogeneities of alloying elements in the 800H ingot are more extensive than those before modification.

4. CONCLUSIONS

- (1) Detailed examination of ESR process in CSMP showed that the appearance of Al, Ti burning loss may be connected to these factors: (a) scale on the surface of the electrodes having not been removed completely; (b) insufficient atmosphere control; and (c) an unsuitable slag composition.
- (2) The major factor in the Ti burning loss is due to an unsuitable slag composition. By the addition of a certain amount of 4% TiO_2 into slag, the Al, Ti, Si content can be controlled within limits.
- (3) Using a slag mixture containing 30% returned slag would improve the homogeneity of the whole ESR ingot.

REFERENCES

1. 趙鴻燕：“渣成分對高溫合金0Cr15Ni25Ti2MoAlVB電渣重熔Ti燒損率 and 鋼錠表面品質的影響”，特殊鋼(2006)，vol.27(2)，pp. 61-64。
2. 常立忠、楊海森、李正邦，“氬氣保護對低合金鋼電渣重熔錠品質的影響”，特殊鋼(2009)，vol.30(4)，pp. 59-60。
3. 陳青：“電渣重熔金屬元素燒損原因中氧元素的追溯考慮”，科技探索(2010)，vol.369。
4. 王信才：“GH3030合金電渣重熔Al、Ti成分控制分析”，特鋼技術(2006)，vol.2(2)，pp. 7-9。
5. 鈴木章、岡村正義、広瀬和夫：“Electroslag remelting of steels containing Ti and Al”，鉄と鋼(1972)，vol. 67(4)，S255。
6. K. Schwerdtfeger, W. Wepner and G. Pateisky, “Modelling of chemical reactions occurring during electroslag remelting oxidation of titanium in stainless steel.” Ironmaking Steelmaking, (1978), vol. 5(3), pp. 135-143.
7. 傅傑，“高鈦低鋁高溫合金電渣重熔過程鈦的燒損”，鋼冶金過程動力學，冶金工業出版社，(2001)，pp. 117-123。
8. G. Pateisky, H. Biele and H. J. Fleischer, “The Reactions of Titanium and Silicon with Al_2O_3 -CaO-CaF₂ Slags in the ESR Process”, J. Vac. Sci. Technol. (1972), vol. 9, pp. 1318. □