Evolution of Mgo·Al_2O_3 Based Inclusions in Alloy Steel During the Refining Process

Shufeng Yang[1,2], Jingshe Li[1], Lifeng Zhang[2], Kent Peaslee[2], Zaifei Wang[1]

[1]*School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China*

[2]*Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65401, USA*

The transformation of MgO·Al_2O_3 based inclusions in alloy steel during refining has been studied by industrial trials. Besides Factsage software is applied to study the formation and modification of spinel inclusions in alloy steel using calcium treatment during refining process. The results show the transformation sequence of inclusions is: MgO·Al_2O_3 → CaO–Al_2O_3–MgO complex inclusions → MgO·Al_2O_3, and under present experimental condition, in order to avoid forming MgO·Al_2O_3 inclusions the content of dissolved Ca in the molten steel has to reach 1ppm. Also the results show that when more calcium was added into molten steel, the content of Al_2O_3 and MgO will be lower. Besides, increases the content of CaO in the inclusions will increase even if the content of SiO_2 changes little.

Keywords: ALLOY STEEL, NON-METALLIC INCLUSIONS, MGO·AL_2O_3 SPINEL, THERMODYNAMICS

Introduction

There are various factors affecting the quality of steel, and the presence of MgO·Al_2O_3 spinel inclusions is one of them. These inclusions are uneasy to deform when rolling due to their high melting point （2135 °C） and high hardness (HV : 2100~2400 kg/mm^2)，which will lead to surface defects on the casting product [1]. In addition, spinel inclusions tend to accumulate at the inner wall of the submerged entry nozzle, inducing clogging during continuous casting [1-3]. Nowadays the mechanisms of formation of MgO·Al_2O_3 based spinel inclusions are still not clear, though some investigations have been carried out on this topic. Stability diagrams of oxide inclusions have been created corresponding to Mg and Al contents using the thermodynamic data experimentally obtained [4-6]. It has been proven that very small amount of Mg and Al enables the formation of spinel. The effects of slag basicity and composition on spinel formation in Fe-16mass%Cr stainless steel deoxidized by Al were investigated by Okuyama et al [7] and Todoroki [8].Young et al [9] studied the formation mechanism of liquid calcium aluminate inclusions from MgO·Al_2O_3 spinel, and found that spinel reacted with the dissolved Ca forming a liquid calcium aluminate phase. Pretorius *et al* [10] studied the modification of spinel inclusions by Ca- treatment in LCAK steel by industrial experiments and showed the feasibility for the modification of spinel inclusions by Ca-treatment. In the current study, evolution of MgO·Al_2O_3 based inclusions in alloy steel during refining was investigated. Factsage6.0 was applied to calculate formation and transformation of spinel inclusions in alloy steel, as well as the effect of calcium treatment on the composition of molten steel and inclusions. This study focuses on the effect of Ca-treatment on transformation of MgO·Al_2O_3 based inclusions.

Methodology

In the present work, the experimental steel is 30CrMo with a composition (in wt.%) of C 0.30; Si 0.22; Mn 0.52; P 0.015; S 0.007; Mo 0.10; Al_s 0.020; V 0.12; Cu 0.07; Cr 0.94. The process to produce 30CrMo is: Scrap+DRI+hot metal →100t EAF →100t LF－VD →CaSi treatment→CC. The time of LF refining is about 60 min and the time of VD treatment is 40 min. During tapping, aluminum (300 Kg), SiMn (800 Kg), and FeMn (400 Kg) were added in order to deoxidize and alloy. After 30 min of LF refining, 60 kg of aluminum wire, 56 kg of ferromanganese, 113 Kg of ferromolybdenum and 180 kg alloy of standard ferrochromium were added to adjust the composition of the molten steel. The size of the billet is 210 mm. Steel samples under four heats were taken during refining (before (301) and during (302) LF treatment, before (401) and after (402) VD treatment). The temperatures of sampling are 1550 ℃ (301), 1620 ℃ (302), 1625 ℃ (401) and 1565 ℃ (402) respectively. During sampling, the samplers were immerged in the molten steel 300 mm below the surface of bath. The inclusions were observed and analyzed using SEM-EDS. In order to observe three-dimensional morphology of inclusions, the samples were treated by partial acid extraction [11].

Results and Discussion

Variation of Molten Steel Composition

The composition of each sample during the refining process is shown in **Table 1**. The average content of aluminum, calcium and magnesium during each step of the refining process is showed in **Figure 1**, indicating that the dissolved aluminum decreases from 0.0256 % to 0.019 % during the early period of the LF. At the beginning of VD, the aluminum content rises to 0.0217 %. And during the VD process, the aluminum content changes slightly. The calcium content increases from 0.0014 % to 0.0025 % during the early period of LF treatment while it decreases later. At the beginning of VD, the content of calcium is 0.0021 % and decreases sharply during degassing to finish at only 0.0005 %. The content of magnesium remains steady at 0.0005 %~0.0009 % during the entire refining process.

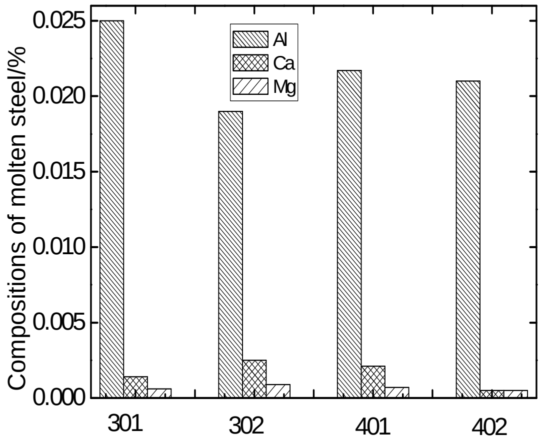


Figure1. Variations of Al,Ca and Mg in molten steel during refining

Table 1. Compositions of molten steel during refining

Samples	Compositions (%)						
	C	Si	Mn	S	Al	Ca	Mg
259301	0.232	0.27	0.91	0.019	0.035	0.0009	0.0005
259302	0.252	0.27	0.011	0.011	0.027	0.0016	0.0006
259401	0.249	0.25	0.004	0.004	0.023	0.001	0.0006
259402	—	—	—	—	0.022	0.0005	0.0005
260301	0.205	0.21	0.90	0.025	0.025	0.0012	0.0006
260302	0.233	0.20	0.95	0.002	0.018	0.003	0.001
260401	0.266	0.23	0.95	0.003	0.021	0.001	0.0006
260402	—	—	—	—	0.021	0.0005	0.0005
261301	0.238	0.27	0.89	0.013	0.017	0.002	0.0006
261302	0.237	0.27	0.94	0.003	0.013	0.003	0.001
261401	0.247	0.26	0.95	0.002	0.021	0.0044	0.0008
261402	—	—	—	—	0.02	0.0005	0.0005

The low aluminum content during the early period of LF treatment may stem from the fact that most of inclusions of deoxidization are removed by floatation. In order to complete deoxidization and to control the content of aluminum, 60kg Al is added during the late period of LF. Thus the content of aluminum increases. Aluminum changes slightly during VD treatment due to the low oxygen. In the trials, Ca-treatment is completed just at the beginning of LF. Sample 301 is selected after Ca-treatment, so its calcium should be the highest. Due to the reaction between calcium and inclusions, the content of calcium decreases gradually. However, the result of the trial shows that the content of calcium increases. Maybe sampling 301 is selected at the time when calcium hasn't diffused uniformly. And the content of calcium still keeps the high level during the late period of LF refining, maybe because calcium which is produced by the reaction between the added Al and CaO in the slag balances the consumption of calcium in the molten steel. Then the content of calcium decreases sharply, because calcium reacts with inclusions and molten steel during VD, and inclusions are removed by flotation.

The Existence Forms of Inclusions in Alloy Steel

There are three kinds of forms of inclusions based $MgO·Al_2O_3$ in alloy steel. One is pure $MgO·Al_2O_3$, mainly containing Mg, Al and O elements, another is $MgO-Al_2O_3-CaO$ complex inclusion, the third is $MgO-Al_2O_3-CaO-SiO_2$ complex inclusion. The size of three kinds of forms of inclusions is 1~3 μm. Those inclusions are very small, so they can't come from refining slag. The current study insist the $MgO·Al_2O_3$ based inclusions can be formed by following several steps: MgO in the slag or lings refractory was reduced by the Al in the molten steel and produce Mg; the Mg dissolve into molten steel; deoxidation product Al_2O_3 reacts with the [Mg] in the steel and formed $MgO·Al_2O_3$ inclusion; $MgO·Al_2O_3$ inclusion react with [Ca] from Ca-treatment or reduced by Al. The reaction equations are followed:

$$3(MgO) + 2[Al] = Al_2O_3 + 3[Mg] \quad \text{(Eq. 1)}$$

$$(MgO) + C = [Mg] + CO(g) \quad \text{(Eq. 2)}$$

$$[Mg] + [O] = (MgO) \quad \text{(Eq. 3)}$$

$$(MgO) + (Al_2O_3) = (MgO·Al_2O_3)\ (s) \quad \text{(Eq. 4)}$$

$$Ca+(x+1/3)[\ MgO·yAl_2O_3] = CaO·\ x\ Al_2O_3·y(x+1/3)MgO+2/3Al \quad \text{(Eq. 5)}$$

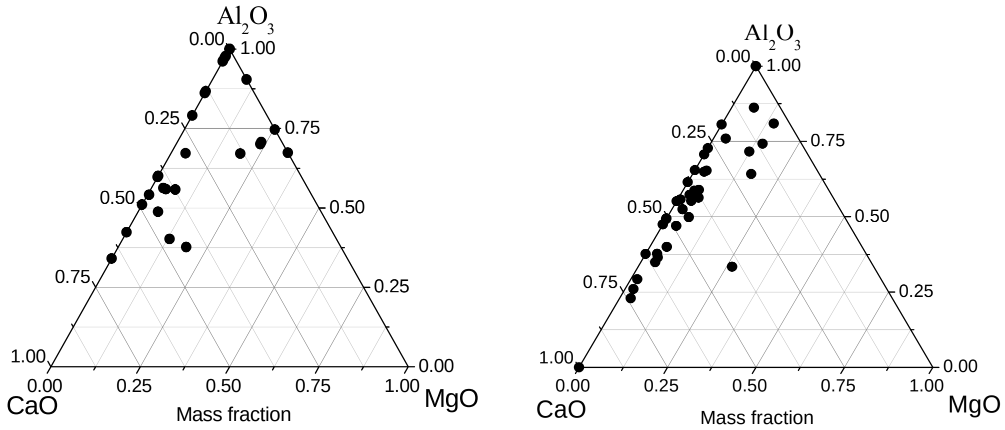
Composition Change of the $MgO·Al_2O_3$ Based Inclusions

For all the steel samples, the composition and size of 10-15 inclusions were analyzed, and in total ~250 inclusions were detected and analyzed using SEM in the current study. **Figures 2** and **3** show the composition distribution in $CaO-MgO-Al_2O_3$ ternary system of the inclusions in steel samples. From **Figure 2(a)**, the inclusions mainly are $MgO·Al_2O_3$, calcium aluminate and $MgO-Al_2O_3-CaO$ complex inclusion. But WANG [12] reported that most inclusions before LF refining were Al_2O_3 inclusions and the average Al_2O_3 content in inclusions was 96.2 mass%. The different results may be caused by the special Ca-treatment process (Ca-treatment at before LF refining) in current study. According to **Figure 2(b)**, after 30 min refining in LF, the content of MgO in the inclusions decreased, while the content of CaO increased and $MgO·Al_2O_3$ inclusions disappeared, The average composition was 51.48 mass% of Al_2O_3, 3.69 mass% of MgO and 44.51 mass% of CaO. **Figure 3(a)** shows at the end of LF refining, the content of MgO in the inclusions changed a little, the content of CaO in the inclusions decreased and $MgO·Al_2O_3$ inclusions weren't observed; during VD refining, the content of CaO in the inclusions changed a little and $MgO·Al_2O_3$ inclusion appeared again as shown in **Figure 3(b)**.

The reason why $MgO·Al_2O_3$ inclusions disappeared, content of MgO in the inclusions decreased and content of CaO in the inclusions increased is that the calcium added into molten steel reacted with $MgO·Al_2O_3$ inclusions and formed $CaO-MgO-Al_2O_3$ complex inclusions, at the same time Mg was produced by reduction of $MgO·Al_2O_3$ inclusions and went to molten steel. The reaction equations are shown as equations (5) and (6).

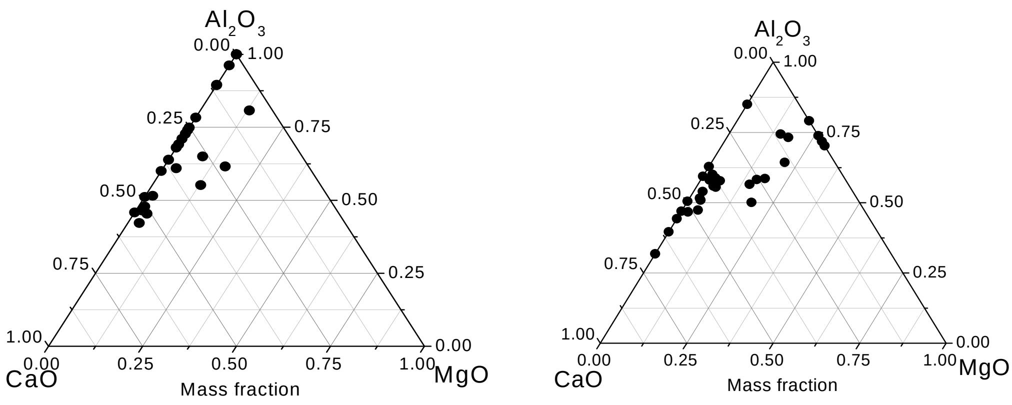
$$Ca+MgO·Al_2O_3=CaO·Al_2O_3+Mg;$$
$$Mg = [Mg] \text{ and } Mg\ (g) \quad \text{(Eq. 6)}$$

Before LF refining, $MgO·Al_2O_3$ inclusions appeared, and during LF refining and VD refining $MgO·Al_2O_3$ inclusions disappeared, but at the end of VD refining $MgO·Al_2O_3$ inclusions appeared again. So the transformation sequence of inclusion in alloy steel in current study is $MgO·Al_2O_3$ →$CaO–Al_2O_3–MgO$ complex inclusions→$MgO·Al_2O_3$. The reason why $MgO·Al_2O_3$ inclusions appeared again may relate to the content of dissolved calcium. According to **Table1**, the average content of total calcium in the molten steel during LF and VD refining exceeds 0.001 %, however, the average content of total calcium in the molten steel at the end of VD refining is 0.0005 %. So in order to avoid forming $MgO·Al_2O_3$ inclusions, the content of dissolved calcium in the molten steel have to reach a certain value. Butin current study the content of dissolved calcium wasn't measured, so it is difficult to know this value. In the later section, thermodynamic calculations were used to get this value. In order to keep a certain content of dissolved calcium, the oxygen potential of molten steel should be low



(a) Before LF (b) After LF

Figure2. Compositions of inclusions during LF



(a) Before VD (b) After VD

Figure3. Compositions of inclusions during VD

enough. Any increase of the oxygen potential from reoxidation may lead to the formation of the secondary spinel inclusions.

Thermodynamic Calculations

Thermodynamics on Formation and Transformation of $MgO\cdot Al_2O_3$ Inclusions

Figure 4 is the inclusions equilibrium diagram of Fe-O-Mg-Al-Ca, and the calcium aluminate inclusions are CaO, $CaAl_2O_4$ and $CaAl_4O_7$ in calculation. From **Figure 4**, when the dissolved aluminum content in molten steel is less than $10^{-2.6}$, the content of dissolved magnesium is less than 10ppm and the content of dissolved calcium in molten steel is about 1ppm, the complex inclusions contained calcium aluminate is the stable form in molten steel. As 30CrMo alloy steel for example, the content of aluminum in molten steel is 0.034 %, the magnesium content is about 0.0005 %, when the dissolved calcium content in molten steel is about 1ppm, the $MgO\cdot Al_2O_3$ spinel can be transformed into a liquid complex inclusions. From **Figure 4,** when the dissolved calcium content in molten steel is increased, liquid complex inclusion region expands rapidly; the lower content of dissolved aluminum in liquid steel, the lower dissolved calcium content required transforming into liquid inclusions from $MgO\cdot Al_2O_3$ spinels.

Effect of Ca-treatment on Transformation of $MgO\cdot Al_2O_3$ Inclusions

The effects of Ca-treatment on transformation of $MgO\cdot Al_2O_3$ inclusions also were calculated by FactSage6.0 thermodynamic software. It should be noticed that the calcium yield was assumed to100 % in the thermodynamic calculations.

Figure 5 shows the effect of Ca-treatment on the compositions of liquid inclusions. According to **Figure 5**, when adding 1ppm calcium into molten steel, $MgO\cdot Al_2O_3$ inclusions have transformed

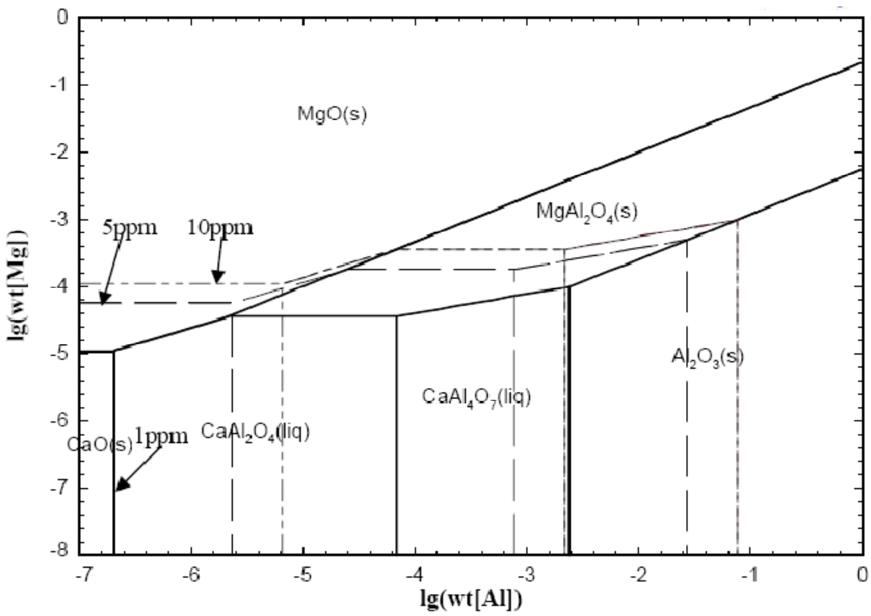


Figure 4. Equilibrium diagram of Fe-O-Mg-Al-Ca at1600℃

into liquid complex inclusions and both the content of Al_2O_3 and MgO in the liquid complex inclusions decrease rapidly, while the content of CaO increases sharply. The content of Al_2O_3 and MgO in the liquid complex inclusions go on decreasing with the increasing amount of calcium added into the molten steel. The content of CaO in the liquid complex inclusions go on increasing with the increasing amount of calcium added into the molten steel, while the content of SiO_2 in the liquid complex inclusions changes little. When the amount of calcium added into the molten steel reaches 10 ppm, the content of MgO in the liquid complex inclusions gets to 7.0 %, the content of Al_2O_3 47.5 %, the content of CaO 44% and the content of SiO_2 1.5 %.

The reason for the increase of both the content of CaO and MgO in the liquid complex inclusions is that MgO in the inclusions is reduced by calcium, producing CaO into inclusions. **Figure 6** is the effect of Ca-treatment on the amount of $MgO{\cdot}Al_2O_3$ in the molten steel. From **Figure 6**, when 2 ppm calcium is added into molten steel, the $MgO{\cdot}Al_2O_3$ inclusions can transform liquid complex inclusions completely.

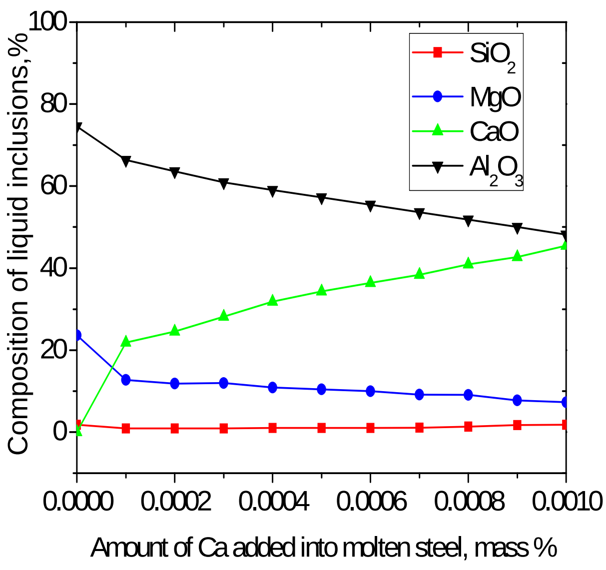


Figure 5. Relation of amount of Ca added and amount of $MgO{\cdot}Al_2O_3$

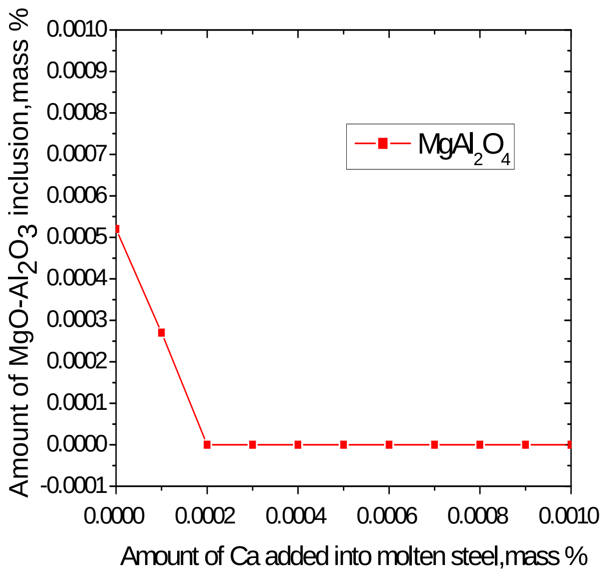


Figure 6. Relation of amount of Ca added and amount of $MgO{\cdot}Al_2O_3$

Conclusions

1. Mainly there are three types of inclusions containing MgO in alloy steel during LF refining: 1) Spinel inclusions; 2) $CaO–Al_2O_3–MgO$ complex inclusions; 3) $CaO–MgO–Al_2O_3–SiO_2$ complex inclusions. The transformation sequence of inclusion during refining is: $MgO·Al_2O_3→CaO–Al_2O_3–MgO$ complex inclusions → $MgO·Al_2O_3$.

2. Under present experimental condition, in order to avoid forming $MgO·Al_2O_3$ inclusions the content of dissolved Ca in the molten steel has to reach 1ppm.

3. Spinel inclusions may form even with low magnesium in the steel. More calcium addition into molten steel lowers the content of the Al_2O_3 and MgO, increases CaO content in the inclusions, while changes SiO_2 content little.

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References

1. H. Todoroki, S. Inada. *Bull. Iron Steel Inst. Jpn*, 2003, Vol. 8, No. 2, p. 575. *

2. Y. Wang, X. Zuo, L. Zhang. *Proceedings of the Seventh International Conference of Clean Steel*, the European Coal and Steel Community, Balatonfüred, 2007, pp. 161-172.

3. Jo S K, Song B, Kim S H. *Metall. and Materials Transactions B*, 2002, Vol. 33B, No. 4, p.709.

4. Joo Hyun Park *Metallurgical and Materials Transactions B*, 2007, Vol.38B, No. 4, p.657.

5. W Y Cha, D S Kim and Y D Lee, et al. *ISIJ International*, Vol. 44, No. 7, 2004, p.1134.

6. H. ITOH, M. HINO, S. BANYA. *Testu-to-Hagane*, 1998, Vol. 84, No. 2, pp. 85-90. *

7. G.OKUYAMA , K.YAMAGUCHI, S.TAKEUCHI , et al . *ISIJ International* , 2000, Vol. 40, No. 2, pp. 121-128

8. K.Mizuno, H. Todoroki, M.Noda, T. Tohge. *Iron Steelmaker*, 2001,Vol. 28, No. 8, pp. 93-101. *

9. Y. Kang, et al. *Steel Research Inter.*, 2006, Vol.77, No. 11, pp. 785-792.

10. E.B. Pretorius, H.G. Oltmann, T. Cash. *AIST2009 Proceeding*, Association for Iron & Steel Technology, St.Louis, 2009, pp. 1035-1049.

11. Zhang Lifeng1, Li Shusen,WANG Jianwei, ZUO Xiangjun. *Iron and Steel*, 2009, Vol.44, No. 3, pp. 75-80. **

12. X. WANG, H. LI, Y. WANG. *AIST2009 Proceeding*, Association for Iron & Steel Technology, St.Louis, 2009, pp. 965-972.

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