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Improving Steel Cleanliness through Slag Refining

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INTRODUCTION

Constructional steel and its many products have undergone significant changes since the initial applications. Some of these were prompted by demands for higher strength and improved economies of construction, and many were caused by developments in joining techniques and fabrication. Constructional steels are widely used for bridges and buildings, requiring good properties of excellent strength, ductility, fracture toughness and weldability. Non-metallic inclusions can generate many defects in the steel product. ^[1-3] Removing more inclusions thus improving steel cleanliness is one of the most important tasks for steelmakers. Slag refining is well used to improve steel cleanliness by absorbing inclusions, lowering sulfur or phosphorus, or adjusting inclusion composition and morphology. ^[4] For traditional refining process of constructional alloy steels, the slag composition locates at A in Figure 1, with 5-7 basicity, ~20% Al_2O_3 , ^[5] by which the non-deformable inclusions, such as C_9A ($C-CaO$, $A-Al_2O_3$), are generated. The ideal slags should be located at B in Fig.1, with 5-10% SiO_2 , 43-47 Al_2O_3 , and 46-54% CaO , by which inclusions with low melting points can be formed, such as $C_{12}A_7$. $C_{12}A_7$ inclusions have melting temperature as low as 1455 °C, spherical shape, and small size, and are slightly deformable during rolling process. $MgO-Al_2O_3$ based inclusions in steels have been noticed by more and more researchers ^[6-10] since the wide use of $MgO-C$ refractories in steel industries from 20 years ago. The current paper is to investigate the steel cleanliness and inclusions in a constructional steel during slag refining process in a laboratory scale.

EXPERIMENTAL METHODOLOGY

Experimental Materials - In order to achieve composition well controlled constructional steel for the current studies, high purity electrolytic iron was melted in a vacuum induction furnace, then high purity electrolytic manganese, single crystal silicon, chromium-iron, molybdenum-iron and granular carbon powders were added into the crucible to adjust the composition of the steel, and to deoxidize the steel. Aluminum metal was then added to the melt to adjust the content of the dissolved aluminum in the steel. The initial dissolved aluminum in the steel ranged from 14ppm to 503ppm. The steel composition is similar to that of 42CrMo steel. The example composition of the steel is shown in Table 1. $CaO-SiO_2-Al_2O_3$ slags were used, which were the mixtures of ultra pure powders of CaO (48%), SiO_2 (6%) and Al_2O_3 . (46%). The original slag basicity $CaO/SiO_2=8$.

Table 1 Original compositions of steel and slag used (wt%)

C	Si	Mn	P	S	Ca	Mg	Cr	Mo
0.42	0.26	0.64	0.01	0.004	0.0010	0.0010	1.14	0.23

Experimental Procedure - A vertical resistance furnace heated by a Si-Mo bar was used, which can reach temperature as high as 2073K. 50g slag and 100g steel sample were melted at 1600°C in a MgO crucible under Ar purging condition. If not specified, the

crucible with steel and slag was stayed in the furnace for 90min, then the crucible was pulled out of the furnace and quenched rapidly in the water. Around 30 experiments were carried out under different conditions. Inclusions in the steel samples were analyzed using SEM-EDS. The composition of steel and slag was also analyzed.

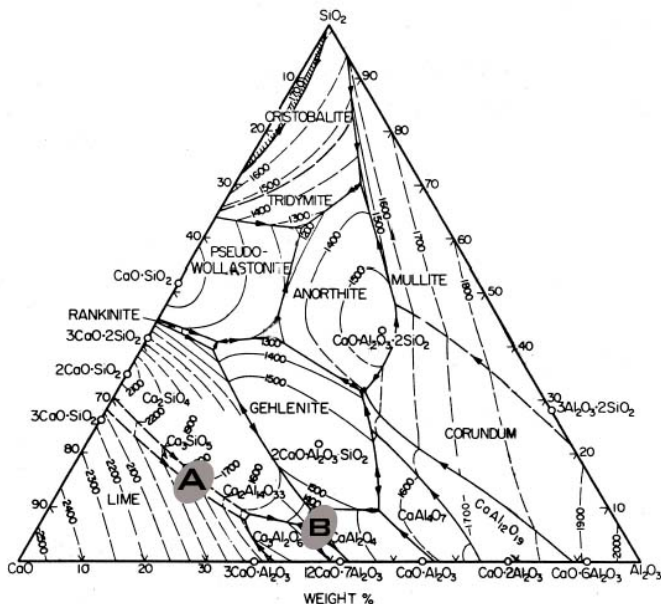


Fig.1 Slags used for the refining process of constructional steels [5]

STEEL CLEANLINESS AND SLAG COMPOSITION AFTER SLAG REFINING

Pre-experiments with the same samples and different reaction times (30min, 60min, 90min, 120min, and 180min) were carried out. As a result, compositions of steel and slag were no obvious change after 90min. Therefore the time to reach equilibration was chosen as 90min. 21 experiments were treated by the current slag refining in 90min.

With 90min reaction time in the MgO crucible, the slag contained 39-44%CaO, 8-10% MgO, 6-11% SiO₂, 39-42%Al₂O₃, <0.2% MnO, and <0.6%FeO. The basicity (%CaO/%SiO₂) was mainly ~7.1-7.6, except one 3.6, one 5.2, and one 6.2 in 21 experiments. The steel composition after slag refining was: C:0.34-0.36%, Si:0.19-0.24%, Mn:0.61-0.64%, Cr:1.10-1.16%, Mo:0.22-0.24%, S:4-12ppm, T.O.:6-15ppm, dissolved aluminum after refining, [Al]_{end}:73-120ppm, Ca:2-10ppm, Mg: mainly 1-16ppm.

The current study indicated that higher FeO+MnO in the slag corresponded more T.O. oxygen in the steel, as shown in Figure 2, which has been reported by many researchers. [3] When slag basicity after refining in the range of 7-8, T.O. and [Al]_{end} decreases with basicity increasing, as shown in Figure 3. It has been reported that the slag with high basicity favors inclusion removal, [11, 12] and high basic slags has a very good capability of assimilating deoxidization products such as Al₂O₃ [12]. Large basicity means more CaO in the slag. However, in the current study, when basicity is 3-7, T.O. changed a little with slag basicity.

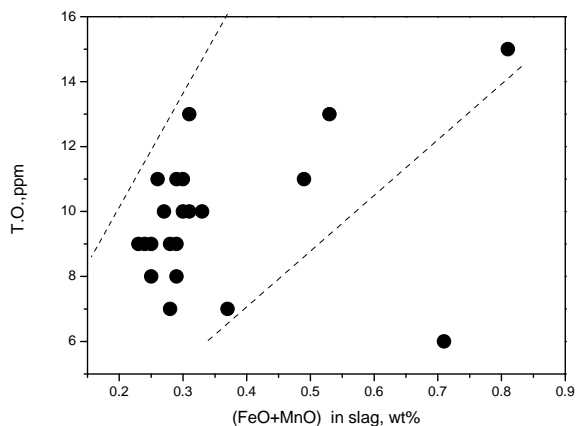


Fig.2 More (FeO+MnO) in slag corresponds high T.O. in the molten steel

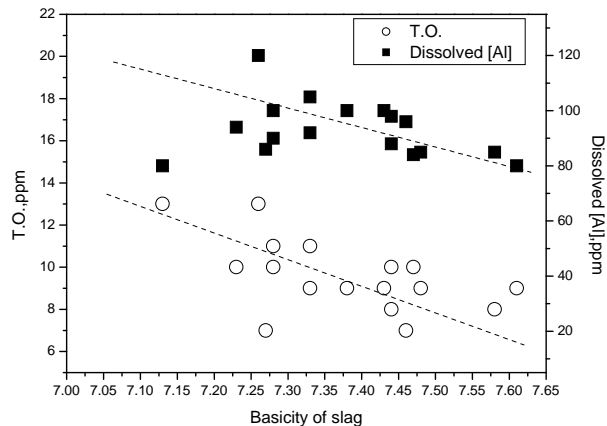


Fig.3 Larger slag basicity (CaO/SiO₂) corresponds less T.O. and dissolved Aluminum in the steel if basicity is over 7

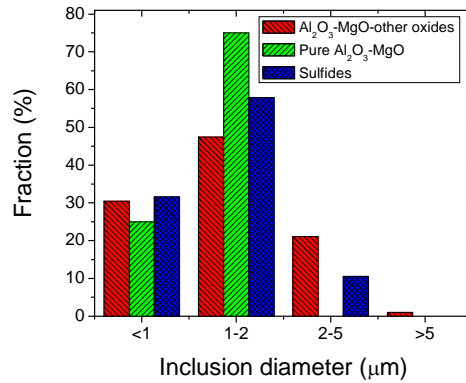


Fig.6 Size distribution of inclusions with 90min reaction time

For 180min reaction steel samples, not so many spherical inclusions were detected. Square shape MgO-Al₂O₃ spinel inclusions and pure MgO inclusions were detected, as shown in Figure 7. The existence of pure MgO inclusions indicates the occurrence of direct dissolution of the crucible materials.

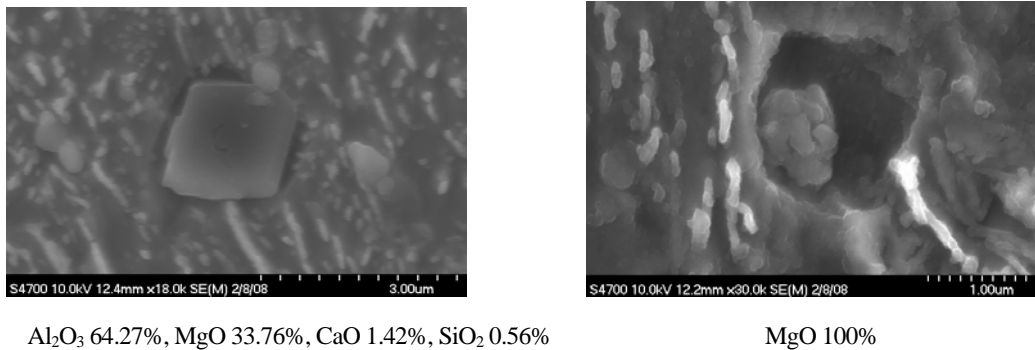


Fig.7 Morphology and composition of inclusions with 180min reaction time

Statistical distribution of the composition of some oxide inclusions is shown in Figure 8: CaO 10-40%, SiO₂ 4-6%, Al₂O₃ 50-55%, MgO 15-35%. In oxide inclusions, the content of SiO₂ was mainly 4-6%, so was neglected, then CaO-Al₂O₃-MgO ternary oxide diagram were drawn, as shown in Figure 9. ~90% inclusions are in solid state, with melting point >1600°C. Around 10% inclusions has melting point of 1500°C-1600°C. Since MgO in inclusions were from the crucible, if we assume that the transfer of MgO from crucible to the molten steel and the slag do not affect the other components in the inclusion, then we can delete MgO to see if a ideal crucible (no reaction with the steel and the slag) is used, what will happen to the inclusions. By this assumption, CaO-Al₂O₃-SiO₂ ternary oxide diagram were drawn, as shown in Figure 10, which indicates again that ~90% inclusions have melting point >1600°C, and 10% inclusions has melting point of 1500°C-1600°C.

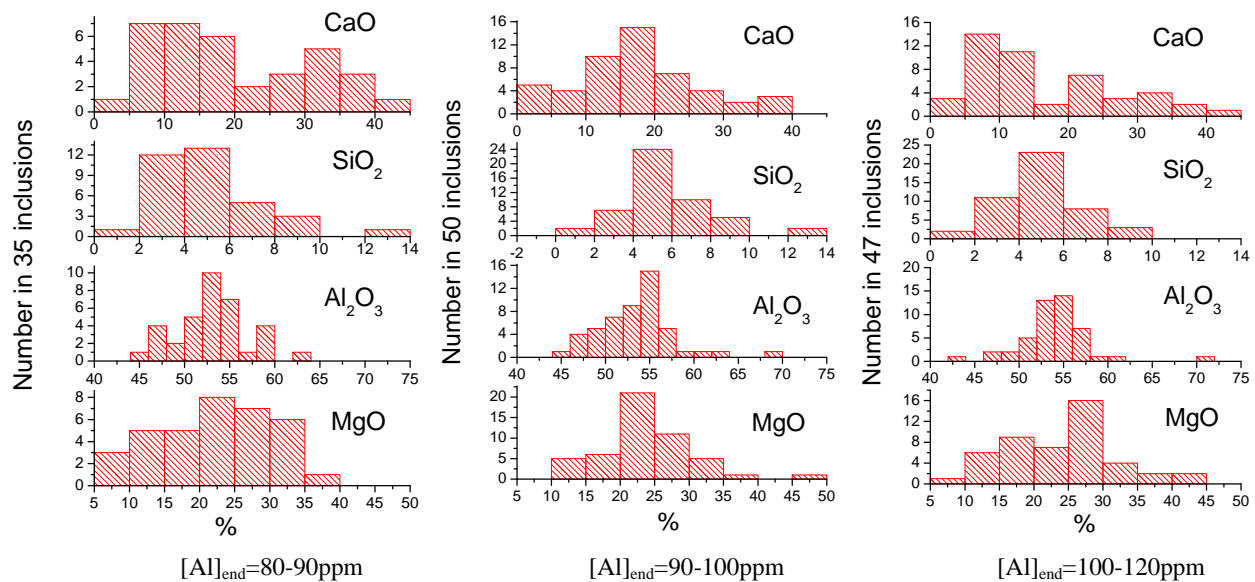


Fig.8 Composition of inclusions corresponding different dissolved aluminum in equilibrium in the molten steel

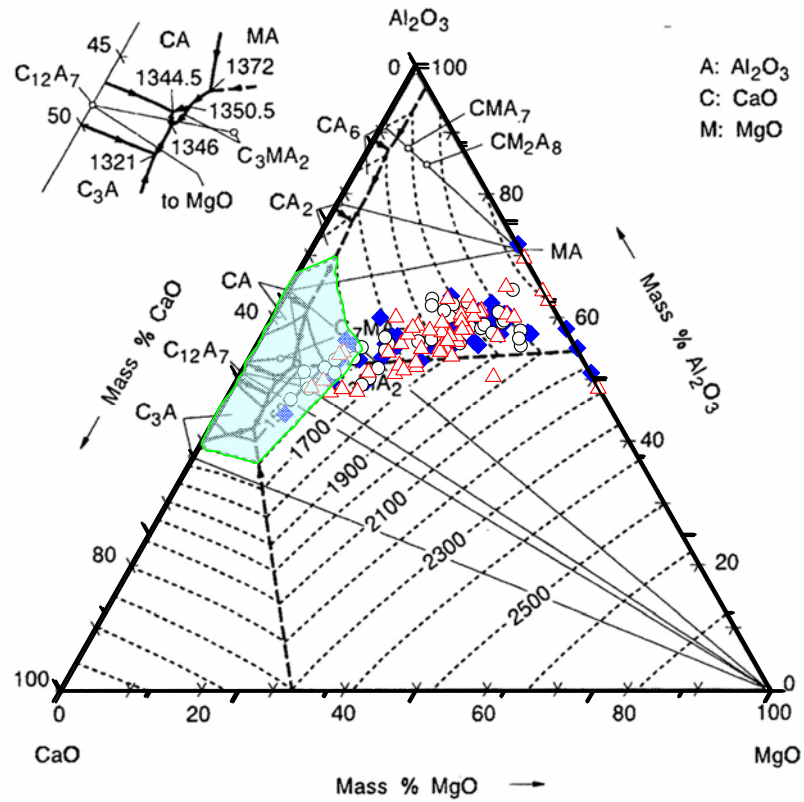


Fig.9 The composition and melting points of inclusions (spheres: [Al]_{end}=80-90ppm, triangles:[Al]_{end}=90-100ppm, diamonds: [Al]_{end}=100-120ppm; shade area with <1600°C melting points; the melting points data from reference [14])

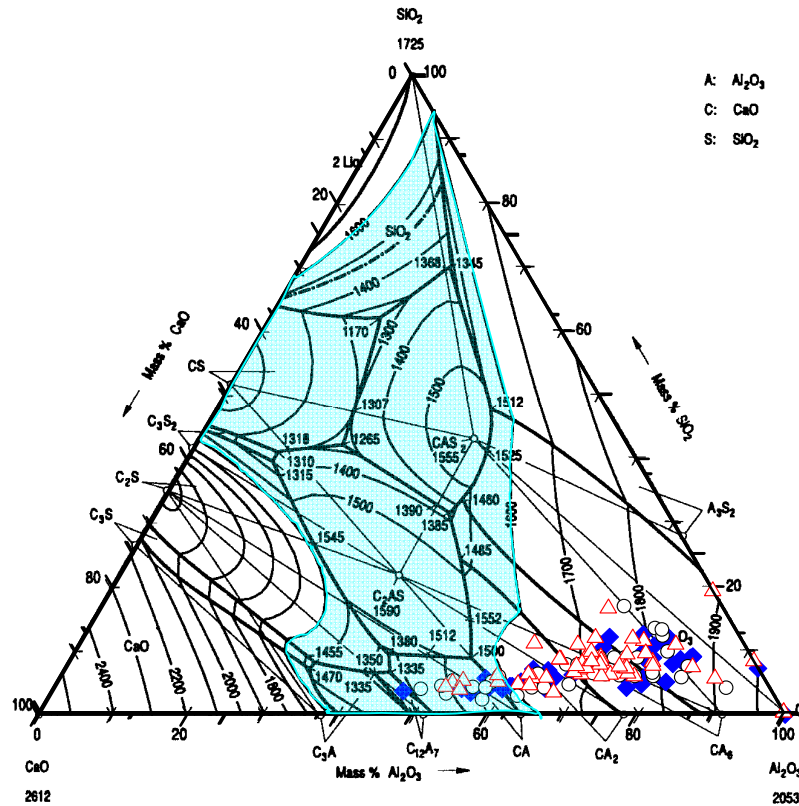


Fig.10 The composition and melting points of inclusions (spheres: [Al]_{end}=80-90ppm, triangles:[Al]_{end}=90-100ppm, diamonds: [Al]_{end}=100-120ppm; shade area with <1600°C melting points; the melting points data from reference [15])

Since liquid inclusions are easy to be removed, and most are deformable during rolling process. Further studies should be carried out in order to modify inclusions from solid state to liquid state. The following object should be achieved:

- For CaO-Al₂O₃ inclusions, or for then CaO-Al₂O₃-SiO₂ inclusions with SiO₂<10%, CaO/Al₂O₃ in inclusions should be ~0.86 in order to form liquid C₁₂A₇ inclusions. For most of the inclusions in the current study, CaO/Al₂O₃=0.1-0.7, so more CaO should be used in the slag phase;
- For CaO-Al₂O₃-MgO inclusions, or for CaO-Al₂O₃-MgO-SiO₂ inclusions with SiO₂<10%, the composition of inclusions should be controlled in the shade area of Figure 9: CaO 40-60%, Al₂O₃ 40-60%, MgO <10%. For most of the inclusions in the current study, MgO=10-35% (Fig.8), and CaO is less than Al₂O₃, so the MgO from lining refractory should be well prevented and more CaO should be used in the slag phase;
- As shown in Fig.10, inclusions containing more SiO₂ tend to be liquid. Suitable increasing SiO₂ in slag may favor to modify solid inclusions into liquid ones. However, SiO₂ tends to pollute steel by reacting with dissolved aluminum.

EFFECT OF DISSOLVED ALUMINUM ON STEEL CLEANLINESS

Effect of the initial dissolved aluminum ([Al]_o) on steel cleanliness with 90min reaction time is shown in Figure 11. Larger [Al]_o corresponds to smaller final T.O. in the steel, smaller SiO₂ content and larger Al₂O₃ in the slag after refining due to the possible reaction between dissolved aluminum and the dissolved oxygen. It should be noticed that Al₂O₃ in the slag after refining is in the small range of 40-42% though increasing with larger [Al]_o, which hints that the main contribution of [Al]_o is not for deoxidation. Fig.11 also indicates there is a critical value of [Al]_o, around 250ppm, at which the final dissolved aluminum ([Al]_{end}) reaches a peak value. 250ppm [Al]_o corresponds to 100ppm [Al]_{end}. This seems very unusual. However, at this critical [Al]_o the value of [Mg] in the steel after refining reaches the minimum value and MgO in the slag after refining reaches maximum value, which hints that the initial dissolved aluminum greatly affects [Mg] in steel, MgO in the slag – the transfer of MgO from lining refractory into steel, thus greatly affects MgO content in inclusions. Thus, the main contribution of [Al]_o is not for deoxidation but for the reaction between steel and crucible MgO lining refractories. As comparison, the effect of [Al]_{end} on steel cleanliness is shown in Figure 12, indicating big difference from those of [Al]_o. Larger [Al]_{end} corresponds to smaller [Mg] in steel and larger MgO in the slag after refining.

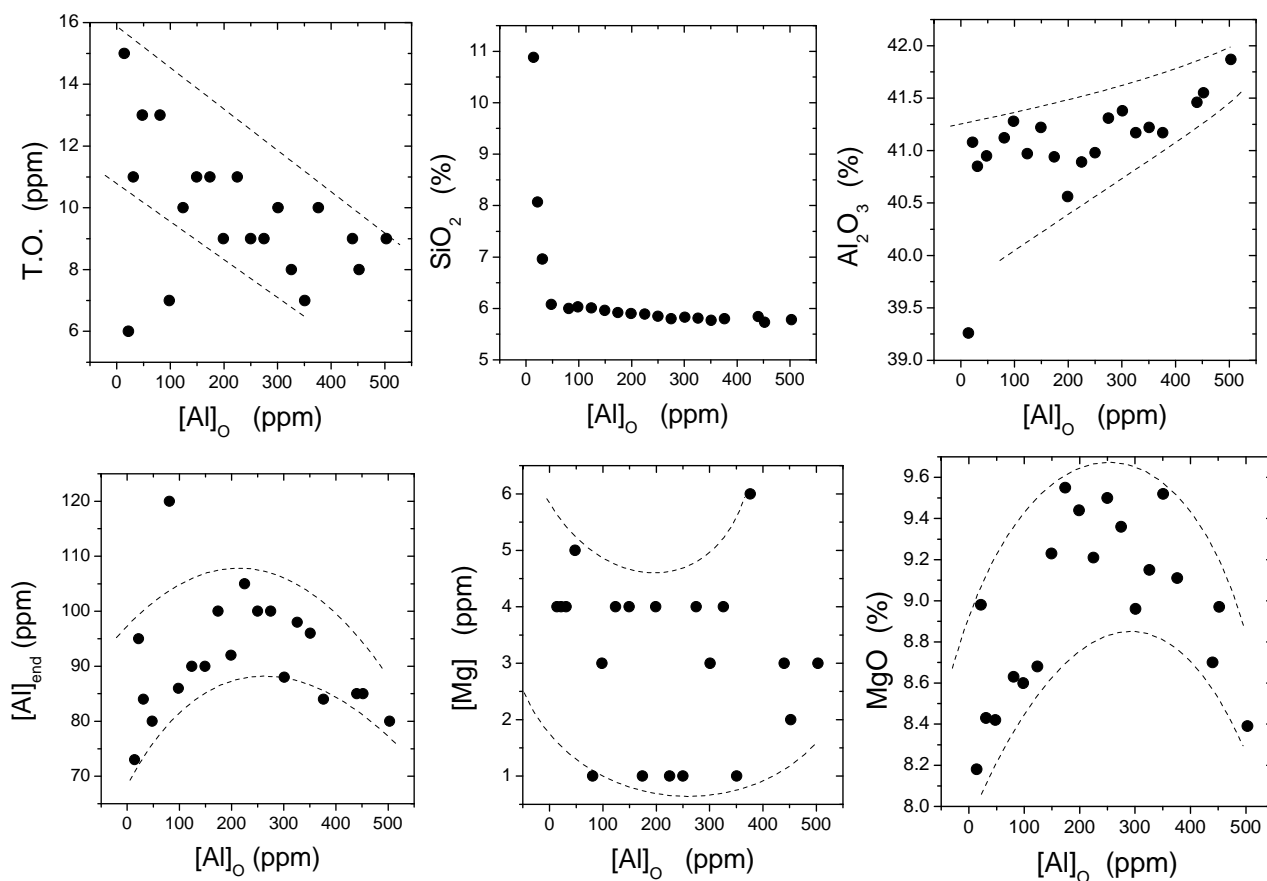


Fig.11 Effect of the initial dissolved aluminum on steel cleanliness

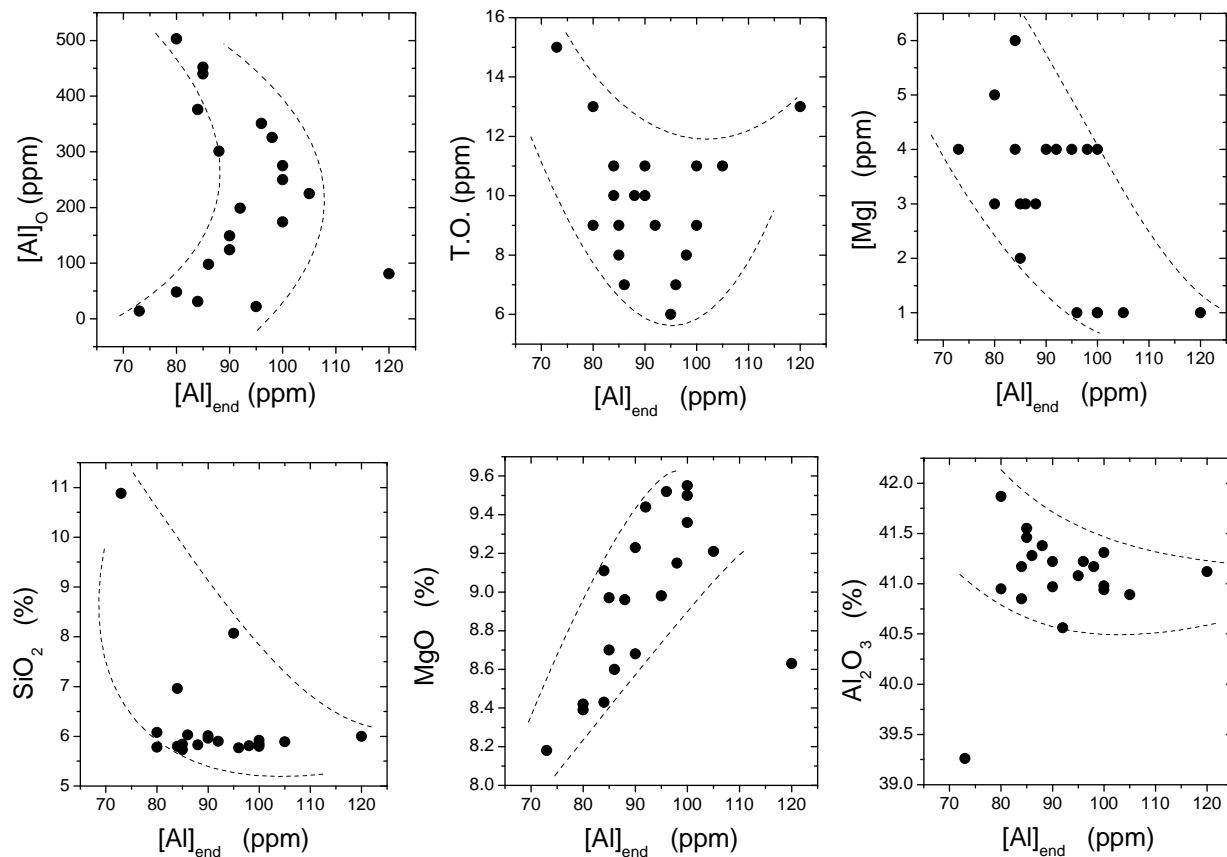


Fig.12 Effect of the dissolved aluminum after refining ($[Al]_{end}$) on steel cleanliness

FORMATION OF MGO-BASED INCLUSIONS

Since all detected inclusions contain MgO, and the only source of MgO is from lining refractory, the mechanisms of MgO transfer from lining refractory to the molten steel should be investigated. After 90min reaction, the mean content of MgO in the slag in 21 experiments is ~9%. If ignoring this MgO, the relative composition of CaO, SiO₂ and Al₂O₃ in the slag is shown in Table 2. Comparing to the original composition, the 1% increasing of SiO₂ is possibly due to the deoxidation by silicon and CaO and Al₂O₃ have no clear change, which indicates again deoxidation by aluminum is minor deoxidation. MgO in the slag increases with reaction time, as shown in Figure 13, though the dissolved aluminum reaches the equilibrium value after 90min.

Table 2 Original compositions of steel and slag used (wt%)

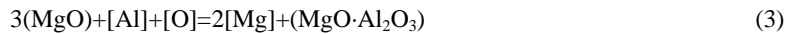
	CaO	SiO ₂	Al ₂ O ₃
Original composition	48%	6%	46%
Ignoring MgO in the slag after refining (90min)	47.65%	6.96%	45.39%

The original slag mass is 50g. After refining the slag mass should be 55g corresponding to 9% of MgO (5g). If all these MgO disperses into the 100g steel with size of 1.5 μ m (Fig.6), the concentration of MgO inclusions in steel will be $\sim 3 \times 10^{17}$ per m³ steel. However, the observation of the crucible after refining indicates that the erosion between slag and the crucible is much more serious than that between steel and the crucible. Some researchers has investigated the dissolution of MgO from crucible into molten slag.^[16] Thus MgO in inclusions in steel have the following two possible mechanisms:

- Mechanism I: direction transfer of MgO from crucible to the molten steel. By this mechanism, inclusions should be the our MgO inclusions or MgO-Al₂O₃ spinel inclusions. 5.5% inclusions detected are generated through this mechanism.
- Mechanism II: dissolution of MgO into the slag and transfer of MgO+CaO+SiO₂ into the molten steel. 89.5% inclusions in the steel generated through this mechanism. It should be noticed that the MgO content of most inclusions is larger than 10%- MgO content in the slag. This indicates that either the transfer of MgO from the slag to the steel is faster than that of CaO and SiO₂ or inclusions by Mechanism II interact with inclusions by Mechanism I in the molten steel.

The reaction by this mechanism includes^[17]





These reactions hint the increasing of [Mg] and consuming dissolved aluminum in the molten steel. These reactions may explain the reason for the critical value of the initial dissolved aluminum, as shown in Fig.11.

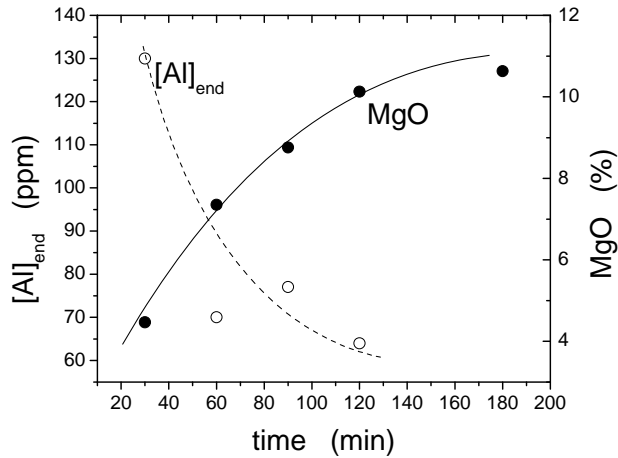


Fig.13 MgO in slag increases with reaction time

Detailed mechanisms of MgO-based inclusions in the molten steel are discussed in another paper by Zhang et al. [17]. As shown in Fig.9, in order to achieve liquid inclusions, MgO content in inclusions should be controlled below 10%, however, the current MgO in inclusions is 10-35%. The following measures will be used in the future experiments:

- Increase CaO in the slag;
- Use more strong and denser MgO crucible or other materials;

In recent 20 years, the lining refractories used in steelmaking, steel refining and continuous casting process are mainly MgO-based. They are much looser than the MgO crucible used in the current laboratory experiments. Thus the dissolution of MgO from lining refractories into the molten steel is a serious issue for steel industries, and has been more and more noticed by steelmakers. [6-10]

SUMMARY

The current paper is to investigate the steel cleanliness and inclusions in a constructional steel during slag refining process in a laboratory scale. With 90min reaction time in the MgO crucible, the slag contained 39-44%CaO, 8-10% MgO, 6-11% SiO₂, 39-42%Al₂O₃, <0.2% MnO, and <0.6%FeO. The basicity (%CaO/%SiO₂) was mainly ~7.1-7.6. The steel cleanliness is: T.O.:6-15ppm, dissolved aluminum after refining:73-120ppm, Ca:2-10ppm, Mg: mainly 1-16ppm. Inclusions include 94% oxide inclusions (5.5% MgO-Al₂O₃ spinel inclusions+89.5% oxide CaO+Al₂O₃+ SiO₂+MgO inclusions) and 6% sulfides, mainly 1-2 μm in diameter and spherical shape. 90% of the inclusions are solid, with melting temperature over 1600°C since they contain CaO 10-40%, SiO₂ 4-6%, Al₂O₃ 50-55%, MgO 15-35%.

All inclusions contain MgO, even for sulfide inclusions, indicating that all detected inclusions were related to MgO crucible since MgO can only comes from the crucible in the current study. The main contribution of [Al]_o is not for deoxidation but for the reaction between steel and crucible MgO lining refractories. There is a critical value of [Al]_o, around 250ppm, at which the final dissolved aluminum reaches a peak value, and the value of [Mg] in the steel reaches the minimum value and MgO in the slag reaches maximum value. MgO in inclusions in steel have two possible mechanisms: I) direction transfer of MgO from crucible to the molten steel, 5.5% inclusions detected are generated through this mechanism; II) dissolution of MgO into the slag and transfer of MgO+CaO+SiO₂ into the molten steel. 89.5% inclusions in the steel generated through this mechanism. The dissolution of MgO from lining refractories into the molten steel is a serious issue for steel industries, and has been more and more noticed by steelmakers.

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