

## **MAGNESIUM: ORIGIN AND ROLE IN CALCIUM-TREATED INCLUSIONS**

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### **Abstract**

Calcium treatment of alumina inclusions, to convert the alumina to molten or partially molten calcium aluminates, is a well-established treatment for steel, to improve the castability of aluminium-killed steel. However, the role of magnesium in calcium-treated steel is not fully clear, nor is the origin of the several percent of magnesium oxide that is often present in calcium-treated inclusions. To study this, steel was sampled after calcium treatment at an industrial steel plant, and the inclusions identified by energy-dispersive X-ray microanalysis (EDX) on polished sections of the samples (analysing the samples in a scanning electron microscope). The predicted fraction liquid in the inclusion was estimated from the ternary alumina-magnesia-lime phase diagram. Inclusions with higher CaO contents generally had lower MgO contents, indicating that the calcium wire is not the origin of the magnesium in the inclusions; this was also confirmed by wet chemical analysis of the calcium wire. Instead, it appears that magnesium-alumina spinel inclusions form during extended ladle contact after aluminium killing and before calcium treatment. While such spinels have been stated to cause poor castability (clogging the submerged-entry nozzle), it is clear that calcium treatment successfully modifies the spinel inclusions to mixed alumina-lime-magnesia inclusions, where the magnesia content contributes substantially to liquefaction of the inclusions: for typical MgO contents of around 10%, the range of Ca:O ratios which yield liquid (or partially liquid) inclusions is extended substantially to lower Ca:O ratios.

### **Background**

Calcium treatment is commonly applied to change the chemical and phase composition of alumina inclusions in aluminium-killed steel [1]. This treatment is based on the unique combination offered by calcium, of the element having a considerably higher affinity for oxygen than aluminium, and its oxide forming low-melting mixtures with aluminium oxide (provided that the calcium aluminate reaction product contains the right ratio of CaO to Al<sub>2</sub>O<sub>3</sub>). Successful calcium treatment relies on the following: injection of the calcium (in wire form) such that the calcium does react with the steel; use of a sufficient amount of calcium; and avoiding reaction of calcium with dissolved sulphur rather than with alumina inclusions [2]. These three requirements are met by control of the injection method, by matching the amount of calcium with the expected inclusion content of the steel, and by avoiding treatment of steel with high dissolved sulphur contents. The result of successful modification is that the solid alumina inclusions are converted into fully or partially liquid lime aluminates, so ensuring clog-free casting of the steel through the submerged-entry nozzle into the continuous caster mould; from a detailed analysis of the link between inclusion composition and casting behaviour, it appears that clogging is avoided if the inclusions contain more than 50% liquid [3].

The calcium-modified alumina inclusions are often considered to be binary  $\text{CaO-Al}_2\text{O}_3$  mixtures. However, the modified inclusions generally contain a significant amount of  $\text{MgO}$  [3,4,5].  $\text{MgO}$  can contribute to the success of calcium modification, as Figure 1 indicates. The strong effect of  $\text{MgO}$  in widening the partially and fully liquid regions is clear in Figure 1a), and this is emphasised by Figure 1b), which shows the effect of increasing Ca:O ratios (that is, greater degrees of modification of alumina inclusions) on liquefaction of the oxide inclusions. Even a small amount  $\text{MgO}$  (as low as 2%) has a remarkable effect, approximately halving the Ca:O ratio where the inclusions are largely liquid. At high  $\text{MgO}$  levels, 15% by mass and above, the amount of liquefaction is limited by formation of the high-melting phases spinel (solid solution based on  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ ) and periclase ( $\text{MgO}$ ). However, even with 20%  $\text{MgO}$  in the inclusion, the Ca:O ratio for 50% liquid formation is less than half of that without  $\text{MgO}$  present.

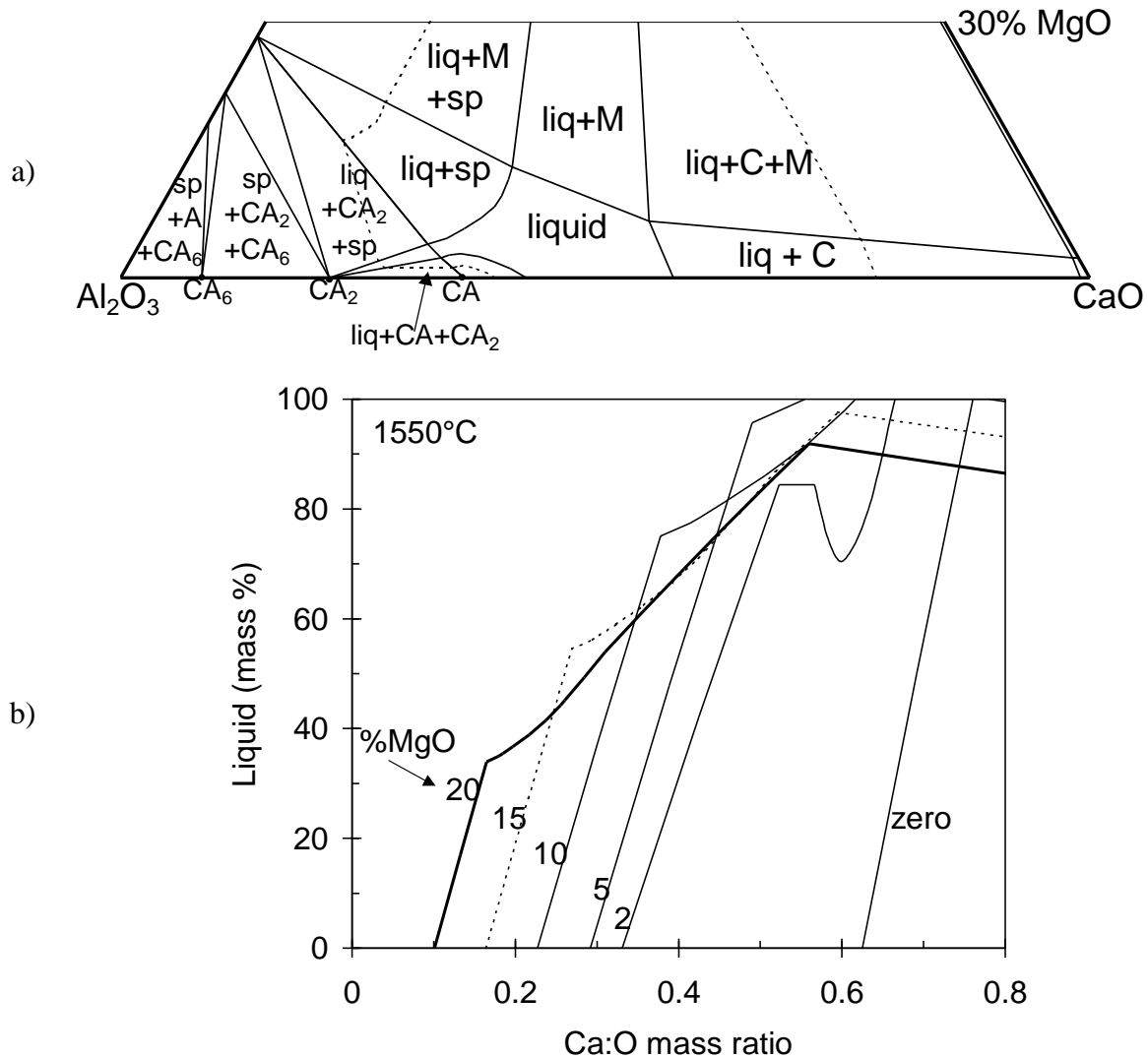


Figure 1. Phase relationships in the  $\text{Al}_2\text{O}_3$ - $\text{CaO}$ - $\text{MgO}$  system at  $1550^\circ\text{C}$ .

a) Isothermal section, in the low- $\text{MgO}$  part of the diagram, as calculated with FACTSage [6]. Compositions plotted as mass percentages; "sp" refers to spinel solid solution, "A" indicates  $\text{Al}_2\text{O}_3$ , "C"  $\text{CaO}$ , and "M"  $\text{MgO}$ . The broken line connects compositions which contain 50% liquid.

b) Mass percentage of liquid in  $\text{Al}_2\text{O}_3$ - $\text{CaO}$ - $\text{MgO}$  mixtures, for different  $\text{MgO}$  mass percentages (as labelled on each curve) and different ratios of calcium to total oxygen masses in the inclusions. Values were derived from the phase diagram shown in a).

These observations imply that it is important to understand the behaviour and origin of MgO in calcium modification of alumina inclusions. To this end, samples were collected from liquid steel after calcium modification, in an integrated steel plant. Aluminium (deoxidant) and calcium wire were also sampled, to test these as possible origins of magnesium in modified inclusions.

### Experimental Method

Steel samples were obtained from an integrated steelworks that produces aluminium-killed low-carbon (0.05% C) steel. The plant uses two ladle furnaces as holding vessels before continuous casting, with holding times ranging from 45 min to 400 min. The ladle slag typically contained 51% CaO, 34% Al<sub>2</sub>O<sub>3</sub>, 10% MgO, and 1% SiO<sub>2</sub>. The total of FeO and MnO in the ladle slag was below 1% in all cases. The ladle refractory was MgO-carbon bricks at the slagline and in the intermediate zone, and alumina-spinel carbon brick in the barrel and floor. Calcium treatment was applied just before sending the ladle to the continuous caster; calcium wire was used for treatment. Calcium yield was around 15%.

Samples were obtained for seven heats (with steel masses ranging from 170 tons to 180 tons). Steel temperatures after calcium treatment varied from 1586°C to 1604°C, with tundish temperatures from 1560°C to 1570°C. The calcium content of the steel was from 17 to 46 ppm in the ladle after calcium treatment, and from 13 to 25 ppm in the tundish. The aluminium content was in the range 0.03-0.05%, and the sulphur 30-50 ppm. "Lollipop" steel samples were taken before and after calcium treatment in the ladle, and in the tundish. Samplers which did not contain zirconium were used, to avoid changes in inclusion composition [5].

Similar to the procedure described before, sections were cut through the lollipop samples, and polished for examination by scanning electron microscopy [5]. Inclusion compositions were found by energy-dispersive X-ray microanalysis (EDX), analysing for Mg, Al, Ca and S. In the diagrams which are presented below, inclusion compositions are presented as ternary mixtures of MgO, Al<sub>2</sub>O<sub>3</sub> and CaO. These compositions were recalculated by assuming that all sulphur is present as CaS (that is, some of the analysed Ca is not present as CaO, but rather as CaS). At least 20 inclusions were analysed per sample.

### Results and Discussion

All the inclusions in the steel sampled before calcium treatment were MgO-Al<sub>2</sub>O<sub>3</sub> spinels. This is shown by their position on the phase diagram (Figure 2a), and also by their angular appearance (Figure 2b). The formation of spinel inclusions is not unexpected, given the low (FeO+MnO) content of the ladle slag, and the long ladle contact time [7]. These spinels form by reduction of MgO from the refractory, diffusion of magnesium into the liquid steel, and reaction with alumina inclusions [7]. Spinel inclusions can lead to severe clogging of the submerged-entry nozzle if the inclusions are not successfully modified by calcium treatment [3].

However, calcium treatment did change the inclusion compositions considerably, away from spinel. As Figures 3, 4 and 5 illustrate, calcium treatment shifted the inclusion compositions to higher CaO contents and lower MgO contents. The overall effect of calcium treatment was to achieve full or partial liquefaction of most of the inclusions that were microanalysed.

This trend of decreasing – but still significant – MgO contents in calcium-treated inclusions was found for all the heats tested in this work; the trend was also reported by Fuhr et al. [3].

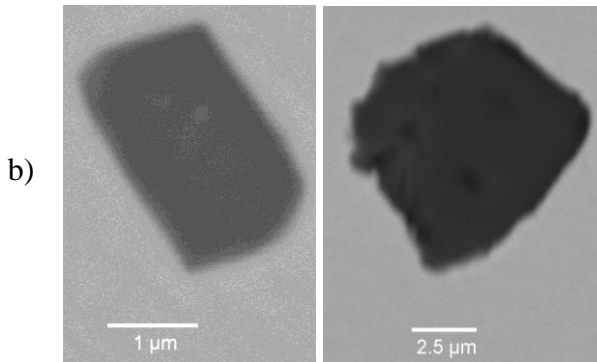
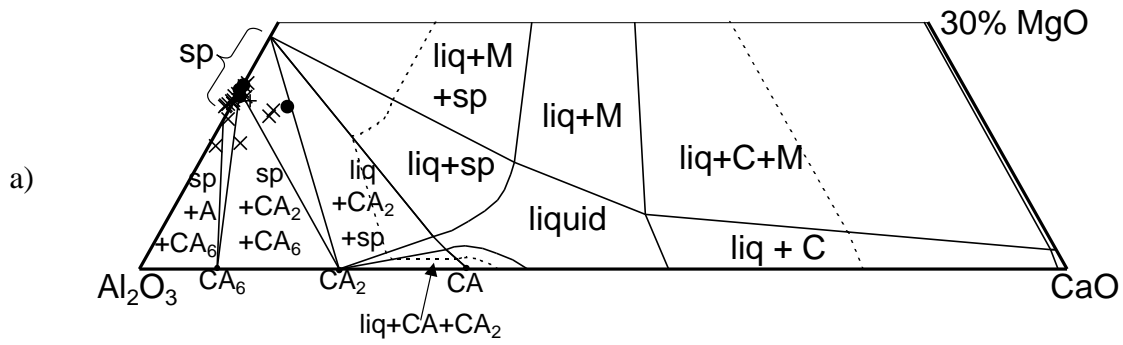


Figure 2. Untreated inclusions, as sampled in ladle furnace:  
 a) Compositions (different symbols are for samples from different heats)  
 b) Microscopical appearance (scanning electron micrograph; backscattered electron image)

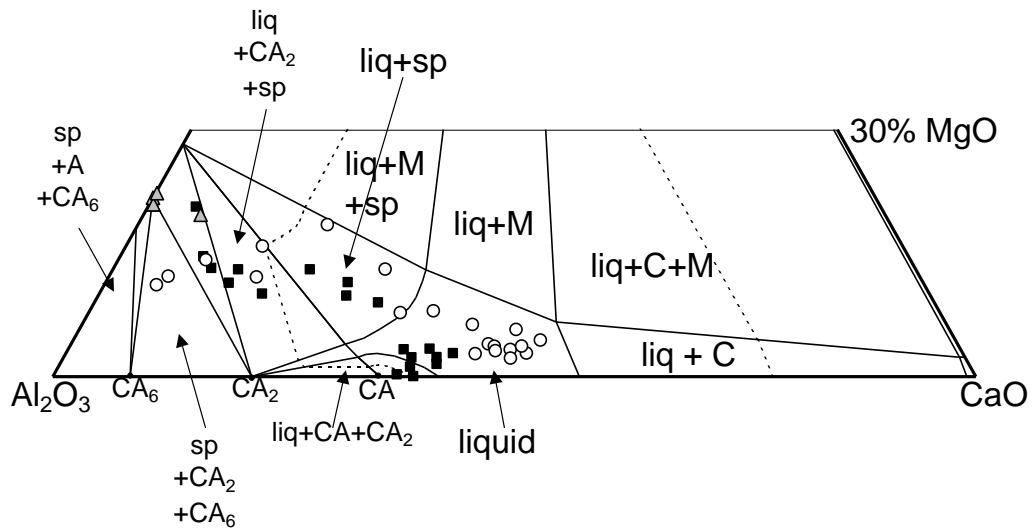


Figure 3. Change in inclusion composition as a result of calcium treatment, for samples from a single heat. The triangles indicate the (spinel) inclusion compositions before calcium treatment, the open circles the inclusions in the ladle after calcium treatment, and the filled squares the inclusions in steel sampled from the tundish.

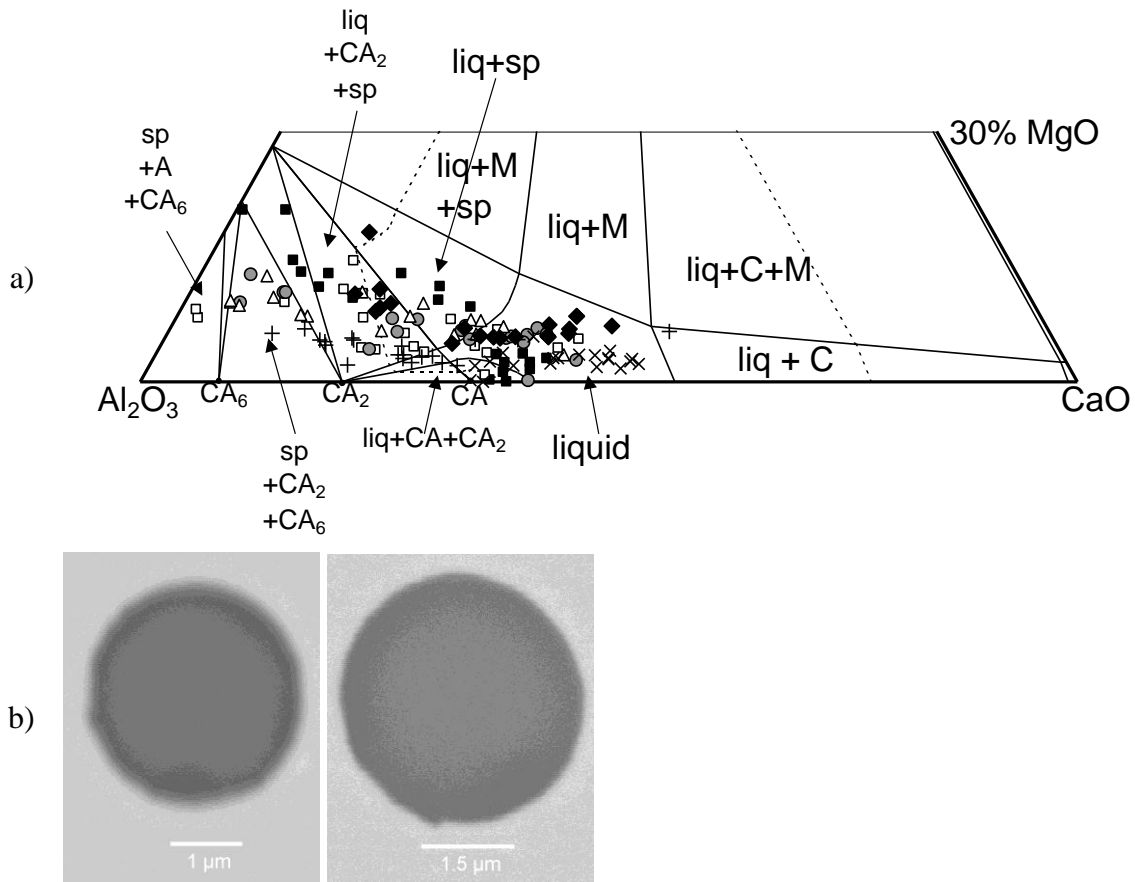


Figure 4. Calcium-treated inclusions, as sampled from the tundish, for 7 heats:  
 a) Compositions (different symbols are for samples from different heats)  
 b) Microscopical appearance (scanning electron micrograph; backscattered electron image)

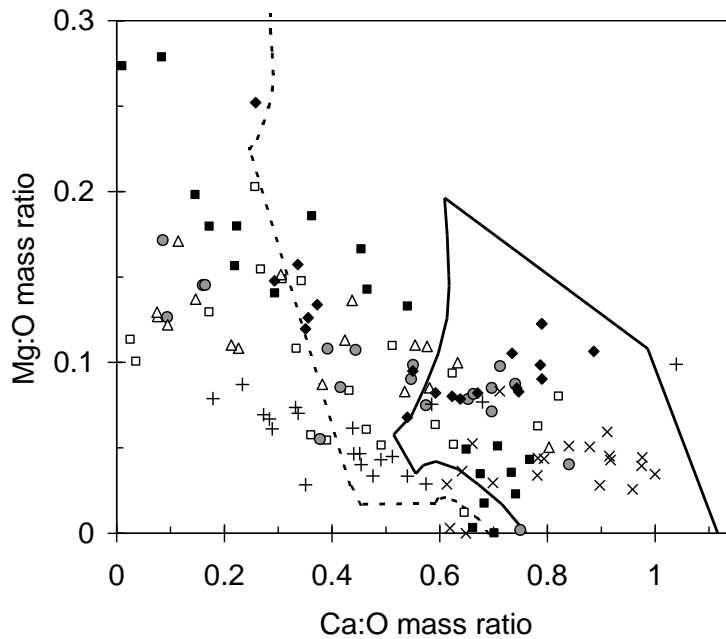


Figure 5. Calcium and magnesium contents (relative to oxygen content) of calcium-modified inclusions, as sampled in the tundish (same data as in Figure 4). Compositions to the right of the broken line contain 50% or more liquid, and compositions within the solid line are fully liquid. Note that the average Mg:O ratio in untreated spinels was 0.27.

From the analyses of calcium-treated inclusions, it is clear that the source of magnesium in the inclusions is not the calcium wire itself (because, if the calcium wire were the source, the MgO content of the inclusions would tend to be *higher* for higher CaO contents, not lower as actually found). This conclusion was supported analysis of the calcium wire by wet chemical analysis, which showed the magnesium content to be negligible, less than 0.01% by mass.

Rather, the MgO in the treated inclusions appears to have been present in the unmodified inclusions, which were of the spinel type. Subsequent calcium treatment serves to remove (reduce) some of the MgO from these inclusions, in parallel with the removal of Al<sub>2</sub>O<sub>3</sub> (the latter is the generally recognised reaction during calcium modification). Despite the lowered MgO content in the modified inclusions, the MgO levels remain significant after calcium treatment – more than 2% by mass in most cases, which is sufficient to contribute significantly to inclusion liquefaction (see Figure 1b).

### Conclusion

The work reported here confirms that MgO can contribute significantly to liquefaction of inclusions by calcium treatment. For the specific operation studied here, the provenance of MgO in modified inclusions was – unexpectedly – spinel inclusions. Calcium modification was clearly successful at modifying such spinels; calcium replaced both magnesium and aluminium in the inclusions. Along the resulting composition trajectory (of increasing calcium and decreasing magnesium contents, see Figure 5) partial and full liquefaction of the oxide inclusions is found at lower Ca:O ratios (that is, with less calcium injected) than would have been the case in the absence of MgO in the starting inclusions: as Figure 5 shows, for calcium modification of the spinel inclusion 50% liquid is found at Ca:O mass ratios of 0.3-0.4 (compared with 0.7 in the absence of MgO), and full liquefaction at Ca:O mass ratios of 0.5-0.6 (compared with 0.76 if no MgO is present).

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