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Abstract

Due to an ever increasing demand for cleaner, high quality steels, there is an increasing push for steelmakers to lower the non-metallic inclusion contents of the steel they produce. Understanding inclusion reactivity in steel is key in producing high quality steels at high production rates. Our current knowledge in controlling and predicting inclusion development during liquid steel processing is limited. In this study, spinel (MgAl₂O₄) inclusions of close to stoichiometric MgO·Al₂O₃ and known size distribution were added to the liquid steel bath prior to assessing their reactivity. The pO₂ of the gas phase was controlled to 10-13 atm throughout the experiment. The inclusions were then tracked for changes in size morphology and composition with time in an aluminium killed steel at 1600 degrees Celsius. It was found that the inclusions were evenly distributed through the melt. There was little change in the average size of the spinel inclusions during the reaction. However, the composition of the inclusions did change. It was found that the Mg: Al mass percentage ratio of the inclusions changed immediately from ~0.5 to 0.08. Other inclusions found in the melt were alumina and complex sulphide inclusions. Of these it was found that the proportion of the alumina inclusion increased with time.

Keywords

steel, mgal₂o₄, changes, spinel, composition, morphology, inclusion, reactivity

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Inclusion Reactivity: Morphology and Composition Changes of Spinel (MgAl_2O_4) in Steel

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Abstract— Due to an ever increasing demand for cleaner, high quality steels, there is an increasing push for steelmakers to lower the non-metallic inclusion contents of the steel they produce. Understanding inclusion reactivity in steel is key in producing high quality steels at high production rates. Our current knowledge in controlling and predicting inclusion development during liquid steel processing is limited. In this study, spinel (MgAl_2O_4) inclusions of close to stoichiometric $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and known size distribution were added to the liquid steel bath prior to assessing their reactivity. The $p\text{O}_2$ of the gas phase was controlled to 10^{-13} atm throughout the experiment. The inclusions were then tracked for changes in size, morphology and composition with time in an aluminium killed steel at 1600°C . It was found that the inclusions were evenly distributed through the melt. There was little change in the average size of the spinel inclusions during the reaction. However, the composition of the inclusions did change. It was found that the Mg:Al mass% ratio of the inclusions changed immediately from ~ 0.5 to 0.08 . Other inclusions found in the melt were alumina and complex sulphide inclusions. Of these it was found that the proportion of the alumina inclusions increased with time.

Keywords- inclusion modificatio; reactivity; clean steel

I. INTRODUCTION

Spinel inclusions (MgAl_2O_4) can be a problem in steel making, limiting productivity by clogging of ladle shrouds and submerged entry nozzles, and causing surface quality issues as a result of their high hardness [1-3]. It is important to fully understand how and when spinel inclusions may form and how they could be modified to aid their removal to the slag phase.

Many studies [2-17] have focused on understanding the formation and modification of spinel inclusions in liquid steel. However, there is still uncertainty with respect to the changes in phase and morphology of the inclusions during steel processing. In particular, there are difficulties controlling the initial composition and phase of the inclusions in what are extremely complex reaction systems, and predicting when an

inclusion is liquid for a given set of conditions. This difficulty in control and prediction has given rise to uncertainty in detailing and understanding inclusion chemistry and morphology changes during secondary refining.

In an effort to improve experimental understanding and control of inclusion formation and development several researchers have used synthetic steel made from high purity reagents to study inclusion modification [15, 17] (as opposed to using steel from the industrial processes). Generally when using this approach there is an attempt to form inclusions in-situ. Even though these studies offer better control over the steel melt compositions, control of the inclusion formation and composition is extremely difficult.

It is difficult to add synthetic inclusions to the liquid steel because of the difficulties in getting inclusions past the liquid steel-gas interface, and doing this without significant agglomeration of the particles. Kang et al.[12] produced synthetic MgAl_2O_4 spinel to study the formation mechanism of calcium aluminate inclusions from spinel. In their experiments, synthetic spinel pellets were placed on top of the melt sample. CaC_2 used as Ca source was positioned in a hole drilled into the melt sample. They analysed the interface between the steel and spinel pellets to determine the reaction phases formed. While this study gives useful information on the reaction chemistry it does not address important size (surface energy) effects and does not readily translate to changes in inclusion size, chemistry and morphology in industrial processing. The present authors [18] have attempted to overcome this issue by doping of the steel with excess synthetic inclusions mechanically encapsulated in steel by sandwiching the inclusions between steel disks/plates. This avoids the issue of inclusions passing through the melt-gas interface, while giving control over the initial composition and size of the inclusions.

In this study the focus was to assess the reactivity of spinel inclusions in Al-killed steel. Controlled additions of inclusions of known size, phase and morphology to liquid steel are used to overcome some of the aforementioned uncertainty issues in the literature. Automatic SEM inclusion analysis is used to assess changes in inclusion chemistry, size and morphology with time in the steel.

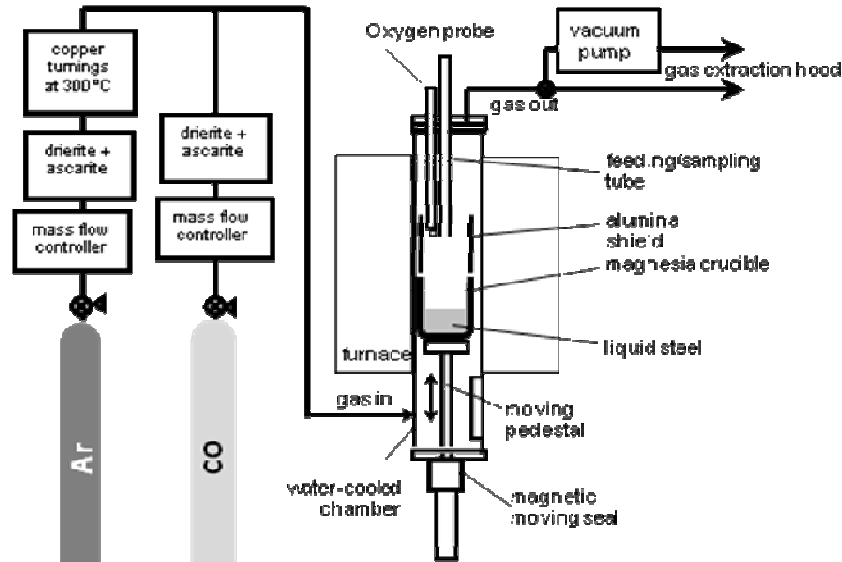


Figure 1. Schematic of set-up used for reactivity experiments

II. EXPERIMENTAL

A. Procedure

A nominal 450g charge of aluminium killed steel and encapsulated spinel inclusions were placed inside an alumina crucible at room temperature. The crucible was then heated in a vertical tube furnace to the experimental temperature of 1600°C (T_E) under 99.99% argon. Once the T_E was reached, the gas atmosphere was changed to a 20% CO-80% Ar mixture to achieve a 10^{-13} atm oxygen potential during the experiment. This value is based on the CO-CO₂ equilibrium at T_E . The input gases were passed through ascarite and drierite prior to entering the furnace to remove CO₂ and moisture.

Time zero was defined as the time when the steel charge reached T_E of 1600°C. At time zero the liquid steel has been present for approximately 8 minutes in heating steel from its liquidus temperature T_L to T_E . T_L for the aluminium killed steel was 1534°C (established via MTDData [19]). The experiment was run for 30 minutes after time zero. Steel suction samples (SS) were made periodically using a 5mm diameter silica tube. At the end of the experiment the crucible containing the liquid steel was lowered into the cooling chamber. This end of experiment steel (EE) was also retained for analysis.

B. Experimental apparatus

The experimental set-up used for the reactivity experiments is shown schematically in Fig 1. The steel melt was contained within an alumina crucible (60mm ID) and was heated in a

vertical tube furnace. The furnace was equipped with a 13 mm port at the top which was used for sampling, and a water cooled chamber at the bottom, into which the crucible can be lowered and rapidly cooled.

C. Materials

The composition of the steels and the typical inclusion types found for the steels used in this study are given in Table 1. The composition of the steels was measured using optical emission spectroscopy. Inclusion analyses were performed by the ASPEX automatic inclusion analysis system [20].

Synthetic MgAl₂O₄ spinel inclusions were prepared from high purity laboratory grade MgO and Al₂O₃ (> 99%) starting materials by reaction sintering. A base mixture of 71.7g Al₂O₃ and 28.4g MgO was dispersed in 500 ml deionised water. The resulting slurry was stirred for 30 minutes, filtered and dried in an oven overnight. The dried powder was mixed again with 4% deionised water as a binder. The moistened powder was pressed into pellets and then sintered at 1600°C for 24 hours. After sintering, the spinel phase was confirmed by X-ray diffraction (XRD). No other phases were identified via XRD.

These synthetic inclusions were encapsulated in steel sandwiches and added to the steel-crucible charge prior to melting. The sandwiches were prepared by pressing two layers of 53-63 μm spinel powder with three layers of an interstitial free steel forming a steel-powder compact. This is then pressure bonded using a pressure of ~4 GPa. The total mass of

TABLE I. COMPOSITION AND INCLUSION TYPE IN STEEL

Metal composition in mass%	C	Mn	Si	S	Cu	Al	Ti	Inclusion type
Inclusion sandwich steel	0.002	0.15	0.005	0.007	0.02	0.038	0.071	Al ₂ O ₃
Experimental melt	0.3	0.23	0.006	0.01	0.008	0.03	0.001	Al ₂ O ₃ & MnS

spinel inclusions added to steel baths was 0.2 g. During pressing the spinel average particle size is reduced to 3.4 μm . This value is based on an optical particle size assessment of the synthetic inclusions after encapsulation.

D. Inclusion Analysis

The SS samples were sectioned vertically whereas EE samples were sectioned both vertically and horizontally. All samples were polished to a 1 μm finish and then analysed using automated SEM/EDX inclusion analysis systems. Two automated SEM/EDX inclusion analysis systems were used. The ASPEX (ASPEX Corporation, Delmont, PA) [20] and a JEOL FEGSEM 7001-F using INCA software (Oxford instruments, Oxfordshire, UK). Although they have similar functionality, the major difference between two instruments is quantifying the composition of inclusions with a similar size from measured X-ray spectra. All ASPEX compositions presented have been manually corrected for atomic number, absorption and fluorescence (ZAF) effects using the GMR Film software [21]. INCA software automatically corrects compositions for ZAF effect using the XPP matrix correction scheme developed by Pouchou and Pichoir [22]. Inclusions were classified based on their composition, neglecting those with a size <1 μm in diameter or with Fe contents >95 mass percent.

III. RESULTS AND DISCUSSIONS

A. Inclusion Size and Distribution

The average sizes of the spinel inclusions measured using ASPEX and INCA systems are compared in Figure 2. All inclusions were in the 2-5 μm size range, with their average size being approximately 3 μm . It can be seen that the size of the spinel inclusions remained largely constant over the reaction time (~30 minutes). This is similar to the original average size of the inclusions and an indication that little or no agglomeration occurred during the experiments. Generally there is good agreement in the size measured by the two

systems though the average size of inclusions was slightly higher using INCA than those from ASPEX.

ASPEX and INCA SEM images of the spinel inclusions were analysed. Both systems showed similar results. The spinel inclusions found had an angular morphology similar to that of the original unreacted spinel and that their morphology did not appreciably change with time. The majority of the spinel inclusions appear as single particles though some appear to be joined with other inclusions. The spinel inclusions were evenly distributed across the areas analysed, with no obvious bias in either the radial or vertical directions.

B. Inclusion Composition

Changes in the composition of the spinel inclusions with time, as represented by the Mg to Al mass ratio (Mg:Al) was assessed using both ASPEX and INCA systems (Figure 3). The unreacted spinel powder as measured by ASPEX and based on original masses used for sintering is also given. It can be seen that the compositions of the spinel inclusions measured by INCA and ASPEX agreed well in both experiments. There is a significant decrease of the Mg:Al ratio from the original values, dropping to ~0.08, which then remains reasonably constant throughout the experiment. This would indicate that a significant amount of reaction has occurred prior to establishing time zero. It is likely that the majority of this reaction has taken place as the steel begins to melt (1534°C) and reach the T_E (1600°C). It indicates that the spinel reaction within the experiment is fast. If Mg:Al changes with time in the steel during this period are to be resolved then future experiments where the inclusion sandwiches are added once the steel is at the T_E must be considered.

Mg:Al ratio changes could be brought about by either magnesium leaving or by aluminium entering the inclusions. Equations 1-5 represent possible reactions that could be responsible for the change in the Mg:Al ratio. Magnesium leaving the inclusion could be going into the solution in the iron (equation 1) or entering the gas phase (equation 2), while

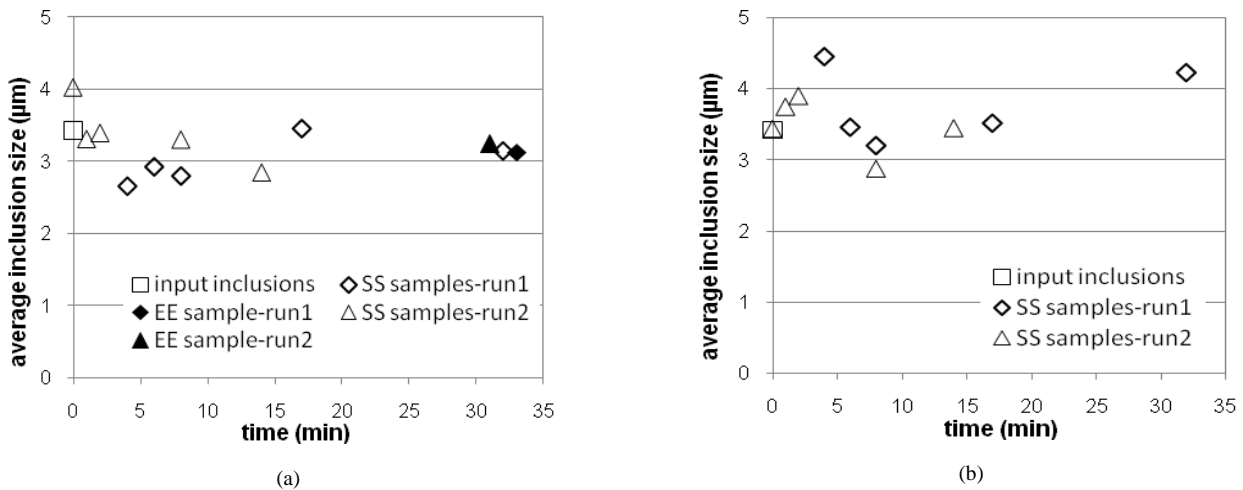


Figure 2. Average size of spinel inclusions found in samples taken at different times during reactivity experiments using (a) ASPEX results (b) INCA results

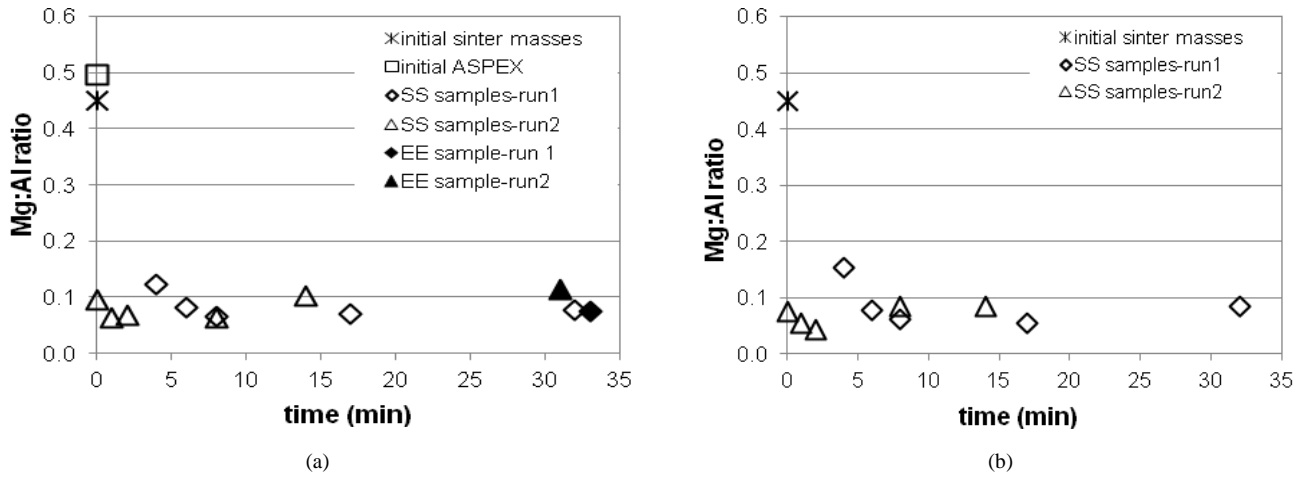
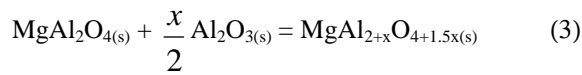
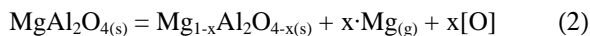
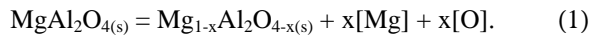
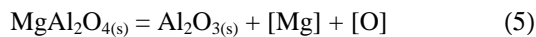
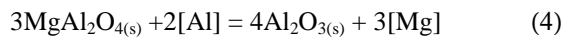


Figure 3. Mg:Al mass ratio of spinel inclusions in samples taken at different times during the reactivity test 1 and 2. (a) ASPEX results (b) INCA results

aluminium entering the inclusion may be described by equation 3. The maximum change in Mg content of the steel based on the change in the composition of the spinel inclusions was ~0.5ppm. The Mg solubility in Fe in the Fe-Mg binary system [23] is ~100ppm at 1600°C. While this does not fully represent the steel used in this study it does indicate that steel is likely to have enough capacity to take up the magnesium.



Alternative reactions that could result in the decomposition of the MgAl_2O_4 spinel inclusion are shown in equations 4 and 5. In these equations the magnesium is shown going into solution in the steel, but again it could also enter the gas phase.



The fraction of total inclusions for alumina and spinel are compared (Figure 4) to assess whether the spinel inclusions could be decomposing. It can be seen the proportion of spinel inclusions remained constant throughout the experiment while the proportion of alumina inclusions increased. As the proportion of spinel inclusions remained constant it is unlikely that decomposition of the spinel inclusions was occurring. The increase in the proportion of alumina inclusions could be due to the $p\text{O}_2$ of $\sim 10^{-13}$ used during the test. The $p\text{O}_2$ in equilibrium with 0.03% [Al] (Table 1) was estimated to be $\sim 10^{-14}$ atm at 1600°C [24-27]. This indicates that there is the potential to

oxidise the [Al] to alumina during the experiment. This would create more alumina inclusions over time.

Mass balances for magnesium and aluminium were carried out for the spinel inclusions found in samples taken at different times. This was carried out to with a view to determine whether the change in the composition of the spinel inclusions was due to magnesium leaving or aluminium entering the inclusion. The primary assumptions made in the mass balance were that

- The inclusions were spherical, with a diameter given by their average diameter as measured by ASPEX.
- The inclusions contained no iron.
- The density of the spinel inclusion at room temperature is $3550 \text{ kg}\cdot\text{m}^{-3}$ [28].
- The original input spinel inclusions had an average diameter of $3.4 \mu\text{m}$.
- Data for spinel inclusions combined with sulfides were neglected

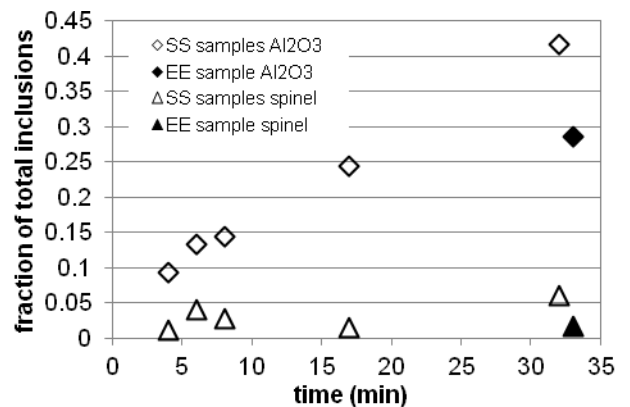


Figure 4. Spinel and alumina inclusions as a proportion of total inclusions.

The mass balance calculations are presented as percentage differences from the input inclusions, as shown in Figure 5.

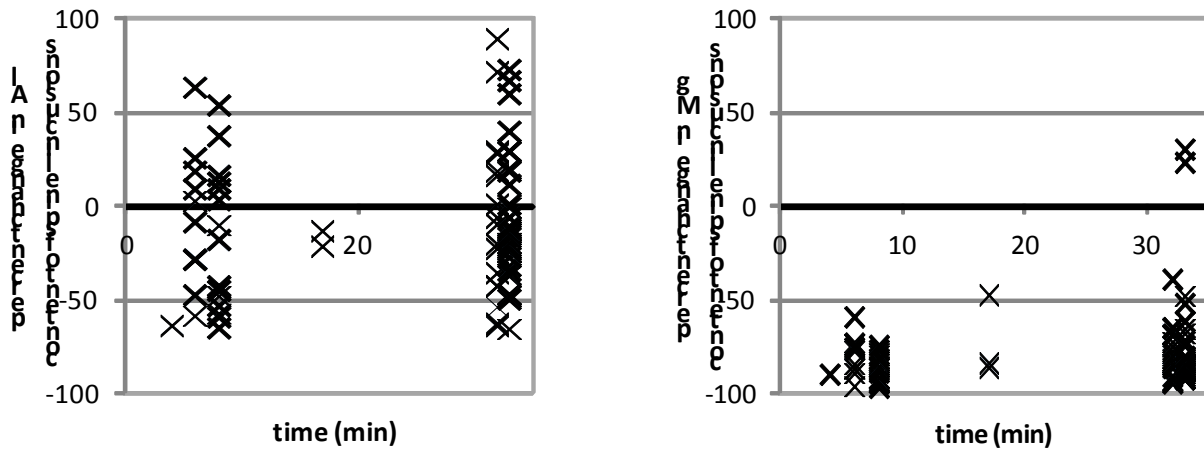


Figure 5. (a) Aluminium mass balance and (b) magnesium mass balance for spinel inclusions found in samples taken during the reactivity testing.

While there is considerable scatter in the data, likely reflecting the use of an average original particle size, it appears that the mass balance indicates that the magnesium content of the majority of the spinel inclusions decreased, indicated by the negative bias of the %Mg change in Figure 5b. The mass balance for aluminium however showed that most of the inclusions were distributed around no change in mass, with some of the larger inclusions skewing the distribution towards an increase in Al content (Figure 5a).

The sensitivity of the mass balance to changes in the size of the original inclusions (from 3-4 μm) was examined. It was found that the trend of the magnesium content in the inclusions to decrease was consistent over the range of original inclusion sizes tested. However, the aluminium content was sensitive to the original particle size used. It could be seen to either increase for small sizes, or decrease at the larger original particle size ranges. This ambiguity in the aluminium mass balance makes it difficult to definitively determine whether or not aluminium is leaving or entering the inclusions. However, the magnesium mass balance shows that magnesium is likely to be leaving the inclusions. Thus the change in the Mg:Al ratio of the inclusions with time is most likely due to magnesium (oxides) leaving the inclusion rather than aluminium (oxides) entering the inclusion. These results are in agreement with literature [3-4]. Verma et al. and Pretorius et al. studied the modification of spinel inclusions by calcium treatment in liquid steel. They found that Mg content of the inclusions in industrial samples decreased sharply after Ca treatment. Their experimental results and thermodynamic calculations also showed that this is due to dissolution of magnesium in liquid steel after the treatment.

Thermodynamic analysis of the system was conducted using MTDATA [19]. Analysis of the Mg-Al-O system was conducted to investigate the change in composition of the spinel inclusions. Isopleths within the Mg-Al-O system, starting with MgAl_2O_4 spinel on one side of the diagram and finishing with Al_2O_3 at the other, were calculated by MTDATA

[19] and is shown in Figure 6. Also shown in the figure are the initial spinel composition and the composition range of spinel inclusions measured after melting. This indicates that the inclusion have reacted from their initial single phase (spinel) to a two phase (spinel-alumina) product.

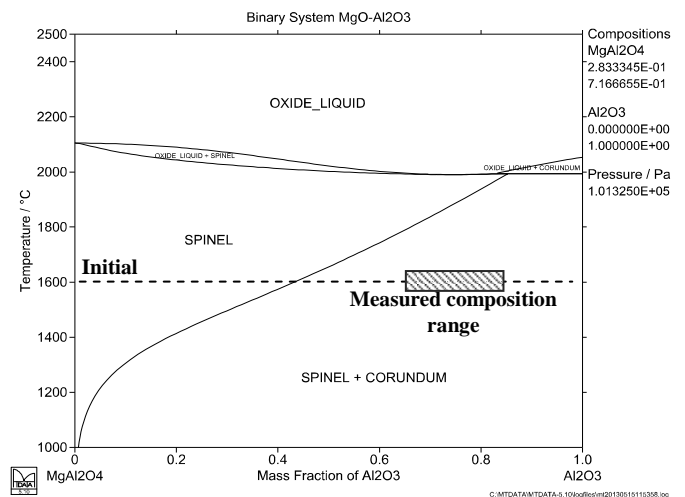


Figure 6. MgAl_2O_4 - Al_2O_3 isopleth as calculated by MTDATA.

Figure 7 shows a comparison of the back scattered electron image and Mg, Al elemental mapping of typical spinel inclusions. The EDS mapping of inclusions showed a Mg depletion in the majority of spinel inclusions. A few inclusions showed a Mg rich core with depletion from the outside of the inclusion see figure 7b. Whilst there is little contrast difference between Mg and Al oxides, the elemental maps show a significant variation between the distributions of Mg and Al in Figure 7 (a) relative to Figure 7 (b). The maps in Figure 7b may indicate that this spinel inclusion contains two phases. This may be a result of magnesia depletion of the spinel inclusion or spinel inclusion may have acted as a nucleation site for Al_2O_3 growth

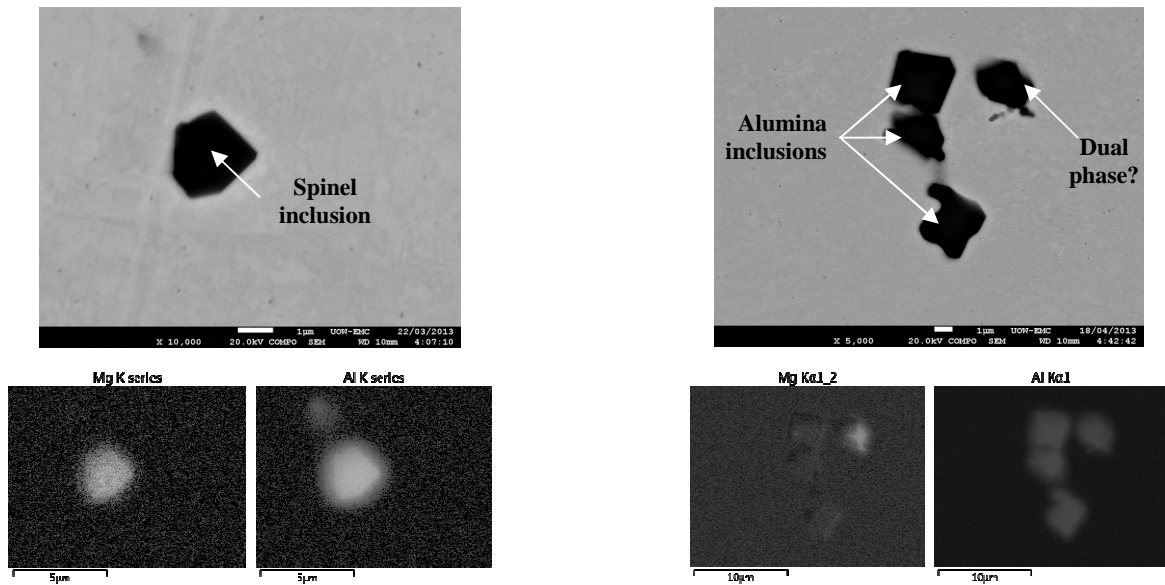


Figure 7. Back scattered electron image and Mg, Al elemental map of Mg containing inclusions (a) single phase from sample taken at 2 min (b) dual phase from sample taken at 30 min (scale bar is 1 μm for micrographs).

C. Matrix effects in EDS analysis of spinel inclusions

It is known that the instrument conditions such as accelerating voltage, counts per spectrum, magnification have an effect on the energy dispersive x-ray analysis of inclusion in steel matrix [3]. These effects were minimized by selecting similar conditions for ASPEX and INCA. They were both operated at 20 kV acceleration voltage. Magnification was set to 450X and 500X for ASPEX and INCA, [3].

ZAF factors can change the analysis when the electron interaction volume is similar to the inclusion volume. The typical measured inclusion studied in this work had an apparent diameter of 2 μm or more, which indicates that the inclusions would be sufficiently large to decrease the effect of the surrounding steel matrix on the EDX microanalysis.

Inclusion analyses via INCA were conducted based on automatic element identification. These analyses were repeated using a fixed element list consisting of Fe, Al, Mg, Mn, S and Ti. By doing this more Mg containing inclusions were found in the steel samples. However, the Mg:Al ratio of the inclusions detected previously did not change. This finding was consistent with literature [3]. Even though, matrix effect on the quantitative analysis of spinel inclusions can be improved by changing the instrument conditions of either ASPEX or INCA, this should not affect the significant change in Mg:Al ratio during reaction.

CONCLUSIONS

The reactivity of MgAl₂O₄ spinel inclusions in liquid steel was studied. The approach used allowed control of the initial size, composition and phase of the inclusions. The key findings were:

- The change in the size and composition of spinel inclusions was similar using ASPEX and INCA.

- While much of the reaction of the MgAl₂O₄ spinel occurred prior to sampling of the liquid steel making assessment of the rate of change of the inclusion composition impossible, it was found that the average Mg:Al ratio of spinel inclusion decreased from 0.49 approximately to 0.08. Further there was plausible evidence presented indicating that it was Mg being lost from the inclusion rather than Al being added to the inclusion that resulted in this change in Mg:Al ratio.
- There was little change in the size of the spinel inclusions and there was little indication that these inclusions agglomerated in the steel.
- In general, the spinel inclusions showed little association or interaction with the other inclusions in the steel and the number of alumina inclusions in the steel increased with time. The increase in the number of alumina inclusion is likely a result of oxidation of the aluminium in solution in the steel

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