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Section B

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Sulfide Report XVIII.

THE EFFECT OF IMPURITIES UPON SULFIDE
REFRACTORIES

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Abstract

A summary of the effect of metal, carbon, silicon, and oxygen impurities upon the various sulfide refractories is given and the proper procedures for elimination of the impurities are discussed.

CeS which is properly prepared can be handled in air without danger of catching fire or appreciable oxidation. 650 satisfactory crucibles have been made to date using sulfides which were screened and pressed in air with less than 0.5% oxygen pickup. The other cerium and thorium sulfides are even more inert to oxidation than is CeS.

Phase diagram possibilities are discussed for the cerium and thorium sulfide and oxy-sulfide systems.

Further study of ThS has shown that ThS crucibles are the highest melting and the least volatile of the sulfide crucibles and ThS may be used for remelting of some metals up to 2000°C. ThS crucibles appear to be the most suitable containers for metal reductions.

Index to Sulfide Reports

A list of the first twelve sulfide reports along with their Chicago report numbers was given in CT-2290. The Chicago report numbers for subsequent reports are as follows:

- XIII. A High Temperature-High Vacuum Apparatus. CT-2139
- XIV. The Preparation and Use of BaS as a Refractory CT-2232
- XV. The Preparation of Sulfide Crucibles CT-2290
- XVI. The Properties of Sulfide Refractories CT-2291
- XVII. The Use of Sulfide Crucibles for Remelting and Reductions. CT-2453

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Sulfide Report XVIII

The Effect of Impurities upon SulfideRefractories

The group which is to take over the large scale production of sulfide refractories from our group has encountered several difficulties in the preparation of sulfide crucibles which had not caused much trouble here. Since it is suspected that the difficulties are due to impurities which were not present in our materials, a study of the effect of various impurities has been made and a summary is presented in this report.

The troublesome impurities likely to be present can be divided into three groups. The least troublesome group contains various metal impurities such as sodium, magnesium, and calcium which come mainly from the starting oxide material. The next most troublesome impurities are carbon which enters during the conversion of oxide to sulfide in a carbon apparatus and silicon which enters in large part during the metal reduction. The most troublesome impurity is oxygen which may be present in the starting materials or introduced during various steps of the preparation. To avoid confusion, the effect of each type of impurity will be considered separately for each sulfide.

I. CeS

A. Metal Impurities. Sodium, magnesium and calcium sulfides are present up to several percent in Ce_2S_3 as ordinarily prepared and about 0.5% calcium metal is present in cerium metal. When the CeS is prepared by reducing Ce_2S_3 with excess Ce metal and vaporizing the excess Ce metal, the alkali and alkaline earth sulfides are reduced and the metals vaporized. After a $2200^\circ C.$ heating, the metals can not usually be detected spectroscopically and after a $2000^\circ C.$ heating, only traces of Mg and Ca can be detected.

When commercial cerium metal containing several percent iron was used for reduction, the iron was also completely vaporized although the iron rather severely attacks the molybdenum containers and shields. The cerium metal which is used at present does not contain iron and the alkali and alkaline earth metals do not affect the molybdenum. The metallic impurities are somewhat troublesome in that they distill out of the reduction container on to the walls of the vacuum apparatus. They are spontaneously combustible in air and special fire precautions given below must be taken when the vacuum is broken. The cerium metal is added as a hydride and the metal impurities start to distill out towards the end of the dehydriding. The sublimates are much more combustible the higher the pressure of hydrogen during

the dehydrating. To prevent explosion of the sublimates, the preparation is allowed to cool over an hour in vacuum and about 30 minutes in argon. Then the tubes are removed while wearing goggles and asbestos gloves and are allowed to stand overnight in air in a safe place. The slow diffusion of the air into the argon slowly oxidizes the combustible sublimates. However, aside from the fire hazard, the metallic impurities do not cause any difficulty as far as CeS is concerned because of the complete removal during the preparation.

In addition to the metals listed above, commercial cerium oxide also contains fairly large amounts of other rare earths. Their greatest disadvantage is in complication of analyses. It is not known how the properties of CeS are affected by other rare earths. Sm, Eu, Tb and Yb would probably be most objectionable and Nd the least objectionable.

B. Carbon and Silicon Impurities.

The Ce_2S_3 being received at present from the large scale production group contains about 0.5% free carbon by weight or 8 mole Percent in $CeS_{1.5}$. This introduces a rather high mole percent of CeC_2 or CeC when the Ce_2S_3 is reduced by Ce metal. During the high temperature preparation, some of the carbon is removed by the reaction of $CeS + CeC = CS(g) + 2 Ce(g)$. However, this reaction does not progress very far even at $2200^\circ C$. especially as long as excess cerium is still present. At $2200^\circ C$, the pressure in the system is about 10^{-3} mm. due to the escape of CS gas. This corresponds to .03 moles of CS per hour and it would take a very long heating to remove any appreciable amount of carbon. To check this point more definitely, 0.7% carbon was added to CeS. The mixture was gradually heated to $2150^\circ C$ in a vacuum; considerable gas evolution was obtained at $1800^\circ C$. But after it had ceased, not much gas was evolved at higher temperatures even up to $2150^\circ C$ where a pressure of 10^{-3} was obtained. From the pressure, the amount of sublimate, and the weight loss during the heating and from the final analysis, it was concluded that the reaction $3C + CeS = CeC_2 + CS(g)$ or the corresponding reaction to CeC took place at $1800^\circ C$ and the carbide formed did not react further with CeS even at $2150^\circ C$. Therefore any carbon present in Ce_2S_3 used for a CeS preparation will react with cerium metal to form cerium carbide, which can not be removed by vacuum heating even at $2200^\circ C$.

As far as is known at present, the carbide impurity has only one bad effect upon CeS. It is not known whether CeC , CeC_2 , or both are present. However CeC_2 hydrolyzes readily in moist air to give off hydrocarbons. CeS itself does not react even with boiling water when pure, but CeS containing carbide impurity reacts with moist air to give off an acetylene odor

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and, of course, to introduce oxide into the CeS. The carbide impurity might also make the CeS crucibles more susceptible to attack in use, but experiments to test this have not been performed.

The presence of carbide also interferes with analysis of CeS. Acetylene causes precipitation of silver acetylide during the sulfur analysis and raises the sulfur value. The acetylene liberated during the oxidation number determination would make the oxidation number appear low if the acetylene is not dissolved. Actually because cerium carbide does not give acetylene exclusively and because the acetylene does not seem to precipitate silver quantitatively and because of the rather high solubility of acetylene in water, the analyses are not in serious error with the usual magnitude of carbon impurity.

Although it would be very desirable to eliminate the carbon impurity by obtaining Ce_2S_3 which is low in carbon, many satisfactory CeS crucibles have been made here from $CeS_{1.5}$ containing 0.5 wt.% or 8 mol.% of carbon. However, it should not be difficult to prepare Ce_2S_3 containing less than 0.2 wt.% carbon as will be pointed out below.

Silicon is present in the starting oxide material and also to some extent in the cerium metal, but usually not in high enough concentration to be serious. Silicon is believed to be introduced during the metal reduction due to reduction of SiO_2 by the alkaline earth metal vapors and by cerium vapor. As carried out here, the only source of silicon during the reduction is from the zircon crucible which is used as a shield for the molybdenum container. The silicon enters the gaseous phase as either SiO or Si . There is also the possibility of ZrO formation in the gaseous phase which may result in zirconium contamination. The apparatus which is being used for large scale production elsewhere contains hot quartz which is another source of SiO or Si vapor in addition to the zircon crucible which is much hotter than the zircon in our apparatus due to water cooling of our glass tube and the use of Mo radiation shields inside the zircon.

No data can be given for the extent of contamination of the CeS by silicon and no data are available on the effect of silicon upon the performance of the sulfide crucibles. Some experiments with cerium metal have indicated that there may be a high enough gaseous silicon concentration in the apparatus to cause appreciable contamination, but the results are not definite as yet. A suitable analytical method will have to be devised to check silicon contamination. All that can be said is that the method used here will give much less silicon contamination since there is no hot quartz in the system and the zircon crucible is much cooler than in the large scale

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apparatus. It is not known whether the greater silicon contamination can account for differences in behavior of CeS prepared by the two groups.

G. Oxide Impurity.

Oxygen is a troublesome impurity which may be present in the starting sulfide material, the reducing cerium metal, or which may be introduced in the handling of the metal or sulfide at various stages of preparation.

Oxide impurity is troublesome since cerium oxide is not reduced readily to a solid divalent state and the oxide impurity will be found in a separate oxy-sulfide phase with an oxidation number close to three while the CeS phase will have an oxidation number of two. The eutectic between CeS and the oxysulfide phase is rather low melting and the presence of much oxide in CeS will cause distortion and slumping of the crucibles during sintering. Also during the sintering, the eutectic liquid will tend to segregate on the exterior of the crucible and the cooler portions of the crucible will be coated with the black oxysulfide. This oxysulfide is rather brittle and portions of the crucible in contact with the segregated oxysulfide are brittle and tend to chip.

Also as has been pointed out in OT-2433, the presence of the oxy-sulfide phase makes the CeS crucibles more susceptible to attack during use as containers for metal reductions. No experiments have been performed to determine the effect of oxide impurity upon the performance of CeS crucibles as remelt containers. The oxide impurity does affect the appearance of the crucibles. Crucibles made from the relatively oxide free CeS have much smoother surfaces, are not appreciably brittle, and are easy to sinter without distortion. However, CeS crucibles with oxidation numbers as high as 2.15 and containing as much as 8 atomic percent of oxygen have apparently been used satisfactorily by the consumers for remelting. To be used satisfactorily as a metal reduction container, the CeS should have less than 4 atomic percent of oxygen and an oxidation number less than 2.02.

To prevent trouble due to oxide impurity, the starting Ce_2S_3 and Ce should be as free of oxide as possible and the various precautions given in OT-2290 for the handling of the metal hydride and sulfide should be carried out to prevent introduction of oxygen. Fortunately, it is possible to remove a great deal of the oxygen during the preparation so that if the original materials contain some oxide or contamination accidentally occurs, it is still possible to prepare pure CeS. Cerium oxides and oxysulfides can be reduced at high temperatures and low pressure to volatile CeO. To accomplish this, approximately 30-40% Ce metal is added in excess of that required for the reaction $Ce_2S_3 + Ce = 3 CeS$. The excess of metal

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not only reduces alkali and alkaline earth sulfides, but it will reduce trivalent cerium oxide or oxy-sulfide to volatile CeO . The metal impurities are removed at $800-1200^{\circ}C$ and CeO is first removed above $1700^{\circ}C$. To obtain almost complete removal of the oxide in a short time, a heating at $2100-2200^{\circ}C$ is required. At this temperature practically all of the oxide is removed as CeO and all the excess Ce metal is vaporized as metal. The 40% excess of cerium and the $2100-2200^{\circ}C$ heating will give practically oxide free CeS even when starting with Ce_2S_3 containing 10 atomic percent of oxygen per atom of Ce . With much lower preparation temperatures, the rate of reduction of oxide is much slower and the removal of oxide is not complete in the time required to completely vaporize the cerium metal. However, a shorter heating is required and the preparation is much easier if relatively oxide free materials can be used, and every attempt is made to prevent oxide contamination before the heating even though it is possible to remove the oxygen. The proper handling of the metal hydride is the most important factor in preventing oxygen contamination.

Since cerium has a vapor pressure of almost 0.1 atmospheres at $2200^{\circ}C$, there is little danger of free cerium metal remaining in the preparation. Also all evidence to date indicates that CeS does not have an appreciable range of solid solubility. It apparently can not dissolve either Ce metal or Ce_3S_4 to any large extent. In *OT-2291*, it had been reported that it was believed that a range of solid solubility from $CeS_{0.8}$ to CeS existed, but it has been since shown that the evidence was in error due to neglect of oxide and carbide content. $CeS_{0.939}O_{0.021}$ with an oxidation number of 1.92 is the preparation with the lowest oxidation number which has been prepared here and it appears quite definite that the difference between 1.92 and 2.00 is due to the presence of carbon which probably does not contribute to the oxidation number analysis as discussed above in connection with carbide impurity. All samples with oxidation numbers above 2.00 have contained an oxy-sulfide phase with oxidation number above 2 and a CeS phase which undoubtedly has an oxidation number of almost exactly 2.0. Microscopic analyses of CeS samples by Dr. Barlett have indicated a high temperature solid solubility of Ce_3S_4 or the oxy-sulfide phase in CeS but it was a very small solubility. Therefore on the basis of evidence to date, CeS is a definite compound with no appreciable range of solid solubility and any samples with oxidation numbers differing appreciably from 2.0 contain phases other than the CeS phase.

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Neglecting cerium polysulfides, the phase diagram of the cerium-sulfur system consists of two sulfide phases. The CeS phase with NaCl structure has no appreciable range of solid solubility and melts above 2300°C and probably not over 2500°C. The Ce₃S₄ cubic phase has a continuous range of solid solubility from CeS_{1.33} to CeS_{1.5}. The melting point does not vary much over the range and is between 1850 and 1950°C. The eutectic between CeS and Ce₃S₄ is at about 1750°C. Addition of oxygen lowers the melting point of the Ce₃S₄ to Ce₂S₃ region as well as lowering the eutectic melting temperature between CeS and Ce₃S₄. Oxygen distributes itself between CeS and Ce₃S₄ with most of it in the Ce₃S₄. When much oxygen is present, the Ce₃S₄ is probably converted to Ce₂SO₂. The eutectic between Ce₂SO₂ and CeS appears to melt below 1650°C.

To aid in the duplication of the preparation of very pure CeS, the log of a preparation run is given. Preparation B-4-74-A was made by mixing 332.2 grams of CeH₃ with 612 grams of Ce₂S₃ from batch 2H. Batch 2H analyzed S/Ce = 1.46 and therefore contained an oxygen content of O/Ce = 0.1 since due to presence of sodium and magnesium sulfides, an oxide free preparation has an analysis of S/Ce = 1.56 when all the metal is counted as cerium. The heating tubes which are described in OT-2290 were loaded in a dry box and the following log gives the pressures at various times during the preparation.

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TIME	PRESSURE	HEATING
11:40		Mechanical and diffusion pumps turned on.
11:50	50×10^{-3} mm.	
12:00	25×10^{-3} mm.	
12:10	11×10^{-3} mm.	
12:20	3×10^{-3} mm.	
12:30	5×10^{-4} mm.	Diffusion pumps turned off.
12:33		Converter set at lowest heating.
12:40	0.5 mm.	Heating increased one division.
12:45	1. mm.	" " " "
12:48	1.3 mm.	" " " "
12:50	1.8 mm.	" " " "
12:53	2.3 mm.	" " " "
12:56	2.5 mm.	" " " "
1:00	3.0 mm.	Heating increased several divisions.
1:03	3.3 mm.	" " " "
1:05	3.8 mm.	
1:10	4.0 mm.	
1:50	6.2 mm.	
1:53	8. mm.	First metallic sublimate on glass. Temperature of preparation about 750°C. Diffusion pumps turned on. Increased heating one division
1:55		Temperature 790°C.
1:56		" 845°C., heating increased
2:02	9.5 mm.	one division.
2:06	8. mm.	Temperature 850°C.
2:08	9. mm.	Temperature 890°C.
2:10	6. mm.	Temperature 960°C.
2:12	3. mm.	Temperature 1170°C.
2:14	0.5 mm.	
2:15	20×10^{-3} mm.	
2:17	8×10^{-3} mm.	
2:19	4×10^{-3} mm.	
2:30	1×10^{-3} mm.	Increased heating
2:50	3×10^{-4} mm.	Temperature of 1850°C observed. Converter turned off to change leads for high temperature heating.
2:51	5×10^{-5} mm.	Converter on for high tempera. heating
3:05	1.5×10^{-3} mm.	Temperature of 2240°C observed.
3:10	6×10^{-4} mm.	Converter turned off.
3:50		Broke vacuum with argon.
4:30		Removed tubes to stand overnight in air.

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The preparation analyzed $CeS_{0.936}O_{0.021}$. The oxidation number of this preparation was discussed on the previous page. A sample has been sent to Dr. Barlett for microscopic analysis. The bottom half of the preparation had sagged as if it had partially melted or softened which had not occurred before in any of the preparations at lower temperatures. Usually when the starting Ce_2S_3 has less oxide, the preparation is not heated over $2150-2200^{\circ}C$. observed.

The details of the preparation are the same as described in CT-2290 and CT-2139 except for the following details. All difficulties with spraying of powder during the dehydrating have been eliminated by tamping the powder around a rod which is pulled out when the container is full. This leaves a hole extending to the bottom which prevents hydrogen liberated at the bottom of the container from lifting all of the powder right out of the container. Two sheets of .002 inch Mo foil are now used between the Mo container and the zircon crucible for insulation and the number of radiation shields above the container have been increased to five or six to raise the attainable temperature.

Very sensitive adjustment of heating is now obtained by using a coil of large variable inductance in series with the heating coils. Pressure above 1 mm. during the dehydrating are measured with a butyl phthalate manometer. The manometer is provided with a stopcock on the evacuated side to allow reevacuation from time to time.

Dr. Johnson has reported that their CeS has been very inflammable and that they have had difficulties obtaining oxygen free material. They probably have not heated the CeS to a high enough temperature to remove excess cerium and to obtain CeS in a nonreactive state. Also they may grind the CeS too fine. Here, the CeS is ground for four hours in a ball mill at which time 65% passes 325 mesh. The coarse powder is saved for the next grinding. Some of our powder has been sent for particle size determination. CeS prepared here is only very slowly oxidized. A sample of powder which analyzed $CeS_{0.996}O_{0.043}$ when first prepared had oxidized to $CeS_{0.966}O_{0.07}$ after standing out in air for 35 days. The powder is handled and crucibles are pressed in air with no special precautions. Dr. Johnson's difficulty will undoubtedly disappear upon raising the preparation temperature; for we definitely do not have to take any elaborate precautions in handling CeS . CeS which is properly prepared can be handled in air without danger of catching fire or appreciable oxidation. We have made 650 satisfactory sulfide crucibles to date and we have screened and pressed all our sulfide powders in air with less than 0.5% oxygen pickup. If a very oxide free CeS were desired, screening in inert atmosphere might be necessary; but pressing could still be done in air.

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Trouble was experienced for a while in hydriding of cerium metal due to the oil used to pack the metal. However, recent shipments of cerium which is now being recast in sticks have caused no difficulty whatever. The recast sticks are apparently less porous and do not absorb oil. The surface is easily cleaned by machining and the oil removed with benzene, and hydriding proceeds very readily.

In summary, the most important factors in the preparation of pure CeS are the use of Ce_2S_3 which is low in oxide, the use of excess cerium metal, and a high preparation temperature.

II. Ce₃S₄

A. Metal Impurities.

Since Ce_3S_4 crucibles are being made here by pressing a mixture of Ce_2S_3 and CeS powders and sintering, all metallic impurities come from the Ce_2S_3 . During the sintering, the CeS reduces the sodium and magnesium sulfides liberating the metals of which all of the sodium and practically all of the magnesium can be removed at the sintering temperature of 1750°C observed, but most of any calcium present will remain. Since the metal impurities start to distill out at 900-1200°C the escape of the gaseous metals does not cause blistering as in the case of the escape of CS noted below since the metals vaporize at temperatures at which the sulfide is still very hard and can not be readily deformed. As far as is known now, these impurities do not seriously affect the properties of Ce_3S_4 , but their presence may result in contamination of a remelt. The use of pure Ce_2S_3 would be required to obtain Ce_3S_4 free of the metallic impurities.

B. Carbon Impurity.

Here again it is the impurity in Ce_2S_3 which causes trouble. Any carbide in CeS will not react with Ce_2S_3 , but free carbon in Ce_2S_3 will react according to the equation $Ce_2S_3 + C = 3/5 Ce_3S_4 + 1/5 CeC_2 + 3/5 CS(g)$. Using Ce_2S_3 and 0.5% carbon, 120 volumes of CS gas will be given off per volume of Ce_3S_4 at 1700°C if the carbon completely reacts. Since the crucible material becomes soft enough to be distorted by a moderate force at the sintering temperatures, the formation of CS gas blows blisters on the crucibles. This effect is especially pronounced in crucibles with thick bottoms or wall sections. To prepare satisfactory crucibles, Ce_2S_3 with less than 0.2% carbon would have to be used. Nothing is known of the effect of silicon contamination.

C. Oxide Impurity.

Oxide can come from the Ce_2S_3 or it may come from the CeS if it has not been treated at a high enough temperature. Pure

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Ce_3S_4 can be sintered above $1750^\circ C$ observed without distortion, but the presence of 5 mol percent oxide will cause distortion and slumping even at $1650^\circ C$. Aside from lowering of melting point, the presence of oxide does not affect the quality of the crucible as far as is known now. It is conceivable that oxide or carbide impurities in the crucibles may be attacked more readily than the pure sulfide and initiate attack under conditions where a pure crucible would not be attacked. This has been shown to be true under some conditions for CeS crucibles and has been indicated as a possibility for the various thorium sulfides, but Ce_3S_4 crucibles have held up so well even when containing oxide impurities that no evidence is available as to whether the oxide impurity causes trouble. Oxide impurity can not be removed from the Ce_3S_4 by heating and can be avoided only by using oxide free starting materials.

III. Ce_2S_3

A. Metal Impurities:

It has been shown above that metal impurities in the Ce_2S_3 used to prepare CeS do not cause much trouble and that the contribution to Ce_3S_4 impurities does not seem to be troublesome aside from possibility of contamination of a remelt. A Ce_2S_3 crucible will be affected much more by these impurities since there is only partial removal of sodium and magnesium and practically none of calcium during the sintering so that the impurities may be very high. Heating Ce_2S_3 as received for 20 minutes at $1725^\circ C$ observed produces a 2.4% loss in weight due to vaporization of the sodium and magnesium sulfide impurities. The sodium and magnesium sulfides are volatile due to the reactions $Na_2S(s) = 2Na(g) + S(g)$ and $MgS(s) = Mg(g) + S(g)$. If all the metal is counted as cerium, the analysis changes from $S/Ce = 1.55$ to $S/Ce = 1.50$ as a result of the heating. If sodium sulfide is analyzed as a cerium sulfide, $S/Ce = 3.0$. If magnesium sulfide is analyzed as a cerium sulfide, $S/Ce = 5.8$. From the loss of weight and change in analysis of the Ce_2S_3 , the composition of the sublimate is $S/Ce = 3.8$. Since some sulfur is lost as a result of the reaction $3Ce_2S_3 = 2Ce_3S_4 + S(g)$, it is seen that the sublimate is largely sodium which can be checked by analysis of the sublimate. However, the impurities will be troublesome only in as far as they contaminate the melt. If contamination is serious, the impurities can be eliminated by using a purer CeO_2 starting material. The ordinary commercial grade of CeO_2 has several percent of sodium, magnesium, and calcium. Magnesium is a somewhat undesirable impurity during the conversion of oxide to sulfide since it is much more difficult to convert MgO to MgS than it is to convert sodium, calcium, or cerium oxides. Therefore the presence of magnesium makes it somewhat more difficult to remove the last traces of oxygen during the conversion to sulfide. If these impurities are to be avoided, pure CeO_2 is available from the Lindsay Light and Chemical Co., West Chicago, Illinois, or from Rohm and Haas, Philadelphia, Penn.

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B. Carbon Impurity.

Carbon impurity is even more serious for Ce_2S_3 than for Ce_3S_4 since 240 volumes of CS are given off per volume of Ce_2S_3 for completion of reaction at $1700^\circ C$ and the reaction will go further to completion with the higher sulfide. Very serious blistering is obtained when Ce_2S_3 containing 0.5% carbon is used to prepare Ce_2S_3 crucibles. Also the presence of carbon means that CS gas will be escaping from the crucible during use and it may cause contamination of the melt.

If carbon free Ce_2S_3 is not available and it is desired to prepare either Ce_2S_3 or Ce_3S_4 crucibles, the Ce_2S_3 may be vacuum heated to allow the reaction $Ce_2S_3 + C = 3/5 Ce_3S_4 + 1/5 CeC_2 + 3/5 CS(g)$ to go to completion to use up all the carbon. The material must be heated above its melting point to obtain complete reaction within an hour. After conversion of the carbon to carbide, the Ce_2S_3 may then be used to prepare Ce_2S_3 or Ce_3S_4 crucibles without blistering troubles since CeC_2 does not react with Ce_2S_3 at sintering temperatures. However, the vacuum heating is a very troublesome operation since it must be done carefully or the Ce_2S_3 will be sprayed out of the crucible by the escaping gas and it is an unnecessary operation if Ce_2S_3 can be obtained which is low in carbon. The Ce_2S_3 should have considerably less than 0.2% carbon to be used for Ce_2S_3 crucibles.

Carbon is introduced into the Ce_2S_3 during the conversion from oxide by one of two methods. The container used is made of graphite or carbon and due to attack by the sulfur gases, there is some disintegration of the container which introduces carbon powder into the Ce_2S_3 . However, this should not be serious since the Ce_2S_3 prepared here has always contained less than 0.1% carbon and with the small samples prepared here, the chance of contamination from the container would be much more likely than with the large charges used for large scale production. The other method of introduction of carbon is by use of $CS_2 + H_2$ instead of H_2S to convert the oxide to sulfide. The following calculations give the reason for carbon deposition. The figures given are based on the data given in CC-1334, "The Thermodynamic Properties of Common Gases".

- (1) $CS_2(g) + 2H_2(g) = C(s) + 2H_2S(g)$, $K_1 = 1800$ at $1000^\circ K$.
- (2) $CS_2(g) + H_2(g) = CS(g) + H_2S(g)$, $K_2 = 200$ at $1000^\circ K$.
- (3) $CS(g) + H_2(g) = C(s) + H_2S(g)$, $K_3 = 10$ at $1000^\circ K$.

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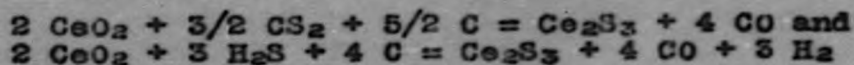
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Equal amounts of CS and H₂S are formed by reaction (2). Thus it is easily seen that the CS will be reduced by hydrogen at pressures greater than 0.1 atmospheres. Reference to the entropy values given in CC-1334 shows that CS₂ can be reduced by hydrogen to carbon at all temperatures and carbon deposition can be prevented only if CS is not reduced. Therefore, at 1000°K. or 700°C, CS₂ should be completely reduced to solid carbon if the hydrogen pressure is greater than 0.1 atmospheres.

At higher temperatures, higher pressures of hydrogen can be allowed without carbon deposition due to the increased stability of CS. The temperature would have to be over 900-1000°C before a hydrogen partial pressure approaching an atmosphere could be used with CS₂ without carbon deposition.

Therefore if CS₂ and H₂ are passed through the apparatus while it is heating up or while it is cooling down, carbon will be deposited from temperatures somewhat below 1000°C to temperatures low enough for the reaction rate to be slow. To avoid carbon deposition, CS₂ must not be passed through the apparatus unless the temperature is at least 1000°C. It is possible to obtain Ce₂S₃ which is both free of oxygen and carbon, for preparations have been made here which contained less than 0.1% oxygen or carbon. These preparations were made by the action of H₂S on CeO₂ in a graphite apparatus at about 1300°C.

The use of CS₂ has several advantages over H₂S. CS₂ is easier to dry and handle, it carries more sulfur per gaseous volume, and it does not attack carbon as extensively as does H₂S. In both cases, CS appears to be the intermediate reactant at high temperatures due to the reactions CS₂ + C = 2 CS and H₂S + C = CS + H₂. It can be seen that H₂S uses up twice as much carbon as does CS₂ per gram atom of sulfur. When the apparatus is at maximum temperature, the net reactions are



At lower temperatures, especially at the beginning of the reaction, H₂O and S₂ are also products of the reaction with less carbon being used up. For example with H₂S, the net reaction at temperatures below 1000°C for the first stage of the reaction is 2 CeO₂ + 2 H₂S = Ce₂SO₂ + 2 H₂O + 1/2 S₂. Since H₂S can be used at a lower temperature than CS₂ + H₂, H₂S can be used for the first stage of the reaction with little carbon attack. Thus the difference in the behavior of H₂S and CS₂ is not important if the CS₂ is used properly.

At this group, the H₂S is dried by P₂O₅. The P₂O₅ is packed in a drying tube with a sealed-in porous glass filter on the side towards the apparatus to prevent the carrying of P₂O₅ dust into the apparatus. If the H₂S available contains excessive amounts of water, it can be first dried by a less efficient drying agent such as alumina to remove most of the water.

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More effective use of CS_2 can be obtained by using a carrier gas other than H_2 . If no hydrogen is present, the CS_2 will not be reduced to carbon. Hydrogen can be used if the partial pressure of the CS_2 is increased by warming the liquid CS_2 so that the pressure of CS_2 is greater than that of the hydrogen. Helium would be a satisfactory carrier gas which is cheap and easily purified. Also H_2S would be a satisfactory carrier. If the CS_2 is warm so that most of the sulfur comes from the CS_2 , the amount of H_2S required would not be large and it could be easily dried by P_2O_5 . H_2S would be much better than H_2 because it would not have any reducing action. With no H_2 present, there is little chance of CS_2 decomposing to give much carbon. For example, at $500^\circ C$, the S_2 partial pressure would have to be less than 8% of the CS_2 pressure to allow decomposition of CS_2 to carbon and at higher temperatures the increased stability of CS_2 prevents carbon deposition. So it can be seen that much is to be gained by substitution of another gas in place of H_2 as carrier for CS_2 . In any case using either H_2S or CS_2 , there is danger of carbon deposition if part of the apparatus is considerably below $1000^\circ C$ when the entering gases pass through a region hotter than $1000^\circ C$, for the CO and CS formed in the hot region may disproportionate in the cold region to give carbon and CO_2 or CS_2 . This is easily prevented by proper design of apparatus. Nothing is known of the effect of silicon.

C. Oxygen Impurity.

As pointed out above, Ce_2S_3 to be used for CeS preparation should be as free of oxide as possible down to 1 to 2 atomic percent. The effect of oxide upon Ce_2S_3 crucibles is practically identical with the effect upon Ce_3S_4 crucibles described above, and the oxide content should be kept low. This is done by treatment at a high enough temperature for a long enough time with CS_2 or H_2S or both. The oxide impurity is not removed by vacuum heating of Ce_2S_3 .

IV. Thorium Sulfides.

A. Metallic Impurities.

Since quite pure ThO_2 is readily available, no trouble is experienced with introduction of metallic impurities from the starting oxide material. Thorium metal sometimes contains small amounts of Be, Mg, and Ca, but these are largely removed during the preparation of the sulfides and are not likely to cause any difficulties.

B. Carbon Impurity.

All thorium sulfides made to date have been made from ThS_2 prepared here which has had less than 0.05% carbon and no trouble has been experienced with carbon. If ThS_2 containing

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0.2-0.3% carbon is used, the same difficulties that were described in the case of the cerium sulfides would be experienced with the thorium sulfides. The thorium metal being used to reduce ThS_2 contains appreciable amounts of inclusions which may contain carbides as well as nitrides and oxides. These inclusions are found apparently intact in the sulfides prepared by use of the metal, but no experiments have been performed to test their effect upon the performance of the crucibles.

C. Oxide Impurity.

Oxygen is a serious impurity in the preparation of thorium sulfides since it is difficult to obtain oxide free metal and it is not as easy to remove oxygen during the preparation as it is in the case of CeS . ThS_2 which contains less than 1 atomic percent of oxygen has been prepared here by the action of H_2S upon ThO_2 at 1500°C in a carbon apparatus. If oxide free ThS could be prepared, then oxide free Th_4S_7 and Th_2S_3 would be easily made by mixing the ThS_2 and ThS .

All of the ThS preparations to date have contained at least 10% of a residue insoluble in acid which shows up microscopically as a separate phase. This residue appears to come from the metal used in the reduction and is undoubtedly largely oxide although it may contain nitride and carbide. Excess thorium metal can not be used to reduce the ThO_2 to gaseous ThO as in the case of CeS because thorium is so non-volatile even at 2200°C (10^{-5} atm.) that the excess thorium metal can not be removed by vaporization, and it has been shown that the presence of excess thorium metal makes the ThS crucibles much less suitable as containers for remelting. Experiments are in progress now to remove the oxide by adding excess cerium metal to a mixture of $\text{ThS}_2 + \text{Th}$ and distilling off the excess cerium at 2200°K as in the case of CeS . Preliminary results have indicated that oxide is removed and it might be possible to prepare oxide free ThS by this method. Because of the large demand for cerium sulfide crucibles, it has not been possible to do much work on the thorium sulfide crucibles. As soon as the large scale CeS crucible production has been taken over, more extensive work on the thorium sulfides is planned. ThS , in particular, appears very promising for certain purposes. It is the most stable, least volatile, and highest melting of the sulfides and can be used for metal remelting at temperatures as high as 2000°C .

In Sulfide Report XVII (CT-2433), it was shown that crucibles made of CeS containing appreciable amounts of oxy-sulfide impurity were not satisfactory containers for metal reductions while pure CeS crucibles were satisfactory containers. The experiments have been repeated with thorium sulfide crucibles and $\text{ThS} \cdot 0.22\text{ThO}_2$ crucibles were found to be satisfactory containers for the preparation of cerium metal by reduction of cerium chloride

by calcium. From these tests, it appears that oxide impurity does not have the serious effect upon ThS that it does upon CeS. Also experiments have shown that uranium can be heated in ThS-0.22ThO₂ crucibles at 1900°C for long periods of time with no detectable attack of the crucible. Clean ingots are obtained which break cleanly from the crucible.

From the above results and the other promising properties of ThS, further work on the development of ThS crucibles appears very worthwhile and pure oxide-free ThS may prove to be even more promising than impure ThS being used at present.

In CK-1714, a preliminary phase diagram of the thorium sulfide system based on the X-ray work of Strotzer und Zumbusch, Z. anorg allg Chem 247, 415 (1941) was given. Dr. Zachariassen has examined thorium sulfides of a wide range of compositions and has shown the German work to be in error. His results were summarized in Sulfide Report XVI (CT-2291). Additional data has been obtained on some of the temperature points and our present knowledge is summarized here. The temperatures are still too uncertain and insufficient points have been studied to draw a reliable phase diagram.

There are four thorium sulfide phases below ThS₂. ThS with NaCl crystal structure apparently has no appreciable range of solid solubility and melts above 2300°C. Th₂S₃ also appears to have no appreciable range of solid solubility and melts around 2000°C. The eutectic between ThS and Th₂S₃ is at about 1900°C. Th₄S₇ melts at about 1800 to 1900°C and apparently has a range of solid solubility from ThS_{1.7} to ThS_{1.9}. ThS₂ melts at 1905°C and apparently has a range of solid solubility down to ThS_{1.9}. The eutectic between the Th₄S₇ and the ThS₂ phases is around 1800-1850°C. When oxygen is present in the ThS, it appears to always exist as a separate ThO₂ phase. Oxide in ThS₂ is found as a separate ThO₃ phase. In Th₂S₃, probably only ThO₂ will be found while both ThO₃ and ThO₂ may be found in Th₄S₇. It is doubtful whether divalent or trivalent oxysulfides will be found with pure thorium but addition of enough cerium should stabilize a mixed thorium-cerium M₂SO₂.

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