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An improved method to dissolve alloyed plutonium residues

L. Pescayre *, C. Passot, D. Cardonna, H. Chollet

CEA/DAM, Centre d'Etude de Valduc, 21120 Is sur Tille, France

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Abstract

An improved method to dissolve alloyed plutonium has been investigated. The purpose is to recycle plutonium residues which contain gallium greater than 15 wt%. The process consists of two main steps: oxidation by a moist Ar/O_2 mixture and then HNO_3/HF dissolution. The burning process is shown to be efficient to oxidize only the plutonium. The only oxide species obtained is PuO_2, which is suitable for a HNO_3/HF dissolution at 70 °C. The global recovery yield is higher than 97%.

Keywords: Actinide alloys and compounds; Gas–solid reactions; Mechanochemical processing; Corrosion; Oxidation

1. Introduction

The activities of the Valduc Nuclear Centre generate various plutonium metal residues which do not meet the required purity specifications to be reused directly. A nitric acid based process has enabled the recovery of the majority of the plutonium scrap in a purified form since the 1970s. It consists of four main stages:

- Direct dissolution of the metal in NH_2SO_3H,
- transformation in plutonium nitrate,
- purification by anionic resin,
- conversion into plutonium dioxide and metal.

However, this process is not efficient and not safe for alloyed plutonium residues (gallium greater than 15 wt%). A new method for the first two stages has been developed in the last 4 years. The first step is an oxidation of the metal by a moist Ar/O_2 mixture. The second step is an aqueous dissolution in a mixture of HNO_3/HF (10 M/0.05 M). The purpose is to develop a procedure and equipment for efficiently recovering the residues: complete burning, i.e. no plutonium metal remaining, good kinetics and recovery yield greater than 80%.

2. Experimental procedure

The first apparatus, for producing oxide, consists of a large horizontal muffle furnace. A gas line feeds a mixture of moist oxygen and argon into the furnace (Fig. 1). Oxygen and argon can be mixed in varying amounts. Gas is forced through the bubbler, which contains water, and then into the furnace assembly. The flow is measured before entering the glove box. The sample is placed in a "stainless steel/tantalum/stainless steel" cell (Fig. 2) inside an AISI-316 stainless steel furnace. A thermocouple is connected to a temperature sensor, regulating the heating of the furnace wall to 550 °C ± 5 °C.

The water vapour concentration varies between 0 and 1.4% by volume and the gas mixture varies between 15 and 25% O_2 at 45 l/h to study the impact on the burning rate. The samples are weighed before and after oxidation to determine the amount of unburned metal remaining. The oxide is ground with a mortar and pestle to verify that there is no metallic particles inside oxidized surfaces.

Each equipment component is used in several runs and then visually checked to determine its capacity to withstand the conditions encountered in the process.

The second apparatus consists of a Uranus B6 (EN 1.4539 X1 Ni Cr Mo Cu 25-20-5) stainless steel vessel, which exhibits very good corrosion resistance to the dissolution acid mixture, surrounded by an electric resistance heater (Fig. 3). A cooling component is present on the top of the vessel head. Gas is extracted and trapped in columns filled with soda solution.

Dissolution is made using 0.05 M HF and 10 M HNO_3. The mixture is thermostated at 70 °C with a coated thermometer and agitated with a mechanical stirrer during working hours for a total reaction time of 2 × 6 h. Liquid samples are taken using pipettes to determine plutonium concentrations by an UV/visible spectrophotometer (wavelength of 830.5 nm).

3. Main results

The experimental results are summarized in Table 1. As noted in some Refs. [1,2] the corrosion rate of alloyed plutonium

* Corresponding author. Tel.: +33 380235064; fax: +33 380235219.
E-mail address: laurent.pescayre@free.fr (L. Pescayre).

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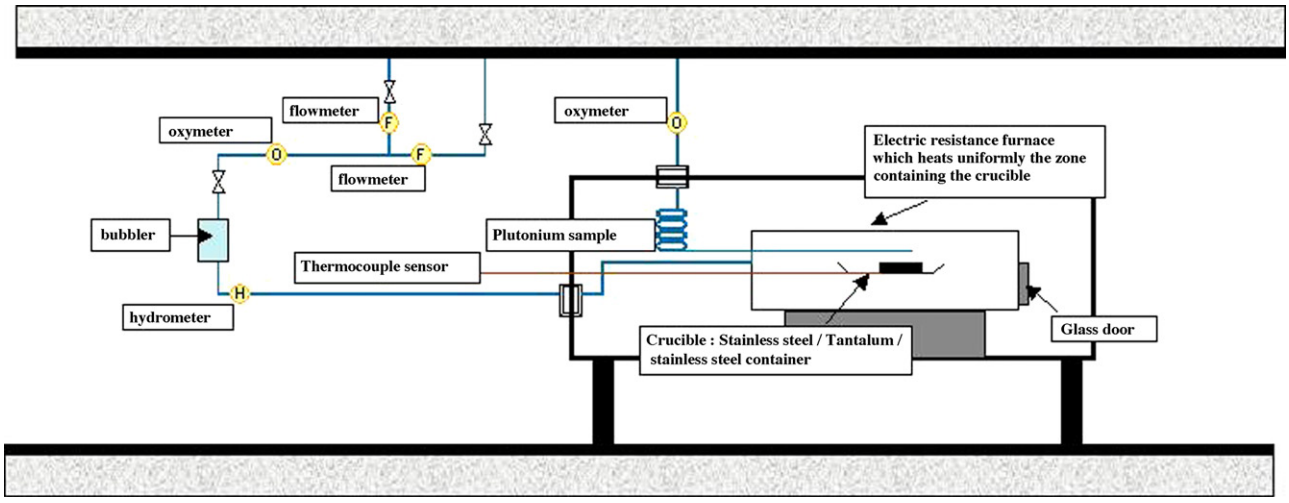

Fig. 1. Horizontal furnace and gas line.

Table 1
Experimental conditions and results of four typical first stage runs

Run	Sample weight (g)	Alloyed element (wt%)	Time (h)	T (°C)	H_2O (ppm)	Flow (l/h)	O_2 (%)	Initial weight/final weight	Result
1	30.58	18	4.5	450	0	45	25	0.95	About 50% oxidized
2	41.75	16	2	450	14000	45	15	0.90	Complete oxidation
3	39.66	21	2	450	14000	45	25	0.91	Complete oxidation
4	122.72	23	2	450	14000	45	15	0.91	Complete oxidation

increases substantially with moisture. A water vapour concentration of 1.4% by volume increases the rate of burning. Each sample is completely oxidized after 2 h (Fig. 4). A general trend is that the burning rate is not very sensitive to the gallium concentration in the metal between 16 and 22%. Varying the gas mixture (Ar/O_2 15% and Ar/O_2 25%) has little impact on the burning rate. It varies between 20 and 110 g/h depending of the surface area.

Plutonium behaves much like other active metals, forming a protective layer of oxide on the surface. The transport of the oxygen, from the surface to the oxide metal interface, determines the oxidation rate of plutonium [2]. A greater rate could be obtained with a mechanical system which breaks the protective dioxide layer. Development of a new furnace device with this system is in progress (Fig. 5).

It seems there is no residual plutonium metal after burning, as seen by the observed increase of the sample weight caused by the complete oxidation to PuO_2. X-ray diffraction of one of the products exactly gives the pattern and lattice constants of fcc PuO_2 (other oxides are not observed). This result confirms that the combustion product of the plutonium metal is PuO_2.

However, metallic grains or droplets are present inside the product. They are not extracted for the dissolution stage. In order to identify their nature by scanning electron microscopy (SEM) analysis, they were manually extracted from the plutonium oxide and spread with a blade on the surface of the container. The

Fig. 2. Stainless steel/tantalum/stainless steel crucible and alloyed metal.

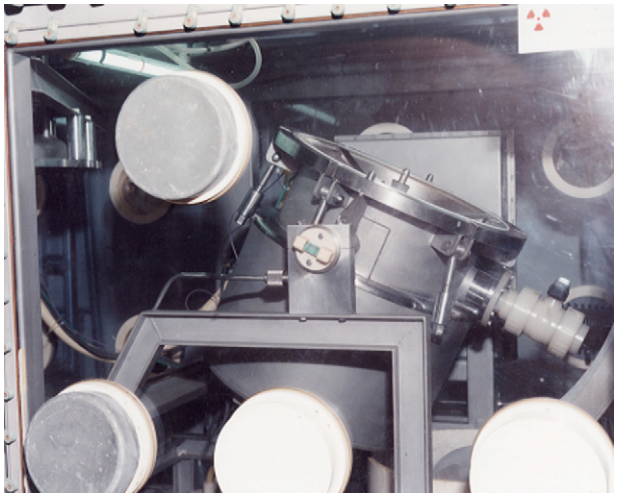

Fig. 3. Vessel used for dissolution.

Fig. 4. Product, after burning sample.

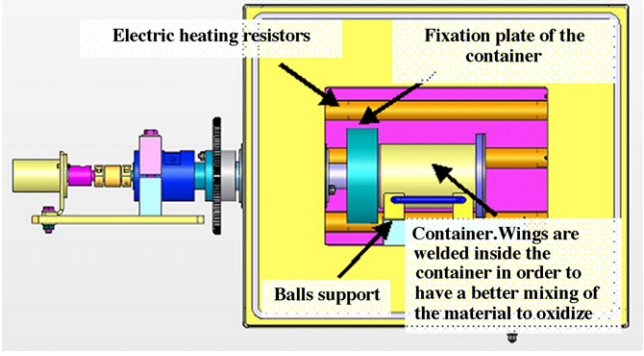

Fig. 5. Pilot device.

analysis showed they are gallium particles that segregated during the combustion, because of good resistance to oxidation (Fig. 6).

The apparatus materials used for the experiments show a great oxidation resistance. The AISI-316 stainless steel furnace can is unaffected after all the runs. The "stainless steel/tantalum/stainless steel" crucible is in excellent shape at the end of these experiments. Those materials are then well suited for use in this process.

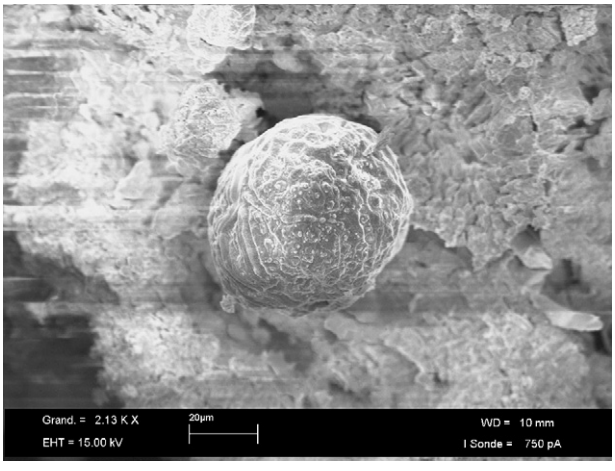

Fig. 6. Gallium particle (SEM).

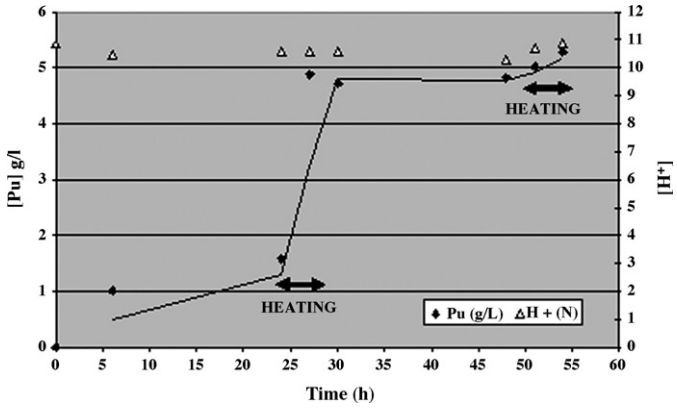

Fig. 7. Pu concentration (g/l) and HNO_3 concentration (N) during dissolution.

It is well-known that the solubility and reactivity of plutonium dioxide obtained by direct oxygen oxidation varies inversely to the oxidation temperature [1]. The dissolution in HNO_3/HF of plutonium oxide, obtained by burning the metal, has been already studied to determine the effect of each the important variables on the dissolution (temperature, HF concentration, HNO_3 concentration, surface area of the PuO_2) [3]. An investigation was done to check that the plutonium oxide powder produced is suitable for a HNO_3 (10 M)/HF (0.05 M) dissolution at 70 °C.

Two 6-h runs are necessary to dissolve the powder efficiently. After rinsing, the insoluble solid residue contains less than 2 g of plutonium (determined by gamma counting) for about 150 g of impure oxide to be dissolved. The global recovery yield is higher than 97%. The dissolution rate results from the burning temperature, the HF concentration and the dissolution temperature (Fig. 7). The solution thus produced is suitable for purification by anionic resin.

4. Conclusions and perspectives

In order to recycle alloyed plutonium residues, an improved and safer method, based on a burning stage and an HNO_3 (10 M)/HF (0.05 M) dissolution at 70 °C stage, has been successfully tested. The process is efficient (the recovery yield is higher than 97%). The equipment components have been successfully tested to withstand the conditions encountered in the process.

Development of a new furnace device is in progress to improve the burning kinetics. A mechanical system will be used to break the protective dioxide layer.

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