Optimization of Desulphurization Process using Lance Injection in Molten Iron

Wenjun MA,^{1)*} Haibo LI,¹⁾ Yang CUI,¹⁾ Bin CHEN,¹⁾ Guoliang LIU¹⁾ and Jianli JI²⁾

1) Shougang Research Institute of Technology, Room 1107, Shougang Research Institute of Technology, No.69, Yangzhuang Road, Shijingshan District, Beijing, 100043 China.

2) Shougang Qian'an Iron & Steel Co., Ltd, Room 606, Yang DianZi Town Riverside Village, Qian'an, 064404 China.

(Received on April 11, 2016; accepted on October 5, 2016; J-STAGE Advance published date: January 26, 2017)

A kinetic model of the 60% Mg and 40% CaO injection desulphurization was established. The simulation results from the model were verified by sampling, and it was in accord with the sampling results. By analyzing the model, the desulfurization process of high sulfur molten iron had three stages, incubation stage, rapid desulfurization stage and slow desulfurization stage. In order to improve the dynamic conditions and the utilization rate of the desulfurization agent, for the molten iron of sulfur content $\geq 0.035\%$, a new injection desulphurization mode was developed and applied. The smaller injection rate of powder and the larger flow rate of nitrogen were used in the slow desulfurization stage. Compared with the conventional process, the consumption of the desulfurizing agent is reduced by 10–20% by using the two-stage injection method.

KEY WORDS: injection desulphurization; kinetic model; two-stage injection method; utilization rate.

1. Introduction

In recent years, in order to improve the profit of the products and expand the market competitiveness of products, the research on the high efficiency and low cost production technology of the low sulfur and ultra-low sulfur steel has become a focus. It has been proved that the hot metal pre-treatment desulfurization technology is currently the most economical and efficient measure of desulphurization. The proportion of hot metal desulphurization is close to 100% in the some steel plant.

The injection method and the Kanbara Reactor (KR) method are the most extensive and most representative hot metal desulphurization technology.

In Japan, Kanbara *et al.*¹⁾ succeeded in performing sulfur removal to < 30 ppm by the KR method. The KR method using mechanical stirring can provide a good dynamic condition for desulfurization, and the desulfurization agent the lime system.^{2–5)} The sulfur content can be controlled under 10 ppm by the KR method in the some steel plants.

For the deep desulfurization (sulfur content ≤ 30 ppm after desulfurization) hot metal using the injection method, the desulfurization agent generally used the magnesium system with good reaction kinetics and thermodynamics.^{6–9)} A wide variety of materials including Na_2CO_3 , CaO, CaC_2 and Mg have been used to desulphurise iron, but to facilitate desulphurization efficiency and satisfy environmental requirements; nowadays many steel works employ magne-

sium alone or in combination with various alkaline metal oxides as the primary desulphurisation agents.¹⁰⁾ By using the injection method, the sulfur content can be controlled at 30–50 ppm.

For the injection desulphurization method, favorable dynamic conditions are necessary. In order to get a higher desulfurization efficiency, these parameters, the gas flow rate, the rate and depth of injection, the geometry and location of the submerged lance, were studied.^{11–13)}

In a steel plant in China, hot metal is desulphurised in the 210 t transfer ladle by injection of 60% Mg and 40% CaO using nitrogen as a carrier gas. With the adjustment of product structure, the proportion of the deep desulfurization hot metal increased to more than 95%. Some problems, the high consumption of desulfurizer, the large amount of slag, and the unstable resulphurization, are also gradually revealed. It seriously impacted on the normal production and the cost control.

In this work, the process of injection desulphurization was investigated by a kinetic model. The changes of sulfur content were analyzed. The result from the model was verified by sampling. According to the result, a new injection desulphurization mode was developed and applied.

2. Mathematical Modelling

Seshadri *et al.*¹³⁾ established the mathematical model of the lime and top slag, but it is not taken into account the magnesium desulphurization. The kinetic model has been proposed based on the following assumptions and considerations: (1) particles of the CaO and Mg are spherical; (2)

* Corresponding author: E-mail: mawenjun2929@163.com
DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-167>

the desulfurizing agent does not contain any sulfur; (3) the rate of injection and the temperature and melt weight remain constant; (4) the amount and composition of the top slag are time-dependent and are determined by the carry-over slag and the rate of injection; (5) the fraction of particles entrapped in the melt and those accommodated at the bubble-metal interface remain constant; (6) the mean diameter of the bubbles is a function only of the metal density; (7).

The total rate of desulfurization can be written as the sum of the contributions of the top slag and CaO and Mg, as given by the equation:

$$V_{total} = V_{CaO} + V_{Mg} + V_{top} \dots\dots\dots (1)$$

2.1. Desulphurisation Rate of Top Slag

The restriction factor of top slag desulphurisation was the sulfur diffusion in the top slag. The mass transfer equation of top slag desulphurisation can be expressed as:

$$J_{[S]} = L_s \cdot K_s \cdot \left(C_{[S]} - \frac{C_{(S)}}{L_s} \right) \dots\dots\dots (2)$$

The molar volume concentration is converted into the mass fraction, and the effect of the mix time on the desulphurisation rate was considered. The rate of top slag desulphurisation can be expressed as:¹⁴⁾

$$-\frac{d[\%S]}{dt} = \frac{A_{top} \cdot \rho_z}{W_m} \cdot K_s \cdot L_s \cdot \left\{ [\%S] \exp(-t_{mix}/t) - \frac{(\%S)}{L_s} \right\} \dots\dots\dots (3)$$

The sulfur content of top slag can be expressed as:

$$(\%S) = \frac{(\%S)_o \cdot W_{so} + \{[\%S]_o - [\%S] \exp(-t_{mix}/t)\} \cdot W_s}{W_{so} + I_p \cdot t \cdot \eta} \dots\dots (4)$$

2.2. Desulphurisation Rate of CaO

The desulfurization behavior of CaO has been investigated,^{12,14,15)} and the restriction factor of desulphurisation was the sulfur diffusion in the boundary layer of hot metal. The mass transfer equation of the process can be expressed as:

$$J_{[S]} = K_m \cdot (C_{[S]} - C_s^e) \dots\dots\dots (5)$$

The molar volume concentration is converted into the mass fraction:

$$-\frac{d[\%S]}{dt} = \frac{A_1}{V_m} \cdot K_m \cdot ([\%S] - [\%S]_e) \dots\dots\dots (6)$$

where A_1 is the total contact surface area of particles and the hot metal, and it can be calculated.¹⁵⁾ The effect of the mix time on the desulphurisation rate was considered. The rate of top slag desulphurisation can be expressed as:^{14,15)}

$$-\frac{d[\%S]}{dt} = \frac{6 \cdot \beta \cdot I_p \cdot \phi_1 \cdot \tau_p \cdot \rho_m}{d_s \cdot W_m \cdot \rho_s} \cdot K_m \cdot \{ [\%S] \cdot \exp(-t_{mix}/t) - [\%S]_e \} \dots\dots\dots (7)$$

2.3. Desulphurisation Rate of Mg

Magnesium existed in two forms at the molten iron temperature. A part of magnesium formed bubbles and react with the sulfur in the molten iron. The other part was dis-

solved in molten iron and react with the sulfur in molten iron. Irons *et al.*'s¹⁶⁾ report showed that the proportion of bubbles and the dissolved magnesium was 1:9.

During the desulfurization process of magnesium bubbles, the restriction factor was the sulfur diffusion to the bubble surface in the boundary layer. The mass transfer equation of the process can be expressed as:

$$J_{[S]} = K_b \cdot (C_{[S]} - C_{[S]}^b) \dots\dots\dots (8)$$

The molar volume concentration is converted into the mass fraction, and the effect of the mix time on the desulphurisation rate was considered. The rate of the desulphurisation of magnesium bubbles can be expressed as:¹⁷⁾

$$-\frac{d[\%S]}{dt} = K_b \cdot A_b \cdot \{ [\%S] \cdot \exp(-t_{mix}/t) - [\%S]_b \} \dots\dots (9)$$

where A_b is the specific surface area of the gas-liquid interface, and it can be expressed as:

$$A_b = \frac{6 \cdot Q \cdot \tau_{RT} \cdot \rho_m}{W_m \cdot d_b} \dots\dots\dots (10)$$

During the desulfurization process of dissolved magnesium, at the initial stage, the restriction factor was the diffusion of the dissolved magnesium at the solid-liquid interface. At the later stage, the restriction factor was the diffusion of the sulfur at the solid-liquid interface. The rate of the desulphurisation of magnesium bubbles can be expressed as:¹⁷⁾

$$-\frac{d[\%S]}{dt} = 0.4167 \cdot k \cdot \rho_m \cdot [\%S] \exp(-t_{mix}/t) \cdot [\%Mg] \exp(-t_{mix}/t) \dots\dots (11)$$

Based on the material balance, the dissolution rate of magnesium can be expressed as:

$$\frac{d[\%Mg]}{dt} = \frac{100 \cdot B_1 \cdot \phi_2 \cdot I_p}{W_m} - 0.75 \cdot \{ 0.4167 \cdot k \cdot \rho_m \cdot [\%S] \exp(-t_{mix}/t) \cdot [\%Mg] \exp(-t_{mix}/t) \} + \dots\dots (12)$$

2.4. Mathematical Equations

According to the above analysis, the total rate of desulfurization can be expressed as:

$$V_m = -\frac{d[\%S]}{dt} = \frac{A \cdot \rho_z}{W_m} \cdot K_s \cdot L_s \cdot \left\{ [\%S] \exp(-t_{mix}/t) - \frac{(\%S)}{L_s} \right\} + \frac{6 \cdot \beta \cdot I_p \cdot \phi_1 \cdot \tau_p \cdot \rho_m}{d_s \cdot W_m \cdot \rho_s} \cdot K_m \cdot \{ [\%S] \cdot \exp(-t_{mix}/t) - [\%S]_e \} + \frac{6 \cdot Q \cdot \tau_{RT} \cdot \rho_m}{W_m \cdot d_b} \cdot K_b \cdot \{ [\%S] \cdot \exp(-t_{mix}/t) - [\%S]_b \} + 0.4167 \cdot k \cdot \rho_m \cdot [\%S] \exp(-t_{mix}/t) \cdot [\%Mg] \exp(-t_{mix}/t) \dots\dots\dots (13)$$

Equations (4), (12) and (13) formed a closed set of equations. Seshadri *et al.*¹³⁾ reported that the calculation process of the sulfur mass transfer coefficient (K_s , K_m , K_b), and the sulfur partition coefficient (L_s), the average residence time of particles and bubbles (τ_p , τ_{RT}), were described in detail. Wang *et al.*^{17,18)} studied the function equation of the powder penetration ratio (β) and the mixing time (t_{mix}) by the water

model experiment.

3. Results and Discussion

To solve the above differential equation of first order, first of all, the unknown parameters, K_s , K_m , K_b , L_s , τ_p , τ_{RT} , β , t_{mix} were calculated.^{13,17,18)} In addition, characteristics of the desulphurization reagent, carrier gas, liquid iron, top slag, lance and ladle car were presented in **Table 1**.

The gas flow rate of injecting, the injection rate of powder, and other parameters were set according to the prototype. In addition, the initial sulfur content of the slag was sampled and analyzed. The other process parameters can be obtained according to the above. The initial sulfur content of the hot metal and the total injection time were the initial conditions of the model.

The mathematical model was calculated by using the MATLAB program, with an algorithm based on an explicit Runge–Kutta (4) formula. The instantaneous concentration of sulfur in the hot metal in the desulfurization process was

obtained. Moreover, the change trends of the sulfur content at different initial conditions can be obtained.

3.1. Change of the Sulfur Content

In the steel plant, the sulfur content in molten iron ranged 0.022% to 0.065% and the average was 0.035%. In order to analyze the sulfur change of the different initial content, the initial sulfur content was set to 0.03% and 0.06%. To verify the accuracy of the simulated results, the samples were taken from the hot metal in the different desulfurization time. The compositions of samples were analyzed by ICP-AES and shown in **Table 2**.

Figure 1 showed the simulated and measured results. It can be seen the simulation results were in accordance with the sampling results. The change trends of the sulfur content were shown. But it can be seen that the change trends of 0.06% sulfur and 0.03% sulfur were different. During the first 120 s (seconds), the initial sulfur content of 0.06% and 0.03% were no obvious change. 120 s later, for the initial sulfur content of 0.03%, the sulfur content decreased rap-

Table 1. Parameters used in model.

Parameter	Meaning	Value	Units
<i>Desulphurization reagent characteristics</i>			
ϕ_1	CaO mass fraction of desulfurizing agent	40	%
ϕ_2	Mg mass fraction of desulfurizing agent	60	%
B_1	Proportion of dissolved Mg	80	%
τ_p	Residence time of powder	25.83	s
τ_{RT}	Residence time of Mg bubble	12.45	s
ρ_s	Density of desulfurization agent	1 380	kg/m ³
d_s	Reagent particle diameter	0.001	m
d_b	Diameter of Mg bubble	9.75×10^{-5}	m
K_b	Mass transfer coefficient of sulfur in Mg bubble surface	2.96×10^{-4}	m/s
k	Apparent reaction rate constant	5.21×10^{-5}	–
β	Powder penetration ratio	36.39	%
η	Effective coefficient of powder into the slag layer	40	%
<i>Top slag hot metal</i>			
ρ_z	Density of top slag	3 500	kg/m ³
A_{top}	Reaction area of slag metal interface	8.24	m ²
W_{so}	Initial mass of slag	5 000	kg
(%S) _o	Initial sulfur content of slag	0.5	%
K_s	Mass transfer coefficient of sulfur in slag	4.19×10^{-9}	m/s
<i>Hot metal hot metal</i>			
ρ_m	Density of hot metal	7 138	kg/m ³
W_m	Mass of hot metal	2.1×10^5	kg
K_m	Mass transfer coefficient of sulfur in hot metal	1.56×10^{-4}	m/s
[%S] _o	Initial sulfur content of hot metal	<i>Initial condition</i>	%
<i>Other parameters</i>			
I_p	Injection rate	0.2	kg/s
Q	Gas flow rate	0.0278	Nm ³ /s
t_{mix}	Mixing time of molten pool	124.3	s
t	Total injection time	<i>Initial condition</i>	s

Table 2. Sulfur content of samples.

Number	Initial sulfur content/%	Sulfur content of desulfurization process/%					
		300 s	600 s	900 s	1 200 s	1 500 s	1 800 s
1	0.0294	0.0247	0.0148	0.0039	—	—	—
2	0.0301	0.0281	0.0172	0.0051	—	—	—
3	0.0609	0.0537	0.0375	0.0271	0.0141	0.0101	0.0050
4	0.0593	0.0514	0.0300	0.0236	0.0153	0.0092	0.0041

Fig. 1. Change of sulfur content in desulfurization process.

idly to below 0.005% and the desulfurization rate had not changed significantly in the process. For the initial sulfur content of 0.06%, however, from 120 to 900 s the sulfur content decreased rapidly to below 0.015%. After 900 s, the reduction rate of sulfur content obviously decreased with time. Finally, the sulfur content decreased to below 0.005%.

But there's a phenomenon that the most of the measured data is greater than the calculated data. Because the samples were taken from the upper part of ladle, and the desulfurization agent is injected from the lower part of ladle. The sulfur content of the lower part of the ladle is lower than the upper part, and the 210 t molten iron takes 124 seconds to complete mixing. But in the calculation process, it is assumed that the molten iron is in a state of equilibrium in real time.

3.2. Desulfurization Characteristics of High Sulfur Hot Metal

For the high sulfur molten iron, the desulfurization efficiency was obviously changed with the injecting time. And according to the desulfurization efficiency, the desulfurization process of high sulfur molten iron is defined as three stages as shown in **Fig. 2**. Incubation stage, the sulfur content was no obvious change and preparing for the next stage of rapid desulfurization. Rapid desulfurization stage, from about 120 to 900 s, the sulfur content decreased rapidly to below 0.015%. Slow desulfurization stage, after 900 s, the desulfurization efficiency decreased along with the injecting time.

According to the characteristics of high sulfur molten iron desulfurization process, in slow desulfurization stage, the utilization rate of the desulfurization agent can be improved by adjusting the injection parameters. The injection rate of

Fig. 2. Three desulfurization stages of high sulfur molten iron (I: Incubation stage; II: Rapid desulfurization stage; III: Slow desulfurization stage).

Table 3. Injection parameters of the different processes.

Parameters	Conventional process	Two-stage injection method	
		Early stage (I, II)	Later stage (III)
Injection rate of powder/(kg/s)	0.183–0.217	0.183–0.217	0.133–0.150
Flow rate of nitrogen/(Nm ³ /s)	1.667	1.667	2.167

the desulfurization agent was reduced. In order to improve the mixing of the molten pool and dynamic conditions, the flow rate of nitrogen was increased in this stage.

3.3. Industrial Applications

Based on the desulfurization characteristics of high sulfur hot metal, two-stage injection method was developed and applied. The injection parameters were given as follows.

The injection time of two-stage injection was the same as the conventional process. The injection time was determined by the initial sulfur content. When the initial sulfur content was greater than or equal to 0.035%, the injection time was more than 1 800 s, and the lance was replaced at the half of injection time in order to improve the service life of the lance. For the two-stage injection method, at the first half of the injection time, the injection parameters were the same as the conventional process. The injection parameters were adjusted after the lance replacement. This was done to avoid the impact on the cycle because of the adjustment parameters.

Industrial tests of two-stage injection method were carried out. The initial sulfur content of tested ladles was above 0.035%, and the sulfur content after the desulfurization and the steel tapping were required above 0.005% and 0.012%. **Tables 4** and **5** showed the industrial data of 4 ladles. The final sulfur content after the desulfurization achieved the target value below 0.005%.

The changes of sulfur content during the smelting process were analyzed as shown in **Fig. 3**. The average sulfur content changes used the conventional process was given. It can be seen that the control of sulfur content used two-stage injection method was the same with the conventional

Table 4. Industrial test data of first stage injection.

NO.	Initial S/%	Steel grade	Target S/%	First stage injection				
				Injection time/s	Desulphurizer consumption/kg	Flow rate/(Nm ³ /s)	Injection rate of powder/(kg/s)	Pressure/(Mpa)
5 102 446	0.041	M3A33	0.005	660	150.19	1.688	0.211	0.423
5 202 464	0.041	SPHC-P	0.005	720	150.00	1.600	0.200	0.425
5 302 495	0.052	SDX51D	0.005	840	177.90	1.655	0.200	0.464
5 202 475	0.040	SPHC	0.005	720	149.00	1.598	0.208	0.439
5 302 510	0.060	SPHC-W1	0.005	960	208.30	1.667	0.213	0.441

Table 5. Industrial test data of second stage injection.

NO.	Initial S/%	Steel grade	Second stage injection					Final S/%
			Injection time/s	Desulphurizer consumption/kg	Flow rate/(Nm ³ /s)	Injection rate of powder/(kg/s)	Pressure/(Mpa)	
5 102 446	0.041	M3A33	660	119.73	2.000	0.173	0.473	0.0033
5 202 464	0.041	SPHC-P	720	120.12	1.987	0.168	0.442	0.0041
5 302 495	0.052	SDX51D	840	149.20	2.006	0.164	0.448	0.0037
5 202 475	0.040	SPHC	720	109.49	2.019	0.170	0.463	0.0041
5 302 510	0.060	SPHC-W1	960	174.31	2.043	0.174	0.471	0.0036

Fig. 3. Change of sulfur content (After Des.: After desulfurization, TSC: temperature sample carbon, TSO: temperature sample oxygen).

method. For the two-stage injection trials, the 5 ladles molten iron of the sulfur content more than 0.035% were selected, and they are of different steel kinds and in different cast times. The target sulfur content after Des is the same $\leq 0.005\%$. But before TSC, according to steel kinds, the steel scraps of different sulfur content were added into the molten steels. Therefore, the sulfur content of different heats are different in TSC. With the slag-steel reaction and the oxidation reaction, the sulfur content of all heats are decreased from TSC to TSO. During the process from TSO to Slab, the sulfur content of all heats is no significant change. Finally, the sulfur content met the requirement of slabs (Requirement of slab sulfur content: M3A33 $\leq 0.010\%$, SPHC-P/SDX51D $\leq 0.012\%$, SPHC/SPHC-W $\leq 0.015\%$). Finally, the sulfur content met the requirement of slabs.

For the molten iron of sulfur content $\geq 0.035\%$, the

two-stage injection method was adopted in the steel plant. Compared with the conventional process, the consumption of the desulfurizing agent is reduced by 10–20% by using the two-stage injection method.

4. Conclusions

A kinetic model of the injection desulfurization was established. The changes of sulfur content were analyzed. For the high sulfur molten iron, a new injection desulfurization mode was developed and applied. The following conclusions were obtained.

(1) The kinetic model of the 60% Mg and 40% CaO injection desulfurization was established. The result from the model was verified by sampling, and it was in accord with the sampling results.

(2) For the high sulfur molten iron, the desulfurization efficiency was obviously changed with the injecting time. The desulfurization process of high sulfur molten iron is defined as three stages, incubation stage, rapid desulfurization stage and slow desulfurization stage.

(3) For the two-stage injection method, at the first half of the injection time, the injection parameters were the same as the conventional process. In order to improve the dynamic conditions and the utilization rate of the desulfurization agent, the smaller injection rate of powder and the larger flow rate of nitrogen were used.

(4) Compared with the conventional process, the consumption of the desulfurizing agent is reduced by 10–20% by using the two-stage injection method.

Nomenclature

A_1 , A_b : Surface area of powder particles in contact with molten iron, bubble-melt interface (m²).

$C_{[S]}$, $C_{(S)}$, C_S^e , $C_{[S]}^b$: Molar volume concentration of hot metal, top slag, reaction equilibrium, bubble-melt interface (mol/L).
 $J_{[S]}$: Mass flux of sulfur (mol/(m²·s)).
 L_s : Sulfur partition ratio between top slag and melt.
 $[\%Mg]$: Instantaneous concentration of magnesium in hot metal (%).
 $[\%S]$, $[\%S]_o$, $[\%S]_e$, $[\%S]_b$: Instantaneous concentration of sulfur in hot metal, initial sulfur concentration in hot metal, sulfur concentration of reaction equilibrium, sulfur concentration of bubble desulfurization equilibrium (%).
 $(\%S)$, $(\%S)_o$: Instantaneous concentration of sulfur in top slag, initial sulfur concentration in top slag (%).
 v_{total} , v_{CaO} , v_{Mg} , v_{top} : Desulfurization rate of total, CaO, Mg, top slag (%/s).
 W_s : Instantaneous mass of top slag (%/s).

REFERENCES

- 1) K. Kanbara, T. Nisugi, O. Shiraishi and T. Hatakeyama: *Tetsu-to-Hagané*, **58** (1972), 34.
- 2) K. Nakanishi, N. Bessyo, S. Takada, A. Ejima, M. Kuga, J. Katsuki and M. Kawana: *Tetsu-to-Hagané*, **64** (1978), 1528.
- 3) N. Kurokawa, S. Matsuo, H. Jouguchi, K. Yamada and Y. Watanabe: *Sumitomo Met.*, **45** (1993), 52.
- 4) N. Kikuchi, S. Nabeshima, S. Takeuchi, T. Yamauchi, Y. Kitano and S. Ogura: *Tetsu-to-Hagané*, **90** (2004), 322.
- 5) N. Kikuchi, S. Nabeshima and Y. Kishimoto: *ISIJ Int.*, **52** (2012), 1809.
- 6) S. Yamaguchi, T. Uemura, H. Nashiwa and H. Sugita: *Ironmaking Steelmaking*, **4** (1977), 276.
- 7) D. A. R. Kay, S. V. Subramanian and R. V. Kumar: *Can. Inst. Min. Metall.*, **17** (1986), 25.
- 8) G. A. Irons and C. Celik: *Ironmaking Steelmaking*, **19** (1992), 136.
- 9) G. A. Irons and R. I. L. Guthrie: *Ironmaking Steelmaking*, **8** (1981), 114.
- 10) J. Diao, B. Xie and S. S. Wang: *Ironmaking Steelmaking*, **36** (2009), 543.
- 11) J. Y. Choi, D. J. Kim and H. G. Lee: *ISIJ Int.*, **41** (2001), 216.
- 12) G. A. Irons: *Ironmaking Steelmaking*, **16** (1989), 28.
- 13) V. Seshadri, C. A. da Silva, I. A. da Silva and P. von Kruger: *ISIJ Int.*, **37** (1997), 21.
- 14) L. H. Luo, Z. S. Zou and A. H. Liu: *J. Northeast. Univ. (Nat. Sci.)*, **19S** (1998), No. 1, 176.
- 15) Y. F. Zhao and G. A. Irons: *Ironmaking Steelmaking*, **21** (1994), 309.
- 16) G. A. Irons and R. I. L. Guthrie: *Metall. Trans. B*, **12B** (1981), 755.
- 17) N. Wang, Y. S. Zou and Z. S. Zou: *J. Iron Steel Res.*, **12S** (2000), 16.
- 18) N. Wang, Y. S. Zou and Z. S. Zou: *J. Iron Steel Res.*, **12S** (2000), 10.