Phase Relations in Ce–Al–Fe–S Based Grain Refiners for Steels

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In the present investigation the phase relations within the Ce–Al–Fe–S system have been clarified, using a combination of optical microscopy and WDS microprobe analyses. As a starting point high-purity charge materials of cerium, aluminium and FeS₂ are melted and superheated to about 2 000°C within small tantalum crucibles inside a dedicated laboratory furnace filled with cleaned argon. The phases detected in the as-solidified samples were CeS, Ce₃Al, Fe₂Ce and γ-Fe, along with Ce₂O₂S, which is an undesirable reaction product in CeS-based grain refiners. It is concluded that FeS₂ can be used as a sulphur source for addition up to about 4 wt% sulphur. At higher levels the Fe–Ta interaction becomes so vigorous that tantalum no longer acts as an inert refractory metal and wetting becomes a major problem. In contrast, aluminium is an essential alloying element in the sense that it prevents the grain refiners from disintegrating in contact with air due to internal oxidation of free cerium by promoting the formation of Ce₃Al.

KEY WORDS: steel grain refiners; manufacturing; oxygen control; pyrite additions; cerium sulphide formation.

1. Introduction

Currently, structural steels are strengthened by a series of different techniques. Usually a fine grain structure is achieved by combining heat treatment and thermo-mechanical processing. The energy saving potential of applying cheaper and faster strengthening methods is great and highly interesting in a time where access to energy is predicted to decline. For example, adding a specially designed master alloy with the ability to produce a fine grain structure in steel is possible and also to some extent exploited by the steel manufacturers.¹⁻³

Several systems with the potential of being used as grain refiners for steel have been studied over the last ten years. One of the most promising ones is the cerium–sulphur system.⁴ Cerium has a strong affinity to sulphur and will, almost always, form a compound with sulphur when both elements are present in molten steel.⁵⁻⁶ A fine distribution of CeS particles in the steel matrix during the austenite to ferrite transformation can shift the nucleation process from the austenite grain boundaries to sites located intragranularly.⁷ This process has been studied extensively since the nineteen seventies in low alloy steel weld metals, where complex oxide and sulphur inclusions contribute to acicular ferrite formation.⁸⁻¹¹ Acicular ferrite has a plate like structure offering a combination of high strength and toughness. Acicular ferrite can only be achieved if the number density of CeS particles in the steel matrix is sufficiently high.¹²⁻¹³ Unfortunately, modern steelmaking involving continuous casting does not allow large additions of ferroalloys late in the process due to practical problems related to a severe temperature drop after the addition and incomplete dissolution and mixing of the alloy in the liquid. Therefore, in order to maintain a good nucleation potential, the master alloy needs to be highly concentrated and contain between 5 and 10 wt% sulphur.¹² Cerium is in this context interesting, since it can dissolve large amounts of sulphur in the liquid state.¹⁴ By fully exploiting the potential of cerium as a sulphur carrier, effective grain refiners can also be produced for continuously cast steels containing a high number density of embedded CeS particles.

A major problem with cerium is that the metal is not protected by a stable oxide layer,¹⁵ meaning that it will gradually disintegrate in contact with air. However, previous experiments have shown that balanced aluminium additions are beneficial to stabilise cerium during storage in an oxygen-rich environment, due to the resulting Ce₃Al compound formation.¹⁶ All melting trials with cerium preformed in the present investigation are therefore carried out using aluminium as an alloying element, along with FeS₂ (pyrite) acting as the sulphur source. However, oxidation of the cerium melt (i.e. Ce₂O₂S formation) may still occur during heating if the oxygen level in the furnace is not kept extremely low.¹⁶ One way to overcome this problem is to use a furnace equipped with a graphite heating element, which will act as an oxygen scavenger at elevated temperatures due to the increased affinity of carbon towards oxygen. This, in combination with rapid heating of the melt, makes it possible to reduce the oxygen pick-up from the surrounding gas atmosphere to an acceptable level.¹⁶

The binary phase diagram which exists today for Ce–S is not fully established within the composition range of specific interest (i.e. from zero and up to 50 at% S).¹⁷ Therefore, the liquidus temperature is only indicated by a dotted
line, suggesting a solubility of sulphur in cerium at 2000°C of about 33 at% sulphur (10 wt% sulphur). The main objective of the present study is thus to provide new and more accurate information about the solubility of sulphur in liquid cerium, and in particular how elements such as aluminium and iron influence the CeS formation and the resulting phase relations. This is done using microprobe and optical microscopy for characterisation of the different constituent phases in the as-solidified samples, and point counting for quantitative volume fraction measurements.

2. Experimental

2.1. Materials

A key issue in the manufacture of CeS-based grain refiners for steel is to use an appropriate sulphur source that does not lead to undesirable side reactions and a low sulphur yield. Therefore, sulphur cannot be added in a pure form because the boiling point is too low, which means that the element will evaporate during heating. A better solution would be to use FeS2 (99.9%) as a sulphur source, as done in the present investigation, because FeS2 is easy to obtain, is richer in sulphur compared to FeS and more stable than elemental sulphur at elevated temperatures. The two other charge materials used were cerium and aluminium metal with 99.9% and 99.999% purity, respectively. These materials were obtained from different commercial manufacturers, i.e. Alfa Aesar, PI-KEM, and Hydro Aluminium.

To avoid oxygen contamination of the charge materials, an argon filled glove box with oxygen and humidity levels 0.1 ppm was used for storage. All materials were charged into the tantalum crucibles inside the glove box.

2.2. Furnace

Figure 1 shows a schematic illustration of the small vacuum furnace used in the melting experiments. This furnace was originally designed for in-situ wetting angle measurements. As a consequence, the furnace is only equipped with a sample holder capable of heating substrates/crucibles with an outer diameter of 10 mm. Small tantalum crucibles were therefore machined to fit this sample holder. Tantalum has good refractory properties, is easy to machine and has a low solubility in contact with liquid cerium.

To protect the sample from oxidising the vacuum chamber was constantly flushed with high purity argon during the experiments. The argon flowing out of the furnace passes through a zirconia oxygen sensor (Sensotec RX2100), which measures the partial pressure of oxygen. The RX2100 can measure a partial pressure of oxygen from 1 to 10 atm with an accuracy of ±1%. When starting the argon flushing, the oxygen partial pressure will after a certain period of time stabilise itself at around 1 atm. Such low oxygen levels are obtainable by passing the argon through a separate furnace, containing heated magnesium, before entering the vacuum furnace.

The heating element is made of graphite, as are all other heated parts of the furnace. A calibrated two-colour pyrometer, with an operating temperature range from 900–2400°C, continuously measures the temperature of the crucible. In-situ photography of the crucible is also possible during the experiments, as shown in Fig. 2.

2.3. Melting Experiments

Four different levels of sulphur additions in cerium were investigated. In addition, 2 and 5 wt% aluminium was added to promote Ce3Al formation. This gives a total of eight melting experiments for the four different nominal sulphur levels aimed at; 0, 2, 4 and 6 wt%, respectively. The weight of each sample was approximately 0.8 g and the targeted chemical compositions are listed in Table 1.

According to the Ce–S phase diagram, the desired solubility level of sulphur can only be achieved if cerium is melted and superheated to about 2000°C. Figure 3 shows a
record of the actual crucible temperature and the partial pressure of oxygen ($p_{O_2}$) in the surrounding gas atmosphere inside the furnace during a typical melting experiment. As the temperature in the furnace is rising, the $p_{O_2}$ is decreasing due to the increased affinity of carbon towards oxygen at elevated temperatures. Oxygen pick-up in the melt during heating will primarily occur within the intermediate temperature range below 1600 to 1800°C, where the protection provided by the graphite heating element is low.\(^{(16)}\)

2.4. Optical Microscopy

Standard metallographic techniques were used to prepare cross-section samples for optical microstructure characterisation. Because cerium corrodes vigorously in water, wet grinding was carried out using an alcohol-based lubricant. The microstructure was readily revealed in the optical microscope without etching. Metallographic examination was performed using a conventional Zeiss reflecting light optical microscope.

2.5. Volume Fraction Measurements

Standard point counting techniques were used to measure the volume fraction of the different constituent phases present in each sample.\(^{(15)}\) This was done employing an optical microscope, equipped with an 11×11 ocular grid at 200× magnification. A total of six different fields were counted per sample, from which the mean values and the standard deviation of the means were calculated. The measured volume fractions can then be compared with the calculated ones, based on the following equation:

$$f_{\text{CeS}} = \frac{m_{\text{CeS}}}{m_{\text{alloy}}} / \rho_{\text{CeS}}$$

where $m_{\text{alloy}}$ is the total weight of the samples and $m_{\text{CeS}}$ is the total mass of CeS in the alloy, assuming 100% sulphur yield. The symbols $\rho_{\text{alloy}}$ and $\rho_{\text{CeS}}$ in the equation represent the corresponding densities of the two phases.

In order to ensure a highest possible confidence in the calculations, measured values for $\rho_{\text{alloy}}$ should be used. In the present investigation, the Archimedes principle of buoyancy was adopted to measure the density of samples No. 1, 4, 5 and 8. By extrapolating the data between the limits 0 to 6 wt% S, separate density plots for the two different aluminium levels were constructed, as shown in Fig. 4.

2.6. Microprobe Analyses

A JEOL JXA-8500F electron probe micro analyser (EPMA) was used to study the as-solidified microstructures of the samples. The JXA-8500F is a high performance thermal field emission electron microprobe analyser and is equipped with 5 wavelength dispersive X-ray spectrometers (WDS) and a backscatter electron (BSE) detector. A cross-section of each sample was prepared and the different phases characterised and identified using BSE imaging and WDS analyses. All these investigations were carried out at an acceleration voltage of 15 keV and a probe current of 30 nA.

3. Results

In the following, the main results from the microstructure and phase characterisations will be presented. Note that the chemical analyses reported below refer to samples No. 4 and 8, which contains a representative selection of the phases being present in all eight samples.

3.1. Microprobe Investigation of Sample No. 4

Figure 5 shows measured element distribution maps for aluminium, iron, cerium and oxygen in sample No. 4. The scanned area is indicated by the rectangular box in the upper right corner of the BSE image. In addition, five WDS point analyses have been carried out at the surface positions indicated by the arrows in the electron micrograph. The results from the point analyses are summarised in Table 2.

The main elements found in positions 1 and 2 are cerium and oxygen. Because this area shows signs of surface corrosion, it is reasonable to assume that the $\gamma$-Ce has been oxidised either during or immediately after the microstructural

![Fig. 4. Plots showing the measured density of the Ce–2wt%Al and the Ce–5wt%Al base alloys, respectively as a function of the added sulphur content.](image)

![Fig. 5. BSE image of sample No. 4 along with element distribution maps for aluminium, iron, cerium and oxygen. The arrows indicate the position of the five point analyses reported in Table 2.](image)

![Table 2. Point analyses of various phases detected in sample No. 4. The numbers are given in at%.](table)
preparation. Hence, this phase is most likely $\gamma$-Ce provided with a surface layer of Ce$_2$O$_3$ or CeO$_2$. In point analyses 3, 4 and 5 the ratio between the constituent elements corresponds to the intermetallic phases Ce$_3$Al, CeS and Fe$_2$Ce, respectively. Therefore, sample No. 4 contains a mixture of the four constituent phases Ce$_3$Al, CeS, Fe$_2$Ce and $\gamma$-Ce. A lamella-shaped ternary eutectic is also present, being encircled by the rectangular box in Fig. 5. As judged from the element distribution maps this eutectic phase consists of Ce$_3$Al, Fe$_2$Ce and $\gamma$-Ce.

### 3.2. Microprobe Investigation of Sample No. 8

Figures 6(a) and 6(b) show two BSE images of sample No. 8 at high and low magnification, respectively. The five point analyses shown in Table 3 were carried out at the surface positions indicated by arrows in the electron micrographs. The main elements found in position 1 are iron and tantalum. This shows that some reactions have occurred between iron dissolved in the melt and the tantalum crucible. The amount of tantalum found in the as-solidified structure is relatively small. However, near the crucible wall the Ta–Fe reaction is more vigorous, as can be seen from the segment delimited by the rectangular box in Fig. 7. The phases observed in positions 2 and 3 are Ce$_3$Al and CeS. The phases in position 4, on the other hand, are too small to be analysed separately. However, by increasing the electron beam diameter, the average composition within the encircled area in Fig. 6(a) can be measured. The point analysis from position 4 suggests a eutectic phase consisting of Ce$_3$Al and Fe$_2$Ce. In position 5 the ratio between the constituent elements points toward Ce$_2$O$_2$S, which is the most stable cerium oxysulphide.\(^{16}\)

### 3.3. Microstructural Evolution in Samples No. 1 to 4

Figure 8 shows four light optical micrographs of samples No. 1, 2, 3 and 4. In these micrographs different grey-tone levels are used to display the three main constituent phases CeS, $\gamma$-Ce and Ce$_3$Al, ranging from bright to dark. In-between these phases, the ternary eutectic is located, forming a fine dispersion of grey particles in the image. By comparing the images, the microstructural changes that occur due to the sulphur additions can be qualitatively observed. It is evident that cerium to an increasing extent reacts and forms CeS when sulphur is added.

In Fig. 9 the results from the quantitative volume fraction

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**Table 3.** Point analyses of various phases detected in sample No. 8. The numbers are given in at%.

| No. | O  | S  | Ta  | Al  | Ce  | Fe  |
|-----|----|----|-----|-----|-----|-----|
| 1   | 4.9| 0.2| 52.7| 4.5 | 1.2 | 36.5|
| 2   | 3.3| 0.3| 0.1 | 23.0| 73.2| 0.1 |
| 3   | 1.2| 47.0| 0.0 | 0.2 | 51.4| 0.2 |
| 4   | 6.6| 0.1| 0.0 | 20.4| 59.6| 13.3|
| 5   | 35.9| 20.0| 0.0 | 0.3 | 43.5| 0.3 |

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**Fig. 6.** BSE image of sample No. 8 at (a) high and (b) low magnification, respectively. The arrows indicate the position of the five point analyses reported in Table 3.

**Fig. 7.** Light optical micrograph of sample No. 7 at the interface between the tantalum crucible and the as-solidified microstructure. The area encircled by the rectangular box shows how the dissolved iron has reacted with the tantalum crucible.

**Fig. 8.** Light optical micrographs of samples No. 1, 2, 3 and 4.
measurements of the same phases are presented graphically. A closer inspection of the trend lines shows that increased sulphur addition promotes both the CeS component formation and the formation of the ternary eutectic phase consisting of Ce$_3$Al, Fe$_2$Ce and γ-Ce. Therefore, a corresponding reduction in the free Ce$_3$Al content is also observed because more Ce$_3$Al will be tied-up in the ternary eutectic phase as the sulphur level increases. Moreover, it follows from Fig. 9 that the homogeneity of the samples is very good, as evidenced by the small error bars in the graphs representing the standard deviation of the measurements.

3.4. Microstructural Evolution in Samples No. 5 to 8

Figure 10 shows four light optical micrographs of samples No. 5, 6, 7 and 8. As already pointed out in the previous section, the main constituents in the micrographs (CeS, γ-Ce and Ce$_3$Al) are displayed by their different greytone levels ranging from bright to dark, respectively. In between these phases, the eutectic phase forms a bright lamella structure. Also the amount of CeS is seen to increase when more sulphur is added to the samples.

Finally, the results from the quantitative volume fraction measurements carried out on samples No. 5, 6, 7 and 8 are presented graphically in Fig. 11. As for the 2 wt% Al samples, the sulphur additions promote formation of CeS and a eutectic phase, which in this case consists of Ce$_3$Al and Fe$_2$Ce. Also a corresponding reduction in the free Ce$_3$Al content is observed with increasing sulphur additions as more Ce$_3$Al becomes tied-up in the eutectic phase.

4. Discussion

In the following, the conditions for CeS formation and the subsequent precipitation reactions occurring during cooling due to the FeS$_2$ and aluminium additions to liquid cerium will be discussed more in detail, starting with an analysis of the sulphur yield in the samples.

4.1. Sulphur Yield Using Pyrite as Charge Material

In the melting experiments pyrite (FeS$_2$) is used as a charge material because it is rich in sulphur. However, this mineral is not stable at elevated temperatures, since it will start to dissociate at 743°C, leading to S$_2$(g) formation:

$$\text{FeS}_2 = \text{FeS} + \frac{1}{2} \text{S}_2(g) \quad \text{(2)}$$

Still, the S$_2$(g) being released can dissolve in the cerium melt and in the limiting case lead to 100 wt% yield of sulphur, according to the overall dissolution reaction:

$$\text{FeS}_2 = \text{Fe} + 2\text{S} \quad \text{(3)}$$

In the other extreme, the S$_2$(g) will just evaporate, which means that the sulphur yield is comparable with that of using pure FeS, in which only one mol of sulphur dissolves in the melt per mol iron added:

$$\text{FeS}_2 = \text{Fe} + \text{S} + 1/2 \text{S}_2(g) \quad \text{(4)}$$

In the latter case the advantage of using FeS$_2$ compared to FeS as a sulphur source is questionable, since reaction (4) implies that all S$_2$(g) is lost to the surrounding atmosphere.

The actual amount of sulphur being retained in the samples as CeS after the FeS$_2$ addition can be calculated from Eq. (1), using the measured volume fraction data for CeS reported previously in Figs. 9 and 11 and the corresponding density data for the samples provided in Fig. 4. The meas-
ured sulphur content in each sample is then plotted as a function of the total amount of sulphur added to the Ce–Al base alloys. The results are shown graphically in Figs. 12(a) and 12(b).

It is evident that the measured sulphur content falls between that calculated for 100% yield of FeS$_2$ and FeS, respectively, as indicated by the dotted lines in the graphs. This essentially means that a significant fraction of the S$_2$(g) being released by the decomposition of FeS$_2$ redissolves in the melt and combines with cerium to form CeS. Hence, there is an advantage of using FeS$_2$ compared to FeS as a sulphur source during manufacturing of CeS-based grain refiners because of the opportunities pyrite offers in minimising the iron content for a given target sulphur level.

4.2. Phase Relations within the Ce–Al–Fe–S System

Currently, there is no phase diagram available for the quaternary Ce–Al–Fe–S system. However, the results from the quantitative phase detection in Secs. 3.2 and 3.3 show that both Ce$_3$Al, Fe$_2$Ce and CeS are present in the as-solidified samples. These are intermetallic compounds that are known from the binary phase diagrams.20–22) Whereas CeS is a high melting point phase ($T_m$= 450°C), Ce$_3$Al and Fe$_2$Ce are low melting point compounds ($T_m$= 932 and 655°C, respectively), which together with cerium ($T_m$= 795°C) constitute the two different eutectic phases detected in the present investigation. None of these eutectic phases have previously been reported in the literature and their melting range and precipitation sequence are therefore not known. However, based on the results from microprobe investigation summarised in Figs. 5 and 6 schematic drawings of the ternary and binary eutectic phases have been made. These are presented in Fig. 13 and provide further information about their morphology and internal phase distribution.

In addition, a cerium oxysulphide phase is observed in the as-solidified samples, which is the result of an undesirable reaction between CeS and oxygen at elevated temperatures. The WDS point analyses referred to in Sec. 3.2 suggest that its composition is close to Ce$_2$O$_2$S. Calculated values for the critical $p_{O_2}$ needed to form (1) Ce$_2$O$_2$S, (2) Ce$_2$O$_3$ and (3) CeO$_2$ at the different temperatures16) In Fig. 14 these $p_{O_2}$ values are superimposed on the measured temperature $T$ and the partial pressure of oxygen ($p_{O_2}$) inside the vacuum furnace during a typical rapid heating cycle (i.e. $T$= 1000°C/min). The dotted lines show the corresponding partial pressure of oxygen needed to form (1) Ce$_2$O$_2$S, (2) Ce$_2$O$_3$ and (3) CeO$_2$ at the different temperatures.16) In Fig. 14 these $p_{O_2}$ values are superimposed on the measured temperature and oxygen profiles shown previously in Fig. 3. It follows that Ce$_2$O$_2$S is the most stable oxide compound at all relevant temperatures and therefore the most likely phase to form during manufacturing of CeS-based grain refiners for steel.

4.3. Upper Limit for the Sulphur Addition Using Pyrite

The results summarised in Figs. 12(a) and 12(b) show that a sulphur content of about 3.5 wt% can be obtained in the as-solidified samples by adding 6 wt% of sulphur to the melt in the form of FeS$_2$. At this level of FeS$_2$ addition, wetting of the tantalum crucible by the melt starts to become a problem, although the solubility limit of sulphur at 2000°C
is not exceeded. The wetting is caused by reactions between iron and tantalum, as shown previously in Fig. 7. The problem becomes much greater at higher iron levels. An example of this is contained in Fig. 15, which shows a photograph of the tantalum crucible after 8 wt% of sulphur addition using pyrite. In this case the reaction is so vigorous that most of the melt has run over the crucible rim and started to attack the outside walls as well.

Due to this wetting problem sulphur additions based on FeS₂ should be restricted to about 4 wt%. This corresponds to approximately 3 wt% of sulphur retained in the grain refiners, as shown previously in Figs. 12(a) and 12(b), or a volume fraction of CeS close to 0.16.

4.4. Stability of the CeS-based Grain Refiners during Long-term Storage in Air

All samples have been re-examined after 10 months of air exposure. The two base alloys containing no sulphur (No. 1 and 5) show good stability, although the Ce–2wt%Al sample is prone to surface oxidation. The remaining Ce–2wt%Al samples containing sulphur (No. 2, 3, and 4), on the other hand, reveal extensive volume expansion and surface cracking. An example of this is shown in Fig. 16(a) for sample No. 3. Obviously, the CeS compound formation results in a microstructure being vulnerable to internal oxidation, which, in turn, leads to fast deterioration of the γ-Ce phase. Higher aluminium levels are therefore required to stabilise the master alloy in order to ensure that all free cerium is tied-up as Ce₃Al. It follows from Fig. 16(b) that a 5 wt% aluminium addition will have the necessary stabilising effect at all relevant sulphur levels. This amount of aluminium can be added without affecting the solubility of sulphur, as shown previously in Fig. 12(b), and will later be transferred to the liquid steel in an intermetallic form where it will dissolve and act as a deoxidiser.

5. Conclusions

The basic conclusions that can be drawn from this investigation are as follows:

CeS-based grain refiners can be produced from high-purity charge materials of cerium, aluminium and FeS₂ which are melted and superheated in tantalum crucibles under the shield of cleaned argon. However, to prevent cerium from oxidising due care must be taken to restrict the supply of oxygen from the surrounding gas atmosphere during manufacturing.

The phases detected in the as-solidified samples are CeS, Ce₃Al, Fe₃Ce and γ-Ce, along with Ce₂O₂S, which is an undesirable microconstituent in the grain refiners. Both Ce₃Al, Fe₃Ce and γ-Ce are inclined to form low melting eutectics, whereas the stable high-temperature phase CeS constitute a discontinuous dendritic network within the grain refiners.

Although pyrite decomposes at 743°C to FeS and S₂(g), the sulphur yield using FeS₂ is significantly higher than that calculated for pure FeS. This is a considerable advantage, because less iron in this way will be charged into the system for a given target composition of sulphur.

The melting experiments show that pyrite can be used as a sulphur source up to about 4 wt% sulphur added. At higher levels the Fe–Ta interaction becomes so vigorous that tantalum does no longer act as an inert refractory metal and wetting becomes a major problem. Eventually, this will force the melt to run over the crucible rim and lead to attacks on the outside walls as well.

Finally, an evaluation of the stability of grain refiners during long-term storage in air shows that they are prone to volume expansion and surface cracking due to internal oxidation of γ-Ce. In practice, the problem can be overcome by balanced aluminium additions, which will tie-up all free cerium in the form of Ce₃Al.

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