Formation of MgO·Al₂O₃ Inclusions in High Strength Alloyed Structural Steel Refined by CaO–SiO₂–Al₂O₃–MgO Slag

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(Received on August 8, 2007; accepted on April 14, 2008)

Present paper focused on the formation of MgO·Al₂O₃ inclusions in high strength 42CrMo alloyed structural steel refined by CaO–SiO₂–Al₂O₃–MgO slag. Soluble aluminum contents in molten steel were less than 0.0100% when steel/slag equilibrium was established.

It is found by pre-equilibrium experiments that 90 min are sufficient for the attainment of equilibrium of slag–metal at 1873 K. Spinel inclusions dispersed widely in the steel, with sizes between 2 μm and 4 μm. Magnesium content in molten steel influences the morphology of spinel inclusions greatly. With the rise of magnesium content in steel, globular spinel inclusions were modified into angular ones. However, trace amount of Ca in inclusions is effective to change the spinels from angular shape to globular shape. Solubility of MgO in slag was also discussed. It is shown that MgO in slags are saturated and activities of MgO can be considered as unity. Observed log \( \frac{X_{MgO}}{X_{Al_2O_3}} \) of inclusions increases with the growth of observed log \( \frac{a_{MgO}}{a_{Al_2O_3}} \) of molten steel as well as the rise of observed log \( \frac{a_{MgO}}{a_{Al_2O_3}} \) in slag, both exhibiting good linear relation.

MgO–MgO·Al₂O₃–Al₂O₃ stability phase diagram was obtained. It is found that aluminum and magnesium contents in molten steel mainly position in the MgO·Al₂O₃ formation zone, which is essentially pre-requisite for the formation MgO·Al₂O₃ in steel. Silica in slag is helpful to stabilize MgO·Al₂O₃ phase, because it would react with calcium and aluminum in molten steel. In the scope of soluble aluminum contents, magnesium content influences the transformation among MgO–MgO·Al₂O₃–Al₂O₃ ternary phases greatly, which is the reason for the formation of rectangular MgO inclusions.

KEY WORDS: MgO·Al₂O₃ spinel; slag; inclusion; equilibrium; high strength alloyed structural steel.

Table 1. Chemical compositions of 42CrMo steel material (mass%).

| C   | Si   | Mn   | P   | S   | Cr  | Mo |
|-----|------|------|-----|-----|-----|----|
| 0.42| 0.25 | 0.65 | 0.01| 0.002| 1.15| 0.2|
unless specially stated. After held at 1 873 K for a certain time (the equilibrium time was confirmed by pre-equilibrium experiments), the magnesia crucible containing the sample was picked out and quenched rapidly in water.

2.1. Pre-equilibrium Experiments

Before equilibrium experiments, pre-experiments have been carried out to find the holding time for attainment of equilibrium between slag and molten steel. The crucible containing slag and steel was held at 1 873 K for a different period of time. Then, the crucible was pulled out and quenched rapidly in water. The steel sample and slag sample were prepared for chemical composition analysis.

2.2. Equilibrium Experiments

After the time for attainment of equilibrium is determined, the melts were held at 1 873 K for a time needed to reach the slag–metal equilibrium without stirring for the purpose of eliminating oxides by flotation and establishing the equilibrium between slag and steel. Then, the crucible containing the sample was picked out and quenched rapidly in water.

The steel samples as well as slag samples were prepared for chemical analysis. Thirty inclusions on the cross-sectioned plane of the sample were randomly chosen and they were analyzed by SEM-EDS to get the overall and statistical information of inclusions such as morphology, size and chemical compositions and so on.

In the present study, a metal sample (0.5 g), 10 cm³ of water and 5 cm³ of HNO₃ (1/11001) were added into a decomposition blocked beaker of 200 cm³ capacity and afterwards slowly heated until no air bubbles emerged out from the solution. Then 5 cm³ HCl (1/11001) was added into the beaker and heated continuingly in order to decompose the metal sample by heating. Water and all acids used were ultra pure grade. After dissolving the sample, the solution was transferred to the measuring flask (100 cm³) using ultra pure water with filtration. Residue was remained in the filter paper. The content of Al in the sample solution (cooled down to room temperature), which was regarded as acid-soluble Al, was analyzed by ICP emission spectrometry. Acid-soluble Ca and Mg content in steel were analyzed in the same method.

It should be noted is that a part of inclusions such as MgO·Al₂O₃ inclusions could dissolve into the acids but not all of them. The extent of dissolving of inclusions in acids depends on the sizes, amounts of inclusions themselves. As a result, the analyzed acid-soluble Al and Mg are different from the actual acid-soluble Al and Mg in steel.

Total oxygen content in the sample was determined by fusion and the infrared absorption method. The composition of the slag was analyzed by an X-ray fluorescence spectrometer.

3. Results and Discussion

3.1. Time for Attainment of Equilibrium

The chemical compositions of the melts and slags obtained in the pre-equilibrium experiments are listed in Table 2.

It is found that after held for 90 min, total oxygen contents in the melt changed very little. That indicates 90 min is sufficient for the floatation of inclusions in molten steel up to slag. While aluminum contents in the melts changed little after the melt were held for 60 min, as shown in Fig. 1. It could be concluded that 90 min are sufficient to attain equilibrium between slag and metal.

3.2. MgO·Al₂O₃ Inclusions Detected in the Steel Samples

The analyzed compositions of the steel and slag after equilibrium experiments are listed in Table 3.

It was found by the observation using SEM-EDS that MgO·Al₂O₃ inclusions widely dispersed in steel samples. In particular, they were very small (about 2–4 μm), globular, uniformly distributed particles other than angular particles reported except in experiment No. 4, as shown in Figs. 2–8.

Magnesia content in spinel inclusions increased with the growth of magnesium content in the melts. Particularly, many rectangular MgO particles existed in steel sample No. 6 in which magnesium content is 0.0010%, highest among all the melts. The reason for this will be discussed in details later. Something noticeable is that increase of magnesium content in molten steel modifies spinel inclusions from spherical to sharp angular, while trace amount of calcium in inclusions might be helpful to modify the inclusions to be spherical as indicated in the Figs. 2–8.

3.3. Deoxidation Equilibrium of Aluminum

When the equilibrium establishes between slag and molten steel, aluminum and magnesium in molten steel are in equilibrium with the slag. Therefore, the following reaction

\[(\text{Al}_2\text{O}_3) = 2\text{[Al]} + 3\text{[O]} \]  

(1)
where $K_i$ is the equilibrium constant, $a_{[i]}$ is the activity of component $i$ in steel, which is calculated by the standard state of infinite dilute solution, and $a_j$ is the activity of component in slag, whose standard state is pure solid. The activities of $[\text{Al}]$, $[\text{O}]$ can be calculated with the following Eqs. (3) and (4),

$$\log a_{[\text{Al}]} = \sum e_i^{[\text{Al}]} [\text{mass}\%] + \log[\text{mass}\%\text{Al}] ......(3)$$

$$\log a_{[\text{O}]} = \sum e_i^{[\text{O}]} [\text{mass}\%] + \log[\text{mass}\%\text{O}] ......(4)$$

Where $e_i$ is the first order interaction coefficient between elements $i$ and $j$, which are given in Table 4. Suito et al. deduced a regression equation for the calculation of the activ-
ity of alumina in CaO–SiO$_2$–Al$_2$O$_3$–MgO slag at 1 873 K as follows\textsuperscript{(12)}:

$$\log a_{\text{Al}_2\text{O}_3} = \{ -0.275(\%\text{CaO}) + 0.167(\%\text{MgO}) \} / (\%\text{SiO}_2)$$

$$+ 0.033(\%\text{Al}_2\text{O}_3) - 1.560 \ldots \ldots \ldots \ldots \ldots (5)$$

Substituting the activity of Al$_2$O$_3$ estimated by Eq. (5) using the slag compositions given in Table 3, Eqs. (3) and (4) to Eq. (2), dissolved oxygen content can be calculated. The oxygen contents in the molten steel in equilibrium with alumina in slag phase at 1 873 K are obtained and given in the above Table 3.

### 3.4 Saturation Behavior of MgO in Slag

Ohta \textit{et al.}\textsuperscript{(12)} plotted the iso-solubility lines of MgO in (CaO+MgO)–SiO$_2$–Al$_2$O$_3$ quasi-ternary system, as shown in Fig. 9. The heavy lines represent the boundaries of different phases, and the light lines represent the iso-solubility lines of MgO. It can be seen from the iso-solubility lines of MgO that, with the increase in Al$_2$O$_3$ content for a given SiO$_2$ content, the solubility of MgO in the MgO-saturated phase increases until the MgO–MgO·Al$_2$O$_3$ double saturated phase boundary and, thereafter, decreased in the MgO·Al$_2$O$_3$-saturated phase.

Compositions of the slags listed in Table 2 are projected in this quasi-ternary system, as indicated by the triangles in Fig. 9. Slag Compositions of the slags in experiments No. 1 and No. 3 locate near the saturated boundary of MgO and CaS and in the MgO·Al$_2$O$_3$ saturated phase respectively, where the MgO solubility is between 5% and 10%. Because the MgO content in slag No. 1 and No. 3 are 7.38% and 6.98%, so activity of MgO in slag No. 1 and No. 3 can be considered as unity. In experiments No. 5 and No. 7, slag compositions locate near the phase boundary of MgO–MgO·Al$_2$O$_3$ with MgO solubility between 10% and 15%. Because MgO contents in slag No. 5 and No. 7 are between 11.5% and 12.31% in experiments, activities of MgO in these two slags can be considered as unity, too. As far as other slags, MgO contents are higher than their solubility, so activities of MgO in these slags can also be considered as unity.

### 3.5 Equilibrium among the Observed MgO·Al$_2$O$_3$-inclusion/Steel/Slag

According to Suito and Inoue\textsuperscript{(16)}, inclusion composition can be estimated from thermodynamic calculation as a function of steel composition and temperature, provided that the equilibrium between steel and inclusion is established. The inclusion composition is theoretically similar to the slag composition at the equilibrium among inclusion/steel/slag, but it seems impossible. Okuyama \textit{et al.}\textsuperscript{(17)} proved that the reaction between inclusions and steel is fast enough to establish the local equilibrium between inclusions and molten steel.

$$\log a_{\text{Al}_2\text{O}_3} = \{ -0.275(\%\text{CaO}) + 0.167(\%\text{MgO}) \} / (\%\text{SiO}_2)$$

$$+ 0.033(\%\text{Al}_2\text{O}_3) - 1.560 \ldots \ldots \ldots \ldots \ldots (5)$$

### Table 4. Interaction coefficients\textsuperscript{(13)} applied in thermodynamic calculations at 1 873 K in present works.

| \( i \) | C | Si | Mn | P | S | Cr | Mo | Al | O |
|---|---|---|---|---|---|---|---|---|---|
| Al | 0.091 | 0.0056 | -- | 0.033 | 0.030 | 0.012 | -- | 0.045 | -- |
| O | -0.436 | -0.131 | -0.021 | 0.07 | -0.133 | -0.04 | 0.0035 | -3.9 | -0.2 |
| Mg | -0.15\textsuperscript{(14)} | -0.09\textsuperscript{(15)} | -- | -- | -1.38 | 0.05 | -- | -0.12 | -430 |

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It could be found that the slope of the fitted line of the experimental data obtained by a linear regression analysis. It was found that observed log(XMgO/XAl2O3) was plotted, indicated in Fig. 11 as solid squares. The dotted line is the fitted line of the experimental data obtained by a linear regression analysis. It could be found that observed log(XMgO/XAl2O3) increased with the growth of observed log(aMgO/aAl2O3), exhibiting good linear relation. Slope of the line is about 0.70.

It should be noted here that because in steel sample No. 6 inclusions detected and analyzed by SEM-EDS were pure MgO, XMgO was zero and log XMgO is not right in math. As a result, the numbers of data points in Figs. 10 and 11 were six rather than seven.

Two reasons result in the scatter of the data points and the deviation between the slopes of fitted line and unity.

3.6. MgO/MgO·Al2O3/Al2O3 Stability Phase Diagram

In order to study MgO/MgO·Al2O3 and MgO·Al2O3/Al2O3 boundaries, thermodynamic calculation has been made to obtain the stability diagram of these three different phases in steel. The used equations are listed as follows:

Calculation of MgO/MgO·Al2O3 boundary

\[ 4(MgO) + 2[Al] = MgO·Al2O3 + 3[Mg] \] (12)

\[ \log K_{12} = -33.09 + 50.880/T \] (13)

\[ K_{12} = \frac{a^4_{[Al]} a_{MgO}^2}{a^4_{[Al]} a^2_{MgO}} \] (14)

Calculation of MgO·Al2O3/Al2O3 boundary

\[ 4(Al2O3) + 3[Mg] = 3(MgO·Al2O3) + 2[Al] \] (15)

\[ \log K_{16} = 34.37 - 46.950/T \] (16)

\[ K_{16} = \frac{a^4_{[Al]} a_{MgO·Al2O3}}{a^4_{MgO·Al2O3} a_{[Al]}^2} \] (17)

According to Hino et al.20) when MgO/MgO·Al2O3 boundary was calculated at 1873 K, activity of MgO·Al2O3 was taken as 0.8 while that of MgO as 0.99 because of very small solubility of Al2O3 into MgO. When MgO·Al2O3/Al2O3 boundary was calculated, activity of MgO·Al2O3 was taken as 0.47 while that of Al2O3 as unity because of negligibly small solubility of MgO into Al2O3. Oxygen concentration was taken into account when calculate the activity coefficient of Mg in present paper. It was taken as 0.0005%, which is about the average of the dissolved oxygen contents of present work. Compared with magnesium, influence of dissolved oxygen content on the activity of alumina was omitted here because e^O_{Mg} is much smaller than e^O_{Al}. During the calculation of the activity coefficients, it is found influence of dissolved oxygen content on the activity coefficient of aluminum can be omitted. Substituting Eqs. (3), (8) to Eqs. (14) and (17), the phase stability diagram calculated, as shown in Fig. 12.

It could be found that in the scope of dissolved aluminum of present paper, tiny increase of magnesium content in the molten steel would promote the transformation of MgO·Al2O3 and MgO. It is obvious that the Mg and Al contents in the molten steel mainly existed in the spinel formation zone, which is the primary reason for MgO·Al2O3 inclusions formation. In Experiment No. 6, in which inclusions were mainly rectangular MgO inclusion as discussed above, the data point of it (indicated by the bold arrow) positioned rightly at the boundary of MgO/spinel. The diagram consisted with the experimental results very well.

Itoh et al.21) evaluated the stable formation region of MgO·Al2O3/Al2O3.
spinel inclusions in liquid steel by assuming an ideal solid solution behavior of spinel during de-oxidation process. In their work, when aluminum content in molten steel is lower than 0.0010%, MgO inclusions will form in molten steel directly. However, in present work, MgO can not form directly because there was no magnesium in molten steel at the very beginning of these experiments. All the MgO inclusions are evolved from MgO·Al2O3. The spinel inclusion region is narrower than that predicted by Itoh et al.

Todoroki et al.10,19 evaluated the stable formation region of spinel inclusions in 304 stainless steel refined by CaO–(SiO2)–Al2O3–MgO–CaF2 slag. In their work, the shape of spinel inclusion region is similar to that in present paper, but the threshold value for Al2O3/MgO·Al2O3 and MgO·Al2O3/MgO transformation is lower than that predicted in present work. The difference originates from the distinction of the chemical compositions in the melts.

According to Todoroki et al.,10,19 silica in slag will react with soluble aluminum and magnesium, which retards and even prohibits further transformation of MgO·Al2O3 inclusion to MgO inclusions or CaO–Al2O3–MgO system inclusions. In their paper, activity of silica in slag was estimated as about 0.0001 using the regression formula given by Ohta and Suito.10 In present paper, activity of silica in slag varied from about 0.0003 to 0.006, calculating with this regression formula. It is found that activity of silica in slag of experiment No. 6 is about 0.0003, which is the lowest one among all the slags. Correspondingly, the magnesium content in the melt is 0.0010% which is the largest one among the melts. It is noticeable that in experiment No. 6 (aluminum content is 0.084%, and magnesium content is 0.0010%), spinel inclusions were transformed into rectangular MgO particles. Furthermore, it could be found that MgO content in inclusions increases with the decrease of silica content in slag as shown by the EDS results in Figs. 2–8 and Table 3.

Conclusions could be drawn here that in scope of aluminum content in present paper, tiny fluctuation of magnesium content in molten steel influences transformation among MgO/MgO·Al2O3/Al2O3 inclusions in the molten steel greatly. When the magnesium content reached a threshold value, spinel inclusions would be transformed to magnesia inclusions. Silica in slag consumed soluble aluminum especially magnesium in molten steel, thus prohibited the transformation of spinels into MgO inclusions stabilized the existence of MgO·Al2O3 inclusions.

4. Conclusions

Laboratory scale experiments as well as thermodynamic calculations have been done to investigate the formation of MgO·Al2O3 inclusions in high strength alloyed structural steel. The following conclusions were obtained:

(1) Pre-equilibrium experiments have been done and it is found that 90 min are sufficient for metal–slag to attain equilibrium.

(2) Inclusions existing in the 42CrMo alloyed structural steel are mainly MgO·Al2O3 spinels. Contents of MgO in inclusions increase with the rise of Mg content in molten steel. Spinel inclusions evolved gradually from globular ones into angular ones with the rise of Mg content in molten steel. Trace amount of calcium in inclusions is helpful to modify the angular spinels to globular inclusions in spite of the rise of Mg content in molten steel, which is very positive to improve the fatigue life of the high strength 42CrMo alloyed structural steel.

(3) MgO in slags during experiments in present paper are saturated; thus, activity of MgO could be considered as unity;

(4) Observed log(aMgO/aAl2O3) of the inclusions linearly increases with the increase of observed log(aMgO/2aAl) in molten steel and with the rise of observed log(aAl/aMgO) in slag, exhibiting good linear relation. But the slopes of the fitted lines are not unity. The reason is that silica in slag influenced greatly the MgO content in inclusions, thus the MgO content in spinels depend not only on MgO but also silica content in the slag.

(5) Stability phase diagram of MgO/MgO·Al2O3/Al2O3 was obtained. It shows that aluminum and magnesium contents in experiments of present paper mainly position in MgO·Al2O3 formation zone, which is the primary reason for the widespread existence of MgO·Al2O3 spinel inclusions in steel. Silica in slag stabilized the existence of MgO·Al2O3 inclusions.

Acknowledgements

The authors are grateful to the team of National Basic Research 973 Program of China (No. 2004CB619106) for support of this works.

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