PROGRESS OF PRODUCTION TECHNOLOGY OF CLEAN STEEL IN BAOSTEEL

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ABSTRACT: The progress in control technology of carbon, nitrogen, total oxygen, phosphorus, and sulphur as well as inclusions in steel is made at Baosteel. The purity obtained in IF steel and pipeline steel is introduced.
KEYWORDS: clean steel, IF steel, pipeline steel, steelmaking

1. Preface

The so-called clean steel generally is the steel in which the content of impurity elements, such as phosphorus, sulphur, total oxygen, nitrogen, hydrogen (including carbon sometimes) and inclusions, are very low. The so-called impurity elements vary with different grades of steel. Some element is harmful to certain steel grade, but may be less harmful or even useful to another steel grade. In other words, the control elements are different for different performance demands of steel. For IF steel, the content of carbon, nitrogen, total oxygen and inclusions should be as low as possible in order to gain good flexibility, high r value, perfect surface quality. The high quality pipeline steel requires ultra low sulphur, low phosphorus, low nitrogen, low total oxygen content and a certain ratio of Ca/S.

Since the mid 1990's, Baosteel has endeavored to develop the melting technology of clean steel. The research work concentrates on the development of relatively individual technologies and mass production of high cleanliness steel (IF steel, pipeline steel etc.).

This paper presents the progress of production technologies of clean steel in Baosteel.

2. Progress of individual production technology of clean steel

2.1 Production technology of ultra-low sulphur steel

The desulphurization in hot metal is a kind of economical and effective desulphurization method, which has been widely used in steelmaking production. Two kinds of desulphurization patterns in torpedo car (CaO based flux, CaC_2 based flux) and hot metal ladle (Mg based flux) were developed in Baosteel. When the original sulphur content is between 150ppm(1ppm=10^{-4}%) and 300ppm, the lowest sulphur content of hot metal can range from 10ppm to 30ppm after the desulphurization.

It is well known that desulphurization ability of BOF is fairly limited. When the original sulphur content in hot metal is very low, the sulphur pick-up phenomenon in BOF often occurs because of the addition of lime and scrap with higher sulphur content. In general, it is difficult to steadily produce the steel with sulphur content less than 30ppm only by hot metal pretreatment. So the development of desulphurization technology of molten steel after tapping is necessary

Three kinds of desulphurization patterns in refining stage have been developed one after another in Baosteel. Their basic futures are as follows.

a. Desulphurization pattern by adding desulphurizer in RH (pattern A)

- Develop high effectual $CaO-CaF_2$ based desulphurizer.
- Add desulphurizer to vacuum vessel through alloy chute.
- Control the amount of carry-over slag of BOF as low as possible, and carry out the ladle slag conditioning.

b. Desulphurization pattern of powder injection in RH (pattern B)

- Develop $CaO-Al_2O_3$ based premelted desulphurizer
- Adopt a low lance position to make powder into molten steel fully.
- Carry out deoxidation of molten steel and ladle slag.

C. Desulphurization pattern in LF (pattern C)

- Develop $CaO-Al_2O_3$ based desulphurizer.
- Optimize deoxidation pattern of slag.
- Adopt strong stirring pattern so as to promote the reaction between slag and molten steel.

The results of industrial desulphurization trial are shown in Table 1:

Table 1 Results of desulphurization trial

Pattern	$[S]_i$ (ppm)	$[S]_f$ (ppm)	De-S rate（%）
A	28.4	16.2	43.0
B	61.9	35.8	42.2
C	67.0	8.7	87.0

$[S]_i$: original average sulphur content；

$[S]_f$: average sulphur content after desulphurization

It can be seen from Table 1, the desulphurization rates are about 40% for desulphurization patterns in RH. These patterns are suitable as the supplement means of sulphur content control. At the same time, it can be seen that the desulphurization patterns in LF have very high desulphurization rate, and its average desulphurization rate reaches 87%. The sulphur content in molten steel can be below 10ppm and its average content is 8.7ppm.

2.2 Production technology of low phosphorus steel

In Baosteel, the follow process trials, which are correlated with the phosphorus control, have been researched:

① Hot metal pretreatment (De-Si, De-P, De-S) + BOF process with small slag volume (slag volume index=0.3)------- (pattern A).

② Hot metal pretreatment (De-S) + BOF process with large slag volume (slag volume index=1.0) -------- (pattern B).

③ Hot metal pretreatment (De-Si, De-P, De-S) + BOF process with large slag volume (slag volume index=1.0)------- (pattern C).

④ BOF pretreatment (De-P) + BOF process with middle slag volume (slag volume index=0.6)------- (pattern D).

The dephosphorization results of above patterns are shown in Fig.1

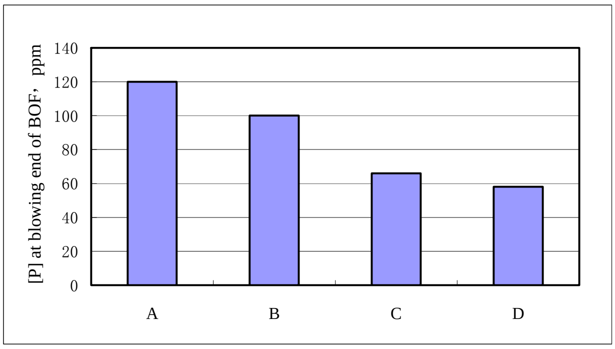

Fig.1 Comparison of average [P] at blowing end of BOF for different patterns

As shown in Fig.1, the average phosphorus contents obtained by using pattern C and pattern D are respectively 66ppm and 58ppm. Therefore the pattern C and pattern D are all the effective production process for low phosphorus steel.

2.3 Production technology of low oxygen steel

A series of measures aiming at reducing Al_2O_3 inclusions, total oxygen content and preventing from slag entrapment have been adopted for low oxygen steel (such as IF steel) in Baosteel.

- Use slag stopper to control the slag thickness at less than 70mm in ladle.
- Ladle slag conditioning: add Al dross on slag to decrease T.Fe content during turndown.
- Control [O] at RH decarburization end and circulation time after RH decarburization.
- Adopt tundish purification technology.
- Use a high viscosity mold powder to prevent from the entrapment.
- Maintain reasonable Ar flowrate from immersed nozzle and liquid level stabilization in mold during continuous casting.

1) Ladle slag conditioning treatment

The relation between T.Fe in slag and T[O] of molten steel in tundish after ladle slag conditioning is shown in Fig.2. From Fig.2, it can be seen that T[O] in tundish decreases with the decrease of T.Fe in slag. Generally, it is favorable to decrease T.Fe in slag to less than 8% for the production of low oxygen steel (T[O]≤30ppm).

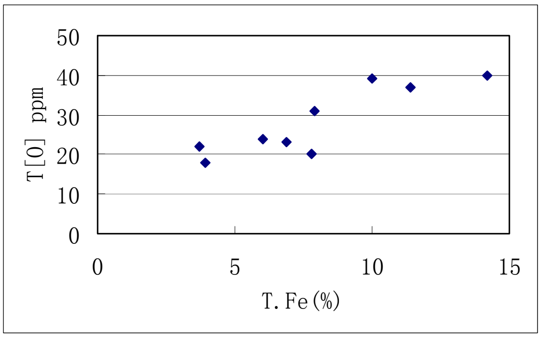

Fig.2 Relation between T.Fe in slag and T[O] in tundish

2) Relation between [O] at RH decarburization end and T[O] in tundish

Fig.3 shows the Relation between [O] at RH decarburization end and T[O] in tundish. As shown, the T[O] in tundish increases with the increase of the [O] at RH decarburization end. So it is important to decrease the [O] at RH decarburization end for the increase of cleanliness of molten steel.

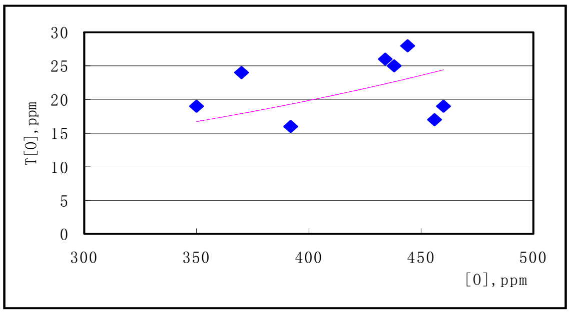

Fig.3 Relation between [O] at RH decarburization end and T[O] in tundish

3) Effect of the tundish flux basicity on T[O]

Fig.4 shows the changes of T[O] in the course of casting for different basicity of tundish fluxes. As shown, the T[O] in the tundish can be reduced by using a higher basicity tundish flux.

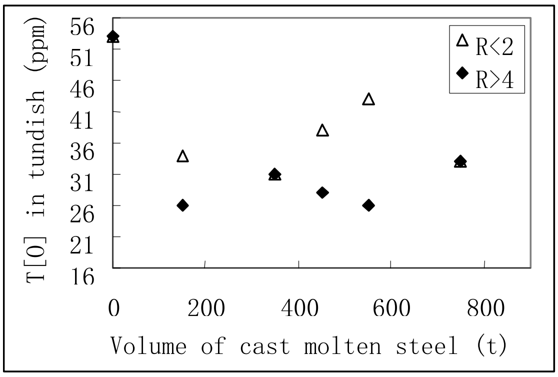

Fig.4 T[O] in tundish in course of cast for different tundish fluxes

($R=CaO/SiO_2$)

Fig.5 and Fig.6 show the number and area percentage of inclusions in response to different basicity of tundish fluxes. It can be seen from Fig5 and Fig 6 that number and area percentage of inclusions are lower with a high basicity tundish flux.

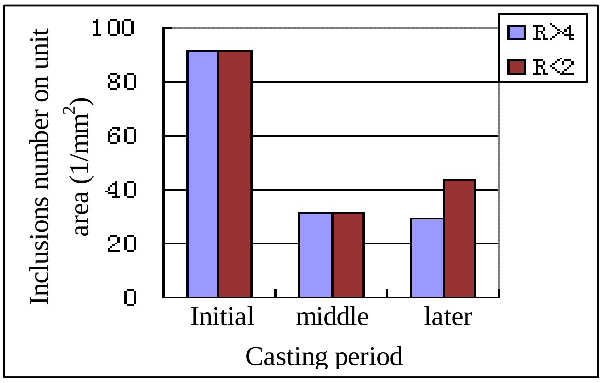

Fig.5 Inclusion number on unit area in course of casting for different fluxes

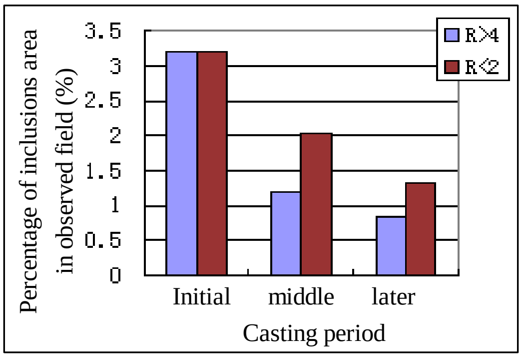

Fig.6 Percentage of inclusions area in observed field in course of casting for different tundish fluxes

4) Effect of fluid flow control in tundish on steel cleanliness [1]

Fig.7 shows the removal efficiency of macro-inclusions, the total oxygen and micro-inclusions with different flow control devices. The above three efficiencies are 80%, 54%, 25% respectively in tundish with device A (two dams and one weir with filter). The industrial trail results show great advantage to remove micro-inclusions with filter. The removal efficiency of micro-inclusions is 10% without filter but is 22% with filter.

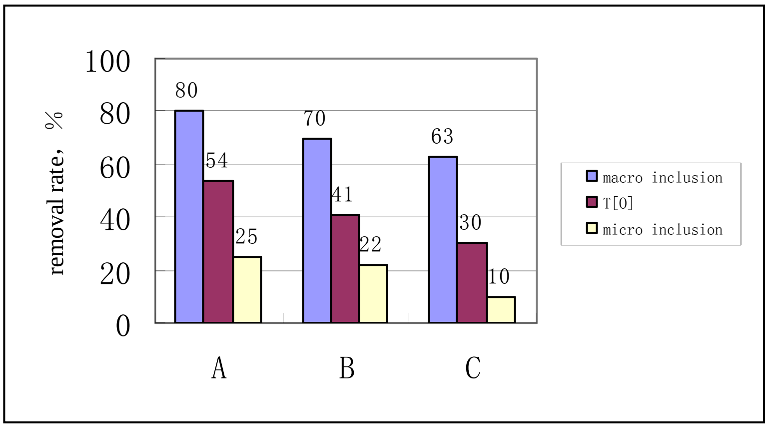

Fig.7 Effect of flow control devices on inclusions removal

(A-2 dams and 1 weir with filter, B-1 dam and 1weir with filter, C- 1 dam and 1weir without filter)

2.4 Production technology of low nitrogen steel

The decrease of nitrogen content in BOF blowing end and prevention of nitrogen pick-up are the two main ways to produce low nitrogen steel.

2.4.1 Low nitrogen blowing process in BOF

The low nitrogen blowing process in BOF is employed in the production of low nitrogen steel:

- Controlling the nitrogen content of hot metal and the ratio of hot metal.
- Optimizing the slag-forming and blowing pattern in BOF.

After adoption of the low nitrogen blowing process in BOF, the nitrogen content at blowing end can be controlled below 13ppm.

2.4.2 Prevention technology of nitrogen pick-up of molten steel

The different tapping patterns will influence the degree of nitrogen pick-up of molten steel. As shown in Fig.8, the opening tapping (aluminum-free tapping) is beneficial to the decrease of nitrogen pick-up.

Fig8 shows that the amount of average nitrogen pick-up for killing tapping is 16.8ppm, but only 5ppm for opening tapping.

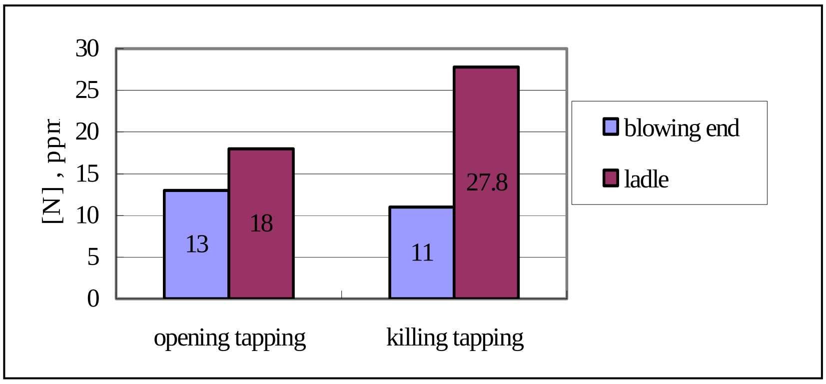

Fig.8 Comparison of Nitrogen pick-up for opening tapping and killing tapping

On a slab caster, the largest nitrogen pick-up generally occurs between ladle and tundish[2]. For this reason, the shrouding tube is used, and the small gap between the ladle and the shrouding tube is sealed by Ar and fiber cone. Currently, the nitrogen pick-up can be controlled within 1.5ppm during continuous casting.

After adoption of above measures, the low nitrogen steel with nitrogen less than 20ppm could be mass-produced in Baosteel.

2.5 Production technology of ultra-low carbon steel

2.5.1 Technology of decarburization in RH

The control technologies of decarburization in RH are outlined in the following two points.

- Control of carbon, oxygen content before RH decarburization
- Technology of decarburization in RH

1) Control of carbon, oxygen content before RH decarburization

The [C] and [O] before and after decarburization in RH are shown in Fig.9. According to Fig.9, the initial [C] and [O] within square frame are more suitable for RH decaburization. In this case, the [C] and [O] after RH decarburization and Al consumption for deoxidation are at lower level, which benefits to cleanliness of molten steel.

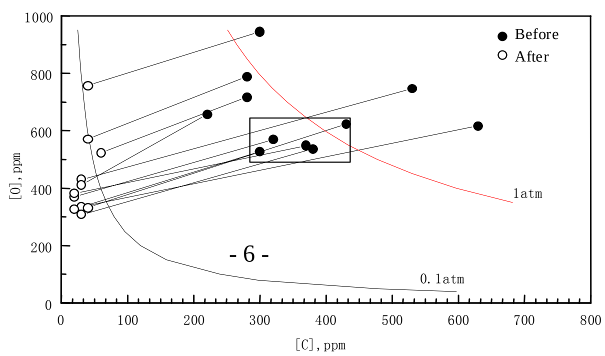

Fig .9 [C] and [O] content before and after RH decarburization

2) Technology of the increase of decaburization rate

A lot of basic researches show that the main means of increasing RH decarburization rate is to increase circulation flowrate of molten steel in RH. The circulation flowrate can be expressed as the following.

$$Q = 7.43\times10^{3} G^{1/3} D^{4/3} (\ln p_1 / p_2)^{1/3}$$

Q– circulation flowrate ,kg/min

G-lift gas flowrate ,m^3/min

D-snorkel diameter ,cm

P_1-atomosphere pressure,torr

P_2-vacuum vessel pressure ,torr

It can be seen from above formula that the circulation flowrate can be increased by the increase of lift gas flowrate and enlargement of snorkel diameter as well as the decrease of vacuum vessel pressure. Among them, the change of the snorkel diameter has the most important effect on the circulation flowrate.

The key device parameters of $1^{\#}$ RH and $2^{\#}$ RH in Baosteel are shown in Table 2

Table 2 Device Parameters of RH of No.1 steelmaking shop in Baosteel

Item		$1^{\#}$ RH	$2^{\#}$ RH
Capacity (Ton/heat)		300	300
Diameter of snorkel (mm)		500	750
Lift gas flowrate (Nl/min)		1200~1400	2000~3000
Blowing oxygen	Pattern	OB	MFB
	Flowrate (Nm^3/hr)	1000~1500	2000~2800
Capacity of vacuum pump under 0.5 Torr (kg/hr)		950	1100

Fig.10 shows the changes in [C] with time during RH decarburization.

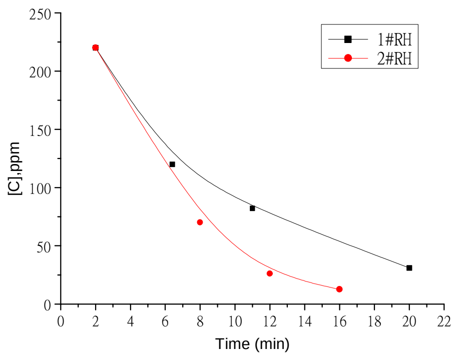

Fig.10 Comparison of decarburization rate of 1#,2# RH in Baosteel

As shown in Table 2, compared with 1# RH, the diameter of snorkel and lift gas flowrate as well as the capacity of vacuum pump in $2^{\#}$ RH are further increased. As shown in Fig.10, the decarburization rate can be increased and the treatment time can be reduced greatly through the improvements.

2.5.2 Prevention technology of carbon pick-up of molten steel

Among many factors resulting in the carbon pick-up of molten steel, it is an important reason that the refractory and flux used in steelmaking contain excessive carbon content. The relative researches concentrate on two areas in Baosteel.

1) High basicity tundish flux

Compared with the conventional tundish flux ($R=CaO/SiO_2<2$), the high basicity tundish flux ($R>4$), which is newly developed, has lower carbon content. Fig.11 shows the changes of carbon content in the course of casting for different basicity of tundish fluxes. As shown in Fig.11, the decrease of carbon content in tundish flux is beneficial to the decrease of carbon pick-up of molten steel.

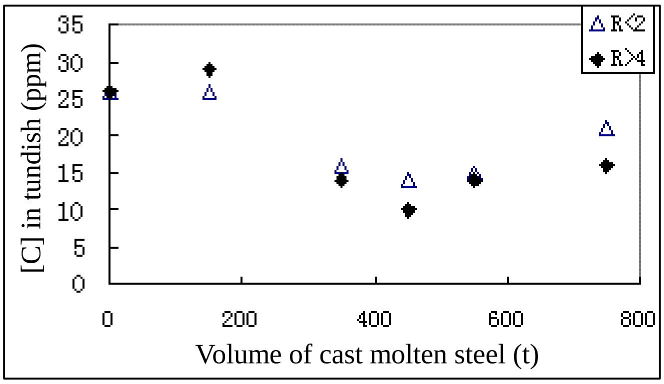

Fig.11 Relation between [C] in tundish in course of casting for different tundish flux

2) High viscosity mold powder with low carbon content

The decrease of carbon content in mold powder is a direct way to avoid the carbon pick-up of ultra low carbon molten steel. Additionally, the increase of the viscosity of mold powder is favorable to prevent carbon pick-up because of the reduction of diffusion rate of carbon from the mold powder to molten steel.

The high viscosity mold powder with low carbon content has been adopted. The comparison of carbon pick-up before and after mold power improvement is shown in Fig.12.

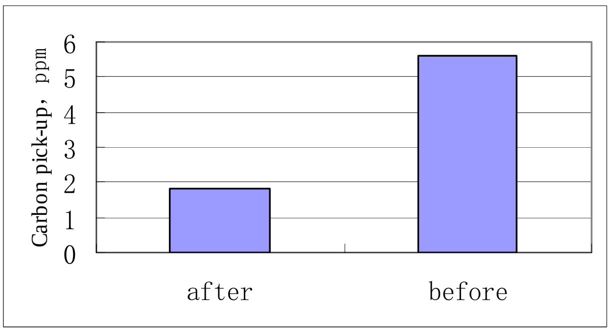

Fig.12 Comparison of carbon pick-up before and after mold powder improvement

According to Fig.12, the amount of carbon pick-up has been decreased by 3.8ppm after mold powder improvement.

3) Carbon-free ladle refractory

Fig.13 shows the effect of different refractory on carbon pick-up of ultra-low carbon steel. As shown, the effect of different ladle refractory on carbon pick-up is quite evident. The tests show that Al_2O_3-MgO based pouring material for ladle bottom and MgO- Al_2O_3 based pouring material for slag line of ladle don't result in the carbon pick-up of molten steel.

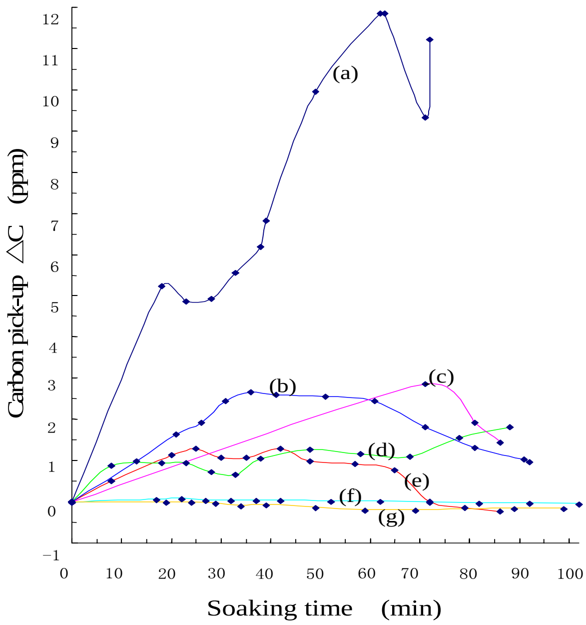

Fig.13 Effect of refractory on carbon pick-up of clean steel

((a)—Pyrophyllite-silicon carbon based brick; (b)—MgO-C based brick for BOF; (c)—MgO-Al_2O_3-SiC based pouring material; (d)—MgO-C based brick for slag line of ladle; (e)—MgO-C based brick with low carbon; (f)—Al_2O_3-MgO based pouring material; (g)—MgO-Al_2O_3 based pouring material)

3.Progress of comprehensive level of clean steel in Baosteel

On the basis of individual technology researches of clean steel, the combination trials have been carried out for IF steel and pipeline steel. The mass-production technologies of clean IF and pipeline steels have been developed successfully. Table 3 shows the average cleanliness of IF steel and pipeline steel at different periods.

Table 3 Average cleanliness of IF steel and pipeline steel at different periods ppm

Year	Pipeline steel					IF steel		
	[S]	[P]	T[O]	[N]	[H]	[C]	[N]	T[O]
1996	32	134	35	47		50	24	50
1999	16	89	24	30	2	23	16	28
2003	9	54	16	30	1.5	16	15	19

It can be seen from Table 3 that the cleanliness of IF steel and pipeline steel makes a sustained progress and has achieved the international advanced level.

4. Conclusion

1) The individual production technologies of clean steel have been developed in Baosteel, which have established a substantial foundation for production of high quality products and possess very high practical value.
2) The IF steel with [C]≤20ppm, [N]≤20ppm, T[O]≤20ppm and pipeline steel with [S]≤10ppm, [P]≤50ppm, T[O]≤20ppm, [N]≤30ppm, [H]≤1.5ppm can been mass-produced in Baosteel. The cleanliness of two kinds of steel has achieved the international advanced level.

REFERENCE

1 Fei H C, Zhang L F etc., The second International Conference on Continuous Casting of steel in developing country, Oct. 1997, 77-82

2 C.Marique etc., Ironmaking and Steelmaking, 1988,Vol.15, No.1,38-42

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