A Novel Powder Metallurgy Technique for Introducing Synthetic Inclusions into Liquid Steel

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Abstract. Previous studies have shown that it is extremely problematic to add synthetic inclusions successfully into liquid steel for clean steel experiments. Small micro-particles encapsulated in a metallic parcel are difficult to pass through the melt-gas interface and inclusions tend to agglomerate then float up to the liquid surface. In this study, powder metallurgy is used to distribute cerium oxide particles of a known size from 1µm to 14µm within a small-scale steel ingot. Carbonyl iron powder has been mixed with 0.1 wt.% cerium oxide (CeO₂) and then sintered in an electrical furnace to produce sintered ingots of 500 grams. A series of induction furnace melting trials using a total of 400 grams of electrolytic iron and cerium oxide sintered ingot have been undertaken. The work has included extensive FE-SEM analysis using the INCA Feature® to characterise synthetic cerium oxide inclusions from both the sintered ingots and trial ingots. The INCA Feature® results showed that the size distribution and number of cerium oxide inclusions agreed well between the sintered ingot and trial ingot. The synthetic cerium oxide inclusions are homogeneously dispersed through the bottom, centre and top of the trial ingot with approximately 16 number counts/mm². Analysis suggests that more than 95% of the cerium oxide from the sintered ingot has been distributed throughout the trial ingot. The work has also been upscaled from 400 grams up to 1.5 kg and has been successful. The method developed will be useful for further studies into steel cleanness of high value alloyed steels.

1. Introduction

It is well established that non-metallic inclusions are detrimental to the castability of clean steels and also to the mechanical properties of the downstream rolled and finished product. For example, tyre wire steel is drawn down to very fine wire (~150 µm diameter) and incorporated into the tread of automobile tyres to provide strength. An excessive level of hard non-deformable inclusions, such as alumina (Al₂O₃), can increase the risk of wire breakage during the drawing process. In bearing steels, non-metallic inclusions can act as stress raisers which can initiate micro-cracks and spalling leading to total bearing failure. Therefore, it is necessary to control and improve the operating practices during the steel manufacturing process to improve the overall cleanness of the steel.

Introducing synthetic inclusions into liquid steel is an important step in the study of inclusion removal at a laboratory level. There are only a few published papers for introducing synthetic inclusions into liquid steel. Dogan et al. [1] published some work in 2012, where they sealed cerium oxide (CeO₂) powder in-between two pieces of steel plate. The plates were than pressed together using 50 tonnes of pressure to seal the oxide particles into the compressed steel sample and remove any entrapped gas. This steel sandwich was then added to the steel liquid. Their results showed that 9% of total inclusions contained the cerium element. A similar pressing method was described in a Japanese patent...
(JP2005091017) in July 2005 [2]. Alumina particles were spread on the surface between a steel plate and a metallic foil, then pressed at high pressure.

Powder metallurgy techniques [3, 4] have showed promising results where oxide particles and powder metal can be compacted by hot isostatic pressing [5, 2] or hydraulic pressing [6]. A major advantage of these methods is that oxide inclusions of known chemical composition, inclusion size and density can be chosen [6].

The objectives of this study were to find a technique, which can introduce the synthetic inclusions into a steel melt for cleanness studies. The new method should allow the addition of inclusions into the steel melt of a known quantity and inclusion size and that these inclusions are homogeneously dispersed through the bottom, centre and top of the sample.

2. Experimental materials and methods

2.1. Manufacturing sintered cerium oxide ingots

The sintered cerium oxide ingots were manufactured by Tata Steel’s Ceramics Research Centre (CRC), IJmuiden. In this study, powder metallurgy was used to distribute cerium oxide particles homogeneously in an iron matrix.

Carbonyl iron powder with a grain size of approximately 10 µm was mixed together with 0.1 wt.% cerium oxide powder with a grain size of from 1 µm to 14 µm and 1.0 wt.% of the binder bisstearoylethylene diamide in a container called a Turbula Mixing System. The amount of iron powder, cerium oxide and binder were mixed for approximate 1 hour.

Approximately 200 gram of the powder mixture was then pressed in a cylindrical mould (Ø 50 mm) with 60 MPa of pressure using a hydraulic press. The pressed sample was then heated to 600 °C at a heating rate of 3 °C/min in atmospheric conditions to remove the binder. The sample stayed at this temperature for 1 hour before it was allowed to cool down following a natural cooling curve.

After debinding, the sample was put in a hydrogen furnace (see Figure 1), to sinter the sample. A temperature program was applied with a heating rate of 5 °C/min, and the sample held at 600 °C for one hour, before further heating until a top temperature of 1300 °C was reached. The holding time at the top temperature was 30 minutes, before the sample was cooled down following a natural cooling curve. The density of the ingot is approximately 7.2 g/cm³ after sintering.

2.2. Introducing synthetic inclusions into liquid steel

Figure 1. Hydrogen furnace at CRC, Tata Steel, IJmuiden, used for sintering the cerium oxide ingots.
The sintered cerium oxide ingot was added together with electrolytic iron at a 400 gram scale. A 45 kW induction furnace based at the Materials Processing Institute (the Institute) was used for melting the samples. The induction furnace was purged with argon to remove any traces of oxygen. Alumina crucibles were used in these experiments. A graphite sleeve manufactured in the workshop of the Institute was placed around the alumina crucible to improve melting performance.

Several techniques of placing the sintered cerium oxide ingot within the electrolytic iron have been tested. The electrolytic iron and sintered cerium oxide ingot were melted out in the induction furnace and the temperature raised to 1610 °C and held for 5 minutes. The induction furnace was then shut down and the melt temperature quickly cooled down to room temperature. The melt temperature was measured using a type-S thermocouple submerged in the liquid steel.

Figure 2 shows a schematic diagram of the experimental induction furnace set-up used at the Institute.

2.3. SEM mapping technique
The work has included extensive Field Emission Gun Scanning Electron Microscopy (FEG-SEM) using the Oxford Instruments INCA Feature® software to characterise synthetic cerium oxide inclusions from both the cerium oxide sintered ingots and trial induction furnace ingots. INCA Feature® is an automated procedure that analyses particle features detected within a designated sample area. The data can then be processed to give several parameters including (a) inclusion counts/mm², (b) inclusion area %, (c) inclusion size and (d) particle shape for each detected phase analysed. The analyser was able to measure very small sized particles < 1µm upwards within the designated analysis areas.

3. Results and discussion
3.1. Metallography of the sintered ingots
Samples of the sintered cerium oxide ingots, manufactured at CRC, have been cut, ground and polished to a 1µm finish, suitable for SEM investigation. The samples have been examined using the Institute’s FEG-SEM, equipped with an Oxford Instruments Energy-Dispersive X-ray Spectroscopy (EDX) analyser.

Each sample was mapped to detect every cerium oxide particle, so that a distribution of cerium oxide inclusions within the ingot could be determined. Figure 3 shows the location of cerium oxide inclusions detected within a sample area of 17 mm². It was seen that the cerium oxide inclusions were dispersed homogeneously in the sintered ingot, from a small inclusion size of 1 µm through to 50 µm. The increase in inclusion size was caused by agglomeration during pressing. The INCA Feature® analysing software was able to detect the size of each cerium oxide inclusion, so that a size distribution could be made for the ingot, which is shown in Figure 4. The major inclusion sizes were from 1 µm to 7 µm. No contamination of the inclusions in the sintered ingot was found.
The INCA Feature® results showed that the number of cerium oxide inclusions was around 45 number counts per millimeter square.

![Figure 3. SEM map of cerium oxide inclusions using INCA Feature®.](image1)

![Figure 4. Size distribution of cerium oxide inclusions in the sintered ingot.](image2)

### 3.2. Metallography of the induction furnace samples

To find the best yield of the cerium oxide inclusions in the steel samples, three trials using 280 gram of electrolytic iron and 120 gram of the sintered cerium oxide ingot were undertaken.

Each trial used a different technique by placing the sintered cerium oxide ingot in different positions, as seen in Figure 5 and as follows:

1. CeO$_2$-iron ingot at the bottom of the electrolytic iron in the crucible.
2. CeO$_2$-iron ingot in the middle of the electrolytic iron in the crucible.
3. CeO$_2$-iron ingot closer to the bottom but surrounded by electrolytic iron in the crucible.

The third control trial showed that the maximum recovery of cerium oxide from sintered cerium ingot was achieved in the melted-out samples, as detailed in Table 1.

![Figure 5. Position of material for the three induction furnace trials.](image3)

| Trial | Ingot Top (number counts/mm$^2$) | Ingot Centre (number counts/mm$^2$) | Ingot Bottom (number counts/mm$^2$) | Ingot Average (number counts/mm$^2$) |
|-------|----------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| 1$^{st}$ | 10.4                             | 12.4                                | 9                                   | 10.6                                |
| 2$^{nd}$ | 15.9                             | 15.5                                | 12.1                                | 14.5                                |
| 3$^{rd}$ | 20.3                             | 16.7                                | 15.2                                | 17.4                                |
A sample area of 17 mm$^2$ was scanned using INCA Feature$^\text{®}$ for the three trials. Figure 6 shows the distribution of the cerium oxide inclusions at the centre of each sample. The SEM maps showed similar results to the sintered cerium oxide ingot, in that the cerium oxide inclusions were homogenously distributed within the samples of the three trials.

The second and third trials showed that the number of cerium oxide inclusions were around 16 number counts per mm$^2$, which had dropped from 45 number counts per mm$^2$ for the sintered cerium oxide ingot, which was initially added to the melt. This was consistent with 30% of the sintered cerium oxide ingot having been added to the induction furnace trial samples. It was therefore concluded that 95% of the cerium oxide inclusions were recovered from the sintered cerium oxide ingot into the induction furnace trial samples.

![Figure 6](image6.png)

**Figure 6.** INCA Feature$^\text{®}$ map of cerium oxide inclusions at the centre position of the induction furnace samples.

Figure 7 shows the size distribution of cerium oxide inclusions for the three trials at the centre location of the melted-out ingot. Analysis showed that the major cerium oxide inclusion sizes were from 1 µm to 7 µm. No larger inclusion sizes from 14 µm to over 30 µm were recorded from the melted-out ingot. This can be explained if the larger size inclusions detected from the original sintered ingot were due to the agglomeration of particles during the sample preparation process. Once these large oxide inclusions get into the liquid melt, the agglomerated inclusions are separated into their original particle size.

More in-depth calculations of the stability of the CeO$_2$ inclusions in the liquid melt was conducted using the thermodynamic software FactSage 7.2 utilising databases FactPS, FToxid and FTmisc. The oxygen activity was calculated with an input O$_2$ content of 0.01 ppm, coming from the argon used in the induction furnace. The temperature ranged used in the calculations was 1200 °C to 1650 °C. Results of the FactSage calculations, indicated that Ce$_2$O$_3$ is stable in the liquid iron and would be duplexed with FeO after solidification. SEM elemental results confirm that FeO-Ce$_2$O$_3$ inclusions were found, which is shown in Figure 8.

![Figure 7](image7.png)

**Figure 7.** Size distribution of cerium oxide inclusions at the centre of the induction furnace samples.

![Figure 8](image8.png)

**Figure 8.** SEM elemental maps confirming inclusions to be FeO-Ce$_2$O$_3$
4. Conclusions
A powder metallurgy technique has been developed to enable the addition of synthetic inclusions of known size, composition and density into liquid steel. The sintered cerium oxide ingot was added with electrolytic iron and melted-out in an induction furnace. Metallographic assessment of the samples showed that the cerium oxide inclusions were homogenously dispersed through the sample from top, centre and bottom. Analysis suggested that more than 95% of the cerium oxide from the sintered ingot had been distributed throughout the trial ingots produced during the experiments.

This technique is therefore useful for future steel cleanliness studies for high value alloyed steels.

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