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Analysis of Slag Formation During UF_4 Magnesiothermic Reduction

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Abstract — *Metallic uranium is a fundamental raw material for producing nuclear fuel elements for research reactors and irradiation targets for producing ^{99}Mo, as U_3Si_2, UMo alloy, UAl_x, and uranium thin foils. Magnesiothermic reduction of UF_4 is a possible route in the nuclear fuel cycle for producing uranium as a metal ingot. The main concern about the reducing scale to produce low-enriched (metallic) uranium (LEU) (around 1 kg) is the relatively low yield compared to calciothermic reduction. Nevertheless, the magnesiothermic reduction has the advantages of having lower cost and being a safer method for dealing with uranium processing. The magnesiothermic process, as a batch, is closed inside a sealed crucible. In the present study, in order to have a qualitative idea of the kinetics during the ignition moment, the slag projected over the lateral inner face of the crucible was used to sketch the general magnesiothermic evolution. The methods used were metallographic observation and X-ray diffraction followed by Rietveld refinement. The results of these analyses led to the conception of a general reaction development during the short time between the ignition of the reducing reaction and final settlement of the products. Relevant information from this study led to the conclusion that uranium is not primarily present in the lateral slag projection over the crucible during the reaction, and the temperature level may reach 1500°C or more, after the ignition.*

Keywords — *Metallic uranium, magnesiothermic reduction, UF_4.*

Note — *Some figures may be in color only in the electronic version.*

I. INTRODUCTION

The nuclear research reactor IEA-R1 fuel elements and irradiation targets for producing radioisotopes for nuclear medicine are made using metallic uranium. This element is alloyed to produce subsequent products, such as U_3Si_2, UAl_x, and U-Mo. There are several possibilities in producing metallic uranium,[1–3] the most common being the reduction of uranium tetrafluoride with calcium or magnesium. Magnesiothermic reduction of UF_4 has been a known process since the early 1940s (Refs. 4 and 5). The Nuclear and Energy Research Institute (IPEN-CNEN/SP) decided to use this route in the 1970s to 1980s for the production of 100-kg ingots of natural uranium. For low-enriched (metallic) uranium (LEU) production, it is necessary to handle safe mass (less than 2.2 kg U) to avoid possible hazards. At present, IPEN-CNEN/SP produces LEU ingots of around 1 kg via the magnesiothermic process, and in the future may produce 2 kg or more.[6,7] This range of LEU U weight is rather small if compared to big productions of natural uranium. When bigger quantities are produced, metallic uranium is reported[8] to be produced with a 94% metallic yield. The magnesiothermic process downscaling to produce LEU has few possibilities of achieving this higher metallic yield. This is due to the design of crucibles, with a relatively high proportion of the surrounding area, which is more prone to withdrawing evolved heat from the exothermic reaction during uranium reduction. Normally, calciothermic reduction of UF_4 is preferred worldwide, since the exothermic heat is −460.7 kJ/mol if compared to a smaller amount of

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−209.4 kJ/mol produced using magnesium as the reducer.[9] Nevertheless, IPEN-CNEN/SP chose magnesiothermic because it is easier to do while avoiding the handling of toxic and pyrophoric calcium. Moreover, the magnesiothermic process is less costly, so it brings more economical compensation for its worse metallic yield than the calcium reduction process. In addition, the recycling of slag and operational rejects is highly efficient, and an insignificant amount of LEU is lost.[10]

The magnesiothermic reaction is given by

$$UF_4 + 2Mg \rightarrow U + 2MgF_2 \rightarrow \Delta H = -209.4\,\text{kJ/mol}\,(\text{at } 640^\circ\text{C})\,. \quad (1)$$

As magnesium is less prone to being ignited than calcium, the batch reactor is heated up to a temperature of around 640°C. The routine shows that this ignition normally happens some degrees below this temperature.[8]

This work discusses the formation of slag and its projection toward the wall of the graphite crucible during the magnesiothermic ignition. The evidence in the slag solidification, after the reaction process to reduce UF_4 toward metallic uranium, can guide the interpretation of the reaction blast. Based on X-ray diffraction (XRD) analysis throughout the transversal section of wall solidified slag, it is possible to give a general idea of chemical and physical events.

II. EXPERIMENTS AND RESULTS

IPEN's UF_4 production is made through a wet route.[11,12] The appearance of UF_4 produced is presented in Fig. 1, which is a typical representation of the UF_4 morphology produced by the wet route. As could be noticed in Fig. 1, there are particles of different sizes and morphologies. The UF_4 powder is supplied to produce metallic uranium by UF_4 reduction by magnesiothermic arrangement.

The IPEN's magnesiothermic process of reducing UF_4 to metallic uranium could be synthesized as follows:

1. A single batch uses 1.815 ± 0.005 kg of the mixture Mg + UF_4 (1.540 ± 0.001 kg LEU UF_4) containing 15% excess of stoichiometric Mg content. For the purpose of homogenization, the charge of UF_4 + Mg is divided into ten layers tapped one by one inside the crucible.

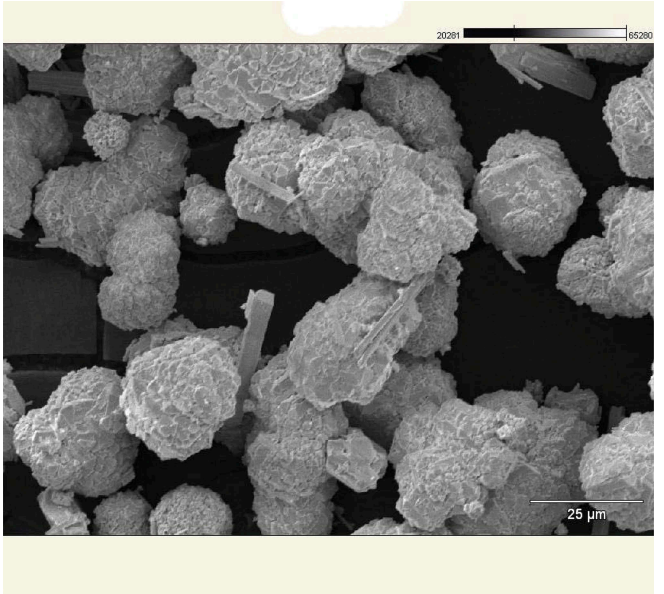


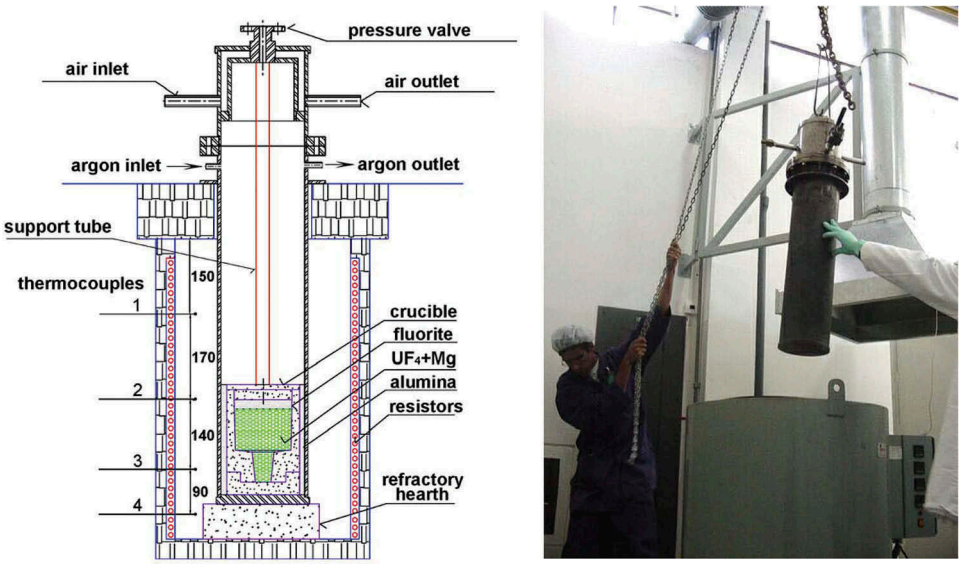
Fig. 1. Scanning electron microscope image of UF_4 powder produced by IPEN's wet route, using $SnCl_2$ as precipitation agent.

2. A variable amount of CaF_2 is tapped over the UF_4 + Mg charge in the crucible to fully complete the reaction volume. This amount is dependent on tapped density and UF_4 + Mg blending, which varies in function with UF_4 fabrication.

3. The crucible is inserted inside a stainless steel cylindrical reactor vessel, made of Grade 310 stainless steel, with argon fluxing during batch processing (1 L/min per 1.67×10^{-3} m^3/s with 2 kg_f/cm^2 per 0.196 MPa of pressure). As shown in Figs. 2a and 2b, the whole crucible + reactor is placed in a resistor pit furnace with four programmable zones having the possibility of raising the temperature up to 1200°C.

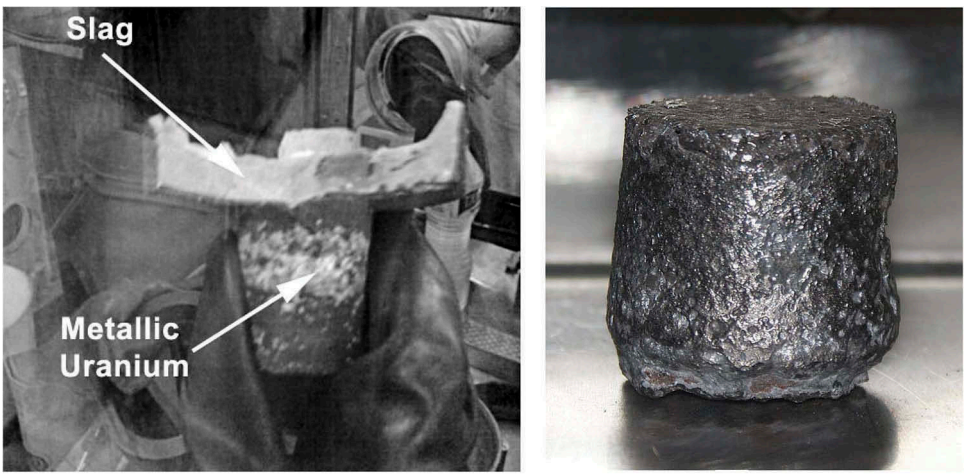
4. The reaction vessel is heated up to 620°C. At this level, the reaction ignition is expected. The total heating time and waiting for ignition is about 10 800 s from heat time to temperature setting point.

5. The reaction of UF_4 with Mg produces an intense exothermic heat release inside the crucible. It produces metallic uranium and MgF_2 slag in liquid form. Both products deposited in the crucible bottom are easily taken apart after opening the crucible. Some slag during the reaction blast is projected over the crucible wall. The full reaction happens during 0.8 to 1.2 s from ignition to final deposit, as indicated by the accelerometer. Figure 3a shows the metallic uranium removed from the crucible with the top slag, and the slag around the ingot is removed afterward (Fig. 3b).



(a) (b)

Fig. 2. (a) Schematic drawing of pit furnace, reactor vessel, and crucible and (b) charging of the reactor vessel inside the pit furnace.



(a) (b)

Fig. 3. (a) Raw metallic uranium and upper deposited slag after their removal from the crucible and (b) metallic uranium after cleaning.

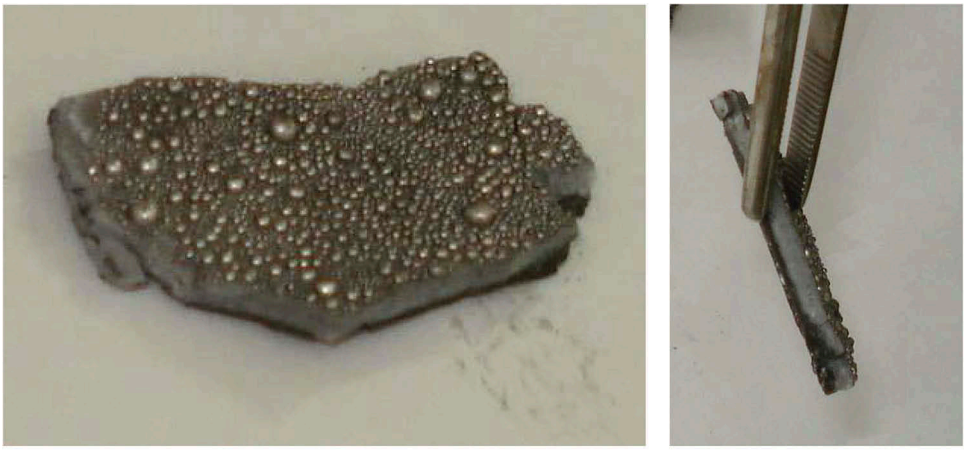
Figures 4a and 4b display the sample of projected slag in the lateral crucible wall, with views of the inner side and transversal section, respectively.

In Fig. 5 it is possible to see in detail different structures deposited during the process of magnesiothermic reaction. It is important to notice that there are four layers in this sample, named in the order of solidification:

Layer 1: This is the layer that had contact with the crucible wall. It is believed to have been formed in the first stage of the blast, when there was the first disarrangement of the initial charge. There was a partial melting of the charge, including the CaF_2 that was originally placed on the top of the charge arrangement to complete the hollow volume inside the crucible. This first layer had a dark color.

Layer 2: This layer follows layer 1 in the sequence of solidification. It has a general view of compressed longitudinal strips parallel to the wall, indicating that this solidification happened under heavy pressure. It has a light greenish color.

Layer 3: Between layers 2 and 3, there is a plane of bubbles of extraneous material if compared to the layer solidification. These bubbles, still under study, seem to be the result of reacting $UF_4 + Mg + U$ nuclei during a reaction that could have been thrown during the blast to this region



(a) (b)

Fig. 4. Wall projected slag analysis. (a) Sample view from the inner side and (b) transversal section view of the slag sample.

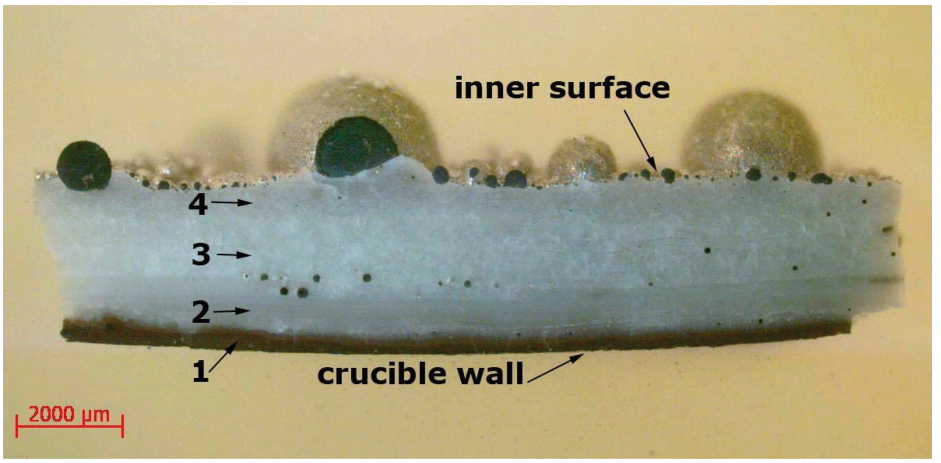


Fig. 5. Lens-magnified view of transversal section view (Fig. 4b).

of ongoing layer solidification. Layer 3 was solidified on the top of this. It resembles much lighter material than layer 2.

Layer 4: This layer is similar to layer 3. It represents the region of last slag crystallization.

X-ray diffractograms of the parallel planes of the transversal sections, obtained by metallographic preparation, were made by polishing along the transverse axis. They are shown in Fig. 6. Uranium could not be identified in these layers, either as metallic U or as UF_4. In general terms, this solidified slag reflects the photography of crystal formation during the events following the ignition of magnesiothermic reaction.

Table I presents the main results of Rietveld refinements of the XRD data, obtained using General Structure Analysis System (GSAS) software.[13] These results were were also considered to discuss a broad guideline of magnesiothermic reaction kinetics accounted by the solidification structures. The crystalline phases found (CaF_2 and MgF_2) were quantified as a function of slag layer. Furthermore, a considerable discrepancy in peak intensities indicated the presence of a crystallographic texture. In this sense, the texture index was refined for each diffractogram, using the spherical harmonics function of GSAS (Ref. 14). From this result, the magnitude of the orientation of crystallites solidified into the material can be evaluated, which can be related to the crystallization process. If the material has no orientation of the crystallites (perfect random distribution), then the index is 1. The higher this value is, the more oriented the crystallites of the material are. Index results above 3 stand for a strong texture of the material, possibly due to crystallization at slow cooling rates.

III. DISCUSSION

Only real-time acoustic and visual inspection results during the crucible opening can be used in studies to

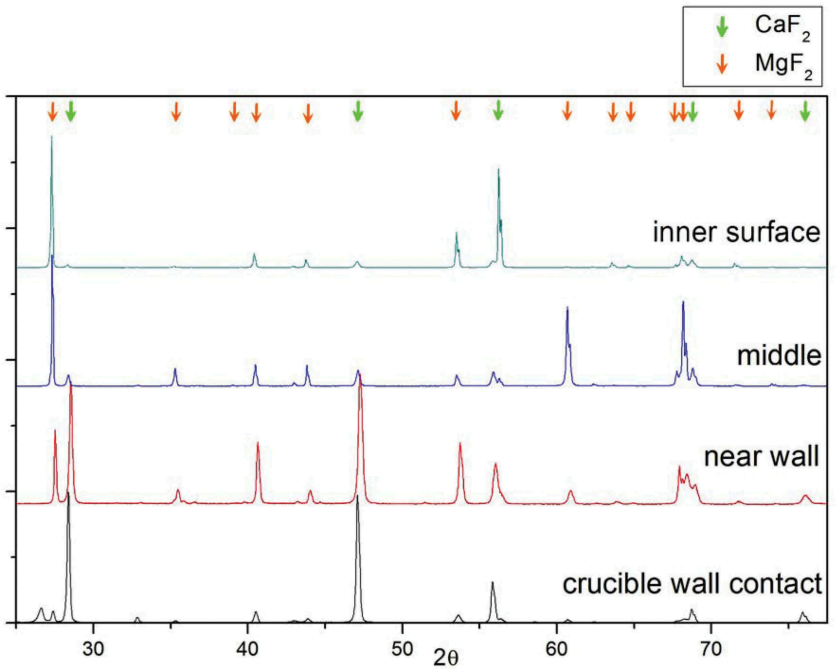


Fig. 6. XRD diffractograms of each layer indicated in Fig. 5.

TABLE I

Rietveld Results for the Major Phases' Contents MgF_2 and CaF_2 Found in the Laterally Projected Slag

XRD Zone	Layer Number	MgF_2 (wt%)	Percent CaF_2 (wt%)	χ^2	Texture MgF_2	Texture CaF_2
Near inner surface	4	81.3	18.7	41.0	2.04	1.68
Middle	3	87.0	13.0	37.2	3.39	1.90
White band near wall	2	66.3	33.7	6.6	8.15	1.03
Crucible wall	1	25.7	74.3	33.9	1.12	1.00

achieve a general idea of the whole reaction ignition by the physical arrangement of the products. Visual inspection results were used to provide a qualitative picture of the reaction events after ignition. This present discussion tries to elucidate the sequence of events just after the ignition of magnesiothermic reaction leading UF_4 to metallic uranium.

It is feasible to suppose that the metallic magnesium also oxidizes during the heating of the load before the ignition, due to oxygen remaining in the atmosphere of the reactants. This, in a certain grade, prevents the reaction from happening before it reaches the ignition moment since there is no a direct contact of magnesium with UF_4. In routine reaction, all reactants reach the temperature level of approximated 640°C, which is considered the ignition temperature. This point is very near to the magnesium melting temperature at 651°C. As a possible hypothesis, the ignition is promoted by magnesium vapor breaking through the thin layer of magnesium oxide covering the magnesium particle. The Mg vapor reaches the nearest UF_4 powder grains. The first reaction happens between a solid UF_4 and magnesium vapor. At this point, it provokes the first spark of ignition promoting a high exothermic reaction (reaction 1) forming locally the first quantity of metallic uranium and magnesium fluoride. Following up is a chain reaction between solid UF_4 grains and Mg vapor. It evolves vigorously throughout the reactants in a driven explosion blast.

This full mass reacts in approximately 0.8 to 1.2 s. In this short time, it is not safe to rely on any equilibrium thermodynamic system. All the physical-chemical events happen very quickly and under a substantial rising of pressure, not yet quantified. After the opening of the reaction chamber, it is observable that even the CaF_2, placed on top of the reactants to compensate UF_4 density

variation, is partially melted. The melting point of CaF_2 is 1418°C. This is an indication that the temperature during reaction reaches values higher than that, probably rising higher than 1500°C. At this temperature, all loaded Mg would be vaporized (boiling point at 1091°C). If any remainder UF_4 exists, it may be present either as a liquid or as a gas (melting point at 1036°C; boiling point at 1417°C).

Analyzing the slag in Figs. 4, 5, and 6, it may be said that there are at least four great events during the reaction moment, characterized by the solidified layers. These events could be discussed on the basis of the relationship between MgF_2 and CaF_2 contents.

Closer to the crucible wall, the solidified slag shows a much greater content of CaF_2 than MgF_2 (3:1 proportion) and displays a dark crystal. This darkness of the crystal, from Rietveld analysis, did not have enough acquired carbon from the graphite crucible. It might have helped to darken the structure of the first layer. As Rietveld's results indicate virtually no texture for CaF_2, it follows that the solidified CaF_2 is near to polycrystalline calcium fluoride formed under high pressure. Calcium fluoride is a crystal that tends to have a dark greenish-violet color. From this analysis, for this first layer, one is able to conclude that the temperature went above the CaF_2 melting point, taking away the CaF_2 put in the top of the charge, in the region of starting ignition; melted it; and projected it toward the crucible wall. The liquefied CaF_2 had a relatively short time to solidify the projected liquid at the crucible wall, with plentiful nucleation sites and limited growing. The texture index near to 1 indicates random orientation of crystallites.

At this stage, it is plausible to say that the magnesiothermic reaction actually happens between the reactants UF_4 and Mg, both in vapor state, since the temperature became high enough for exothermic heat, and produces molten metallic uranium and MgF_2. As observed in XRD analysis, not much uranium, if any, was projected toward the crucible wall. So, only the lighter products (CaF_2 and MgF_2) were blasted toward the wall and solidified. Most liquid uranium droplets went directly toward the crucible bottom and solidified there. All the temperatures were quite above the uranium melting point at 1036°C and even much higher than the MgF_2 at 1280°C. The proportion variation of CaF_2 composing all layers' zones throughout the projected molten material indicates that the temperature was above 1417°C (melting temperature point of CaF_2). Since the appearance of the projected slag displayed no material fluency downward, this is an indication that the difference of temperature was not so high from the melting points under probably high pressure. The texture of crystallized slag rising from layer 2 to 4 may indicate that the crystals were formed under less stress with the process of nucleation and were growing with a relatively high temperature above the melting temperature.

Almost no magnesium was identified inside the slag sample; nevertheless, there is a "layer" of "magnesium bubbles" between layers 2 and 3. It is thought that it was formed by a nonreactant magnesium vapor during the magnesiothermic reaction (15% excess magnesium was added to the reaction charge), as it was blasted toward the solidifying fluoride slag at the crucible wall. It may be said that this layer marked an event after the initial reaction peak since there were already slag layers 1 and 2.

Finally, the last deposition over the final inner layer surface was from magnesium forming bubbles over the inner layer of the slag at temperatures below 651°C, as shown in Figs. 4 and 5. In the transverse views, there are bubbles of many sizes, showing that this process lasted long enough to allow nucleation and growing. In fact, 15% excess of magnesium loaded with UF_4 was more than enough to assure full reaction.

IV. CONCLUSIONS

From the projected slag at the midway point of the crucible wall, the sequence of events just after the ignition of magnesiothermic reaction to produce metallic uranium was analyzed. The major characteristics of these events, based on XRD and Rietveld analyses, reveal the sequence of the reaction just analyzing the crystallization of the slag. The major constituents of the slag were CaF_2 and MgF_2. MgF_2 is crescent in content from the crucible wall toward the inner side. In the same direction the texture of the crystallized materials also increases. There was no fluency of the material, showing that the solidification happened at temperatures above the melting point of CaF_2 (1417°C). From the slag, it is possible to infer the reaction peak moment from a plane formed by small bubbles of projected magnesium inside the slag sample. The further deposited CaF_2 and MgF_2 formed with an increase of crystallographic texture, indicating that the temperature declined as this structure was being formed. Magnesium was deposited finally over the crystallized layer, indicating that this process had enough time to happen, displaying spheres of several sizes and showing that a mechanism of nucleation and growing took place in this process as the crucible decreased its temperature.

These results contribute to a better understanding of the sequence of events that occur during the reduction reaction, which is important to understanding and

improving the production process, especially in terms of yield in obtaining uranium metal properly separated from the slag.

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