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Preparation and Properties of Refractory Cerium Sulfides[1a]

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In a search for new refractories which could be easily formed and sintered into crucibles, yet would be stable and refractory, it was felt that perhaps certain sulfides might be useful. In an effort to choose the most refractory sulfides, preliminary calculations and estimations indicated that the most stable sulfides should lie in the periodic table around thorium and the rare earth metals. Accordingly the sulfides of the most abundant rare earth, cerium, have been investigated and two new compounds have been discovered. These compounds proved to be such good refractories that a rather complete study of their properties was undertaken. The three cerium sulfides are the red sesquisulfide Ce_2S_3, black Ce_3S_4, and brassy-yellow CeS. All three, especially CeS, are useful as refractories at high temperatures. Picon[2a] and Picon and Cogne[2b] have prepared the sesquisulfide and studied the reaction of carbon with it at very high temperatures. They also investigated the chemical reactivity of Ce_2S_3 with many materials.

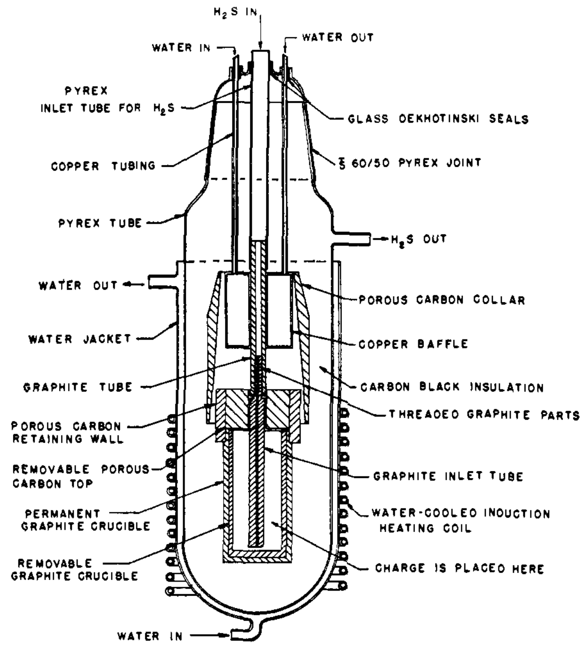

Fig. 1.—Graphite reaction chamber.

Preparation of Cerium Sulfides

Ce_2S_3—Cerium sesquisulfide, Ce_2S_3, is prepared from the dioxide, CeO_2, by passing a current of hydrogen sulfide over it in a carbon furnace at elevated temperatures. The net reactions are

$$6CeO_2 + 4H_2S = 3Ce_2O_2S + 4H_2O + SO_2$$

and

$$2H_2S + 2C + Ce_2O_2S = Ce_2S_3 + 2CO + 2H_2$$

It is entirely possible that the latter reaction proceeds through gaseous CS intermediate, but this has not been shown conclusively. The reaction of CeO_2 with hydrogen sulfide in a porcelain tube will not go to completion and the reaction of CeO_2 with sulfur gas gives as the only solid product, Ce_2O_2S.

The apparatus (Fig. 1) consists essentially of an inductively heated graphite chamber containing about 100 g. of the finely ground oxide and itself contained in carbon black insulation. The entire assembly is contained in an externally water cooled Pyrex tube. The hydrogen sulfide is conducted into the chamber through a graphite inlet tube from which the gas flows over and through the oxide powder. After assembly the hydrogen sulfide flow is adjusted to from 25 to 50 l. per hour and the induction heater started. The temperature is slowly raised until it is 1200–1400°. The temperature is measured by an optical pyrometer by sighting down the carbon inlet tube. Conversion is usually complete in from two to three hours, resulting in a product analyzing 25.5% sulfur corresponding to $CeS_{1.50}$ if the starting oxide is pure, and as high as 26.2% sulfur if the starting material is the commercial grade oxide containing light metal impurities.

"Cerium Black."—A solid solution of Ce_2S_3 in Ce_3S_4 may be prepared by vacuum heating Ce_2S_3 near its melting point.

The Ce_2S_3 is placed in a molybdenum crucible and the crucible placed in the high temperature high vacuum apparatus. A vacuum of 10^{-4} to 10^{-5} mm. is obtained and the heating is started. The temperature is raised to about 1800° for several minutes and then slowly through the melting point to about 2100°. It is necessary to be careful as bumping or boiling may occur on melting and much material may be lost. After several hours of heating at this high temperature the analysis would show about $CeS_{1.40}$.

The high temperature high vacuum apparatus[3] consists essentially of a 4″ Pyrex pipe tee flanged on one end to a Pyrex L and on the other to a 4″ horizontal oil diffusion pump (see Fig. 2). From the bottom of the T and L hang adaptor flanges which connect through standard ground-glass 71/60 joints to Pyrex tubes with a small nipple on the bottom end. The Pyrex tube is surrounded by another Pyrex tube which acts as a water jacket and is held centered by the nipple at the bottom and spacers at the top. A molybdenum or zircon stand is placed in the Pyrex tube (Fig. 3) and on it is placed the molybdenum crucible containing the sample to be heated. This crucible is surrounded by a spiral of 1 to 2 mil molybdenum foil and several radiation shields are placed on top. This

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[1] (a) This work was performed under the Manhattan District Contract No. W-7405-eng-48B from 1943 to 1946. Presented at San Francisco, California, meeting of American Chemical Society, March 1949. (b) Deceased, 1945.

[2] (a) M. Picon, *Compt. rend.*, **195**, 957 (1932); *Bull. soc. chim. France*, [4] **49**, 703 (1941); (b) M. Picon and Cogne, *Compt. rend.*, **193**, 595 (1931).

[3] L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Declassified Atomic Energy Commission Paper, MDDC-367, August 4, 1945.

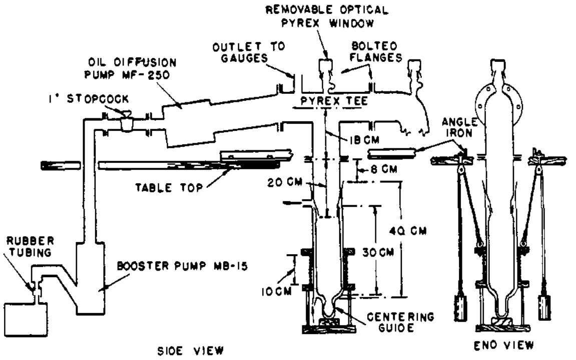

Fig. 2.—Diagram of vacuum apparatus.

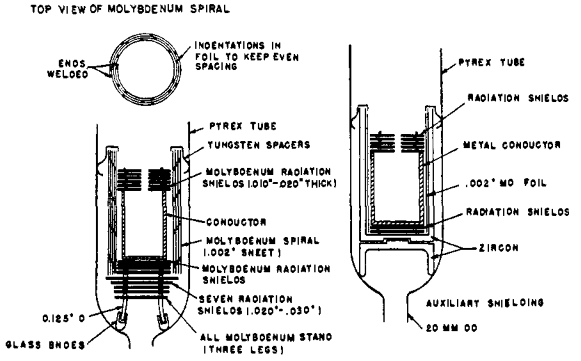

Fig. 3.—High temperature chamber.

molybdenum assembly is held centered in the Pyrex tube by tungsten wire spacers.

The oil diffusion pump is backed by another oil diffusion pump and then by a compound mechanical pump.

Ce_3S_4.—Ce_3S_4 may be prepared either by the reaction of Ce_2S_3 with CeS or by the reduction of Ce_2S_3 with CeH_3. The procedure and apparatus is that used for the preparation of CeS.

CeS.—CeS is prepared by the reaction of Ce_2S_3 and CeH_3. CeH_3 is simply prepared by allowing cerium metal to come into contact with hydrogen at or slightly above room temperature. It is necessary to exert careful control on the rate of hydrogen addition and the cooling of the container, especially if a glass tube is used, as the heat evolved is sufficient to cause the entire mass of metal and hydride to become red hot if the reaction is uncontrolled. The Ce_2S_3 and CeH_3 are both powdered by grinding in a steel ball mill. In the case of the hydride it is necessary to handle it at all times in an inert atmosphere. A "dry" box was especially designed for this operation. The CeH_3 and Ce_2S_3 powders are mixed thoroughly, and placed in a molybdenum container. This is placed in the high temperature high vacuum apparatus described under "Cerium Black" and the equipment evacuated to a good vacuum to insure absence of leaks. The molybdenum crucible is heated slowly until the hydrogen is removed and then heated to about 2200° in a vacuum of about 10^{-4} mm. for several minutes to remove impurities and ensure complete reaction. The following impurities are quite completely removed: alkali metals, alkaline earth metals, iron, oxygen probably as CeO and any excess cerium. A slight excess of cerium hydride is usually used in the preparation to ensure oxygen removal. After cooling, the solid chunks of CeS will fall out of the molybdenum crucibles, after gentle tapping, clearing the crucibles for re-use.

TABLE I

PROPERTIES OF THE CERIUM SULFIDES

Property	CeS	Ce_3S_4	Ce_2S_3
Color	Brass	Black	Red
Crystal density,[5] g./cc.	5.93	5.3	5.2
Melting point, °C.	2450 ± 100	2050 ± 75	1890 ± 50
Temp. at which v. p. = 10^{-3} mm.	1900	1840	Low[a]
Spec. res. ohm-cm.[4]	9×10^{-5}	4×10^{-4}	>1000
Crystal structure[5]	NaCl	Cubic	Cubic
Lattice constant,[5] Å.	5.76	8.606	8.618
Ce–S[5] distance, Å.	2.88	2.97	2.98
Magnetic susceptibility[6] e. m. u. $\times 10^{-6}$	2140	2200	2520
Heats of form. from rhombic S, 298° K., kcal./mole	−117.9	−421.5	−300.5

[a] Ce_2S_3 loses sulfur upon heating.

Properties.—Table I, which lists the physical, chemical and thermodynamic properties of these sulfides, should prove useful in the choice of these as refractories.

There is a eutectic between CeS and Ce_3S_4 at $CeS_{1.15 \pm 0.03}$ melting 2000 ± 75°. In the Table I resistance measurements were made by A. Van Dyken, Jr.,[4] X-ray data by W. H. Zachariasen,[5] magnetic susceptibilities by M. Calvin[6] and heats of formation by Evans.[7] If it is desired to use the heat of formation from S_2 gas, the value −15.5 kcal. per $\frac{1}{2}$ S_2[8] should be added to the values given. The entropy of formation of the sulfides can probably be taken as about −4 cal. per degree per atom sulfur based on the comparison of barium sulfide with calcium sulfide by Kelley.[8] If it is desired to know the entropies of formation from sulfur gas, −19.6 e. u. should be added per $\frac{1}{2}$ S_2. For high temperature estimations of the free energies of formation, the heats and entropies of formation from sulfur gas should be used. Since these sulfides vaporize by decomposition to S gas and the metal gas, these values can be used to calculate the volatility of the sulfides.

The melting point determinations were by direct observation on a melt in a molybdenum or tungsten crucible with an optical pyrometer. Correction was made for absorption of light by the window and an approximate black body correction was made. The vapor pressures were obtained from weight loss assuming unit accommodation coefficient and vaporization as cerium and sulfur atoms. These were qualitatively checked by calculation from heats of formation.[7] The resistance to attack is based on tests of crucibles made of these sulfides.

The details of the preparation of the crucibles

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[4] A. Van Dyken, Jr., private communication, Argonne National Laboratory, Chicago, Ill.

[5] W. H. Zachariasen, private communication, Argonne National Laboratory, Chicago, Ill.

[6] M. Calvin, private communication, October 1944.

[7] M. Evans, Declassified Atomic Energy Commission Paper MDDC-438-I.

[8] K. K. Kelley, Bull. 406, U. S. Bureau of Mines, 1937.

and tests have been given by the authors.[9] It should be pointed out that even though it is thermodynamically possible for attack to take place, often attack does not occur. This is especially true when the sulfide is in a sintered compact form. Indeed, some of the most satisfactory crucibles are not only the ones like CeS which should not be attacked, but also crucibles of Ce_3S_4 which have proved very satisfactory where they should thermodynamically have been attacked. Although CeS is stable toward reduction by very electropositive metals such as alkali and alkaline earth metals, cerium, aluminum, iron, etc., it is attacked by some of the noble metals like platinum and bismuth due to the high stability of the cerium intermetallic compounds. Thus platinum reacts with CeS to form Ce_3S_4 and $CePt_2$.

The spalling resistance of CeS is excellent and small crucibles have been heated at rates of 1000° per minute without spalling or fracture. In the case of Ce_3S_4, crucibles over one inch in diameter cannot be heated faster than 100° per minute and Ce_2S_3 behaves like a conventional refractory with much poorer spalling resistance. Due to oxidation by oxygen or oxygen containing compounds, heating of the sulfide crucibles must be carried out under reduced pressures or in an inert atmosphere, but at temperatures of 200–300° and below a thin protective coating prevents any appreciable oxidation of the sulfides. Slight oxidation at higher temperatures produces a characteristic blue or purple surface coloration. When finely divided the sulfides are much more reactive and are sometimes even pyrophoric. The sulfides can be boiled in water without attack but they react rapidly with cold dilute acids to give hydrogen sulfide and also hydrogen with CeS and Ce_3S_4.

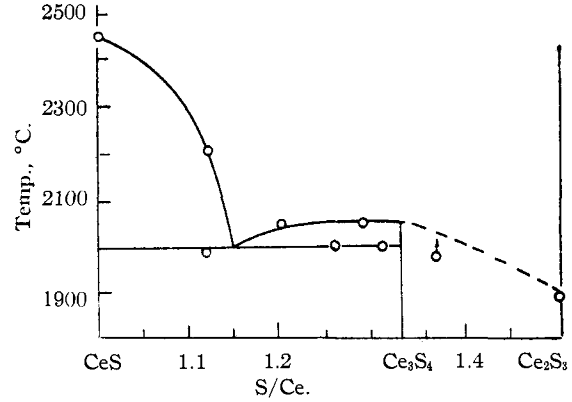

Fig. 4.—Tentative cerium–sulfur phase diagram: δ melting point low because of oxygen pickup.

The mechanical properties of CeS are very similar to those of cast iron and it can be machined. Ce_3S_4 and Ce_2S_3 have mechanical properties more like those of porcelain.

Figure 4 is a tentative phase diagram for the cerium–sulfur system based upon observed melting and solidification points as indicated by circles as well as upon X-ray data,[5] visual examination of the samples for proportion of eutectic mixture and analysis[10] of the eutectic mixture. It was not possible with the present equipment to distinguish between the solidus and liquidus lines in the solid solution region between Ce_3S_4 and Ce_2S_3. The X-ray evidence indicates the sulfur lattice is intact in this range and vacancies are left among the cerium sites as one goes from the ideal lattice of Ce_3S_4 to Ce_2S_3. The magnetic susceptibility data given in Table I indicate that both Ce_2S_3 and Ce_3S_4 as well as CeS have one free "f" electron with any additional electrons for compositions below Ce_2S_3 being involved in bonding between the cerium ions. It is interesting to note that if one fills up the vacancies in the Ce_2S_3 lattice by adding cerium, the lattice actually contracts instead of expanding as might be expected. This is apparently due to the increased bonding resulting from the extra electrons made available by the entering ceriums. In addition to the Ce_3S_4–Ce_2S_3 solid solution range, there is evidence[11,12] that CeS can dissolve an excess of sulfur at very high temperatures. It was found that very small oxide additions to Ce_2S_3 would destroy the cubic structure with the formation of a new structure having a very complicated X-ray powder pattern.

Summary

The methods of preparation, apparatus used, and the physical, chemical and thermodynamic properties of the cerium sulfides have been discussed. The stability and low reactivity of these sulfides should make their use as refractories very useful for many applications, especially where it is desirable to prevent oxygen contamination and one is dealing with very electropositive metals.

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(9) L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, Declassified Atomic Energy Commission Paper, AECD-2253, October 27, 1945.

(10) L. Brewer, L. A. Bromley, A. D. Fong, P. W. Gilles, C. S. Koch and N. L. Lofgren, Declassified Atomic Energy Commission Paper, MDDC-1654, September 22, 1945.

(11) H. B. Barlett, Massachusetts Institute of Technology, private communication, October 1944.

(12) H. B. Barlett and M. Cohen, Massachusetts Institute of Technology, private communication, October 1944.