UNCLASSIFIED

L

HW-38912

Metallurgy and Ceramics
(TID-4500, 10th Ed.)

THE MELTING OF SMALL PIECES OF URANIUM METAL

By

W. R. DeHollander

Pile Metallurgy Unit
Metallurgy Research Sub-Section

September 1, 1955

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission by the
General Electric Company under Contract # W-31-109-Eng-52

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price 10 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION - - - - -	3
OBJECTIVE - - - - -	3
SUMMARY - - - - -	3
DISCUSSION - - - - -	3
CONCLUSIONS - - - - -	6
RECOMMENDATIONS - - - - -	7
ABSTRACT - - - - -	8

THE MELTING OF SMALL PIECES OF URANIUM METALINTRODUCTION

The general practice of melting uranium under protective fluxes is unsatisfactory for small pieces of uranium metal. Unless elaborate precautions are taken to prevent oxidation and to remove all oxide film, the small pieces fail to coalesce into one mass even at temperatures several hundreds of degrees above the melting point. The reason for this is that a strong, rigid layer of uranium oxides on the surface of the metal forms a "skull" which can hold or contain sizeable masses of uranium in the same manner as crucible-type containers.

OBJECTIVE

It was the objective of this work to devise a simple, efficient method of melting and consolidating small pieces of uranium, such as uranium turnings.

SUMMARY

Small uranium pieces, such as turnings, may be melted and consolidated in the manner described. Elaborate preparation of the metal is not necessary. The metal is melted in a magnesium oxide crucible in the presence of barium chloride and metallic calcium and in an inert atmosphere of argon. The method is most appropriate for recovery and consolidation of metal with a high accountability value, such as uranium isotope 235.

DISCUSSION

During the course of some work to demonstrate the effect of calcium oxide on the coalescence of uranium, it became evident that a method was required by which uranium turning fragments could be melted on a small scale with reproducible coalescing behavior. A brief description of several

of the methods used during this experimental program is given below:

(1) The clean uranium metal turnings were placed in crucibles of graphite and/or magnesium oxide and molten calcium chloride, barium chloride or calcium fluoride poured over them. After holding at various temperatures above the melting point of uranium for various times, the fused mass was broken away and the product examined. In almost every instance severe oxidation of the turnings was evident. The liquid salt depth was at least one inch or more. None melted in any sort of reproducible manner.

It could only be concluded that atmospheric oxygen dissolved in the melt and rapidly and efficiently oxidized the uranium.

(2) The clean, pickled turnings were treated as in (1) above, but this time an argon hood was placed over the assembly. The turnings melted in a haphazard fashion but with very poor coalescence. The source of the oxide which prevented free coalescence is unknown but it is probable that it was the result of exposure to air following pickling. This method could probably work adequately if more stringent pickling requirements and exposure conditions were specified.

(3) The clean, pickled, dry turnings were dropped into molten calcium chloride, barium chloride, or calcium fluoride in air. After a waiting period of a few minutes, the system was cooled. Best results were secured with pressed compacts of turning fragments dropped into calcium fluoride. Fair coalescence was evident but the coalescence occurred in a non-reproducible manner. This method showed promise with more development. It was not tried under an inert atmosphere.

(4) All of the above methods were also tried with the addition of various amounts of calcium oxide added to the fused salt. In every instance more severe oxidation occurred and generally the metal was fragmented and powdered in the presence of CaO.

Since the apparent trouble in the above experiments and others, too trivial to mention, appeared to be a result of oxidation, it was reasoned that perhaps the addition of a reducing agent capable of reducing uranium oxides would clean up the surface of the metal by converting the oxide to metallic uranium and a reduction by-product. Then if the flux could dissolve or disperse the reduction by-product, the metal should coalesce. The only reducing agents which are practical are calcium and magnesium metal. Since calcium is less volatile than magnesium at the temperatures of interest, calcium was chosen. The melt-down was performed in the following manner, the details of which are recorded in HWN-325, a personal laboratory notebook.

The uranium metal fragments, which were usually uranium turnings or coarse powders obtained from bomb reductions of uranium oxide or metal dendrites obtained by the electrorefining technique of Marzano and Noland,⁽¹⁾ were freed of greases and oils by thorough washing in soap and water. After rinsing in deionized water and drying in air, ten grams of the turnings were tamped into a small, high-fired magnesium oxide crucible. Note that the metal was not pickled prior to loading. Metallic calcium pellets of requisite purity were sprinkled among the metal fragments in the ratio of about one gram of calcium to ten grams of uranium. The actual amount of calcium necessary is determined by the amount of oxide present on the uranium. In these experiments, the uranium metal was not pickled prior to melting and some of the pieces were heavily coated with oxides. Next, ten grams of anhydrous barium chloride was placed over the crucible contents. The amount of barium chloride was not critical. Generally, sufficient dry granular salt was added such that the metal would be covered by molten salt during the interval of time between the melting of the barium chloride and the melting of the uranium metal.

(1) Marzano, C., and R. A. Noland, The Electrolytic Refining of Uranium, ANL-5102, August 2, 1953, (Secret).

The magnesium oxide crucible was placed inside a close-fitting graphite crucible which was used as the inductor in an induction heater. The magnesium oxide crucible was topped by a lid of magnesium oxide to help confine calcium vapor and then the graphite and magnesia assembly was placed in the coils of a Lepel ten kilowatt, 500 kilocycle induction heater. The crucible was supported on a small plaque of magnesium oxide. Finally an opaque quartz hood with an argon inlet at the top was placed over the entire assembly and argon, gettered by passing over zirconium turnings at 1000 C, was passed into the hood to flow out at the bottom. The necessity of using gettered argon has not been determined. It was used only because this particular source of argon was available. The temperature of the graphite crucible was brought to $1300\text{ C} \pm 25\text{ C}$ as determined by an optical pyrometer. In order to obtain this reading, the quartz hood was momentarily lifted half way and then quickly returned. The temperature was held for six minutes then the crucible was cooled. After leaching away the barium chloride in cold water, clean, bright metal pellets were obtained. All metal which was in contact had coalesced. Those pieces which had not coalesced were not touching since the crucible was flat-bottomed.

Recovery yields have been on the order of 100 per cent down to 95 per cent, depending on the weight of oxide present. The per cent recovery was calculated on the basis of the starting weight considered as uranium. No correction for the amount of oxide was made.

CONCLUSIONS

Small fragments and powders of uranium may be melted and consolidated by the method presented herein when other simple methods fail.

It is felt that the following conditions are necessary and sufficient to accomplish the melt successfully.

1. The metal is degreased.
2. The metal is dry.
3. The metal is not pickled.
4. Thermodynamically stable crucibles are used.
5. Metallic calcium in slight excess of the quantity of oxide present is required.
6. A salt capable of dissolving calcium oxide and stable to uranium is used as flux.
7. Pure inert gas is maintained over the melt.
8. Temperatures of $1300\text{ C} \pm 50\text{ C}$ are required.
9. Time at temperature is dependent on the mass of metal being melted.

RECOMMENDATIONS

It is recommended that this method of melting uranium be considered whenever scrap of high accountability value such as uranium 235 needs consolidation. It is also recommended that the same philosophy involved in this method be employed whenever any highly reactive, refractory metal has to be melted. Some obvious metals might be plutonium, cerium, thorium, neptunium, and possibly beryllium.

William R. DeHollander

W. R. DeHollander

WRD:jw

ABSTRACT

A method of melting small pieces of uranium has been developed. A reducing atmosphere of metallic calcium, together with a solvent flux such as fused barium chloride, is required. The calcium reduces the uranium oxide skull and permits the metal drops to coalesce. The entire melt is performed under argon gas.