Effect of MgO on crystallization behavior of MnO–SiO2–Al2O3 based inclusions in tire cord steel

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\textbf{ABSTRACT}

Increasingly MgO content in refining slag and molten steel is the major cause of corrosion of refractory materials at slag line during the refining process of Si–Mn deoxidized tire cord steel, the effects on the crystallization behavior of typical MnO–SiO2–Al2O3 based inclusions in tire cord steel were studied. The relation between the formation of high melting point and high hardness inclusions (Al2O3, 3Al2O3⋅2SiO2, MgO–Al2O3, and 2MgO–SiO2) with MnO–SiO2–Al2O3 (0wt.%, 4wt.%, 8wt.%, 12wt.%, 16wt.%) MgO system was verified by ICP, XRD, SEM-EDS and FactSage 8.0. The results indicated that the crystallization temperature of MnO–SiO2–Al2O3 system increases with the increase of MgO content. Mg\textsubscript{x}Mn\textsubscript{2-x}Si\textsubscript{2}(1 \leq x \leq 2) solid solution is the main crystalline phase due to isomorphism. Only a small amount of 2MgO-SiO\textsubscript{2} which is not enough to cause wire breakage was formed in the trial with the highest MgO content (16wt.%) after the low melting point MnO–SiO2–Al2O3 composition added different MgO content and the other three kinds of inclusions were not produced in the five trials.

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1. Introduction

As one of the main representatives of clean steel, tire cord steel has more stringent refining conditions. To avoid wire breakage caused by high-melting point and hard large-size Al-containing inclusions, alloys containing Si or Mn are used to control the types of inclusions in the steel as MnO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} inclusions and CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} inclusions in the low-melting point region from their ternary phase diagrams [1, 2, 3]. However, the physical and chemical corrosion of refining slag and molten steel on refractories is a classic problem in changing the composition of refining slag during the refining process. Besides, the compositions of inclusions are controlled by top slag, and their compositions are changing accordingly [4, 5, 6, 7].

Several studies have pointed out that MnO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} is the endogenous deoxidization product inclusion, while CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} inclusions contain MnO or MgO components. As noted by Wang MnO–SiO\textsubscript{2} is the initial inclusion during Si–Mn deoxidation [8]. Once the acid soluble aluminum in the steel begins to increase with the dissolution of the alloy and then MnO–SiO\textsubscript{2} is transformed into MnO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} composite inclusions. CaO–SiO\textsubscript{2}–MnO-(MgO) inclusions are formed by the collision between MnO–SiO\textsubscript{2} and CaO–SiO\textsubscript{2}-(MgO) from the top slag, and these inclusions are going to transform as CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}-(MgO) inclusions. Niu argued the compositions of oxide inclusions in the industrial trials of tire cord steel, and explored the relationship between the size, quantity, melting point and other properties of inclusions and Al\textsubscript{2}O\textsubscript{3} content [9]. For this study, the compositions of Al\textsubscript{2}O\textsubscript{3} in the top slag of different heats were 3.08%, 3.40% and 3.20%, respectively, while the Al\textsubscript{2}O\textsubscript{3} content in the inclusions was up to 50%, which was much higher than that in the top slag. Previous researches have indicated that inclusions have good deformation ability as the Al\textsubscript{2}O\textsubscript{3} content is 20–25%. Both deoxidization products in the steel and the mineral phases from the top slag affect the evolution behavior of inclusions [6, 7, 8]. Al\textsubscript{2}O\textsubscript{3} affects the deformation ability of MnO–SiO\textsubscript{2} inclusions through the formation of composite oxide inclusions with different melting points, while Al\textsubscript{2}O\textsubscript{3} mainly comes from acid soluble aluminum in steel.

The deformation capacity of inclusions during hot rolling is usually expressed by the melting point, viscosity and other rheological properties of inclusions, and the low-temperature deformation capacity of inclusions during cold drawing is evaluated by Young's modulus [10]. Zhang proposed that the aspect ratio of inclusions after hot rolling represents the high-temperature deformation capacity of inclusions [11]. It is found that the CaO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}–MgO inclusions are long chain along the rolling direction through the analysis results of inclusions in once rolled bar. MnO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO inclusions are ‘eye shaped’ with the
surrounding MnO–SiO₂–Al₂O₃–(MgO/CaO) wrapping the central SiO₂-rich phase. Moreover, an about 4μm size of 92.98% SiO₂-rich inclusion was found in the bar. The maximum section sizes of inclusions causing wire breakage during cold drawing were 22 μm and 17.8 μm, and their components were 48.48%CaO-19.39%SiO₂-11.69%Al₂O₃-5.88%MgO-14.54%CaS and 7.48%MgO-17.61%SiO₂-49.88%Al₂O₃-25.02%MgO, respectively. These two inclusions detected at the fracture are not near the low melting point MnO-Al₂O₃. MnO–SiO₂ binary phase diagram and EDS shows that there is a slight difference in the composition of the micro region of samples at different temperatures. Overall, no crystal phases were found at 7 sampling temperatures from Figure 4, and SEM results are consistent with the XRD results. It is a liquid phase as shown in Figure 3, and EDS shows that there is a slight difference in the composition of the micro region of samples at different temperatures.

Table 1. Oxide compositions and liquidus temperatures of MnO–SiO₂–Al₂O₃–MgO.

| No. | SiO₂/g | MnO/g | Al₂O₃/g | MgO/g | TL°/C |
|-----|--------|-------|---------|-------|-------|
| B   | 43.2   | 46.8  | 10      | 0     | 1148  |
| C   | 43.2   | 46.8  | 10      | 4     | 1210  |
| D   | 43.2   | 46.8  | 10      | 8     | 1318  |
| E   | 43.2   | 46.8  | 10      | 12    | 1406  |
| F   | 43.2   | 46.8  | 10      | 16    | 1475  |

3. Results

There is no obvious intensity peak as the XRD result shows in Figure 2, that is, no crystalline phase was formed in the sample, and the 0 wt.% MgO content water quenched sample is a homogeneous glass phase according to the SEM.

ICP results of MnO–SiO₂–Al₂O₃–MgO system are shown in Table 2, in which C₇ is 4wt.% MgO air cooled sample, D₉ is 8wt.% MgO air cooled sample. E₉ is 12wt.% MgO air cooled sample, F₄ is 16wt.% MgO air cooled sample. SiO₂/(SiO₂+MnO) ratio of the samples is close to 0.5, and the fluctuation value of MgO content and design composition is 0.09-0.43%. XRD results of MnO–SiO₂–Al₂O₃-4wt.% MgO water quenched samples are shown in Figure 3. Overall, no crystal phases were found.

2. Raw material and trials

The compositions of MnO–SiO₂–Al₂O₃ inclusion system were selected near the low melting point 3MnO-Al₂O₃:SiO₂ primary crystal region of its ternary phase diagram to obtain inclusions with low melting point and fine rheological properties, and Al₂O₃ in the system was determined to be 10wt.%. According to MnO–SiO₂ binary phase diagram and MnO–SiO₂–Al₂O₃ ternary phase diagram, SiO₂/(SiO₂+MnO) = 0.48 was selected. 4wt.%, 8wt.%, 12wt.% and 16wt.% four groups of MgO compositions were designed based on this component, the specific component and liquidus temperature were shown in Table 1. To ensure the same proportions and weights of MnO, SiO₂ and Al₂O₃, MgO content is the weight proportion of MnO–SiO₂–Al₂O₃ system. Precisely weighed each oxide (analytically pure, Sinopharm group), fully mixed it and put it into a graphite crucible. Figure 1 shows the schematic diagram of heating device and heating procedure. Samples were heated in a high-temperature carbon tube furnace under Ar atmosphere to 1600 °C (heating rate, 10 °C/min) and kept for 15 min to melt the sample completely. Then every 50 °C (cooling rate, 3.33 °C/min) was cooled and kept for 10 min, the graphite rod was used to dip the sample for water quenching until the sample became significantly solidified. At this temperature, the crucible was taken out for air cooling as the final sample. ICP and XRD were used to detect the oxide compositions and crystalline phases of the dried samples, and SEM-EDS was used to analyze the microstructure and micro components of each sample. These trials were numbered in the order shown in Table 1, the liquidus temperature of the 0wt.% MgO content was the lowest, and only 1200 °C water quenched samples were taken.
and Mg element is enriched in the crystal phase. Different from the occurrence in 12 wt.% MgO samples, Al in crystalline phases and Mg in the liquid phase of 16 wt.% MgO samples are lower.

4. Discussion

In order to make the glass phase formation mechanism of 0 wt.% MgO system clear, FactSage 8.0 was used to calculate the solidification process of MnO–SiO2–Al2O3-0 wt.% MgO system according to the actual composition detected by ICP, and the results are shown in Figure 11. FactPS and FT oxide databases were chosen to calculate the 'normal equilibrium', all solutions were selected, and 5 °C for the calculation steps. 3MgO·Al2O3·3SiO2 is the first precipitated phase in the system, and its crystallization temperature is about 1148 °C, then MnSiO3 is precipitated, and finally, SiO2 is precipitated. These confirm that the composition point of the system is in the primary crystal region of 3MgO·Al2O3·3SiO2 in the ternary phase diagram. With the decreased temperature of the liquid, the cooling path reaches the interface of the primary crystalline region of 3MgO·Al2O3·3SiO2 and MnSiO3, and the precipitation of these two mineral phases increases. Finally, the liquid phase disappears in a narrow temperature range, three phases are precipitated in this range because of eutectic. Under the condition of high undercooling, if the initial composition of the system is in the low melting point region in the ternary phase diagram, for example, in the primary crystal region of 3MgO·Al2O3·3SiO2, no crystalline phase is formed. But SiO2 is precipitated under the equilibrium cooling condition. Since the design composition of MnO–SiO2–Al2O3 is not in the primary crystalline region of SiO2, the main crystalline phase first precipitated is not SiO2, the high undercooling given by the sampling conditions resulted in the MnO–SiO2–Al2O3-MgO system being in the glass phase when sampled at 1200 °C. FactSage 8.0 was used to calculated the MnO–SiO2–Al2O3 ternary phase diagram. FactPS and FT oxide databases were chosen for 'isotherms and univariants', all solutions were selected, the temperature range is from 1300 °C–1600 °C and 50 °C for the steps.

Table 2. ICP compositions of MnO–SiO2–Al2O3–MgO system/wt.%.  

| No. | SiO2 | MnO | Al2O3 | MgO |
|-----|------|-----|-------|-----|
| C7  | 45.68| 43.47| 10.85 | 4.13|
| D6  | 43.49| 46.46| 10.05 | 8.09|
| E5  | 44.84| 44.94| 10.23 | 12.43|
| F4  | 43.65| 46.95| 9.40  | 15.87|

Figure 1. Schematic diagram of heating device and heating procedure.

Figure 2. XRD and SEM-EDS results of 0 wt.% MgO content system.

Figure 3. XRD results of MnO–SiO2–Al2O3-4 wt.% MgO.

Figure 4. XRD results of MnO–SiO2–Al2O3-4 wt.% MgO.
As shown in Figure 12, it is likely that Al₂O₃ is precipitated from MnO–SiO₂–Al₂O₃ system, the Al₂O₃ content in the system is more than 30%, while 3Al₂O₃·2SiO₂ (mullite) is precipitated, the minimum Al₂O₃ content in the system is about 0.8%, and the SiO₂ content is 92%. The former is difficult for Al₂O₃ in MnO–SiO₂–Al₂O₃ system to reach this content, while the latter forms a SiO₂-rich phase, and the precipitation of pure 3Al₂O₃·2SiO₂ is also difficult to aggregate and grow. The large sizes of Al₂O₃, 3Al₂O₃·2SiO₂ inclusions are not produced during the crystallization of MnO–SiO₂–Al₂O₃ system.

MgO component changes the crystallization properties of MnO–SiO₂–Al₂O₃ inclusions. With the increase of MgO content in the inclusion system, the crystallization ability of the sample and the liquidus temperature of the system gradually increased. The microstructure of the 4 wt.% MgO sample is glass phase and the crystal peak of the 8 wt.% MgO sample at the lowest temperature is detected by XRD, the precipitated crystal phase is olivine with new micromorphology. Crystal phases were

| No. | Si   | Mn   | Al   | Mg  | O    | EDS compositions of MnO–SiO₂–Al₂O₃-4wt.% MgO/wt.% |
|-----|------|------|------|-----|------|
| C₁  | 21.06| 38.46| 5.41 | 3.08| 31.99|
| C₂  | 20.13| 38.50| 5.03 | 3.29| 33.05|
| C₃  | 20.24| 37.15| 5.44 | 2.84| 34.32|
| C₄  | 21.49| 36.72| 5.70 | 3.13| 32.97|
| C₅  | 22.95| 39.22| 6.45 | 2.73| 28.64|
| C₆  | 22.52| 37.15| 5.63 | 3.01| 31.69|
| C₇  | 22.14| 36.34| 6.50 | 3.12| 31.90|

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Figure 4. Micrographs of MnO–SiO₂–Al₂O₃-4wt.% MgO (C1-1600 °C, C2-1550 °C, C3-1500 °C, C4-1450 °C, C5-1400 °C, C6-1350 °C, C7-1300 °C).

Table 3. EDS compositions of MnO–SiO₂–Al₂O₃-4wt.% MgO/wt.%.

Figure 5. XRD results of MnO–SiO₂–Al₂O₃-8wt.% MgO.

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detected at all sampling temperatures in the 12 wt.% MgO and 16 wt.% MgO trials. After fitting according to the strength, all of these crystal phases in these samples had an olivine phase. Equilib module of FactSage8.0 is used to calculate the effect of MgO content on the precipitated phases of MnO–SiO2–Al2O3 system during solidification from Figure 13. FactPS and FT oxide databases were chosen to calculate the 'normal equilibrium', all solutions were selected, and 5 °C for the calculation steps. It is found that when the MgO content in the inclusion system is 4.13wt.%, 8.09wt.%, 12.43wt.% and 15.87wt.%, the liquidus temperatures are 1170 °C, 1275 °C, 1350 °C and 1425 °C, respectively. Chen studied the effect of MgO on the crystallization and structure of CaO–SiO2–B2O3 fluorine-free mold flux, and found that non-bridged oxygen in the system was increased when the MgO content increased from 2wt.% to 10wt.%, the polymerization degree of silicate structure in the melt decreased, which changed the configuration of Si network, then the crystallization properties of the system were affected. For some CaO–SiO2 based systems, the addition of MgO forms melting point compounds such as feldspar, merwinite and calcium olivine, and inhibits the precipitation of crystals instance, high melting point cuspidine and nepheline, therefore, the crystallization temperature is reduced [16]. However, MgO also tends to increase the crystallization ability of the system. Yang studied the CCT curve of CaO–SiO2 based system and found that when the MgO content in the system changes from 0.9, 2.3, 3.4 to 4.9, the incubation period of the crystal changed to 2.3s, 1s, 0s and 0s, respectively. It showed that MgO increased the crystallization ability of the system [17].

Table 4. EDS compositions of MnO–SiO2–Al2O3-8wt.% MgO/wt.%.

| No.  | Si  | Mn  | Al  | Mg  | O  |
|------|-----|-----|-----|-----|----|
| D1   | 22  | 38.7| 5.5 | 5.3 | 28.5|
| D2   | 20.8| 36  | 6.2 | 5.3 | 31.7|
| D3   | 19.9| 36.3| 6   | 5.2 | 32.6|
| D4   | 21.5| 38.9| 5.4 | 6.1 | 28.1|
| D5   | 21.9| 38.3| 5.5 | 5.9 | 28.5|
| D6-left | 22 | 37.1| 6.2 | 4.9 | 29.8|
| D6-right | 22.3| 37.3| 5.5 | 6.2 | 28.7|

Figure 6. Micrographs of MnO–SiO2–Al2O3-8wt.% MgO (D1-1600 °C, D2-1550 °C, D3-1500 °C, D4-1450 °C, D5-1400 °C, D6-1350 °C).

Figure 7. XRD results of MnO–SiO2–Al2O3-12wt.% MgO.

Chen studied the effect of MgO on the crystallization and structure of CaO–SiO2–B2O3 fluorine-free mold flux, and found that non-bridged oxygen in the system was increased when the MgO content increased from 2wt.% to 10wt.%, the polymerization degree of silicate structure in the melt decreased, which changed the configuration of Si network, then the crystallization properties of the system were affected. For some CaO–SiO2 based systems, the addition of MgO forms melting point compounds such as feldspar, merwinite and calcium olivine, and inhibits the precipitation of crystals instance, high melting point cuspidine and nepheline, therefore, the crystallization temperature is reduced [16]. However, MgO also tends to increase the crystallization ability of the system. Yang studied the CCT curve of CaO–SiO2 based system and found that when the MgO content in the system changes from 0.9, 2.3, 3.4 to 4.9, the incubation period of the crystal changed to 2.3s, 1s, 0s and 0s, respectively. It showed that MgO increased the crystallization ability of the system [17]. It is confirmed that the effect of MgO on the crystallization temperature of the system is mainly realized by the formation of different MgO-containing compounds. Compared with Figure 11, MgSiO3 is newly formed in Figure 13 (a), and the melting point of MgSiO3 is 1558 °C Mg2SiO4 and MgMnSiO4 begin to precipitate in 4.13wt.% system at the same time. The melting point of Mg2SiO4 is 1888
and the crystallization temperature of 8.09wt.% system is 105°C higher than that of 4.13wt.% system. The crystallization temperature of 12.43wt.% system increased further. The difference between 15.87wt.% system and 12.43wt.% system is in the content of four phases, the former is more and the crystallization temperature reaches the maximum.

Combined with XRD results (Figure 3), the system formed the glass phases under rapid cooling conditions as the content of MgO in MnO–SiO2–Al2O3 system is less than 8 wt.%. Weak peaks of Mg3Al2Si3O12 were detected in addition to olivine with 12.43 wt.% MgO. This phase is not produced in the calculation of the equilibrium system, whereas the phase is Mn3Al2Si3O12. Mg3Al2Si3O12 is suggested to precipitate under rapid cooling conditions, one possible implication of this is that it has a higher crystallization temperature. XRD results (Figure 7) and FactSage8.0 equilibrium solidification calculation results show that there is no separate MgO·Al2O3 phase precipitation in the low melting
According to the calculation results in Figure 13(a) and Figure 13(b), the XRD results of 4wt.% MgO in Figure 3 and 8wt.% MgO in Figure 5 show that no crystal phase is detected in the water quenched samples. Therefore, it is considered that the crystal phase detected by XRD is MgMnSiO₄ solid solution phase. Due to the existence of isomorphism, some cations in the forsterite and manganese olivine phases are replaced by each other to form a single mixed crystal phase. For the same valence cations, the occurrence of isomorphism is as follows:

\[ I = \frac{(r_1 - r_2)}{r_2} \]  

Where \( r_1 \) is the larger ion radius; \( r_2 \) is the smaller ion radius; \( I < 10\% - 15\% \), complete isomorphism is generally formed; \( I = (10\% - 20\%) - 25\% \), complete isomorphism is formed at high temperature and the solid solution is exsolution as the temperature drops; \( I > 20\% - 25\% \), only incomplete isomorphism can be formed at high temperature, and no isomorphism occurs at low temperature.

The atomic radii of Mg²⁺ and Mn²⁺ are 0.78 Å and 0.91 Å, respectively. \( I = 16.67\% \) is calculated after bringing these atomic radii into Eq. (5). Mg²⁺ and Mn²⁺ belong to equivalent isomorphism and the solid solution may be exsolution as the temperature drops because the range value of \( I \) is the second type. Other high-temperature samples are solid solution phase, except for Mg₅SiO₄ and solid solution detected in the samples with the highest MgO content (16 wt.% MgO). There are not a single magnesium olivine phase and manganese olivine phase, indicating that the solid solution has not been exsolution. Olivine and Mg₅Al₃(SiO₄) were detected in Figure 7. The melting point of manganese olivine is lower than that of forsterite. However, in the equilibrium calculation of the system in Figure 13, the olivine phases contain Mg₅SiO₄, Mn₂SiO₄ and MgMnSiO₄ solid solution which Mg is replaced by Mn, MnMgSiO₄ solid solution which Mn is replaced by Mg, these phases are precipitated at the same time. There are no pure olivine phases detected from XRD results in Figure 7. As the system temperature decreases, Mn₃Al₃(SiO₄) precipitates when the equilibrium phase diagram is lower than 1200 °C, and the minimum water quenching temperature is 1450 °C, a small amount of Mg₅Al₃(SiO₄) is formed under rapid cooling conditions. The XRD-PDF cards data of Mg₃Al₃(SiO₄) solid solution phase and Mg₅SiO₄ have a high degree of overlap. MgMnSiO₄ has a higher matching degree with the detected intensity peak than that of Mg₅SiO₄. EDS analysis results of the crystal phase show that the crystal phase contains Mg and Mn elements. Therefore, it is considered that the crystal phase detected by XRD is MgMnSiO₄ solid solution phase.

Figure 8 shows the columnar crystals in the E1-E4 microstructure diagrams. It can be seen from the equilibrium phase diagram in Figure 13 that olivine precipitates first from the liquid phase. Figure 15 (a) shows the morphology of crystal growth in the low field of view and the solid solution crystallizes in irregular eutectic mode. Figure 15 (b) shows the morphology of the crystals when it reaches the channel formed by pores during water quenching before solidification during liquid phase crystallization. The liquid phase at the pore channel decreases and the crystalline phase crystallizes and sinks at the channel as the red dotted lines show. The crystal phases on the plane are connected with the crystal phases in the channel, indicating that the solid solution is a small plane phase during crystallization. The temperature gradient during rapid cooling determines the growth direction of solid solution precipitation.

Figure 16 presents that Mg is mainly distributed in the crystal phase, and the Mg content in the liquid phase is relatively few. The occurrence of Al is exactly the opposite of that of Mg. Si, Mn and O are uniformly distributed in the whole field of view. It can be found in Figure 15. P1SEM-Al that there is an Al-rich region with a similar shape in the central region of the crystalline phase, and the Mg content in this region is low, the same phenomenon also exists in the Mg and Al element.
distribution in Figure 16 F4SEM. It can be concluded that the central region of the crystalline phase is the liquid phase region from both the morphological distribution and the element distribution. The crystalline phase grows from low to high along the interface temperature gradient perpendicular to its cross-section, and the liquid phase remains under high undercooling. Hence, it shows the morphology of the external solid solution wrapping the liquid phase. Although the distribution of Mn elements is relatively uniform, the area with relatively concentrated pixel points can be seen from the element distribution diagram. As Figure 16 F1SEM - Mn shows that Mn elements are enriched at the edge of the crystal phase, and the color near the edge of the crystal phase is darker than that in the internal area. It shows that as the Mg$_{12}$Mn$_{2x}$SiO$_4$(1 < x < 2) solid solution is formed, only a small part of Mn$^{2+}$ replaces Mg$^{2+}$ at the beginning, and the Mg$^{2+}$ content in the liquid phase around the crystal decreases during the crystal growth, so the external Mn$^{2+}$ rich solid solution type is formed.

Figure 13. Effect of MgO on the phase of MnO–SiO$_2$–Al$_2$O$_3$ system (a-4.13wt.% MgO, b-8.09wt.% MgO, c-12.43wt.% MgO, d-15.87wt.% MgO).

Figure 14. Line scanning of D6.

distribution in Figure 16 F4SEM. It can be concluded that the central region of the crystalline phase is the liquid phase region from both the morphological distribution and the element distribution. The crystalline phase grows from low to high along the interface temperature gradient perpendicular to its cross-section, and the liquid phase remains under high undercooling. Hence, it shows the morphology of the external solid solution wrapping the liquid phase. Although the distribution of Mn elements is relatively uniform, the area with relatively concentrated pixel points can be seen from the element distribution diagram. As Figure 16 F1SEM - Mn shows that Mn elements are enriched at the edge of the crystal phase, and the color near the edge of the crystal phase is darker than that in the internal area. It shows that as the Mg$_{12}$Mn$_{2x}$SiO$_4$(1 < x < 2) solid solution is formed, only a small part of Mn$^{2+}$ replaces Mg$^{2+}$ at the beginning, and the Mg$^{2+}$ content in the liquid phase around the crystal decreases during the crystal growth, so the external Mn$^{2+}$ rich solid solution type is formed.

Figure 15. Typical crystal growth morphology (a-F3, b-E2).
5. Conclusion

The effects of MgO from slag line on the crystallization behavior of typical MnO–SiO$_2$–Al$_2$O$_3$ based inclusions in tire cord steel were studied by ICP, XRD, SEM-EDS and FactSage 8.0, and the conclusions are as follows:

Crystallization phase of MnO–SiO$_2$–Al$_2$O$_3$ during rapid cooling depends on the primary crystal region of the phase diagram where its composition is located. Spessartine is a glass phase under the condition of liquid phase water quenching. Large particle Al$_2$O$_3$, 3Al$_2$O$_3$·2SiO$_2$ inclusions are not produced during the crystallization of MnO–SiO$_2$–Al$_2$O$_3$ system. As MgO content in MnO–SiO$_2$–Al$_2$O$_3$ system increases from 4.13wt.% to 15.87wt.%, the high melting point Mg containing oxide is formed, and the crystallization temperature of the system increases with the increase of MgO content. The inclusion system in the spessartine region does not form magnesium aluminium spinel when different MgO contents are introduced. Mg$_x$Mn$_{(2-x)}$SiO$_4$ solid solution is the main crystalline phase in MnO–SiO$_2$–Al$_2$O$_3$–MgO system. The solid solution formed by magnesium olivine and manganese olivine does not occur dissociation at low temperatures. There is no 2MgO-SiO$_2$ crystal produced in the system as the MgO content is less than 12wt.%.

Declarations

Author contribution statement

Qiang Zeng: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Jianli Li: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Qi Xu: Performed the experiments.

Yue Yu: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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