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The Melting and Casting of Uranium
in Sulfide Crucibles [†]

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Abstract

Uranium has been successfully cast at temperatures as high as 1900-2000°C. in crucibles made from CeS , $\text{CeS}_{1.38}$, ThS , $\text{ThS}_{1.75}$, and $\text{ThU}_{0.7}\text{S}_2$ with the sulfur pickup in all cases less than 0.15 weight percent, in some cases at low temperatures being less than 0.005 percent. A summary of actual sulfur absorption for different experimental temperatures and crucible types is given.

The effect of the molten mixture of U and U-UBr_3 ($\text{Br/U} = 2$) upon some sulfide refractories was investigated. The results indicate that only ThS_2 and divalent sulfides like ThUS_2 , US , ThS , etc., would withstand the U- UBr_3 mixture.

Uranium may be separated from metal salt mixtures (CaCl_2 , SrBr_2 , BaI_2 , etc.) by distillation of the salt and fusion of the U in a sulfide crucible.

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The Melting and Casting of Uranium in Sulfide Crucibles

Fusion of Uranium in Sulfide Crucibles

The crucible materials used for this series of metal fusion were prepared by procedures standard for sulfide preparation described elsewhere. The fusions were conducted in an evacuated system, the crucibles with contained metal being placed in molybdenum crucibles inductively heated. To maintain a temperature control an optical pyrometer was used.

Before the metal samples were placed in the crucibles each was polished to insure the purity of the ingots. To remove the melted ingots from the crucibles in most cases the crucibles had to be cracked, although in two instances, ingots 2 and 5, removal was accomplished by slight tapping.

To remove the crucible material from the surfaces of the ingots, each was treated with dilute HCl. After the acid treatment the metal pieces were sampled through use of a cold chisel against a steel surface, the samples for analysis being roughly taken from the central portion of the ingots.

It should be mentioned that the experiments were conducted on a rather small scale, the samples being approximately five grams, thus making the possibility of contamination of the analysis samples from residual crucible material considerably greater. Additionally, the ratio of crucible wall area to ingot weight being rather large, the introduction of sulfur

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from the sulfide crucible would be more important for these small samples than for larger ingots where this ratio would be decreased.

The following table gives the results of sulfur analysis upon the ingots after fusion, with conditions of fusion and crucible materials used also being given.

Table I

Uranium Fusions

Ingot No.	Fusion Temp.	Sulfur Pick-up (ppm)	Cruc. Type	Cruc. Compn.	Ingot Appear.
(Initial metal)		1			
1	1300°C-5 min.	10	Ce "Brass"	CeS	shiny
2	" "	13	Th "Black"	ThS _{1.75}	"
3	1475°C-30 min.	40	Ce "Brass"	CeS	"
4	" "	60	Ce "Black"	CeS _{1.38}	rough
5	" "	15	Th "Black"	ThS _{1.75}	(partly shiny)
6	1900°C-4 min.	240	Ce "Brass"	CeS	dull
7	" "	1100	Th "Silver"	ThS _{1.22}	rough

In all cases the metal ingots obtained were sound and easily separated from the crucible materials either by dilute acid treatment or by filing. A comparison of the two types of crucible materials used, the low sulfur content and the high sulfur content sulfides, indicates that at low temperatures there is no appreciable difference between their effects

upon the uranium ingot. There was, however, a difference between the case of mechanical separation of the ingot from the crucible material. For example, when a CeS or a ThS crucible was used the metal walls and bottom were coated with a thin layer of the sulfide approximately 0.1 mm. thick, whereas when a $\text{CeS}_{1.38}$ or a $\text{ThS}_{1.75}$ crucible was used the sulfide material was only stuck to the ingot spottedly, the metal itself being visible. This rather firm weld between the crucible and ingot in the former case was not a source of trouble, however, since the crucible material should be dissolved away quite easily.

Considering the results of the 1900°C fusion the analysis would indicate that the ThS was not as satisfactory as CeS as a refractory. However, this may be accounted for by the difference in composition between the crucibles associated with ingots 6 and 7, the thorium sulfide material having considerably more sulfur content. From the analysis, the actual ThS content of the crucible was approximately 60%, the remaining material being principally Th_2S_3 .

An explanation of the comparatively small sulfur contamination during fusion of uranium in high sulfide crucibles, $\text{ThS}_{1.75}$ or $\text{CeS}_{1.38}$ for example, is that the reducing conditions at the metal crucible interface produce a very thin layer of the reduced sulfide which protects the higher sulfide

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from further attack. This thin coating is left on the ingot when removed from the crucible.

Uranium-Uranium Bromide in Sulfide Crucibles

The effect of a UBr_3 -U metal mixture upon the sulfide crucibles was investigated using a mixture $Br/U = 2$. Crucibles prepared from ThS_2 and $Th_{1/2}U_{1/2}S$ withstood such a fused mixture for 4-1/2 hours at $900^\circ C$., the only apparent change being a darkening of the crucible surfaces. After one half hour treatment, a $CeS_{1.5}$, a $CeS_{1.4}$, and a $ThS_{1.75}$ crucible were attacked, the evidence being cracking of the crucibles and formation of white sublimates in the quartz reaction tube. These results are in contrast to the lack of attack of the crucibles by such fused halides as $CaCl_2$, $SrBr_2$, or BaI_2 . Therefore, it would appear from these incomplete results that only ThS_2 or the divalent sulfides such as US , $Th_{1/2}U_{1/2}S$, ThS , and perhaps CeS would be satisfactory containers for a mixture of both U and UBr_3 .

Fusion of Powdered Uranium in Sulfide Crucibles

Powdered uranium, obtained through the decomposition of the hydride, upon being fused in crucibles of both general types, high sulfur and low sulfur, produced shiny ingots of metal with an oxide slag easily separable from the main body of the ingot. The treatment for 5 minutes at 1250 - $1350^\circ C$. was sufficient to give a good collection of the small particles of metal into a single piece.

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Separation of Volatile Halides from Uranium

To isolate uranium metal contained in a salt bath from an electrolytic reduction, the salt containing the metal was heated in an evacuated system to a temperature above the melting point of the U and the boiling point of the salt in the vacuum. All crucible materials tested, $\text{ThU}_{0.7}\text{S}_2$, $\text{CeS}_{1.38}$, and $\text{ThS}_{1.75}$, gave no evidence of attack when CaCl_2 , SrBr_2 , and BaI_2 were distilled from the crucible leaving behind a metallic button with a silvery surface. After 900°C . for 1 hour and $1500-1550^\circ\text{C}$. for 15 minutes, all of the halides were removed with the metal being quite well aggregated into one ingot.

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