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PREPARATION AND FORMING OF HIGH-PURITY CERIUM OXYSULFIDE

E.E. Ketchen

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PREPARATION AND FORMING OF HIGH-PURITY CERIUM OXYSULFIDE

E. E. Ketchen
Isotopes Division

MARCH 1968

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PREPARATION AND FORMING OF HIGH-PURITY CERIUM OXYSULFIDE

E. E. Ketchen

ABSTRACT

High-purity Ce_2O_2S powder was prepared by the reaction of CeO_2 with Ce_2S_3 at 1000-1200°C. The intermediate compound Ce_2S_3 was prepared by the reaction of H_2S with CeO_2 at 1200°C. The purity of the product was estimated by melting-point determinations. Theoretically dense (5.99 g/cm^3) compacts of Ce_2O_2S were obtained by hot pressing at 1500°C.

INTRODUCTION

One of the possible uses for fission-product ^{144}Ce is to supply heat for conversion to electric power in thermoelectric, thermionic, or thermodynamic converters. These devices are designed primarily to provide a reliable and predictable supply of power for aerospace and remote marine and terrestrial applications. The compounds selected for use in heat conversion devices, especially in thermionic systems, must have excellent stability at high temperatures, good thermal conductivity, and high density. The physiochemical properties of Ce_2O_2S make it a good candidate for these applications.

Cerium oxysulfide has a hexagonal structure[1] which is derived from the cubic Ce_2O_3 by replacing one of the oxygen atoms with a sulfur atom. Cerium oxysulfide, like Ce_2O_3, is not reduced to a lower oxidation state even at temperatures up to 2000°C. In contrast, the cerium of CeO_2 can be reduced from Ce^{4+} to Ce^{3+}. Cerium oxysulfide, unlike Ce_2O_3, can be conveniently prepared at a temperature of <1250°C and can be exposed to air at 200°C for short periods of time without significant oxidation. At high temperatures, the thermal conductivities of Ce_2O_2S are expected to be of the same order of magnitude as metallic materials due to the nature of sulfur bonding.[2]

Four reactions are reported in the literature for the preparation of Ce_2O_2S:[3,4]

$$4CeO_2 + 4H_2S(g) \rightarrow 2Ce_2O_2S + 4H_2O(g) + S_2(g) \quad (1)$$

$$2CeO_2 + S_2(g) \rightarrow Ce_2O_2S + SO_2(g) \quad (2)$$

$$Ce_2S_3 + 2H_2O(g) \rightarrow Ce_2O_2S + 2H_2S(g) \quad (3)$$

$$2Ce_2O_3 + Ce_2S_3 \rightarrow 3Ce_2O_2S. \quad (4)$$

Of the four reactions, the first two appear attractive because the CeO_2 can be readily prepared; however, these reactions were found to give poor yields and erratic results. The third reaction was eliminated because all of the CeO_2 must be converted to Ce_2S_3. The fourth reaction was discarded because Ce_2O_3 is unstable in air and must be handled in an inert atmosphere.

The reaction of CeO_2 and Ce_2S_3 to produce Ce_2O_2S was developed in this work. The preparation of Ce_2O_2S from CeO_2 and Ce_2S_3 was selected because it is necessary to convert only a fraction of CeO_2 to Ce_2S_3 and because the two reactants can be handled in air at temperatures below 300°C.

PREPARATION OF Ce_2S_3

The preparation of Ce_2S_3 by the reaction of CeO_2 and H_2S at 1200-1400°C for 2-3 hr is reported by Eastman et al.:[5]

$$4CeO_2 + 8H_2S(g) \rightarrow 2Ce_2S_3 + 8H_2O(g) + S_2(g). \quad (5)$$

This method of preparation is similar to Eq. (1) except that the reaction is carried to completion. To define the temperature necessary for completion of the reaction in a reasonable time, 15-g batches of CeO_2 were reacted in a graphite boat enclosed in a mullite tube (Fig. 1) with H_2S flowing at 35 liters/hr. The flow of H_2S was maintained until the temperature was <200°C. Helium was then substituted for H_2S, and the helium flow was maintained until the reaction products cooled. The reaction was 80-90% complete after 5 hr at 1150°C and 100% complete after 2 hr at 1250°C.

The purity of Ce_2S_3 was determined by x-ray diffraction analysis and by dissolution of the product in 10% acetic acid. The impurities, Ce_2O_2S and CeO_2, are insoluble or only slightly soluble in dilute acetic acid. The dissolution method of analysis has a lower limit of detection (<0.5%)

than x-ray diffraction (3-5%). Of the ~50 preparations made, 90% yielded Ce_2S_3 without any impurities detectable by x-ray analysis.

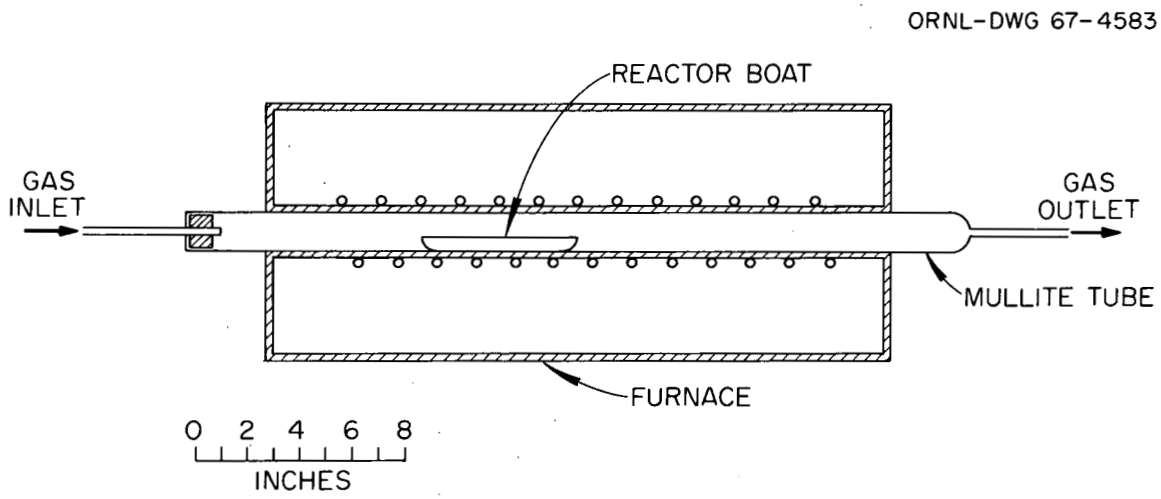

Fig. 1. Reactor for Ce_2S_3 Preparation

LABORATORY PREPARATION OF Ce_2O_2S

Two possible reactions were proposed for the preparation of Ce_2O_2S from Ce_2S_3 and CeO_2:

$$2Ce_2S_3 + 6CeO_2 \rightarrow 5Ce_2O_2S + SO_2(g) \quad (6)$$

$$2Ce_2S_3 + 4CeO_2 \rightarrow 4Ce_2O_2S + S_2(g) \quad (7)$$

Four mixtures of CeO_2 and Ce_2S_3 with molar ratios varying from 2:1 to 3:1 were pressed into 6-mm-dia pellets (Table 1). The pellets were heated in a helium atmosphere of a graphite furnace in the following sequence: 1 hr at 1000°C, 3 hr at 1350°C, and 1 hr at 1550°C. The Ce_2O_2S prepared with the 2:1 molar ratio had the highest melting point (Table 1). (A melting point of 2000 ± 200°C is reported for Ce_2O_2S by Eastman et al.[3]) The only impurity (identified by x-ray diffraction) was ~3% CeO_2 in the Ce_2O_2S prepared from the mixture with a mole ratio of 3 (Eq. 6). Since x-ray diffraction analysis was inconclusive on the three other products, the melting point of the product was used as a measure of the purity in these experiments. Hence, under the above conditions, Eq. (7) is the predominant reaction.

Table 1. Melting Points of Ce_2O_2S Products Prepared from Various Mole Ratios of CeO_2:Ce_2S_3

CeO_2:Ce_2S_3	Melting point, °C
3.00	1960
2.66	1965
2.33	1980
2.00	1995

The laboratory preparation of small batches of Ce_2O_2S from CeO_2 and Ce_2S_3 mixtures was investigated at 1000°C. Mixtures of CeO_2 and Ce_2S_3 powder with ratios of 2-2.7 were reacted at 1000°C in a molybdenum crucible for 2 hr under a reducing helium atmosphere. For CeO_2:Ce_2S_3 ratios of 2, 2.3, and 2.7, the respective Ce_2O_2S products contained 5-10% Ce_2S_3, 5% CeO_2, and 15-20% CeO_2.

Since the Ce_2O_2S product contained either Ce_2S_3 or CeO_2 (when the reaction was carried out at 1000°C), methods of purification were investigated. Cerium sesquisulfide is soluble in 10% acetic acid, but Ce_2O_2S will not go into solution. This solubility difference enabled the development of a purification method to remove Ce_2S_3 from the Ce_2O_2S product. A batch of 5 g of 80-85% Ce_2O_2S—15-20% Ce_2S_3 product was leached overnight in a 10% acetic acid solution. The resulting Ce_2O_2S product weighed 4.4 g, had a melting point of 2045°C, and was determined to be single phase Ce_2O_2S by x-ray analyses. When other batches of Ce_2O_2S powder were leached with 10% acetic acid, the resulting single phase Ce_2O_2S had melting points up to 2060°C.

INFLUENCE OF IMPURITIES ON MELTING POINT OF Ce_2O_2S

To determine the effect of CeO_2 and Ce_2S_3 on the melting point of Ce_2O_2S, samples were prepared by adding CeO_2 or Ce_2S_3 to pure Ce_2O_2S. The melting point curves for Ce_2O_2S containing various amounts of CeO_2 and Ce_2S_3 are shown in Figs. 2 and 3. In all cases, the melting points of Ce_2O_2S were lowered by the addition of CeO_2 or Ce_2S_3, and data show that the melting point is indicative of the purity of Ce_2O_2S powder.

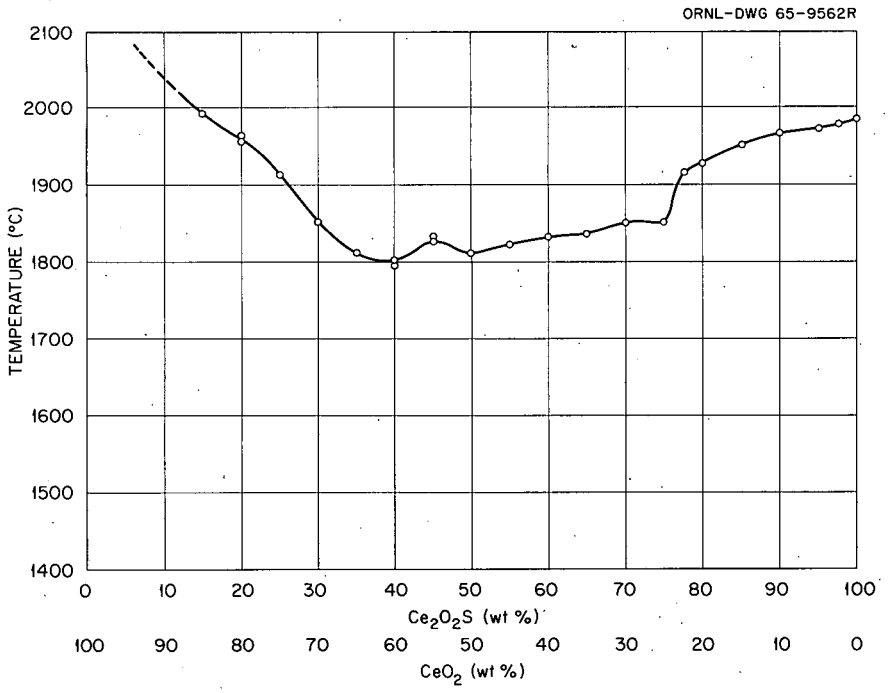

Fig. 2. Melting Points of Ce_2O_2S as a Function of CeO_2 Content.

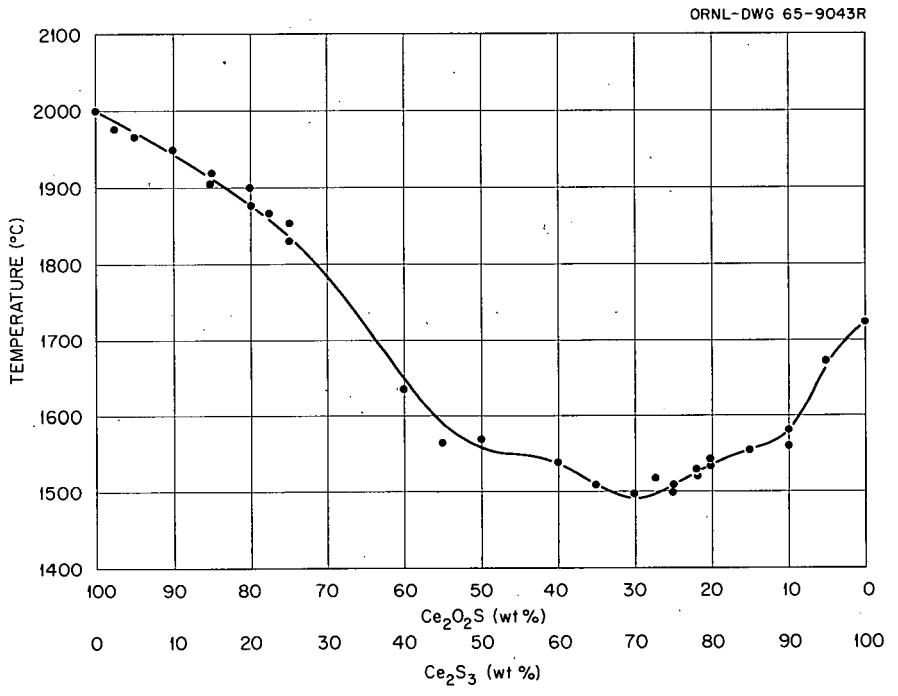

Fig. 3. Melting Points of Ce_2O_2S as a Function of Ce_2S_3 Content.

PILOT PLANT PRODUCTION OF Ce_2O_2S

A pilot plant apparatus (Fig. 4) was used to prepare pound quantities of Ce_2S_3 and Ce_2O_2S. The CeO_2 was heated in the apparatus over a 24-hr period in a H_2S flow of 35 liters/hr. The temperature was held at 1200°C for 2 hr. The H_2S flow was maintained until the temperature fell to 1000°C at which time a helium flow was substituted. The Ce_2S_3 was 97% pure (3% Ce_2O_2S).

The preparation of Ce_2O_2S on a pound scale was investigated using the same equipment. Approximately 125 g of the reactants with a CeO_2:Ce_2S_3 ratio of 2 were loaded on each of the top four trays of the reactor. The results of the pilot-plant-scale run differed considerably from the small-scale (10 g) experiments. After reaction for 16 hr at 1000°C, the reaction was 60-70% complete. The reaction was >90% complete after 16 hr at 1200°C. The melting point of the Ce_2O_2S was 1945°C.

The difference in the purity of Ce_2O_2S produced on a small scale and that produced on a pilot-plant scale could be due to the difference in the rate of sulfur removal from small and pound-scale batches. In Eq. (7), which is believed to be the predominant reaction, sulfur must be removed to complete the reaction. Since the removal of sulfur is important, the purity of the product could probably be increased by increasing the reaction temperature from 1200 to 1250-1300°C to aid sulfur removal.

CERIUM OXYSULFIDE PELLET FABRICATION

Three methods of forming Ce_2O_2S into dense bodies were investigated: pressing-sintering, casting, and hot-pressing. Of these, hot-pressing was the most successful.

The highest density obtained by pressing and sintering at 1725°C for 15 min was 5.1 g/cm^3. Prolonged sintering at 1725°C resulted in a decrease in density. No significant sintering was obtained at temperatures of <1500°C. The Ce_2O_2S melted at 2100°C and cast into molybdenum molds had a density of 5.3 g/cm^3. The low densities resulted primarily from pipes produced by shrinkage on cooling.

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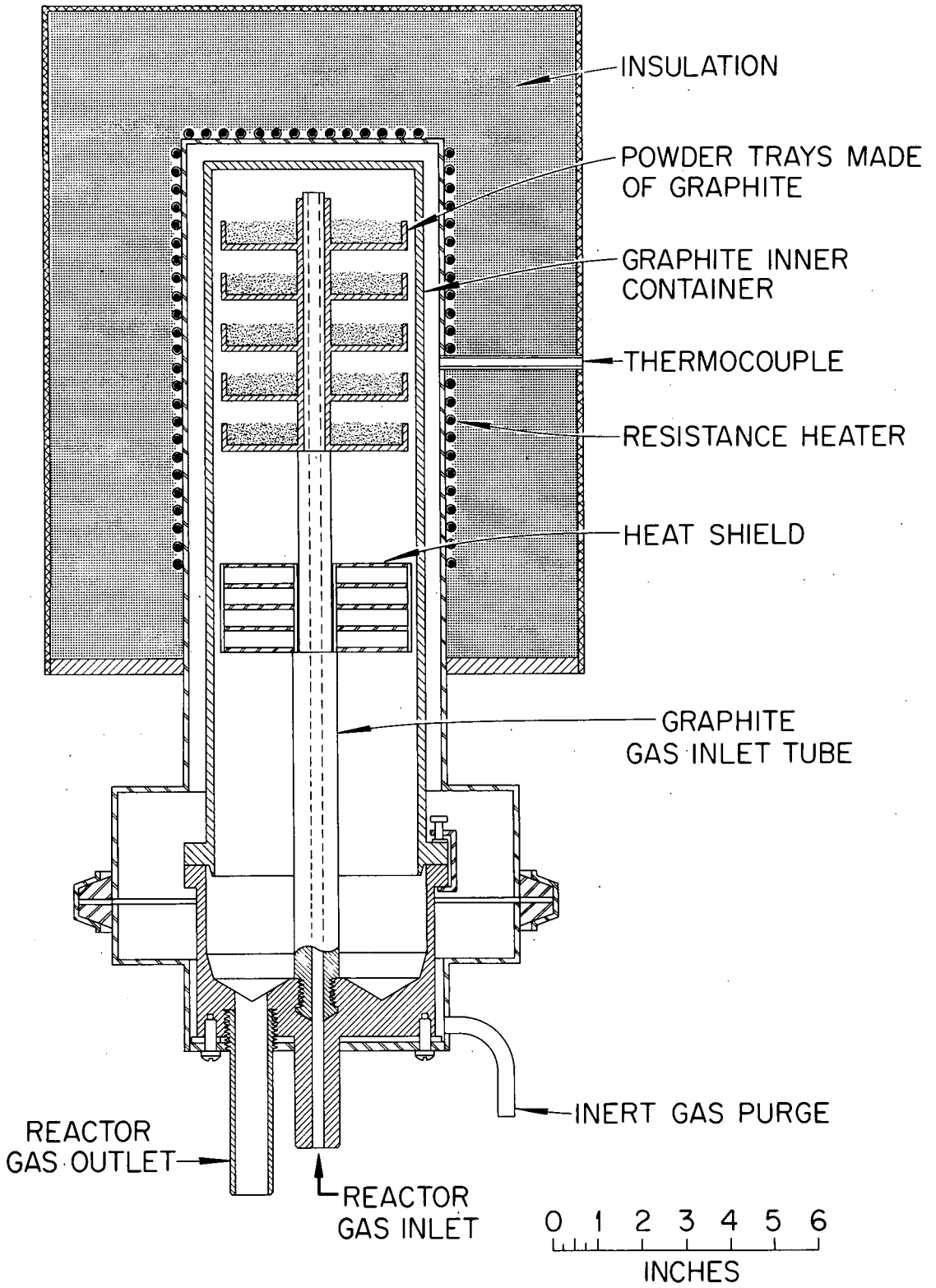

Fig. 4. Cerium Sulfide and Oxysulfide Reactor

Pellets with essentially theoretical density (5.99 g/cm^3) were obtained by hot-pressing Ce_2O_2S in graphite dies at 1500°C for 10 min. The microstructure of a hot-pressed sample (density, 5.88 g/cm^3) is shown in Fig. 5. The light gray phase is Ce_2O_2S, the dark gray phase is Ce_2S_3, and the black areas are voids.

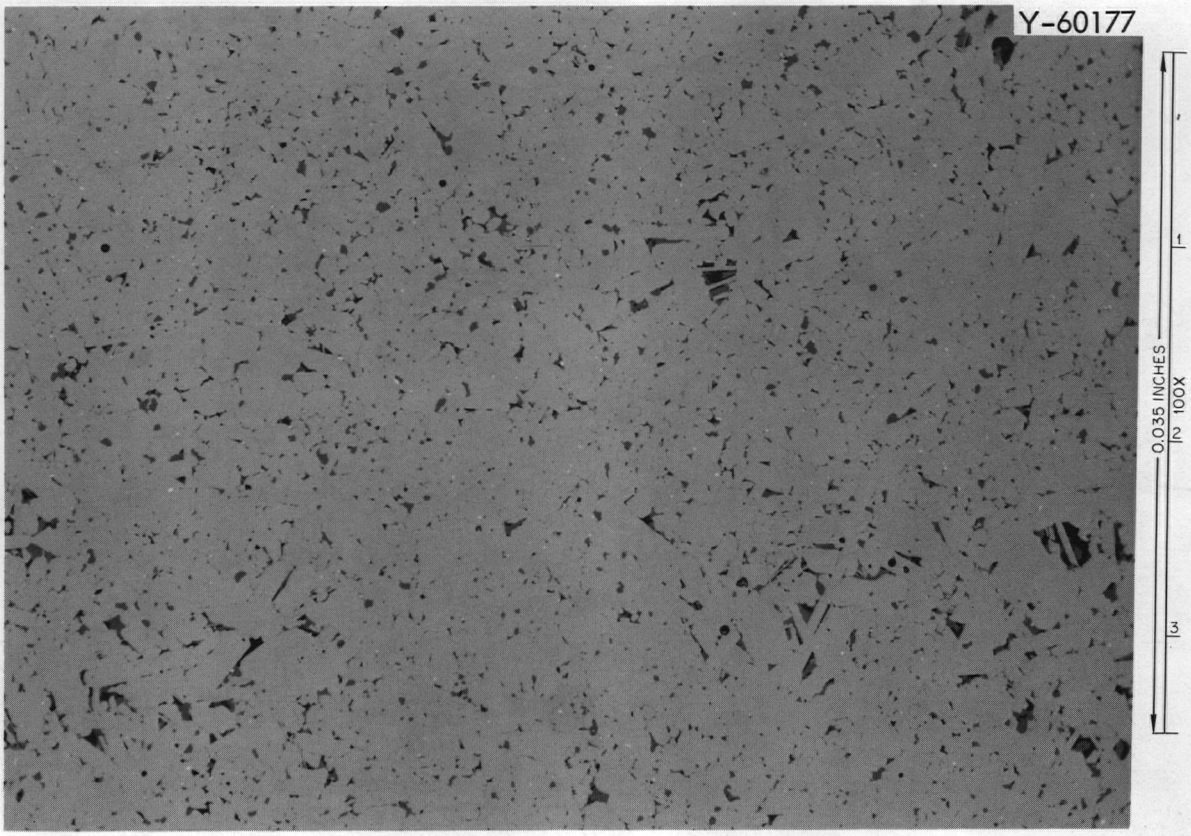

Fig. 5. Photomicrograph of a Hot-Pressed Sample of Ce_2O_2S with a Density of 5.88 g/cm^3. The light gray phase is Ce_2O_2S, the dark gray phase is Ce_2S_3, and the black areas are voids.

CONCLUSION

The preparation of Ce_2O_2S in pound quantities by reaction of CeO_2 and Ce_2S_3 was demonstrated with nonradioactive materials. The product purity was demonstrated to be acceptable by determining melting points to be in the range of 1950-2000°C compared with a reported value of 2000°C for Ce_2O_2S. The fabricability of Ce_2O_2S into dense forms by casting and hot pressing was demonstrated. The techniques and equipment developed in these experiments can be extended to the preparation of radioactive ^{144}Ce source forms.

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