DO NOT REMOVE THIS PAGE

REPORT NO. Ct-2433
THIS DOCUMENT CONTAINS 7 PAGES OF
TEXT AND 0 PAGES OF FIGURES.
THIS IS COPY 34 OF 62 SERIES A

CLASSIFICATION: ~~SECRET~~

ISSUED TO: H.A. Wensel

THIS IS A CLASSIFIED DOCUMENT

1. THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN MEANING OF THE ESPIONAGE ACT, U.S.C. 50; 31 AND 32. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

2. BEFORE THIS DOCUMENT CAN BE READ BY A PERSON OTHER THAN THE ONE TO WHOM IT WAS ASSIGNED, HIS NAME MUST BE ON THE LIBRARY LIST OF THOSE AUTHORIZED TO READ MATERIAL ON THIS SUBJECT, OR PERMISSION MUST BE OBTAINED FROM THE ASSISTANT DIRECTOR OR THE DIRECTOR OF THE INFORMATION DEPARTMENT, OR THROUGH AN APPROPRIATE SECTION CHIEF OR HIGHER OFFICER WHO MUST BE CONVINCED THAT THE PERSON NEEDS TO READ THE DOCUMENT FOR THE SUCCESS OF HIS WORK.

3. THIS IS A CLASSIFIED DOCUMENT AND IS TO BE KEPT ONLY IN A GUARDED AREA. SECRET MATERIAL MUST BE KEPT IN A LOCKED SAFE OR A LOCKED FILING CASE WITH TUMBLER LOCK. CONFIDENTIAL MATERIAL MUST BE KEPT IN AT LEAST A LOCKED FILING CABINET.

4. A SECRET OR CONFIDENTIAL DOCUMENT IS NOT TO BE COPIED OR OTHERWISE DUPLICATED WITHOUT PERMISSION OF THE ORIGINATING OFFICE. EXTENSIVE NOTES ON THE CONTENTS OF A SECRET REPORT MAY BE TAKEN ONLY IN A BOUND NOTEBOOK WITH NUMBERED PAGES, HAVING THE DESIGNATION SECRET. THIS MUST BE SAFEGUARDED IN THE SAME WAY AS A SECRET REPORT. OTHER NOTES MUST BE AVOIDED, BUT IF MADE MUST BE DONE IN A FORM MEANINGLESS TO ANYONE BUT THE WRITER AND LATER DESTROYED.

5. THE PERSON OR OFFICE TO WHOM A SECRET OR CONFIDENTIAL DOCUMENT IS ISSUED IS ACCOUNTABLE FOR THE DOCUMENT AT ALL TIMES. A SYSTEM OF ACCOUNTABILITY BY SIGNED RECEIPTS OR A SIGNED RECORD BOOK MUST ALWAYS BE USED. PERMISSION FOR TRANSMISSION TO ANOTHER OFFICE OTHER THAN THAT OF THE ASSIGNEE MUST BE OBTAINED THROUGH THE INFORMATION OFFICE AND RECORDED THERE.

6. AS SOON AS THE DOCUMENT IS NO LONGER NEEDED, IT IS TO BE RETURNED TO THE INFORMATION OFFICE WHEREUPON THE INDIVIDUAL WILL BE RELIEVED OF THE RESPONSIBILITY FOR ITS SAFEKEEPING.

7. THE FORM BELOW IS USED IN ROUTING THIS REPORT AND MUST BE SIGNED BY EACH PERSON WHO READS IT.

ROUTE TO	READ BY	DATE	ROUTE TO	READ BY	DATE

11-21-44

DECLASSIFIED

CT-2433
1 - M

Metallurgical Project

A. H. Compton, Project Director

. . . . . .

University of California Project

W. M. Latimer and E. D. Eastman, Project Directors

. . . . . .

THE USE OF SULFIDE CRUCIBLES FOR REMELTING AND REDUCTIONS

L. Brewer, L. A. Bromley, N. Lofgren,
P. Gillis and W. Gwinn

November 21, 1944

ABSTRACT

Th_4S_7, Th_2S_3, ThS, Ce_2S_3, Ce_3S_4, and CeS have been satisfactorily used for remelting of cerium metal in a vacuum at 1500°C. Results of tests are given and the effect of oxide impurities in the sulfide crucibles is considered. Cerium halide reductions have been carried out in CeS crucibles. If the CeS is not pure, the crucible is badly cracked. Pure CeS crucibles are satisfactory containers for the metal reduction reaction.

CLASSIFICATION CANCELLED
DATE FEB 19 1957
For The Atomic Energy Commission
H. R. Carroll
Chief, Declassification Branch

Photostat Price $ 1.80
Microfilm Price $ 1.80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

XVII. THE USE OF SULFIDE CRUCIBLES FOR REMELTING AND REDUCTIONS

In order to determine the proper purities and porosities required to make the sulfide crucibles most resistant to attack in use and to determine the best uses for each sulfide material, various experiments have been performed at Berkeley using cerium and uranium ~~as stand-ins~~. dele

Previous experiments have determined the effects of U, Ce, Ba, Sr, $U+UBr_3$, $U+CaCl_2$, $U+SrBr_2$, $U+BaI_2$ and $U+SrI_2$. The results of testing of BaS are given in Sulfide Report XIV (CT--2232). The results of most of the tests of other sulfides are given in Sulfide Report XI (CK-1714) and "The Thermodynamics of High Vacuum-High Temperature Systems Applied to Refractories" (CC-1802) with a summary in Sulfide Report XVI (CT-).

The present report presents results of recent tests. The tests of crucibles for remelting purposes will be discussed first.

A. The Use of Sulfide Crucibles for Remelting.

Previous tests have indicated that cerium is much more destructive to refractories than uranium and it is a more satisfactory ~~stand-in~~. dele Therefore all present work has been done with cerium. Previous experiments extending up to 1300°C. have indicated that all the sulfides except BaS were satisfactory for remelting of cerium. This was very promising since even the best oxide refractories are reported to be badly attacked at 1000-1200°C. To test the sulfide crucibles under very severe conditions, cerium was heated for fifteen minutes in each of the sulfide crucibles at 1500°C. in a vacuum. The sulfides tested were Th_4S_7, Th_2S_3, ThS, Ce_2S_3, Ce_3S_4, and CeS. The cerium used was Ames cerium which was prepared by calcium reduction and contained a considerable amount of calcium. The calcium impurity increases the reactivity of the cerium, but the presence of calcium duplicates more closely the remelting conditions.

271

002

Table I gives the composition, firing conditions, and porosities of the crucibles used in the tests. No oxygen analyses were performed on the Ce_2S_3 and Ce_3S_4 used, but they contain at least 2 to 5% oxide which comes from the starting Ce_2S_3 material. They also contain sodium, magnesium, and calcium sulfides as impurities which also come largely from the starting Ce_2S_3 material. The other sulfides were analyzed for sulfur and the oxidation number determined by the methods given in Sulfide Report XII (CC-2078). The difference between sulfur and oxidation number gives oxygen content. The firing temperatures given are temperatures observed with optical pyrometer with no corrections for glass absorption or black body deviations. The true temperatures are about 100°C. higher. The porosities given include closed voids and are determined by comparing observed densities with x-ray densities. The porosities were not actually determined for each crucible but were estimated by comparing shrinkages on firing with shrinkages of similar crucibles for which densities were determined.

TABLE I

PROPERTIES OF CRUCIBLES USED IN TESTS

No.	Composition	Firing Conditions Observed Temperatures		Porosity
433	$ThS_{1.77}\cdot 0.04ThO_2$	1650°C.	30 min.	20%
435	$ThS_{1.75}\cdot 0.04ThO_2$	1695°C.	60 min.	2-5%
430	$ThS_{1.58}\cdot 0.07ThO_2$	1740°C.	15 min.	20%
458	$ThS_{1.53}\cdot 0.08ThO_2$	1750°C.	60 min.	5%
387	$ThS_{0.994}\cdot 0.22ThO_2$	1825°C.	15 min.	10-15%
390	$ThS_{0.994}\cdot 0.22ThO_2$	1900°C.	40 min.	1%
511	$CeS_{1.51}$	1780°C.	10 min.	5-10%
438	Ce_3S_4	1760°C.	15 min.	6%
422	$CeS_{0.967}O_{0.043}$	1600°C.	30 min.	25%
440	$CeS_{1.02}O_{0.04}$	1750°C.	15 min.	2%
501	$CeS_{0.97}O_{0.06}$	Unfired	Unfired	25%

Clean pieces of cerium metal were added to each crucible. The crucibles were N type crucibles and 2.2 to 2.6 grams of metal were added. The crucibles were heated slowly to 900°C. in one hour. The slow heating was required so that the evaporation of the volatile impurities such as Ca and $CeCl_3$ would not spray the cerium metal out of the crucibles. The temperature was then raised to 1500°C. over a period of thirty minutes and then maintained at 1500°C. for fifteen minutes. The crucibles were all heated together inside a Mo crucible which was inductively heated. The pressure read on the Knudsen gauge without trap was 4×10^{-5}mm. just before heating was stopped. After cooling, the crucibles were broken from the ingots and 0.1 g. samples of metal removed for sulfur analysis. Duplicate determinations are bracketed together. Samples from the ingots with very high sulfur content give varying results because sulfide inclusions apparently cause variation in sulfur content through the ingot. Sulfur analyses were performed using the method given in Part IV of Sulfide Report XII (CC-2075). Table II gives the sulfur contents of the ingots and crucibles after the heating at 1500°C. All remelted ingots had a silvery metallic luster when cleaned. Sulfur content is given in p.p.m.

TABLE II. RESULTS OF REMELTING OF CERIUM AT 1500°C.

Crucible	Sulfur Content	Description of Ingot
433 → Por. Th_4S_7	29,800 10,670	Almost flat smooth surface with no wetting of sides of crucible above ingot. A thin layer of crucible stuck to ingot when crucible was broken off. The ingot was silvery when crucible layer was filed off. 0.5% weight loss.
465 → Dense Th_4S_7	5,010 6,880	Same appearance as 433. 0.5% weight loss.
430 Por. Th_2S_3	5,280	Same appearance as 433. 0.5% weight loss.
458 → Dense Th_2S_3	34,600 27,200	Concave surface with wetting of sides of crucible almost up to lip. A thin layer of crucible stuck to ingot. 0.6% weight loss.
387 Por. ThS	7,900	Concave surface with wetting of sides of crucible part way up to lip. A thin layer of crucible stuck to ingot.
390 Dense ThS	18,080	Very concave surface with metal over lip and on outside sides of crucible. Metal had evidently sprayed out over edge. The ingot had lost almost half of its weight. A thin layer of crucible was stuck to ingot.
511 Ce_2S_3	4,110	Slightly concave surface with no wetting of crucible walls above ingot surface. The crucible broke lose from the ingot with practically none of the crucible left on the ingot. 0.5% weight loss.
488 Ce_3S_4	3,490	Exactly same appearance as 511. The crucible broke loose from ingot with practically none of the crucible left on the ingot.
422 Por. CeS	-----	The metal had completely soaked into the crucible leaving no trace although from the weight of crucible and ingot, only 1.6% of the ingot was lost.
440 Dense CeS	1,630	Slightly concave surface with no wetting of walls above ingot surface. A thin layer of the crucible stuck to the ingot which was silvery when cleaned. The weight loss was 0.7%.
501 Por. CeS	------	The ingot had completely soaked into the crucible leaving no trace of metal.

The first conclusion to be drawn by comparison of Tables I and II is that the crucibles with porosities greater than 20% soaked up all the cerium metal at 1500°C. It is clear that the pore size is the determining factor and the high surface tension of the metal prevents soaking into the crucible unless the pores are large. The higher the temperature, the more non-porous must the crucibles be to prevent soaking of the metal into the crucible. Since it is easy to obtain sulfide crucibles with porosities less than 10%, soaking up of metal by capillary action is no problem with sulfide crucibles.

The second conclusion is given by the small weight losses. The spraying of metal which occurred in previous experiments was eliminated by slow heating while volatile impurities were distilled out except in the case of ThS crucible 390. The ThS crucibles are believed to have the highest thermal conductivity of any of the crucibles and due to more rapid heat conduction from the Mo heating crucible, the dense ThS heated more rapidly than the other crucibles and sprayed metal even though the others did not. Therefore, one would conclude that the rate of heating should be slowest when using ThS crucibles and can be increasing more rapidly in going from CeS to Th_2S_3 to Th_4S_7 to Ce_3S_4 to Ce_2S_3 crucibles.

The most remarkable result of these tests is the slight degree of attack of the Ce_3S_4 and Ce_2S_3 crucibles. The attack of any of the crucibles was remarkably small considering the temperature of the experiment, but the ingots contained in the Ce_3S_4 and Ce_2S_3 crucibles broke cleanly from the crucibles. The sulfur pickups of 3000-4000 p.p.m. were very small considering the temperature. The lack of attack is due to a thin imperious film of CeS formed on the surface of the crucible, or to lack of wetting by the metal. When the crucible is broken off the ingot, there is a very thin brassy CeS film on the crucible and on the ingot. The ingot in the CeS crucible had the smallest sulfur pickup, but like the ingots in the thorium sulfide crucibles, there was a layer of crucible material approximately 0.1-0.5 mm. thick which did not break off easily and may represent slight penetration of the crucible by the cerium metal. It is difficult to explain why the ingots in the Ce_3S_4 and Ce_2S_3 crucibles break away cleanly while the ingot in the CeS crucible does not, but the same results were obtained in the lower temperature runs where it was evident that CeS is wet more readily than are the higher sulfides.

The thorium sulfides held up rather poorly compared with the cerium sulfides at the high temperature. This is in contrast to their behavior at temperatures below 1300°C. where the thorium sulfides were as good or better than the cerium sulfides. A possible explanation for the higher sulfur pickups and the 0.1-0.5 mm. thicknesses of crucible remaining on the ingot is the oxide content of these sulfides which varied from 22% ThO_2 in ThS to 5% ThO_2 in Th_4S_7. It is known that the oxides are more readily attacked than the sulfides and the attack of the oxide phase can allow penetration of the crucible by the metal for several tenths of a millimeter and possibility of disengagement of particles of sulfide material from the surface. It is quite possible that oxide free thorium sulfides would give much smaller sulfur pickup and would break cleanly from the ingot. Oxide free sulfides can be made if thorium metal can be purified to reduce the oxide content. Work is in progress to attempt such purification. Such work seems worthwhile since Th_4S_7 and Th_2S_3 appear to be very promising refractories on the basis of the lower temperature experiments.

The smaller sulfur pickups in the cases of the porous Th_2S_3 and ThS crucibles are rather puzzling. A possible chemical explanation is that the higher firing temperature required for production of the dense crucibles has resulted in reaction between ThO_2 and sulfide to give oxysulfides that are more readily attacked than ThO_2. From appearance of the ingots in the crucibles, it appeared that the dense crucibles were more readily wetted by the molten metal.

In summary, these results at 1500°C. indicated that remelting or vacuum heating of cerium containing alkaline earth impurities can be carried out with little attack of the crucibles. The porosities of the crucibles must be 20% or lower to prevent soaking up of the metal. The thorium sulfides give higher sulfur pickups and more evidence of attack which may be due to the high oxide content. Ce_2S_3 and Ce_3S_4 gave ingots which broke away cleanly with 3000-4000 p.p.m. sulfur. CeS gave an ingot with 1600 p.p.m. sulfur and thin layer of crucible sticking to ingot.

Comparison with previous lower temperature runs shows that Th_4S_7 and Th_2S_3 also give ingots which break cleanly away from the crucible when the heating is below 1300°C. Also the sulfur pickups at the lower temperatures were always less than 400 p.p.m. and less than 100 p.p.m. in many cases. It should be noted that the product remelts are usually not made above 1200°C. Comparison of these results with results obtained in oxide crucibles indicate that the sulfide crucibles are far superior.

The resistance of the sulfides to attack at 1500°C. may prove valuable if it is desired to purify a metal by vacuum heating at a high temperature. While all the alkali and alkaline earth metals except Be can be removed by vacuum heating at 1200-1300°C., Al, Cr, and Mn can not be removed unless the temperature is raised to about 1500°C. Even higher temperatures are required to remove Be and B by simple distillation of the metal, but it should be possible to obtain complete removal of Be and B as BeS and BS gases even at temperatures as low as 1200-1300°C. by vacuum heating in a Th_4S_7, Ce_3S_4, or Ce_2S_3 crucible. It has been shown in experiments which have been reported in previous reports that Be in uranium can be decreased to below 0.05 p.p.m. by melting for five minutes at 1300°C. in a high sulfide crucible.

B. THE USE OF SULFIDE CRUCIBLES FOR METAL REDUCTIONS.

271 006

The previous tests with Ba, Sr, and mixtures of U with various halides which were mentioned in the introduction showed that the higher sulfides are attacked too severely to be used as containers for reductions. However, CeS, ThS, US, and solid solutions of these monosulfides did resist attack and they appear satisfactory as containers. Dr. William Gwinn has carried out further tests on CeS crucibles with varying amounts of higher sulfide impurity in the CeS. Crucibles of composition $CeS_{0.990}O_{0.073}$ were not attacked by the following mixtures at 800-900°C.: (1) molten calcium metal, (2) calcium metal + $CaCl_2$, and (3) a mixture of LiCl, KCl, $CaCl_2$, and $CeCl_3$.

However when Ca + LiCl + KCl + $CaCl_2$ was heated in the crucible or when $CeCl_3$ was reduced by Ca in a LiCl + KCl bath, the crucible was severely cracked. Examination of the crucible material between cracks indicated no chemical attack of the CeS since the brassy color of the CeS was quite evident. Previous microscopic examination of polished section of crucibles of this composition at M.I.T. had shown that $CeS_{0.99}O_{0.073}$ consists of two phases. There is the brass CeS phase and a blue phase which is undoubtedly Ce_3S_4 containing a large percentage of oxygen. The CeS grains average about 75 microns in diameter and are completely separated from each other by the blue phase. Since previous experiments have shown that the higher sulfides are severely attacked by the reduction mixture, the cracking of $CeS_{0.99}O_{0.073}$ crucibles is probably due to attack of the higher sulfide between the grains which results in intergranular cracking. To check this, the reduction experiments were repeated with crucibles of composition $CeS_{0.967}O_{0.043}$ which had been shown under the microscope to consist of a continuous field of CeS with small patches of the blue phase. These crucibles showed no cracking whatever during the reduction although heating was very rapid and every attempt was made to make the test as severe as possible.

It is clear from these experiments that in order to be satisfactory, CeS crucibles used for reductions must have so little higher sulfide in them that the CeS grains are no longer separated by the higher sulfide phase. CeS samples with oxidation numbers 2.12, 2.10, 2.09, 2.05, and 2.02 have been sent to M.I.T. to determine the maximum allowable oxidation number above 2.00 for which the CeS grains are not surrounded by the higher sulfide. The CeS preparations have been running somewhat high in oxidation number because of rather high carbon and oxide contents of the Ce_2S_3 we have been receiving. Dr. Johnson at M.I.T. expects to have the preparation difficulties overcome shortly and he should be able to prepare Ce_2S_3 on a large scale with little oxide or carbon contamination which will allow preparation of purer CeS.

Tests of ThS as a reduction container will also be run shortly. The ThO_2 impurity in the present ThS crucibles may cause some trouble.