

ROLE OF SLAG ON SECONDARY REFINING PROCESS

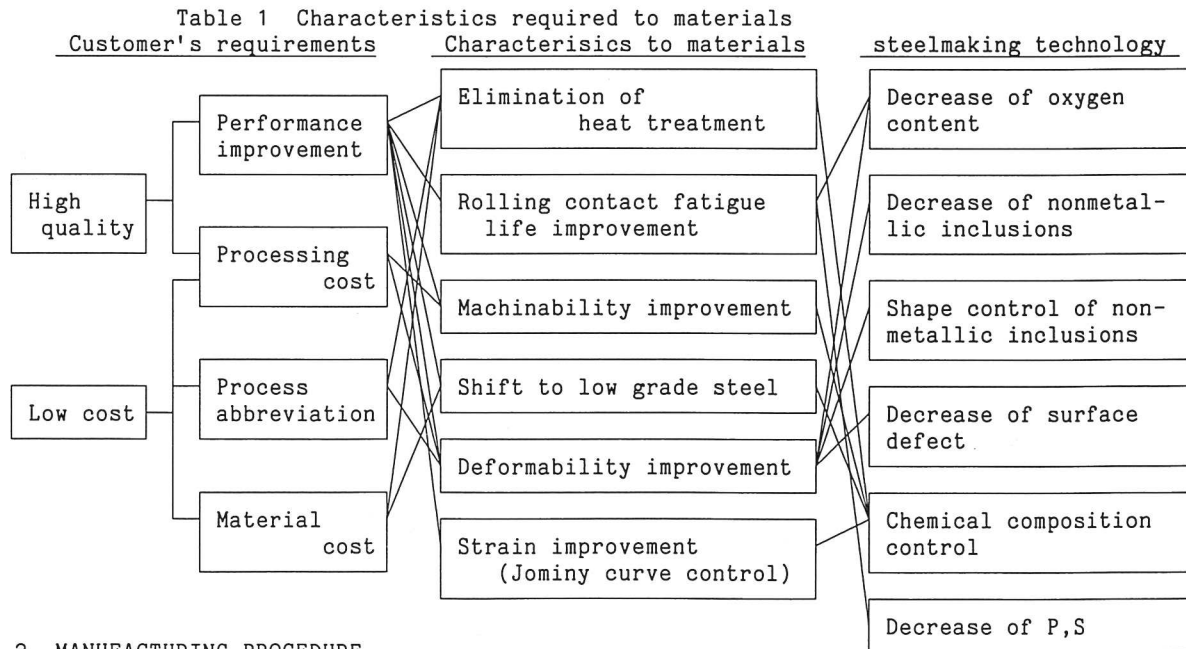
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Synopsis: Recently customer's requirements for structural steel have diversified and become rigorous. To satisfy them , secondary refining process which is LF(Ladle Furnace) - RH(RH degassing unit) and AR (Aichi advanced Refining furnace) - LD (Ladle Degassing unit) have installed and new technologies have been developed. They made it possible to produce such high quality steel under the conditions of higher productivity and lower cost. In this study , optimum slag composition for oxygen reduction and sulphur control including desulphurization have been investigated. By controlling slag composition ,it become possible to produce ultra low oxygen steel , low sulphur steel and complex S-Pb free cutting steel
 Keywords: Deoxidation ,Desulphurization , Sulphur control, Secondary refining

1. INTRODUCTION

Recently customer's requirements for quality-up of speciality steel have diversified and become rigorous for automobile use as shown in table 1.¹⁾ For the purpose of making lighter automobiles , reduction of oxygen content in steel is demanded to increase strength for parts' miniaturization. Narrow range control of sulphur for structural steel and complex free cutting steel (S=0.040-0.070% , Pb=0.15-0.25%) is demanded to raise the machinability. To satisfy these requirements , optimum conditions on secondary refining process (LF,RH) has been established. This paper describes the production techniques of low oxygen content steel , low sulphur content steel and sulphur control of complex free cutting steel.



2. MANUFACTURING PROCEDURE

Fig.1 and Fig.2 show Aichi's two main production lines and Table 2 shows main the specification of the principal equipments. The 80tEAF line and 50tEAF line produce speciality steel 75,000 t/month and 25,000t/month respectively. The big differences between them are that molten steel is degassed with slag in LF-RH line and without slag in AR-LD line ,

and AR can control its atmosphere in chamber by inert gas.

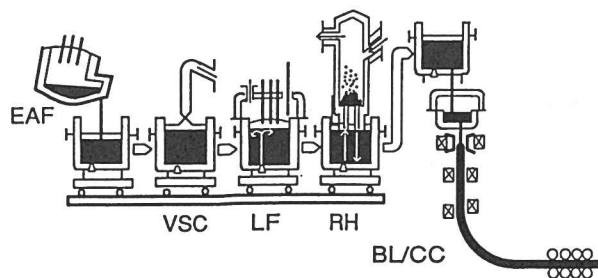


Fig.1 Schematic diagram of 80tEAF line

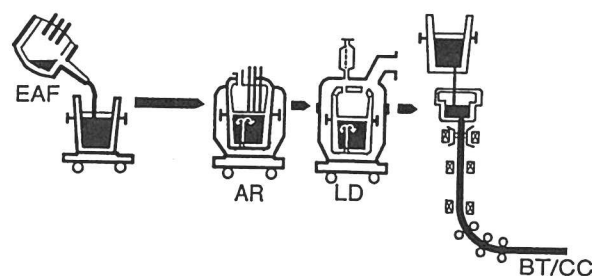


Fig.2 Schematic diagram of 50tEAF line

Table 2 Main specifications of principal equipments in 80tEAF line and 50tEAF line

Items		80tEAF line(LF-RH)	50tEAF line (AR-LD)
EAF	<ul style="list-style-type: none"> • Shell diameter • Transformer capacity • Max.secondary current • Max.secondary voltage • Electrode diameter • Charging weight 	7.1M 75MVA 70KA 940V 24inches 140T	5.8M 30MVA 43KA 597V 20inches 70T
AR/LF	<ul style="list-style-type: none"> • Transformer capacity • Max.secondary current • Max.secondary voltage • Electrode diameter • Treating time 	16MVA 30.8KA 360V 14inches 30-70min.	14MVA 28 KA 290V 14inches 20-40min.
LD/RH	<ul style="list-style-type: none"> • Type of vacuum pump • Treating time 	Steam ejector 20-45min.	Steam ejector 7-20min.
CC	<ul style="list-style-type: none"> • Type of machine • Number of strand • Mold size 	Curved type 2 370 × 480 mm	Curved type 2 135s,185s, 180× 320

3. METHOD OF INVESTIGATION

3-1 Oxygen content reduction

At first step of investigation, the effects of slag composition on deoxidation were studied in LF-RH process. And next, deoxidation rates in both of LF - RH and AR - LD process were investigated to discuss the merits and demerits of them.

3-2 Desulphurization and sulphur control

The influence of slag composition on desulphurization has been studied in AR and LF. And next, the technique of sulphur control during stirring for lead addition were investigated

4. RESULT AND DISCUSSION

4-1 Technique of deoxidation

4-1-1 Effects of slag composition on deoxidation

Main roles of slag on secondary refining are considered as follows.

- Improvement of deoxidationability of deoxidizing elements.
- Absorption and removal of inclusions such as Al_2O_3 .
- Less reoxidation of molten steel by slag.

As reoxidation sources are FeO, MnO and SiO_2 in slag, increase of basicity with increasing deoxidationability of deoxidizing elements is effective way to reduce oxygen contents. The effects of FeO and MnO on deoxidation in case hardening steel are shown in Fig.3. To investigate further detail of influence of SiO_2 on oxygen contents, ($FeO + MnO \leq 0.5\%$) was used. The result is shown in Fig.4.

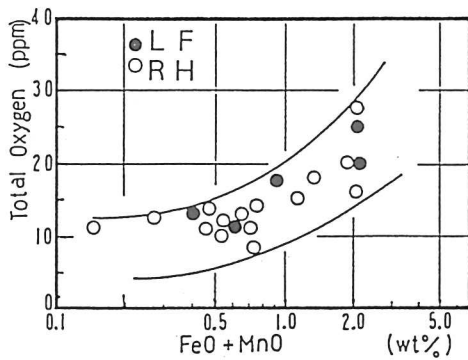


Fig.3 Relationship between (%FeO + %MnO) in slag and total oxygen content of molten steel after treatment in LF and RH

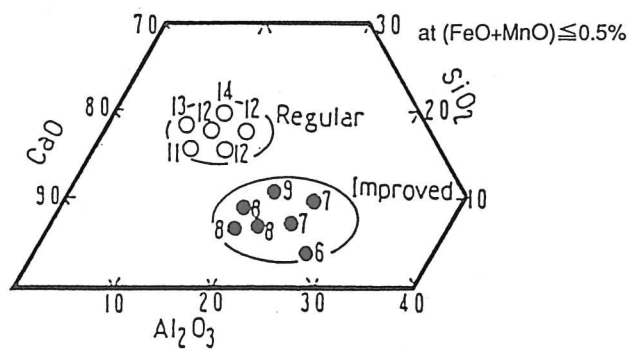


Fig.4 Effect of (%SiO₂) in slag in LF and RH on total oxygen content of products (Numbers beside dots indicate the oxygen content in products at each slag composition.)

Reduction of activity of SiO₂ is a basic policy to reduce oxygen contents and appropriate amount of Al₂O₃ is needed to keep fluidity of slag and prevent refractory erosion at minimum without using excess fluorspar in actual operation. Fig.5 shows the points to make high basicity slag and Table 3 shows the example of slag composition obtained by the operation in accordance with these points.

Table 3 Example of slag composition for high quality steel (wt%)

CaO	SiO ₂	Al ₂ O ₃	MnO	T.Fe	MgO	CaF ₂
60.3	8.5	15.9	<0.1	0.3	5.3	5.2

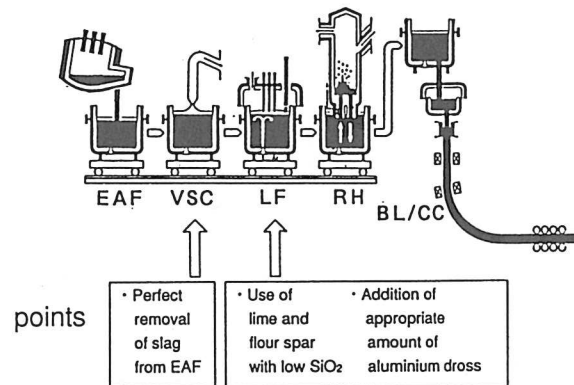


Fig.5 The points to make with high basicity and low (%FeO+ %MnO)

4-1-2 Deoxidation and reoxidation rate comparison between LF-RH process and AR-LD process

Deoxidation behavior in LF-RH and AR-LD process was studied as shown in Fig.6. By using these results, the next analysis was done. By using the assumption that the apparent deoxidation rate during operation is expressed as the balance of deoxidation and reoxidation, the deoxidation equation is written in equation(1).²⁾

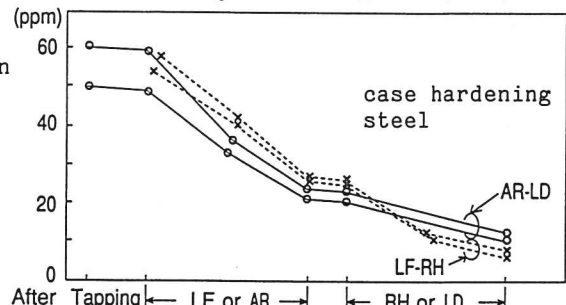


Fig.6 Example of deoxidation behavior

$$(-d[O]/dt)_{Total} = (-d[O]/dt)_{output} - (-d[O]/dt)_{input} \dots\dots\dots (1)$$

Assuming that deoxidation and reoxidation are linear reactions, equation(2) and equation(3) are obtained. $(-d[O]/dt)_{output} = K ([O] - [O]_{eD}) \dots\dots\dots (2)$

$$(-d[O]/dt)_{input} = K_R ([O]_{eR} - [O]_{eD}) + k \dots\dots\dots (3)$$

Then equation(1) is changed to equation(4) by substituting equation(2) and (3) into equ.(1)

$$(-d[O]/dt)_{Total} = K [[O] - (K_R ([O]_{eR} - [O]_{eD}) + k/K + [O]_{eD})] \dots\dots (4)$$

On the other hand, from actual deoxidation behaviors, α and $[O]_e$ which are shown in equation(5) are obtained by data fitting method.

$$(-d[O]/dt)_{Total} = \alpha ([O] - [O]_e) \dots\dots\dots (5)$$

$[O]_{eR}$ and $[O]_{eD}$ are estimated from thermodynamic data, K and K_R are obtained by solving simultaneous equation of equation(6) and (7).

$$\alpha = K \dots\dots\dots (6)$$

$$[O]_e = K_R ([O]_{eR} - [O]_{eD}) + k/K + [O]_{eD} \dots\dots\dots (7)$$

- $[O]_e$: Apparent deoxidation equilibrium value
- $[O]_{eD}$: Equilibrium oxygen contents decided by molten steel composition
- $[O]_{eR}$: Reoxidation equilibrium value decided by slag composition

k : Reoxidation rate by oxidation of Al in molten steel (before Al adding, $k=0$)
 K : Deoxidation rate constant [O] : Total oxygen
 K_R : Reoxidation rate constant α : Apparent reaction rate constant

The result of calculation is shown in Fig.7. AR has smaller K_R than LF, because it can control its atmosphere to prevent oxidation by air. On the other hand, RH has larger K and K_R than LD. It is thought that coagulation of inclusions in RH vessel and removal of them by slag on ladle are promoted during RH degassing, while irregular reoxidation by stuck metal in RH vessel seems to take place little by little. However, since K is one order larger than that of LD, total deoxidationability on LF-RH process is larger than that of AR-LD process. Fig.8 shows total oxygen produced by each processes.

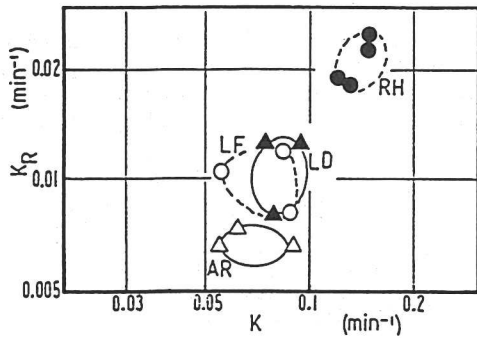


Fig.7 Relationship between K and K_R

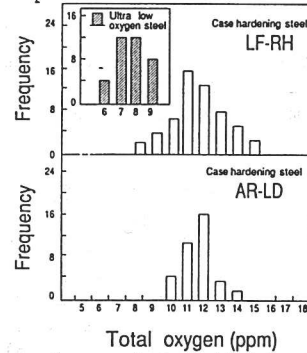


Fig.8 Comparison of deoxidationability in LF-RH and AR-LD process

Although, LF-RH process is advantageous to produce ultra low oxygen steel, the production cost of AR-LD process is much cheaper than LF-RH process. The most suitable refining process has been chosen in accordance with steel grade as shown in Table 4.

Table 4 Choice of process according to steel grade

Steel grade	Total oxygen (ppm)		Process
	Case hardening steel	SAE52100 class	
Ultra low oxygen steel	≤ 9 ppm	≤ 7 ppm	LF-RH with ultra high basicity slag
Low oxygen steel	≤ 15 ppm	≤ 10 ppm	AR-LD with ultra high basicity slag in AR
Normal steel	—	—	AR-LD

4-1-3 Effect of decrease of total oxygen on cold formability and fatigue life

The production technique of low oxygen contents steel has been applied to case hardening steel and ball bearing steel. As a result, cold formability and fatigue life are extremely improved as shown in Fig.9 and Fig.10. Fig.9 shows laboratory data of relationship between

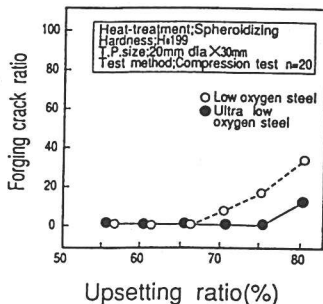


Fig.9 Relationship between upsetting ratio and frequency of crack initiation

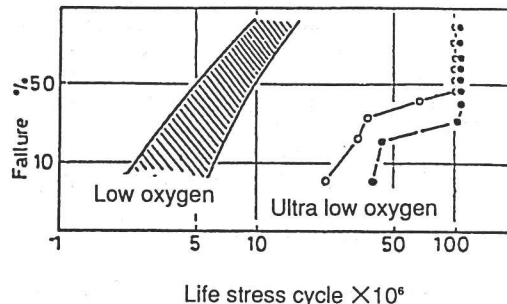


Fig.10 Fatigue life of high carbon ball bearing steel

upsetting ratio and crack ratio. Upper limit of upsetting ratio has improved from 65% to 75%. And at customer's plant the forging crack ratio has been extremely improved. Total oxygen content of ball bearing steel is less than 7ppm, so rolling contact fatigue life has been improved to three times longer.(Fig.10)

4-2 Technique of sulphur control including desulphurization
4-2-1 Desulphurization

As for desulphurization, sulphur content of the molten steel of which initial content is 0.025% could be decreased to less than 10 ppm within 70 minutes of LF refining time by controlling the slag composition (Fig.11:CaO/SiO₂/Al₂O₃=0.2-0.4) and quantity, application of powder injection and strong stirring by double porous plugs(Fig. 12^{3'}). LF has a powder injection equipment. It is used by the way to blow particles under 1mm of 85%CaO - 15%CaF₂ onto the surface of the molten steel (Powder Blowing method). (T.Fe + MnO) content of EAF slag is reduced in shortened slag forming time by it, and in addition, high basic and low oxidized slag can be easily and stably obtained with a small amount of new flux.

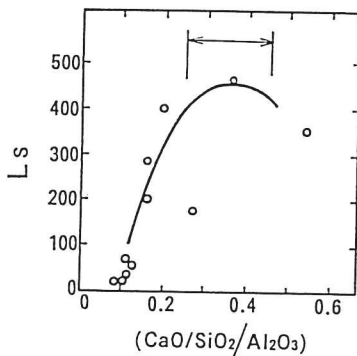


Fig.11 Relation between sulphur distribution coefficient Ls and (CaO/SiO₂)/Al₂O₃

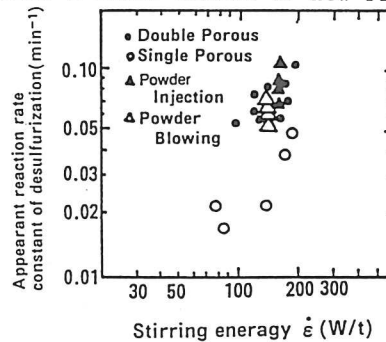


Fig.12 Relation between apparent reaction rate constant of desulphurization(Ks) and stirring energy (ε)

4-2-2 Sulphur control during strong stirring for lead addition

Narrow range control of sulphur for complex free cutting steel (Table 5) is demanded to raise the machinability. In LF-RH process sulphur control is very difficult because sulphur is reduced by slag-metal reaction during lead addition. Then prevention technique of desulphurization is necessary. Desulphurization rate equation and sulphur distribution Ls are expressed equation (8) and (9) respectively. By these equations, the conditions of preventing desulphurization are considered.(Table 6)

Table 5 Example of chemical composition of complex free cutting steel(wt%)

C	Si	Mn	S	Pb
0.45	0.25	0.80	0.060	0.18

$$-[\%S]/dt = k_s \cdot (\rho_s / \rho_m) \cdot (A/V_m) \cdot (L_s[\%S] - (\%S)_o) \quad (8)$$

$$L_s = (\%S)/[\%S] = k_s \cdot (a_{O^{2-}} \times f_s) / ((a_o \times f_s^{2-})) \quad (9)$$

- [%S] : Sulphur content in metal
- (%S)_o: Initial sulphur content in slag
- k_s : Sulphur transfer coefficient in slag
- V_m : Volume of metal
- A : slag-metal intersurface area
- ρ_s : Slag density
- ρ_m : Metal density
- a_{O²⁻} : Activity of O²⁻ in slag
- a_o : Activity of oxygen in metal
- f_s : Activity coefficient of sulphur in metal
- f_{s²⁻} : Activity coefficient of sulphur in slag

Table 6 Conditions of preventing desulphurization

Items	Conditions	Right or wrong
Reduction of the slag-metal intersurface area	① Removal slag	△
	② Low fluidity	×
	③ No stirring	×
Reduction of Ls = Increase of (%S)	④ Reduction of O ²⁻	○
	⑤ Increase of S ²⁻	○
	⑥ Increase of O	×

In table 6 we selected test conditions. In order to decrease Ls, Fe-S alloy and silica sand were added. Fig.13 shows desulphurization ratio during lead addition. In case of slag basicity=1.9 and (%S)=1.8%, desulphurization ratio is almost 0%. Fig.14 shows the operational result of relationship between sulphur content before and after lead addition in above conditions. As a result, sulphur content can be controlled between 0.045% and 0.055% constantly.

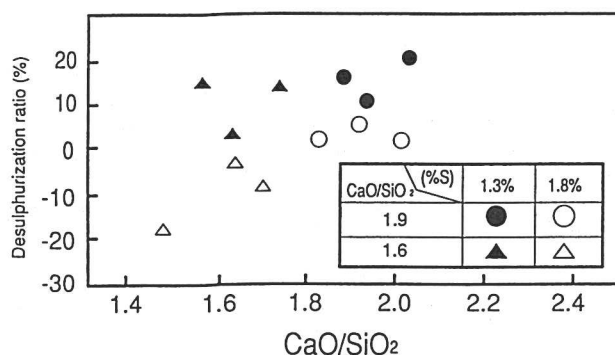


Fig.13 Relationship between desulphurization ratio during lead addition and slag basicity

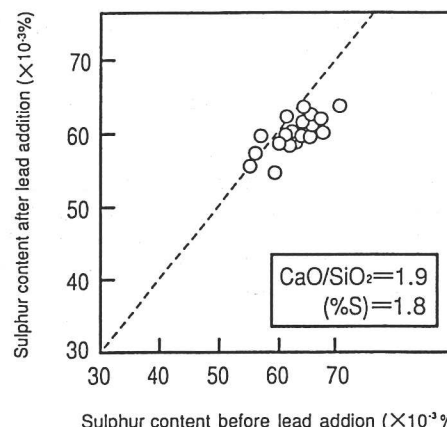


Fig.14 Relationship between Sulphur content before and after lead addition

4-2-3 Slag for sulphur control including desulphurization

According to sulphur level of products, Ls of slag used in secondary refining process are shown in table 7.

Table 7 Slag used in secondary refining process

Steel grade	Sulphur level	Slag weight	Ls
Structural steel	0.010-0.030wt%	2.0 kg/t	200-250
Ball bearing steel /cold forging steel	0.003-0.010wt%	2.7 kg/t	300-350
Special ball bearing steel	-0.002wt%	4.0 kg/t	450-500
Complex free cutting steel	0.055-0.065wt%	1.2 kg/t	30

5. CONCLUSION

- (1) Total oxygen content of case hardening steel and ball bearing steel can be obtained constantly less than 9ppm and 7ppm respectively by controlling slag composition as FeO+MnO is less than 0.5% and slag basicity is over than 7.
- (2) By comparison of deoxidationability and operation cost of LF-RH and AR-LD process, LF-RH has better deoxidationability, but operation cost of AR-LD is much cheaper.
- (3) Ultra low oxygen steel is produced by LF-RH process and can improve the forging crack ratio and contact fatigue life.
- (4) $S \leq 10$ ppm can be obtained by the application of the control of slag composition ($CaO/SiO_2/Al_2O_3=0.25-0.45$) and quantity, powder injection and strong stirring by double porous plugs.
- (5) In complex free cutting steel, narrow range control of sulphur has been established by slag composition control to prevent desulphurization during strong stirring for lead addition.

REFERENCES

- 1) J.Eguchi et al. : Proceeding of 6th IISC Jpn., (1990), 650
- 2) T.Yamada et al. : CAMP-ISIJ Jpn., 1(1988), 1177
- 3) M.Kawachi et al. : Tetsu-to-Hagane Jpn., 72(1986), S218