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# Kinetics of thermal synthesis of cerium sulfides

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ABSTRACT

One of the most promising applications for cerium sulfide is as a refractory for molten metal processing, particularly for reactive actinides. Separate processes were used to synthesize cerium monosulfide, cerium sesquisulfide ($Ce_2S_3$) and cerium hydride ($CeH_2$). High purity $Ce_2S_3$ was produced by reacting ceria ($CeO_2$) and hydrogen sulfide ($H_2S$) in an induction furnace using a carbon catalyst at temperatures above 2000 °C. $CeH_2$ was synthesized from cerium metal and hydrogen gas at 100 °C. $Ce_2S_3$ and $CeH_2$ were subsequently reacted together in an induction furnace at temperatures above 1700 °C to produce CeS. X-ray diffraction was used to analyze synthesized samples and the kinetics of the CeS synthesis reaction was modeled using a diffusion-limited reaction model. The activation energy for the process was estimated to be 190 kJ/mol.

## 1. Introduction

There are four sulfides of cerium which exist with chemical compositions $CeS_2$, $Ce_2S_3$, $Ce_3S_4$, and CeS. Three of the cerium sulfides have been investigated in the past and have properties that can be used in a wide variety of applications from high temperature pigments to semiconductors [1,2]. Cerium disulfide ($CeS_2$) has not been studied in detail, has no known application, and is not encountered during the synthesis of the other sulfides. Although the cerium sulfides are somewhat difficult to produce, their interesting properties and high temperature capabilities have warranted research into the synthesis procedures associated with these compounds. An attractive application of CeS, $Ce_2S_3$, and $Ce_3S_4$ is as high temperature crucibles as they have been shown to have low reactivity to many molten metals including alkali metals and actinides [3].

CeS has 18.6 wt% sulfur and is a cubic crystalline compound with the sodium chloride crystal structure and a brassy-yellow color. It has the best high temperature characteristics of the cerium sulfides with volatilization occurring above 2450 °C, and a vapor pressure of $10^2$ mPa at 1900 °C [4]. Vaporization of CeS takes place congruently leaving the stoichiometry of the bulk material intact below 2500 °C. CeS has good thermal shock resistance like the other sulfides and can be cooled at 1000 °C/min without fracturing [5]. While performing better than the other sulfides in many areas, CeS does have lower oxidation resistance than the other sulfides and will oxidize rapidly in air above 200 °C to the extent that its properties are degraded. This can be avoided by heating in an oxygen free environment.

CeS is an excellent crucible material due to the wetting characteristics it has with other materials. It shows little interaction with nearly all metals except for platinum. Molten platinum reacts vigorously with CeS to produce the intermetallic compound CePt that destroys the crucible. CeS is also non-wetting to actinide metals that are known for heavily corroding crucibles used to process and handle them. This makes CeS an excellent candidate material for crucibles in this and many other applications [6]. Minimal interaction between the crucible and metal allows crucibles to be reused, reducing costs and reducing environmental waste from replacing broken or corroded crucibles.

At present there is little reported literature on the synthesis of the sulfides of cerium, especially CeS. This sulfide has the most beneficial properties and the largest potential to be used in an industrial setting among the cerium sulfides. An objective of the present work was to determine the feasibility and details associated with a particular reported procedure for CeS synthesis. Another objective of the work was to quantify the kinetics associated with the synthesis reaction. A detailed synthesis procedure coupled with the kinetics data would greatly assist in the large-scale production of CeS. Thermodynamic modeling for the reactions associated with the synthesis of $Ce_2S_3$ and CeS was done by Hogan [7].

## 2. Experimental procedures

Several notable methods have been reported for the production of CeS, each one involving the reaction of cerium sesquisulfide $Ce_2S_3$ with another cerium bearing material to produce CeS. The

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conditions associated with the synthesis of $Ce_2S_3$ and CeS are briefly outlined in this section and details can be found in Gibbard [8].

### 2.1. Cerium sesquisulfide synthesis

The two methods used to produce $Ce_2S_3$ are sulfidation by $CS_2$ and sulfidation by $H_2S$ [3]. The former procedure was not used in these studies because of the long reaction time reported and the significant amounts of carbon and oxygen impurities present in the final product.

In 1950 Eastman produced $Ce_2S_3$ through the reduction of ceria with $H_2S$. It was speculated that the reaction steps were

$$6CeO_2 + 4H_2S \rightarrow 3Ce_2O_2S + 4H_2O + SO_2 \tag{1}$$

followed by

$$Ce_2O_2S + 2H_2S + 2C \rightarrow Ce_2S_3 + 2CO + 2H_2. \tag{2}$$

Eastman also indicated that the second reaction step could involve a gaseous CS species as another intermediate. The reaction required at least 2 h at a temperature of 1500–1700 °C to go to completion. This process produced high purity $Ce_2S_3$ in a much shorter time than the alternative method of sulfidation by $CS_2$ [3]. The drawbacks of the $H_2S$ method include the use of corrosive $H_2S$ and the need for higher reaction temperatures.

### 2.2. Cerium monosulfide production

Several notable methods for the production of cerium monosulfide include aluminothermic reduction [9], carbothermic reduction [10], electrolytic reduction [5] and reduction by cerium hydride [4]. The different reaction methods were compared to determine which method had the most desirable qualities. The last method involving cerium hydride $CeH_2$ was selected.

Cerium hydride can be used to reduce $Ce_2S_3$ to CeS following the reaction

$$Ce_2S_3 + CeH_2 \rightarrow 3CeS + H_2. \tag{3}$$

The experimental conditions reported for this reaction include a temperature of 2200 °C and a pressure of $10^1$ mPa [4]. Only a few minutes were needed for the reaction to proceed to completion. A variation of this method was used by Krikorian who produced CeS by arc melting $Ce_2S_3$ with cerium metal in an argon atmosphere [11].

A significant advantage of this method over the other methods includes the use of additional cerium-bearing material in the process to increase yield and enhance the purity of the resulting CeS. A slight excess of $CeH_2$ is used when combining the reactants to eliminate impurities such as oxygen from the final product. Some challenges encountered when using this method include the high reaction temperature and the production and handling of $CeH_2$ which oxidizes readily when exposed to air. This method of CeS production was chosen due to the high purity reported; it does not require any further purification steps which cause a loss of product and decreased reaction yield. Additionally, only a few minutes are required at high temperature for the reaction to go to completion as compared to the hours needed for the other types of reduction processes.

## 3. Experimental apparatus

The method chosen for the production of CeS involved three processes each needing its own specifically designed reactor. Reactors were constructed with a capacity to produce a few grams of the CeS at a time. The different reactors are briefly described in this section and details can be found in Gibbard [8].

### 3.1. Ceria sulfidation reactor

Cerium sesquisulfide was made by the reaction of ceria with hydrogen sulfide at 1500 °C in the presence of carbon. The ceria sulfidation reactor consisted of a 2.5 cm inner diameter jacketed chromatographic column with a 5 cm outer diameter. Cooling water was circulated through the jacketing to prevent overheating of the column. The column was placed in a fume hood within a three-turn induction coil made from 0.25 in. copper tubing. The induction coil was part of a 5-kW induction power supply which required an independent cooling water system.

The ends of the reactor column were sealed with PTFE caps that contained polymeric o-ring seals that fit against the glass reactor column. The end caps contained threaded channels through them allowing for stainless steel gas lines to be attached at both ends. A 0.375 in. stainless steel sight tube was connected to the top end cap to give a clear line of sight for temperature measurement by an Omega 2-color infrared pyrometer and a 0.25 in. stainless steel gas line was used to bring gasses into the column through a T-joint. The pyrometer was selected to keep temperature measurement equipment out of the magnetic field of the induction heater and was calibrated by correlating the melting temperature of pure metals (copper, nickel, and platinum) to the reading on the pyrometer at melting in the experimental setup. This calibration was used to verify the adequacy of the grey body approximation used. Eastman reported that the reaction of ceria with hydrogen sulfide will not go to completion in the absence of carbon and that a gaseous carbon sulfide intermediate may be involved in reducing $Ce_2O_2S$ to cerium sesquisulfide per reaction (2) [4]. To ensure that the reaction would go to completion the sight tube was fitted with a carbon tip to enhance the production of any beneficial carbon intermediate. The bottom end cap contained 0.25 in. stainless steel fittings to allow for gas to be exhausted through cold water before being vented into the back of the fume hood. Crucibles to hold the reactants were made from 0.625 in. diameter carbon rods which were cut into 0.5 in. segments and had a 0.375 in. hole drilled in the center. Each crucible was surrounded with insulating zirconia felt. A stand made from rolled zirconia felt was used to hold the sample in the center of the reaction column where it would be surrounded by the induction coil. Several layers of carbon felt were placed on top of and below the crucible to provide insulation. A schematic diagram of the setup of the column is shown in Fig. 1(a).

### 3.2. Cerium hydrogenation reactor

Cerium hydride was produced by the reaction of hydrogen gas with cerium metal at 100 °C in a vacuum purged tube furnace. Both cerium metal and cerium hydride are reactive in air and will oxidize spontaneously to produce cerium oxides when exposed. A glove box with an inert argon atmosphere was used when handling these two materials. An oxygen analyzer was used to monitor the oxygen content inside the glove box while handling reactive species. An oxygen content of 500 ppm was maintained when handling these materials.

The reacting gas used in the procedure was pure hydrogen similar to reported work for the production of cerium hydride [12,13]. A stainless steel dilution chamber was set up inside the glove box where the exhaust gas from the reactor could be mixed with argon before being vented out of the system. A dual stage rotary vane vacuum pump was used for purging the tube furnace and for cycling gas through the glove box to reduce the oxygen concentration present.

The glove box contained the equipment necessary to section the cerium metal into pieces as well as a small tube furnace where the reaction was performed. The furnace was equipped with a 1 in. diameter stainless steel tube with fittings to 0.25 in. stainless steel

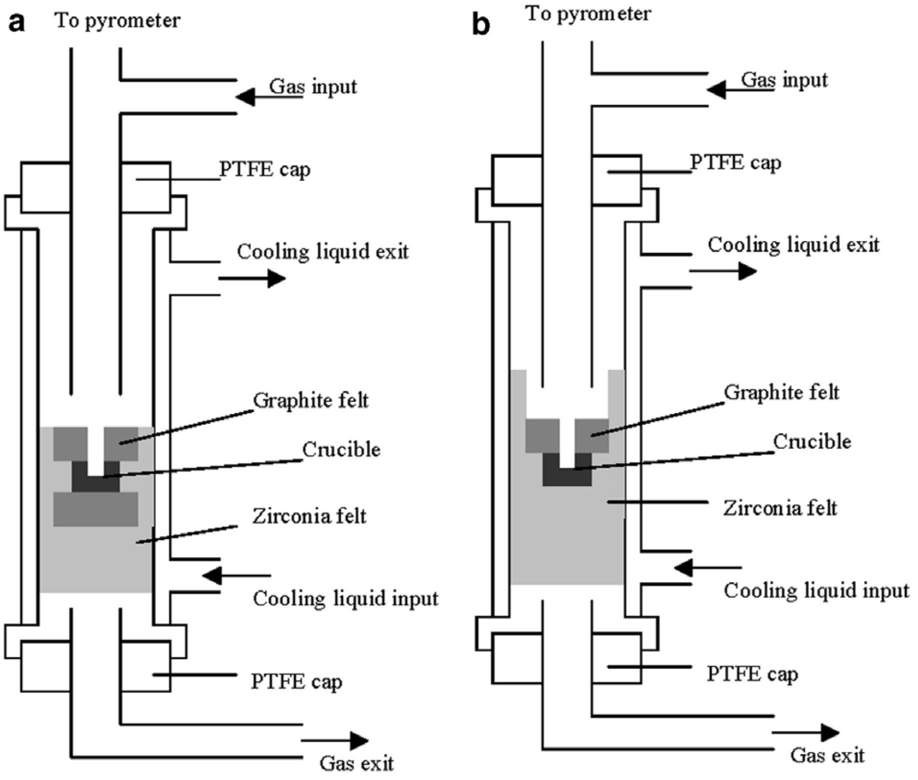

**Fig. 1.** Schematic diagrams of the ceria sulfidation reactor column (a) and cerium monosulfide reactor column (b).

tubes at each end for the entry and exhaust of reaction gasses. A copper boat was made to hold the cerium metal while in the tube furnace with a copper retaining wire to move the boat in and out of the furnace.

### 3.3. Cerium monosulfide reactor

The synthesis of CeS was done in experimental apparatus similar to the ceria sulfidation reactor. A jacketed chromatographic column was used as the reactor and replaced the $Ce_2S_3$ reactor within the induction coil. The bottom end cap of this reactor was a solid PTFE plug and the top end cap contained a stainless steel valve to isolate the contents of the column from atmosphere. The addition of the valve allowed for an inert argon atmosphere inside the column to be maintained while it was moved and connected to a vacuum pump. The reactor and the $Ce_2S_3$ and cerium hydride reactants were assembled in an argon atmosphere glove box. The box was equipped with a microbalance for weighing and mortar and pestle for mixing the two compounds.

The reactant mixture was heated to temperatures from 1200 to 1750 °C and a pressure of $10^3$ mPa to synthesize CeS.

The vacuum required during the reaction allowed for less insulation to be used inside the column as compared to the $Ce_2S_3$ reactor. Zirconia felt was used as a stand for a molybdenum or molybdenum-lined carbon crucible, which was wrapped with more zirconia felt. A small ring of carbon felt was also included above the crucible to act as an oxygen getter in an effort to reduce the effects of any oxygen remaining in the system. A schematic diagram of the setup of the reactor column can be seen in Fig. 1(b).

## 4. Experimental results

The samples produced in the experiments conducted were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD was used to determine the phases present and their relative amounts. Both qualitative and quantitative XRD were performed on the samples synthesized. SEM was used to produce images of the powders made during the experiments from which sizes of individual particles were determined.

XRD samples were obtained by grinding sample pellets in a mortar and pestle to create a fine powder. A glass slide was labeled with the designation of the sample and a 1 cm square piece of double-sided tape was placed in the center of the slide. A portion of the sample powder was placed on the tape and spread with a small spatula to cover the entire area of the tape. Samples were stored in a dessicator and analyzed within four days of being produced.

### 4.1. Cerium sesquisulfide results

Many experiments were performed to determine a synthesis procedure that produced homogeneous $Ce_2S_3$ that was free from oxygen impurities. Initial samples produced were heterogeneous and contained large amounts of oxygen impurities in the form of cerium thiosulfide ($Ce_2O_2S$). Though cerium sesquisulfide was also present in these samples the cerium thiosulfide dominated the XRD patterns. XRD scans on material taken from the core and the surface of a given sample indicated that the cerium thiosulfide was more concentrated in the sample's core than at the sample's surface.

Eastman described the reaction of ceria and $H_2S$ in the absence of carbon and showed that under these circumstances cerium thiosulfide was the only product phase with no production of cerium sesquisulfide [14]. Based on this observation it was decided to increase the carbon content available to react with the ceria powder. Powdered carbon black was mixed with the reactant ceria powder before being loaded into the crucibles. It was found that the oxygen impurities were removed from a previously reacted sample by adding carbon and reheating the sample at 1500 °C under flowing

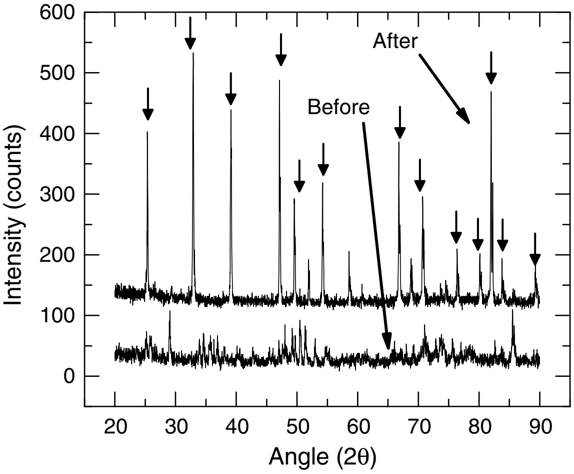

**Fig. 2.** X-ray diffraction scans of cerium sesquisulfide samples before and after purification. The plot associated with the after purification sample was displaced by an intensity of 100 counts. The arrows included are reference markers associated with cerium sesquisulfide.

hydrogen sulfide. XRD scans taken from a $Ce_2S_3$ sample before and after purification are shown in Fig. 2. The presence of the oxygen in the form of cerium thiosulfide was indicated by the presence of its XRD peaks. The absence of these peaks in the purified sample demonstrated the removal of the oxygen by the completion of the reaction between the thiosulfide and $H_2S$.

Samples produced after increasing the carbon content of the reactants had the characteristic red color of $Ce_2S_3$ and were determined to be $Ce_2S_3$ by XRD. Even if a slight stoichiometric surplus of carbon was added to the reactants no carbon peaks were observed in the resulting XRD spectra. This may indicate that excess carbon reacted with oxygen present to produce gaseous carbon monoxide or with the hydrogen sulfide to produce a gaseous carbon sulfide compound.

### 4.2. Cerium hydride results

Cerium hydride is a non-stoichiometric compound with a chemical formula of $CeH_x$ where $x$ varies from 2 to 3. This compound shows a large extent of disorder in the crystal lattice and the amount of hydrogen incorporated can cause shifts in the XRD peak locations and changes their intensities. These factors as well as the reactivity of cerium hydride in air complicated the use of XRD as a characterization technique. Cerium hydride samples were analyzed within minutes of being removed from the inert atmosphere they were stored in to avoid as much oxidation as possible.

The samples that were produced took a black, rough appearance and the XRD spectra showed peaks indicating the presence of cerium hydride. An XRD scan taken from a cerium hydride sample can be seen in Fig. 3. The weak intensity of the peaks and the large amount of noise in the spectrum were indicative of the highly disordered structure of cerium hydride. The peaks were slightly shifted from those documented in the JCPDS data base, presumably due to variation in stoichiometry. If samples were allowed to sit for several weeks, even in an environment with a low oxygen concentration, the resulting powder took on the characteristic yellow color of cerium oxide. This result was verified by XRD.

The cerium hydride was also analyzed to determine the stoichiometry of the compound. Samples were weighed and allowed to oxidize in air for many days. Once the samples had taken on a uniform yellow color they were reweighed and the difference in mass was used to calculate the amount of hydrogen that was originally incorporated into the cerium hydride. The combination of XRD and oxidation results indicated that the cerium hydride produced had a composition of approximately $CeH_{2.7}$ [7].

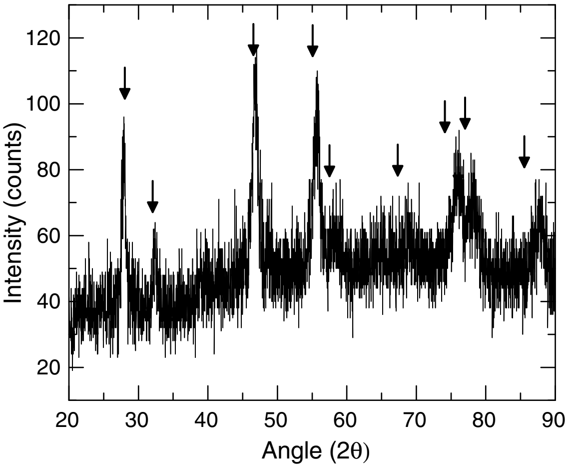

**Fig. 3.** X-ray diffraction scan of cerium hydride sample. The arrows included are reference markers associated with cerium hydride.

### 4.3. Cerium monosulfide results

Qualitative XRD patterns and quantitative XRD data were collected to analyze the synthesized CeS. Quantitative XRD was used to determine the amount of CeS produced during the experiments. These data were used to relate the amount of CeS produced to the degree of completion of the reaction and from this, the kinetics of the synthesis reaction.

Samples taken from the CeS reactor were a brassy yellow color and were shown by XRD to be CeS free of any significant impurities. XRD scans taken of two different CeS samples are shown in Fig. 4. The two samples of CeS were synthesized from independently produced samples of both cerium sesquisulfide and cerium hydride. The reaction conditions associated with these samples were a temperature of 1750 °C for 20 min.

The CeS synthesis reaction was observed to be sensitive to the presence of oxygen in the reactants. If the cerium hydride had oxidized partially before being reacted the resulting CeS sample contained oxygen impurities in the form of cerium thiosulfide. The use of carbon crucibles also changed the structure of the final product.

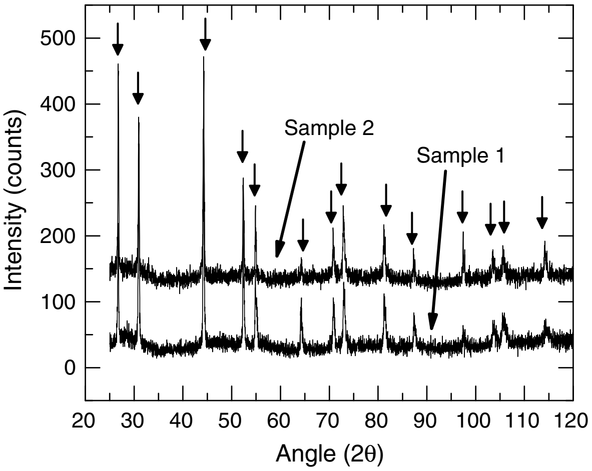

**Fig. 4.** X-ray diffraction scans of cerium monosulfide samples. The plot associated with Sample 2 was displaced by an intensity of 100 counts. The arrows included are reference markers associated with cerium monosulfide.

To prevent this, crucibles used for this reaction were either molybdenum or carbon with a molybdenum foil lining that isolated the contents of the crucible from the carbon.

The experiments performed to determine the kinetics of the CeS synthesis reaction were done at temperatures less than 1750 °C. XRD scans associated with samples produced under these conditions showed peaks from CeS as well as $Ce_2S_3$ and were analyzed further to determine the extent of the reaction.

Quantitative XRD was used to determine the extent of reaction from the relative amounts of the phases present. This analysis was done using the internal standard method where reference samples are made with a known weight of a reference powder before analyzing experimental samples [15,16]. This method avoids complications involving the determination of the X-ray absorption coefficient and density of the material. Alpha-aluminum oxide was used as a reference material in this experiment because its major diffraction peaks do not overlap with those from any of the encountered cerium compounds.

Powders with compositions ranging from 0% to 100% cerium monosulfide were mixed with equal weights of aluminum oxide to produce reference samples. These samples were then analyzed using XRD and the ratio of the peak area of the primary cerium monosulfide peak to the area of the primary aluminum oxide peak was calculated. The area ratio was then plotted as a function of sample composition to determine the calibration constant that would be used to calculate the amount of CeS present in samples with an undetermined composition using the equation

$$(A_{\mathrm{CeS}}/A_{\mathrm{Al_2O_3}}) = k(X_{\mathrm{CeS}}/X_{\mathrm{Al_2O_3}}). \tag{4}$$

The calibration curve produced can be seen in Fig. 5.

Samples produced experimentally were mixed with an equal mass of aluminum oxide and this mixture was then analyzed using XRD. The amount of CeS present in the sample was determined by comparing the relative intensity of the CeS peak to the intensity of the aluminum oxide peak in the sample against the calibration constant calculated from known mixtures in the reference samples. The data taken from this analysis is presented in the Kinetics Analysis section.

Scanning electron microscopy was used to examine the reactant mixture of cerium hydride and $Ce_2S_3$ as well as the synthesized CeS powder. A portion of a $Ce_2S_3$ and cerium hydride mixture was placed on a carbon glue tab attached to an aluminum mount and stored in a sealed jar for transport to the electron microscope. The mount was loaded into the sample stage of the microscope as quickly as possible to prevent any reaction of the powder with the environment. The powder was analyzed to determine the particle sizes of the different materials and the homogeneity of the powder. SEM micrographs of the reactant powders can be seen in Figs. 6 and 7. Particles appeared to be faceted but shaped roughly like spheres. Though some variation existed in the size of the particles the value of 10 μm for the particle diameter was judged to be a reasonable estimate of the size.

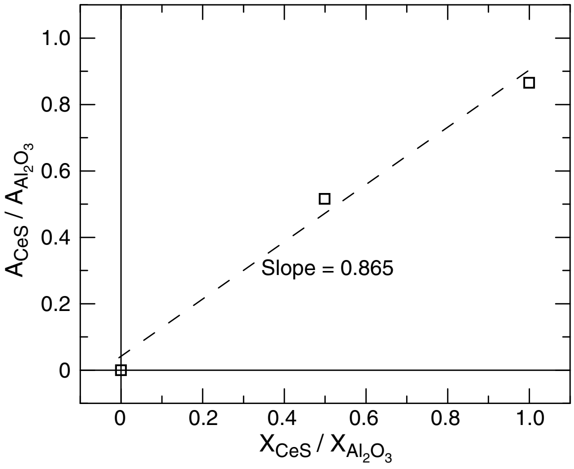

**Fig. 5.** Calibration curve for quantitative analysis.

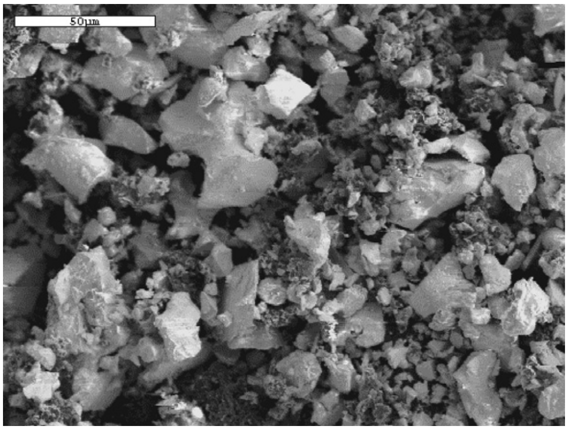

**Fig. 6.** Scanning electron micrograph of the reactant powder at 600×, 50 wt% $Ce_2S_3$ and 50 wt% $CeH_2$.

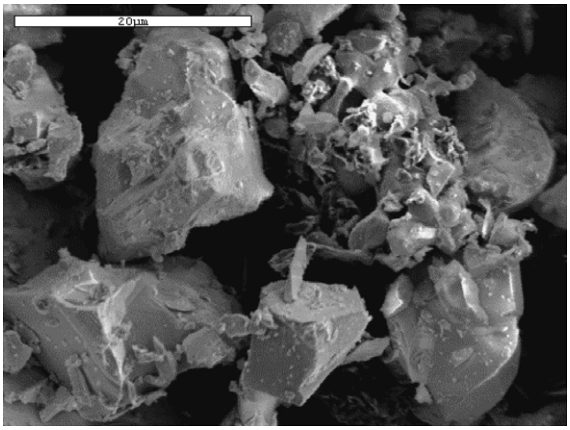

**Fig. 7.** Scanning electron micrograph of the reactant powder at 2500×, 50 wt% $Ce_2S_3$ and 50 wt% $CeH_2$.

A CeS sample from a 1750 °C, 20-min run was removed from the crucible and ground with a mortar and pestle to separate the particles. At high temperatures the CeS tended to sinter together into a solid mass that could be broken apart using moderate force with the mortar and pestle. This powder was also analyzed on a carbon sticky tab on an aluminum mount to determine the size of the powder particles. The resulting SEM micrograph of the powder can be seen in Fig. 8. The approximate particle size of the CeS powder is 10 μm, similar to the particle size of the reactant powder. The major difference between the reactant powder and CeS powder was the particle morphology. While the reactant powder appeared to be more spherical the cerium monosulfide powder was more irregularly shaped.

## 5. Kinetics analysis

The data taken from the XRD analysis was used to determine the kinetics of the reaction between $Ce_2S_3$ and cerium hydride to form CeS. CeS samples were produced at times and temperatures such that the reaction did not go to completion. Experiments were

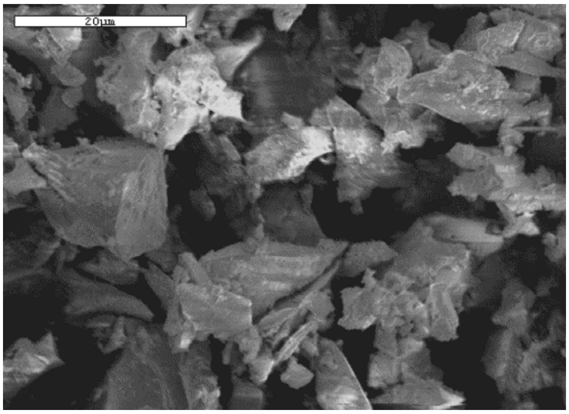

**Fig. 8.** Scanning electron micrograph of CeS powder.

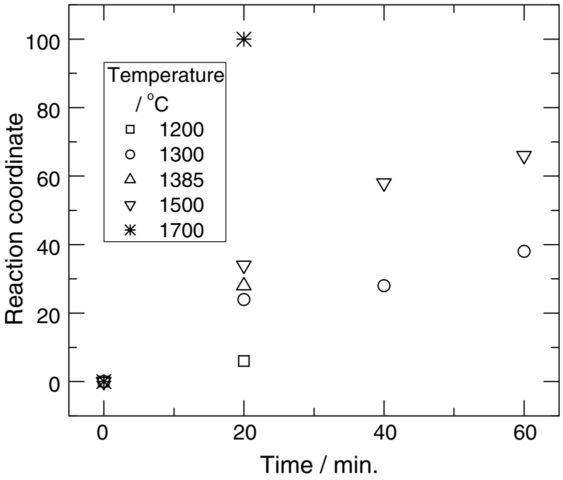

**Fig. 10.** Weight fraction of CeS produced as functions of time for different reaction temperatures.

run at several temperatures for 20 min and again at 1300 °C and 1500 °C for longer times. Very high heating rates were used to prevent reaction during heat-up from affecting the experimental results. Final reaction temperatures were typically reached within 5 s of initial heating. The extent of the reaction was determined from quantitative XRD data and analyzed using an existing model for the rate and type of reaction.

The reaction coordinate was defined as the weight percent of CeS that had been produced during the reaction. The data from experiments run for 20 min is shown in Fig. 9 as a function of reaction temperature. The reaction coordinate was observed to increase with temperature from 5% at 1200 °C to 35% at 1500 °C and then to 100% at 1750 °C. The 100% reaction coordinate at 1750 °C indicated that the reaction had gone to completion and that there were no detectable impurities in the sample of CeS.

The extent of reaction determined by quantitative XRD for samples at different temperatures and several reaction times is shown in Fig. 10. The data associated with the experiments at 1300 °C and 1500 °C were analyzed using the Jander equation for parabolic kinetics [17]. The Jander equation was developed to model the rate of reaction of diffusion-limited processes in spherical particles and was selected since it was considered likely that the CeS synthesis reaction met these conditions.

The equation

$$F = Kt/r^2 \tag{5}$$

where the parameter $F$ was given by

$$F = \left(1 - \sqrt[3]{(1-\alpha)}\right)^2 \tag{6}$$

was used to calculate the value of the rate constant, $K$, at a given temperature where the $t$ is the reaction time, $r$ is the particle radius, and $\alpha$ is the reaction coordinate. The value of $F$ as a function of time, $t$, for the data from experiments at 1300 °C and 1500 °C is shown in Fig. 11. A straight line was fit to the data from which the value of $K$ was determined. The particle radius, $r$, was determined from SEM to be approximately 10 μm. Rate constants calculated using this expression were $K = 6 \times 10^{-4}$ and $K = 4 \times 10^{-3}$ for condition temperatures of 1300 °C and 1500 °C, respectively.

Since experiments were done at more than one temperature it was possible to analyze the results and estimate the activation energy for the rate-limiting step of the reaction. This was done by using the Jander equation to find the rate constant of the reaction which is the slope of the $F$ versus time curve. This value varies with temperature according to the equation

$$K = Ce^{-q/RT} \tag{7}$$

where $q$ is the activation energy, $T$ is absolute temperature, $R$ is the gas constant, and $C$ is a constant. Fig. 12 contains a plot of ln $K$ versus $1/T$, the slope of which is $-q/R$. Although only two points can be produced for this plot since only two temperatures were investigated it is useful to get a rough estimate of $q$. The value of the

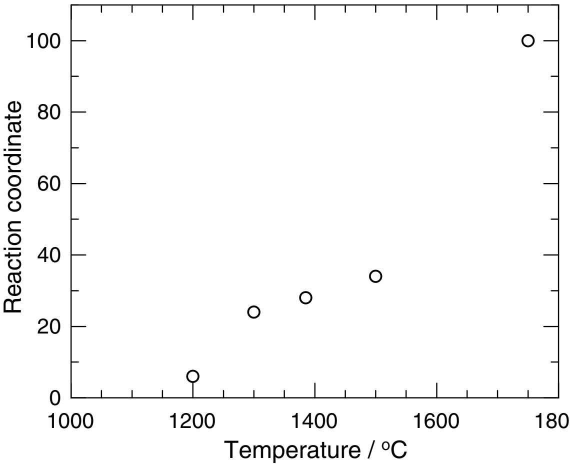

**Fig. 9.** Weight fraction of CeS produced as a function of reaction temperature at 20 min.

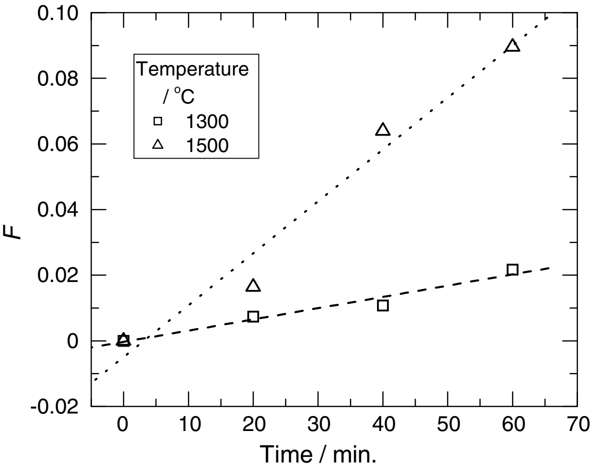

**Fig. 11.** Jander equation $F$ as a function of time at 1300 °C and 1500 °C.

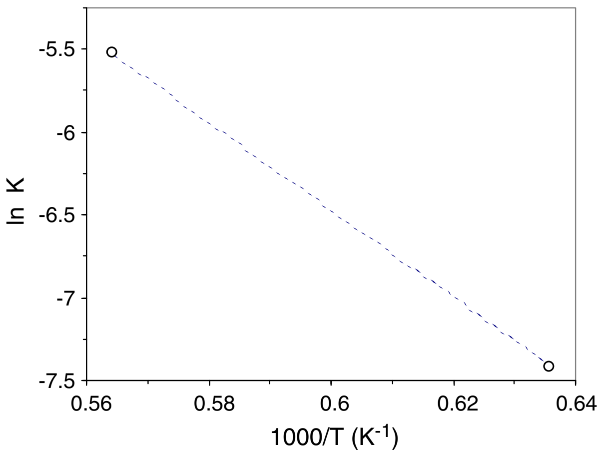

**Fig. 12.** Logarithmic value of rate constant $K$ as a function of $1000/T$ for cerium monosulfide production.

activation energy associated with the diffusion of sulfur or cerium atoms was found to be approximately 190 kJ/mol cerium monosulfide. This value was similar to the activation energy of 195 kJ/mol that was associated with the diffusion process during the removal of oxygen from ceria [19].

## 6. Discussion

The required apparatuses and details associated with procedures for the synthesis of cerium monosulfide, cerium sesquisulfide, and cerium hydride were described. The accompanying XRD scans demonstrated the applicability of these procedures. The synthesis procedure of $Ce_2S_3$ from ceria and $H_2S$ highlighted the use of a purification step that yielded samples of $Ce_2S_3$ without significant impurities. The temperature used for this procedure was 1500 °C and was consistent with that reported in literature. The procedure also demonstrated the importance of including carbon black with the reactants to increase yield. The procedural conditions used for the synthesis of cerium hydride were consistent with literature.

The focus of this work was the synthesis of CeS. As expected, it was observed that a larger extent of cerium monosulfide reaction was produced with longer reaction time and higher reaction temperature. The synthesis temperature of 1750 °C yielded a product of CeS that did not have significant impurities as observed in the associated XRD scan. This temperature was much lower than the temperature reported in literature of 2000 °C [4]. The reaction time for the experiment run at 1750 °C was 20 min, although the reaction could have been complete before the run ended. The time to complete the reaction reported in literature at 2000 °C was a few minutes, which is in agreement with this work where the reaction was completed at this temperature in a very short time. This work also demonstrated that CeS could be reproducibly synthesized at the lower temperature of 1750 °C as opposed to 2000 °C.

The Jander equation used for modeling diffusion-limited reactions fits the data reasonably well although some variation existed that could be caused by the particle size distribution and non-spherical particle morphology. Other models have been developed that take a large particle size distribution into consideration, but the sensitivity of the cerium hydride to air and moisture prevent a more detailed analysis of the sample powder size distribution [18].

Impurities may also play a role in the rate of the cerium monosulfide synthesis reaction. It was indicated that an excess of cerium hydride could be used in the preparation of the reactants in an attempt to reduce oxygen impurities by removing gaseous CeO from the system [4]. This procedure works best at high temperatures where the vapor pressure of the CeO is high, allowing it to be vaporized and removed from the sample by the vacuum system. At lower temperatures, such impurities may not be removed completely and could slow the reaction rate by acting as additional barriers to diffusion. It is presumed that a large amount of CeO is vaporized at 1750 °C where the vapor pressure of CeO is greater than at 1500 °C. This may lead to the large increase in both the reaction rate and purity of the cerium monosulfide that is produced at higher temperatures.

As the reactant mixture is heated through 575 °C cerium hydride releases hydrogen and the cerium is converted to metallic form. The mixture of cerium and cerium sesquisulfide then reacts to form cerium monosulfide. The rate-limiting step in this reaction would be the diffusion of either cerium atoms into cerium sesquisulfide or of sulfur atoms into the metallic cerium. This could be verified by measuring the diffusion rates of cerium and sulfur atoms through the cerium sulfides and comparing the activation energy for these processes to the activation energy for the cerium monosulfide production reaction.

The XRD data show that the cerium sesquisulfide peak falls below the 3–5% detection limit before the reaction is within 5% of completion which may be due to an increasing amount of disorder in its structure as diffusion takes place. This could be caused by liquid cerium coating the particles since an excess of cerium hydride was used in the reaction.

Potential drawbacks of using the Jander model include the assumptions that the particles are spherical and the particle surface area remains constant. These assumptions are not strictly true as can be seen in the scanning electron micrographs of the reactant and product powders. Reactions taking place with impurities that are present could also complicate the use of the model. Despite these drawbacks, the data fit the Jander model reasonably well and were able to be used to calculate the activation energy for this reaction. The assumption that a 3D diffusion mechanism is taking place is reasonable considering the physical state of the reactants and the resulting state of the CeS product.

## 7. Conclusions

This project was able to produce the required apparatuses and a detailed procedure for the production of cerium monosulfide from cerium sesquisulfide and cerium hydride. The kinetics of this reaction was also investigated using quantitative XRD. Since cerium sesquisulfide was required for the production of the cerium monosulfide, an experimental procedure was developed for its synthesis from cerium oxide and hydrogen sulfide. Cerium hydride was also produced based on methods used in previous literature from cerium metal and hydrogen gas to participate in the reaction to produce cerium monosulfide.

It was found that the cerium monosulfide synthesis reaction fit reasonably well with the Jander model of a diffusion-limited reaction. Most likely the rate-limiting step of the reaction involves the diffusion of either cerium atoms or sulfur atoms. The activation energy for this process was determined to be approximately 190 kJ/mol cerium sulfide.

Additional work with cerium monosulfide will involve larger-scale production followed by pressing the resulting powder into test crucibles and running interaction studies with various molten metals. With the synthesis procedure available it will be possible to tailor the chemistry of the cerium monosulfide using additives such as thorium sulfide in order to further enhance its properties as a crucible material for use with actinide metals.

In addition, more extensive studies could be done on the kinetics of the synthesis reactions of not only cerium monosulfide but also of cerium sesquisulfide. The cerium sesquisulfide reaction appears to involve several intermediate compounds and is still poorly understood. As this compound is essential to the production of cerium monosulfide further investigation of its production would be beneficial to the overall synthesis procedure.

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