Conditions for CeS Formation During Manufacturing of Ce–S–Al Based Grain Refiners for Steels

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In the present investigation the phase relations within the Ce–S–Al 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 Ce2S3 were melted and superheated to about 2 000°C within small tantalum crucibles inside a dedicated laboratory furnace filled with cleaned argon. The main constituent phases detected in the as-solidified samples are CeS, Ce2Al, CeAl and γ-Ce, where the CeS phase constitutes a discontinuous dendritic network within the grain refiners. The melting experiments show that pure cerium can dissolve about 6 wt% of sulphur at 2 000°C, which drops to approximately 1.8 wt% at 1 500°C. The measured sulphur solubility is considerably lower than that inferred from the existing binary Ce–S phase diagram, which therefore should be revised to comply with these new measurements. Because alloying with aluminium reduces the sulphur solubility in liquid cerium, the addition of this element should be restricted if a high volume fraction of CeS is desired in the grain refiners. At the same time the use of Ce2S3 as a sulphur source in replacement of pyrite (FeS2) means that aluminium is not actually needed to prevent the grain refiners from disintegrating in contact with air due to internal oxidation.

KEY WORDS: steel grain refiners; manufacturing; cerium melts; sulphur solubility; cerium sulphide formation.

1. Introduction

The harmful effects of inclusions on steel properties arise from their ability to act as initiation sites for microvoids and cleavage cracks during service. Hence, the use of clean steels is normally considered to be an advantage from a toughness point of view.1,2) On the other hand, it is now widely accepted that non-metallic inclusions also display some positive attributes by virtue of their ability promote grain refinement during solidification and/or in the solid state by a process of heterogeneous nucleation.3,4) Such particles are sufficiently small to be harmless from a toughness point of view,5,6) but at the same time large enough to act as potent nucleation sites during phase transformation.7–9) For example, the phenomenon of intragranular nucleation of acicular ferrite at oxides and sulphides is well known from low-alloy steel weld metals, where the characteristic high number density of such inclusions results in the development of a fine-grained microstructure within the as-deposited material.10–12) Later, the concept has been transferred to wrought steels products, leading to the introduction of the titanium deoxidised steels in the early nineties.13–16) Currently, a wide variety of different steels in which non-metallic inclusions are used to control the microstructure evolution in the solid state have been patented, both in Europe and Japan.17–19) This reflects an increasing interest among the international steel manufacturers to exploit the possibility offered by the technology to produce new low-cost steel grades with unique transformation characteristics on a commercial basis.

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.20) Cerium has a strong affinity to sulphur and will, almost always, form a compound with sulphur when both elements are present in molten steel.21,22) 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.23) Unfortunately, modern steelmaking involving continuous casting does not allow large amounts of ferroalloys to be added late in the process due to the practical problems this will cause in terms of a severe temperature drop and incomplete alloy dissolution and mixing 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% S.24) Cerium is in this context interesting, since it can dissolve large amounts of sulphur in the liquid state.25) 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.23)
of Ce, Al and FeS₂ (pyrite), which are melted and superheated to about 2000°C in tantalum crucibles under the shield of cleaned argon. However, in order 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 observed within the as-solidified samples are CeS, Ce₃Al, Fe₂Ce and Ce, along with Ce₂O₂S, which is an undesirable microconstituent in the grain refiners. Both Ce₃Al, Fe₂Ce and Ce are inclined to form low melting eutectics, whereas the stable high-temperature phase CeS constitutes a discontinuous dendritic network within the grain refiners. The indications are that pyrite can be used as a sulphur source up to about 4 wt% S added, corresponding to about 3 wt% of retained sulphur in the grain refiners. At higher levels the Fe-Ta interaction becomes so vigorous that tantalum is no longer an inert refractory metal and wetting becomes a major problem. Eventually, this will force the melt to run over the crucible rim and also lead to attacks on the outside walls.

In the present investigation, attempts will be made to produce the CeS-based grain refiners without adding iron by using Ce₂S₃ as the sulphur source. According to the binary Ce–S phase diagram the solubility of sulphur in liquid cerium at 2000°C should be of the order of 10 wt%, which is formidable compared to that inferred from other potential systems like Fe–Mn–S and Dy–S but more similar to that of La–S. Although between 2 and 5 wt% of aluminium is needed to improve the long-term stability of the grain refiners in contact with air by promoting the Ce₃Al compound formation, such small aluminium additions would not be expected to impose large restrictions on the sulphur solubility. Still, this needs to be verified experimentally by carrying out a series of exploratory measurements of the phase relations within the ternary Ce–S–Al system. The results will then be compared with those obtained employing pyrite as a sulphur source and eventually used to reassess the Ce–S phase diagram, which is believed to provide misleading information about the sulphur solubility in liquid cerium.

2. Experimental

Figure 1 shows a sketch of the cerium-rich corner of the ternary Ce–S–Al phase diagram and the composition range examined in the present investigation. Specifically, the following three different series are included in the experimental programme, i.e. Series I with no Al additions and 0, 2, 4, 5, 6 and 7 wt% S added, Series II with 2 wt% Al additions and 0, 2, 4, 5 and 6 wt% S added and Series III with 5 wt% Al additions and 0, 2, 4, 5 and 6 wt% S added.

2.1. Charge Materials and Sample Preparation Procedures

The charge mixtures were prepared from high purity raw materials, i.e. γ-Ce, Ce₂S₃ and Al, all with a purity greater than 99.9%. These were obtained from different commercial manufacturers. To prevent the materials from oxidising, an argon-filled glove box with oxygen and humidity levels <0.1 ppm was used for storage, weighing and subsequent charging of the materials into the small tantalum crucibles used in the melting trials. In the present laboratory experiments the typical sample weight is about 0.8 g, which can be measured with an accuracy of about ±0.0001 g.

After weighing the charged tantalum crucibles were transported to the vacuum furnace inside an argon-filled container.

2.2. Melting Experiments

The vacuum furnace, which originally is designed for in situ wetting angle measurements, is equipped with a sample holder capable of heating small tantalum crucibles with an outer diameter of 10 mm. Figure 2 shows a drawing of the main parts of the furnace. The heating element is made of graphite, as are all of the 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. To protect the sample from oxidising, the vacuum furnace is constantly flushed with high purity argon. This, together with the oxygen scavenging effect provided by the graphite heating element at temperatures above 1 800°C, is sufficient to prevent cerium from oxidising during the melting experiments. Further details are given elsewhere.

Figure 3 shows a record of the actual crucible temperature as a function of time during a typical rapid heating cycle at ~1 000°C/min. In these small-scale laboratory experiments it is essential that the heating rate is high enough to kinetically suppress the oxygen absorption from the shielding gas before the graphite takes control of the oxygen level at about 1 800°C. When the target superheat temperature of 2 000°C is reached the samples are held at that temperature for 3 min to allow the Ce₂S₃ to dissolve into the melt. This holding time is sufficient to reach sulphur saturation at 2 000°C because supplementary test results (not reported here) show that there is no real difference in neither the Ce₂S₃ dissolution behaviour nor the subsequent CeS compound formation during cooling between...
samples held at 3 and 6 min.

2.3. Optical and Electron Microscopy

Standard metallographic techniques were employed to prepare cross section samples for microstructure characterisation. Because $\gamma$-Ce corrodes vigorously in water, wet grinding was carried out using an alcohol-based lubricant. In the light microscope the microstructure was readily revealed without etching. The optical examination was performed using a conventional Zeiss reflecting light microscope. In addition, phase characterisation was done employing backscatter electron (BSE) imaging and wavelength dispersive X-ray spectrometry (WDS). These investigations were carried out in a JEOL JXA-8500F electron microscope, using an acceleration voltage of 15 keV and a probe current of 30 nA.

2.4. Volume Fraction Measurements

Standard point counting techniques were used to measure the volume fraction of the different constituent phases present in each sample.29) This was done by taking 10 optical micrographs at a magnification of 200×, which subsequently were provided with 10×20 square grids to ease the point counting. The microstructure data were recorded and processed using the Visual Basic point count programme CPCe V3.5.30) A total of 2 000 points was counted for each sample, from which the mean values and the standard deviation of the means were calculated. The measured volume fractions of the different constituent phases (cp) were then compared with the calculated ones, based on the following equation:

$$f_{cp} = \frac{m_{cp}}{m_a} \rho_a$$

where $m_a$ is the total weight of the alloy and $m_{cp}$ is the total mass of a given phase in the alloy, assuming 100% yield of the charged elements and the formation of stoichiometric compounds. The symbols $\rho_a$ and $\rho_{cp}$ in Eq. (1) represent the corresponding densities of the alloy and the constituent phase being considered in the calculations.

In order to ensure the highest possible confidence in the calculations, measured values for the density of the alloys $\rho_a$ should be used. Archimedes principle of buoyancy was therefore adopted to measure the density of samples from the three different series included in the investigation. By extrapolating the experimental data up to 7 wt% S, separate density plots for Series I, II and III were constructed, as shown in Fig. 4.

3. Results

3.1. Phase Characterisation

In the following, the main results from the microstructure and phase characterisation will be presented. Note that the microstructure data reported below refer to the 5 wt% S samples from Series I, II and III, which contain a representative selection of the phases being present in the alloys mentioned in Fig. 1.

3.1.1. Series I

Figures 5(a) and 5(b) show one optical and one BSE image, respectively at low and high magnification of the 5 wt% S sample from Series I. The numbers are given in at%.

Table 1. Point analyses of various phases detected in the 5 wt% S sample from Series I. The numbers are given in at%.

<table>
<thead>
<tr>
<th>No.</th>
<th>Al</th>
<th>O</th>
<th>S</th>
<th>Ta</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>3.4</td>
<td>46.1</td>
<td>0.0</td>
<td>30.5</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>62.9</td>
<td>0.1</td>
<td>0.0</td>
<td>36.8</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>40.1</td>
<td>17.5</td>
<td>0.0</td>
<td>42.4</td>
</tr>
</tbody>
</table>

Fig. 3. Graphical representation of the measured crucible temperature $T$ as a function of time during a typical rapid heating cycle (i.e. $\sim 1\,000^\circ$C/min).

Fig. 4. Plots showing the measured density of samples from Series I, II and III, respectively as a function of the added sulphur content.

Fig. 5. (a) Optical and (b) BSE micrographs of the 5 wt% S sample from Series I at low and high magnification, respectively. The arrows indicate the position of the three point analyses reported in Table 1.
ratio between Ce and S found in phase No. 1 points toward CeS. In this sample all CeS is present in the form of a discontinuous dendritic network within the matrix, as shown by the optical micrograph in Fig. 5(a). Moreover, it follows that the matrix, corresponding to phase No. 2 in Table 1, consists mainly of cerium and oxygen. Because this area shows signs of surface corrosion, it is reasonable to assume that the γ-Ce has been oxidised either during or immediately after the metallographic preparation. Hence, phase No. 2 is most likely γ-Ce with a surface layer of Ce₂O₃ or CeO₂.²⁶ In addition, needle-shaped particles can also be observed within the microstructure. As judged from the point analysis of phase No. 3 in Table 1, this phase is probably Ce₂O₂S, which is the most stable cerium oxysulphide and therefore will inevitably form in the presence of oxygen.²⁶,²⁸

3.1.2. Series II

Figure 6 shows an optical micrograph of the 5 wt% S sample from Series II at low magnification. Two distinct regions can be detected in this image, i.e. Region I containing CeS dendrites and Region II containing CeS particulates, which is similar to that observed in Series I at 6 and 7 wt% S added (not shown here). Close-ups of Region I and II are shown by the BSE images in Figs. 7(a) and 7(b), respectively. Note that the arrows in the electron micrographs indicate the position of the six point analyses reported in Table 2. The point analyses No. 1 through 5 refer to Region I in Fig. 7(a). The phases observed in position 1 and 2 are CeS and γ-Ce (with a surface layer of CeO₂/Ce₂O₃), respectively. In Region I the CeS forms a discontinuous dendritic network similar to that observed for Series I in Fig. 5. The γ-Ce, on the other hand, is no longer present as an isolated phase, but is part of a lamella-shaped eutectic. It follows from the point analyses of position 3 and 4 in Fig. 7(a) that the ratio between the constituent elements reported in Table 2 corresponds to CeO₂/Ce₃O₇ and Ce₃Al. However, as pointed out in Sec. 3.1.1, the cerium-oxide is probably γ-Ce which has been oxidised during the metallographic preparation. Hence, the eutectic phase consists most likely of γ-Ce and Ce₃Al. In addition, the point analysis carried out in position 5 shows that needle-shaped Ce₂O₂S particles also are present within the sample because of reactions with dissolved oxygen being picked-up from the shielding gas.²⁸

Moreover, it is evident from Table 2 that Region II also contains CeS as shown by the point analysis of position 6 in Fig. 7(b). Their characteristic particulate morphology suggests that they are of a different physical origin compared to the CeS dendrites. In-between, a eutectic phase is observed, which probably is the same as the one detected within Region I. This follows from a comparison of the two BSE images in Figs. 7(a) and 7(b), respectively. In addition, a number of large pores can be seen within the microstructure, which are either gaseous or shrinkage pores. Because these always appear together with the CeS particulates, it is reasonable to assume that they are associated with the conversion of Ce₂S₃ to CeS in regions of the melt already saturated with respect to sulphur (to be discussed later).

3.1.3. Series III

Figures 8(a) and 8(b) show one optical and one BSE image, respectively at low and high magnification of the 5 wt% S sample from Series III. In this case the arrows in the latter micrograph indicate the position of the five point analyses reported in Table 3. It follows from Table 3 that the two phases observed in position 1 and 2 are CeS and Ce₃Al. Adjacent to these, the eutectic phase is located, which according to the point analyses of position 3 and 4 consists of CeAl and Ce₃Al, respectively. Furthermore, the phase observed in position 5 is tantalum. This tantalum stems from reactions with the crucible, which at 2000°C has a limited solubility in liquid cerium.²⁵

In addition to the CeS dendrites observed in Fig. 8(a) the 5 wt% S sample from Series III also contained CeS particulates analogous to that documented for Series II in Fig. 6. For an addition of 6 wt% S the CeS particulate formation is even more pronounced, as shown in Fig. 9(a). At the same
time remnants of an intermediate reaction product are present at the interface between the pores and the surrounding CeS particulates, as evidenced by the electron micrograph in Fig. 9(b). It follows from Table 3 that the phase detected in position 7 adjacent to the CeS in position 6 is Ce$_3$S$_4$. This suggests that the conversion of Ce$_2$S$_3$ to CeS occurs in steps via the intermediate Ce$_3$S$_4$ phase, which results in S$_2$(g) rejection and subsequently pore formation along with CeS particulate precipitation in regions of the melt already saturated with respect to sulphur.

### 3.2. Quantitative Volume Fraction Measurements

In Table 4, the results from the quantitative metallographic examination of the various phases detected in the samples from Series I, II and III are summarised. Included is also the standard deviation in the measurements, which provides a good indication of the samples homogeneity in each case. Note that the volume fraction measurements have only been carried out within Region I. The CeS particulates are excluded from these analyses, as they form in regions of the melt already saturated with respect to sulphur, and are thus of a different physical origin compared to the CeS dendrites.

Figures 10(a) and 10(b) show graphical representations of the measured volume fractions of CeS, γ-Ce, Ce$_3$Al and CeAl in the samples from Series I, II and III as a function of the added sulphur content. The dotted lines in Fig. 10(a) represent the calculated volume fractions of CeS assuming 100% sulphur yield, according to Eq. (1). A closer inspection of the trend lines in Fig. 10(a) shows that the use of Ce$_2$S$_3$ as a sulphur source implies a yield of 100% up to the point where saturation is reached. In the case of the binary Ce–S system (Series I) sulphur saturation at 2000°C is reached at about 6 wt% added, corresponding to a volume fraction of CeS of approximately 0.34 in the as-solidified sample. At this point the CeS particulates start to appear within the microstructure, which suggests that the two phase field region is entered. When aluminium is added the overall picture is similar. Still, the aluminium additions have a marked effect on the sulphur solubility, which at 5 wt% Al is reduced to about 3.3 wt%, corresponding to a

![Fig. 8](image1)
![Fig. 9](image2)

Table 3. Point analyses of various phases detected in the 5 wt% S sample from Series III. The numbers are given in at%.

<table>
<thead>
<tr>
<th>No.</th>
<th>Al</th>
<th>O</th>
<th>S</th>
<th>Ta</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>1.3</td>
<td>47.5</td>
<td>0.1</td>
<td>50.9</td>
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<tr>
<td>2</td>
<td>23.1</td>
<td>3.7</td>
<td>0.1</td>
<td>0.0</td>
<td>73.1</td>
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<tr>
<td>3</td>
<td>45.4</td>
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<tr>
<td>4</td>
<td>22.8</td>
<td>3.8</td>
<td>0.1</td>
<td>0.0</td>
<td>73.3</td>
</tr>
<tr>
<td>5</td>
<td>2.1</td>
<td>4.3</td>
<td>0.2</td>
<td>90.9</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
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<td>1.6</td>
<td>48.3</td>
<td>0.0</td>
<td>50.1</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>1.2</td>
<td>55.7</td>
<td>0.0</td>
<td>43.1</td>
</tr>
</tbody>
</table>

Table 4. Summary of the results from the quantitative volume fraction measurements of the various phases detected in the samples from Series I, II and III.

<table>
<thead>
<tr>
<th>Series No.</th>
<th>Phase detected</th>
<th>wt% S added</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>I</td>
<td>CeS</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>γ-Ce</td>
<td>0.99±0.01</td>
</tr>
<tr>
<td></td>
<td>Ce$_2$O$_4$S</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>0.00</td>
</tr>
<tr>
<td>II</td>
<td>CeS</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>γ-Ce</td>
<td>0.63±0.03</td>
</tr>
<tr>
<td></td>
<td>Ce$_3$Al</td>
<td>0.36±0.03</td>
</tr>
<tr>
<td></td>
<td>Ce$_2$O$_4$S</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>0.00</td>
</tr>
<tr>
<td>III</td>
<td>CeS</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>γ-Ce</td>
<td>0.15±0.02</td>
</tr>
<tr>
<td></td>
<td>Ce$_3$Al</td>
<td>0.84±0.02</td>
</tr>
<tr>
<td></td>
<td>CeAl</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>Ce$_2$O$_4$S</td>
<td>0.01±0.01</td>
</tr>
<tr>
<td></td>
<td>Ta</td>
<td>0.00</td>
</tr>
</tbody>
</table>
volume fraction of CeS of 0.19. Because sulphur ties-up an equivalent (stoichiometric) amount of cerium, the content of free $\gamma$-Ce decreases when Ce$_2$S$_3$ is added to the melt, as shown in Fig. 10(b). At high aluminium levels this reduction in the $\gamma$-Ce content is also accompanied by a change in the phase balance between Ce$_3$Al and CeAl, leading to the displacive behaviour observed in the graph for Series III.

4. Discussion

In the following, the conditions for CeS formation and the subsequent precipitation reactions occurring during cooling following the Ce$_2$S$_3$ and aluminium additions to liquid cerium will be discussed in more detail.

4.1. Phase Relations within Region I

Within Region I the results from the quantitative phase detection show that both CeS, Ce$_3$Al and CeAl are present in the as-solidified samples. These are intermetallic compounds that are known from the binary phase diagrams. Figure 11 shows a sketch of the cerium-rich corner of the ternary Ce–S–Al phase diagram, in which the tie-lines connecting the observed coexisting phases within Series I, II and III are included. It follows from Fig. 11 that the three coexisting phases within phase-field A are $\gamma$-Ce, Ce$_3$Al and CeS, where the former ones also constitute the two eutectic phases shown schematically in Figs. 12(a) and 12(b) being observed at 2 and 5 wt% Al, respectively. The third eutectic phase displayed in Fig. 12(c) forms when all free $\gamma$-Ce in Series III is tied-up with sulphur and aluminium. This occurs when the sulphur level exceeds 4 wt% and the composition shifts to phase-field B in Fig. 11, yielding the three coexisting phases Ce$_3$Al, CeAl and CeS. Beside the quantitative phase characterisation reported in the present investigation, no information is available in the scientific literature about the phase relations within the ternary Ce–S–Al system. This prevents a more in-depth analysis of the precipitation sequence and the thermodynamic stability of the three eutectic phases visualised in Fig. 12.

4.2. Phase Relations within Region II

Region II refers to parts of the melt already being saturated with respect to sulphur. Therefore, the remnants of the phases detected in Fig. 9 conceal details of the dissolution kinetics of Ce$_2$S$_3$ within the two-phase region “liq+CeS” (i.e. Region II in Fig. 9). Figure 13 shows a sketch of the binary Ce–S phase diagram showing the sequence of reactions occurring during conversion of Ce$_2$S$_3$ to CeS within the two-phase region “liq+CeS”.

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gram, which is a useful model system to unravel the reaction sequence. It follows that Step 1 involves conversion of \( \text{Ce}_2\text{S}_3 \) to \( \text{Ce}_3\text{S}_4 \) according to the reaction:
\[
3\text{Ce}_2\text{S}_3 = 2\text{Ce}_3\text{S}_4 + \frac{1}{2} \text{S}_2(g)
\]  

This conversion gives rise to the release of \( \text{S}_2(g) \) bubbles and subsequent pore formation within the interior of the as-solidified samples, as shown previously in Figs. 6 and 7. In addition, the *in-situ* photograph of the tantalum crucible provided in Fig. 14 suggests that some of the gas bubbles also escape from the surface during the melting experiments. This is another indication that sulphur saturation is reached at \( 2000°C \) and explains why the curves in Fig. 10(a), representing the sulphur yield, suddenly flatten out when the solubility limit is reached at the different aluminium levels.

Moreover, Step 2 involves conversion of \( \text{Ce}_3\text{S}_4 \) to \( \text{CeS} \), most probably according to the reaction:
\[
\text{Ce}_3\text{S}_4 + \text{Ce} = 4\text{CeS}
\]  

Because Eq. (3) implies that cerium must diffuse through the \( \text{CeS} \) reaction layer in order to reach the \( \text{CeS}/\text{Ce}_3\text{S}_4 \) interface, a high conversion rate can only be maintained throughout the process if the \( \text{CeS} \) particulates are continuously rejected at the liq/\( \text{CeS} \) interface, as indicated in Fig. 13. This leads to the characteristic “two-phase region” microstructures shown previously in Figs. 6 and 9.

### 4.3. Solubility of Sulphur in Liquid Ce and Ce–Al Melts

The results from the \( \text{CeS} \) volume fraction measurements in Fig. 10(a) provide a good indication of the sulphur solubility in liquid cerium and Ce–Al melts at \( 2000°C \). At this temperature pure cerium can dissolve as much as \( 6 \text{ wt}\% \) of sulphur, which is reduced to \( 4.1 \text{ wt}\% \) at \( 2 \text{ wt}\% \) Al and further to \( 3.3 \text{ wt}\% \) at \( 5 \text{ wt}\% \) Al. Although the measured sulphur solubility is formidable, it is considerably lower than that inferred from the binary Ce–S phase diagram, which suggests that the solubility should be close to \( 10 \text{ wt}\% \) at \( 2000°C \).

In Fig. 15 the new liquidus line representing the sulphur solubility within the Ce–S system is indicated, based on the results obtained in the present investigation. Two other points on the curve are also provided, *i.e.* at \( 1800 \) and \( 1500°C \). These results have been obtained from a series of up-scaled melting experiments carried out in an induction furnace filled with cleaned argon and are sufficiently accurate to be incorporated in the present data collection. As expected, the sulphur solubility is seen to decrease with decreasing temperatures, reaching a value of about \( 1.8 \text{ wt}\% \) at \( 1500°C \). This new liquidus line is believed to be more accurate than the previous one quoted by Massalski. At the same time it is consistent with what one would expect from a comparison with the La–S phase diagram, which appears to be more firmly established and is thus a good benchmark for the present measurements.

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

When pyrite (\( \text{FeS}_2 \)) is used as a sulphur source, previous investigations have shown that aluminium additions are required to prevent the grain refiners from disintegrating during long-term storage in air. By replacing \( \text{FeS}_2 \) with \( \text{Ce}_2\text{S}_3 \) the problem with internal oxidation of free cerium is largely eliminated, as evidenced by the photographs in Figs. 16(a) and 16(b), suggesting that the observed disintegration is mainly associated with the presence of the \( \text{Fe}_2\text{Ce} \) phase in the grain refiners. Therefore, alloying with aluminium is no longer a crucial issue and should thus be restricted if the highest possible sulphur solubility is desired in the liquid state. In this way, the benchmark previously set for the sulphur content in the grain refiners can be met.

### 5. Conclusions

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

1. CeS-based grain refiners can be produced from high-purity charge materials of cerium, aluminium and
Ce$_2$S$_3$, which are melted and superheated in tantalum crucibles under a shield of cleaned argon.

(2) During melting the dissolution of Ce$_2$S$_3$ occurs in steps via the intermediate Ce$_2$S$_4$ phase, which results in S$_2$(g) evolution and subsequently CeS particulate formation. In spite of this decomposition reaction, the observed sulphur yield is close to 100% up to the point where saturation is reached, meaning that both components are fully absorbed within the liquid cerium melt.

(3) The phases detected in the as-solidified samples are CeS, Ce$_3$Al, CeAl and $\gamma$-Ce, along with Ce$_2$O$_2$S, the latter one being an undesirable microconstituent in the grain refiners. Both Ce$_3$Al, CeAl and $\gamma$-Ce are inclined to form low melting point eutectics, whereas the stable high-temperature phase CeS constitutes a discontinuous dendritic network within the grain refiners.

(4) The results show that pure cerium can dissolve up to 6 wt% of sulphur at 2 000°C, which is reduced to about 1.8 wt% at about 1 500°C. This solubility is considerably lower than that inferred from the binary Ce–S phase diagram, which suggests that it should be close to 10 wt% at 2 000°C.

(5) Based on the results obtained in the present investigation the binary Ce–S phase diagram has been revised to comply with the new solubility data. The liquidus line being constructed is believed to be more accurate than the one previously reported in the literature. At the same time it is consistent with what one would expect from a comparison with the La–S system, which appears to be more firmly established and is thus a good benchmark for the present measurements.

(6) Moreover, it is confirmed that alloying with aluminium has a clear negative effect on the solubility of sulphur in liquid cerium. Thus, at 2 000°C it drops from initially 6 wt% to 4.1 wt% at 2 wt% Al added and further to 3.3 wt% at 5 wt% Al added.

(7) In addition, when Ce$_2$S$_3$ is used as the sulphur source in replacement of pyrite (FeS$_2$) the previously experienced problem with internal oxidation of free cerium in the grain refiners is largely eliminated. Therefore, alloying with aluminium is no longer crucial and should thus be restricted if the highest possible sulphur solubility is desired in the liquid state.

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