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CHARACTERIZATION FOR PHYSICAL
MEASUREMENTS** From commercial actinide oxides to
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From commercial actinide oxides to single crystals of their metals and refractory compounds

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Résumé. — Les oxydes commerciaux d'actinide préalablement purifiés par voie aqueuse sont réduits à l'état métallique. Les métaux volatils d'actinides (Am, Bk, Cf, Es) sont obtenus par réduction métallothermique sous vide avec le lanthane comme agent réducteur. Le même procédé est utilisé pour préparer le Cm, Ac, Pu mais avec le thorium comme réducteur. Les U, Np, Pu sont préparés par réduction tantalothermique sous vide des carbures. Les métaux volatils sont affinés par évaporation et condensation sélectives. Le Pa et le Th sont préparés suivant le procédé van Arkel par dissociation thermique des iodures obtenus après réaction de l'iode avec les carbures.

De gros cristaux des métaux les plus volatils (Am, Cm) ont été préparés par transport physique en phase vapeur et recuits à haute température. Des monocristaux de Th et Pa sont produits par le procédé van Arkel. Les composés des actinides sont préparés à l'état polycristallin par synthèse directe à partir des éléments. Les monocristaux de dioxydes, dipnictides et dichalcogénures d'actinides sont préparés par transport chimique en phase vapeur avec le TeCl_4 et I_2 comme agent de transport. Les monopnictures sont obtenus par le procédé van Arkel.

Les monocristaux sont caractérisés par diffraction des RX (méthodes de Debye-Scherrer, Weissenberg, Laue).

Abstract. — Commercial actinide oxides, after purification by standard procedures (extraction chromatography, precipitation, etc.) are reduced to metals. The actinide metals Am, Bk, Cf, Es are obtained by metallothermic reduction in vacuum with lanthanum metal, Cm, Ac, Pu by the same process with Th metal as reductant. U, Np, Pu metals are prepared by tantalothermic reduction of the carbides. These volatile metals are efficiently refined by repeated evaporation and condensation. Pa and Th are prepared in a pure form in a van Arkel process by thermal dissociation of their iodides starting from the carbide. Large single crystals of the more volatile metals (Am, Cm) are prepared by physical vapour deposition and annealing at high temperature. Single crystals of Th and Pa are obtained by chemical vapour deposition with I_2 as transporting agent. Pure actinide compounds in powder form are prepared by direct synthesis from the elements. Composition and structure of the compounds can be controlled by the reaction conditions. Single crystals of the actinide dioxides, dipnictides and dichalcogenides are produced by chemical vapour transport with TeCl_4 or I_2 as transporting agent. Monopnictide single crystals are prepared by chemical vapour deposition using the van Arkel process.

The crystals are characterized by chemical analysis and X-ray diffraction (Debye-Scherrer, Weissenberg, Laue) techniques.

1. Introduction. — Progress in actinide materials science is based on sophisticated investigations of physical properties to understand the electronic structure and the chemical bonding in the actinide elements and compounds. For most of these investigations, samples with well defined structure and of known purity, in some cases single crystals of suitable size, are required.

The preparation of such greatly needed materials was planned in the frame of the Transuranium Institute's programme. This task involved :

— the purification to a suitable purity level of actinide isotopes, commercially available or recovered from waste processing ;

— the preparation, identification and characterization of well defined monophased materials in a suitable form for physical property measurements.

Earlier experience on waste processing and purification of americium oxide [1, 2] had shown the great difficulty to reach high purity level with aqueous purifications processes. In addition, inconveniences like

— high radiation exposure during the work in glove boxes,

— high contamination risk for the prepared product during long and difficult processes,

— large quantity of liquid waste produced to be reprocessed,

are making the time consuming aqueous route in attractive.

On the other hand, pyrometallurgical processes producing metals *via* the vapour phase can yield high purity material [1, 3].

Therefore, the processing concept shown on figure 1 was systematically developed and extended for application to the light actinide elements and their compounds: Pure metals are produced by pyrometallurgical processes, involving physical or chemical vapour transport, the preliminary aqueous purification step being reduced to the elimination of the few specific impurities which are not removed during the preparation and refining of the metal. The compounds are obtained by direct synthesis between the elements.

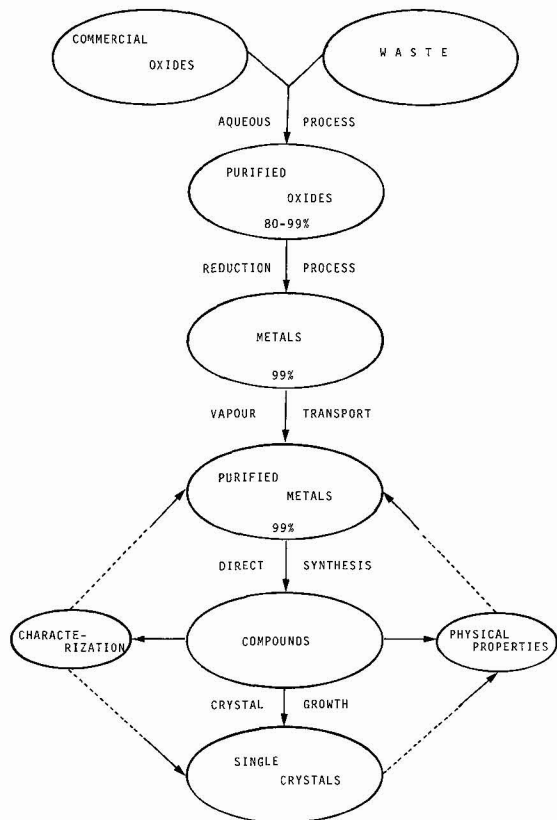


Fig. 1. — Solid state material preparation concept based on high purity actinide metals production.

2. Preparation and refinement of actinide metals.

— 2.1 GENERAL. — There is no single, simple method for producing high purity metals, but a large number of methods exist for producing each of the individual elements. In order to be satisfactory, all fabrication processes should follow some general rules:

— They should be feasible with a reasonable reaction rate.

— It should be possible to recover the desired metal in a single phase.

— It should also be possible to prevent contamination of the desired product by the environment (protective atmosphere or high vacuum for processing, handling and storage, prevention of crucible corrosion by liquid metals ...).

— Where possible a step involving gas phase transport of the element should be used since this always results in a high decontamination factor.

2.2 METALLOTHERMIC REDUCTION OF HALIDES.

— The metallothemic reduction of the actinide halides (commonly fluorides) is thermodynamically feasible (Fig. 2) and was mostly used to prepare the actinide metals [4].

This method shows some disadvantages:

— Very pure anhydrous actinide fluorides are difficult to prepare.

— Actinide fluorides are neutron emitters (α , n reaction) which increase radiation hazards.

— The metals produced can be contaminated by the reaction products, impurities of low vapour pressure and corrosion products of the crucibles.

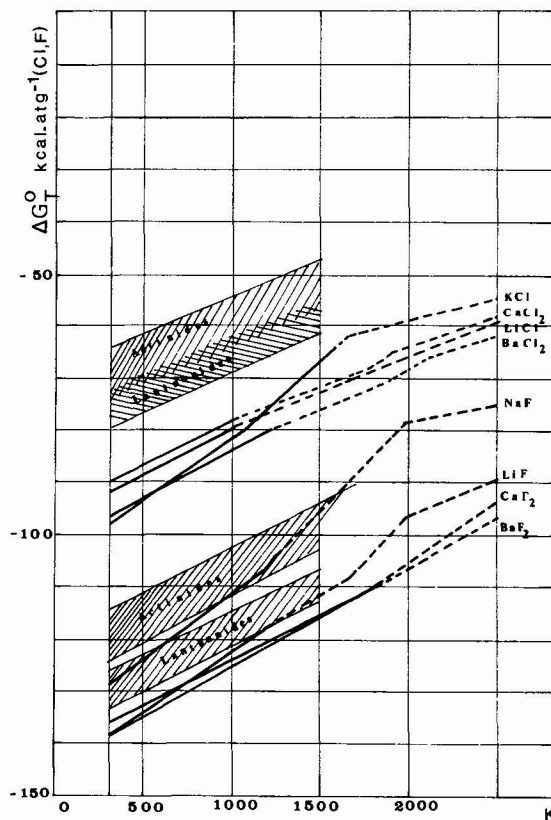


Fig. 2. — Free energy of formation of halides.

2.3 METALLOTHERMIC REDUCTION OF THE ACTINIDE OXIDES.

— The actinide oxides have very large free energies of formation (Fig. 3). The metallothemic reductions have positive or close to zero free energies of reaction. If the vapour pressure of the actinide metal is high enough, in vacuum and in open systems, it will leave the reaction mixture allowing a complete transformation of the reactants.

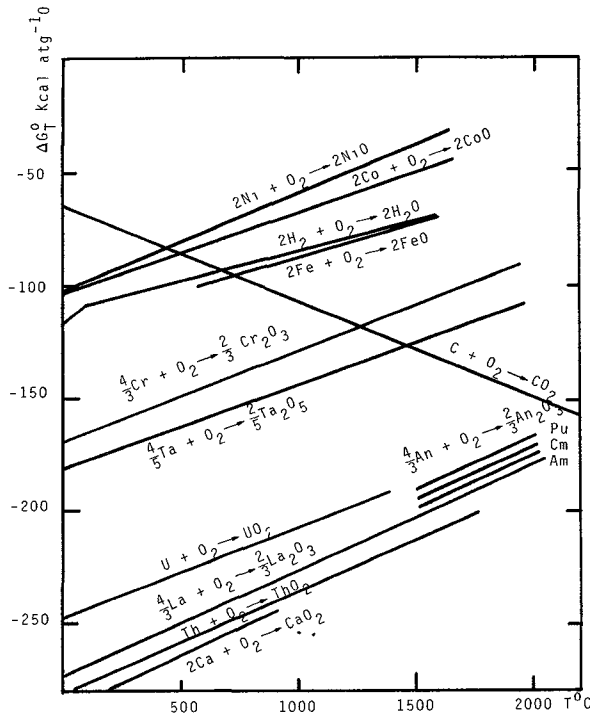


Fig. 3. — Free energy of formation of oxides.

A suitable reductant has to show the following characteristics :

- The free energy of formation of the oxide is at least of the same order of magnitude as that of the actinide oxide.

- The vapour pressure is several orders of magnitude lower than that of the actinide metal (Fig. 4) to prevent coevaporation.

It follows from figures 3 and 4 that lanthanum is a good reductant for Am, Bk, Cf, Es in the temperature interval between 900 and 1 300 °C. To prepare Pu and Cm, thorium can be used at 1 800°C without risk of high contamination level.

Metals which could allow the metallothermic reduction of the oxides of Np, U, Th, Pa, do not exist. Attempts to prepare Np metal with thorium as reductant yielded alloys with more than 1 % of thorium [9].

The actinide oxides (Am, Cf, Cm, Ac) are mixed with freshly prepared La or Th turnings and pressed into pellets at 5 t/cm².

Table I

Oxide	Reductant	Temperatures °C	
		reduction	condensation
AmO ₂	La	1 250	800
CfO ₂	La	1 000	----
CmO ₂	Th	1 750	1 250
AcO ₂	Th	1 750	1 000
NpO ₂	Th	2 000	1 000

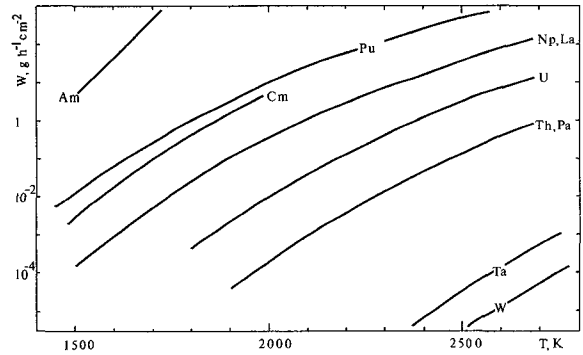


Fig. 4. — Evaporation rate of the actinides and of the metals commonly used as reductors as a function of the temperature.

The reduction occurs in a RF heated tantalum column under a vacuum of 10⁻⁶ torr. Operational conditions and results are summarized in table I.

2.4 METALLOTHERMIC REDUCTION OF ACTINIDE CARBIDE. — Due to the preparation difficulties in the halide reduction process and because of the limitation of the oxide reduction process to the actinide metals of the highest vapour pressure, it was interesting to look for a metallothermic reaction system applicable without restrictions to the production of all the actinide metals.

The carbides constitute a very favourable system.

- The actinide carbide can be prepared in a high purity level by carboreduction of the oxides.

- The free energies of formation of some transition metal carbides are much greater than the free energies of formation of the actinide carbides (Fig. 5).

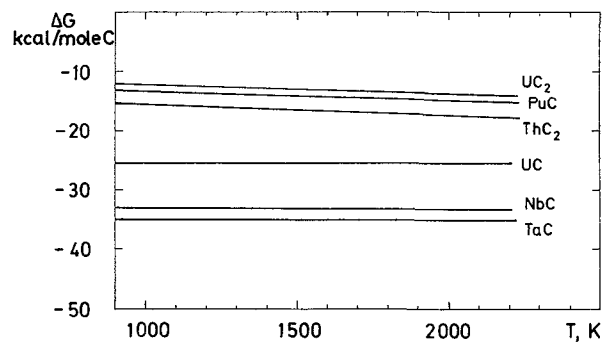
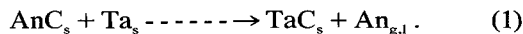


Fig. 5. — Free energy of formation of carbides.

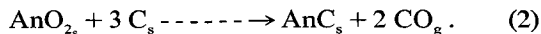
Condensed metal mass (g)	Yield %	Impurities ppm	References
0.2-10	94-98	La : 5	[3, 4, 5]
0.001	----	----	[7, 8]
0.2-1	90	Th : 500	[6]
----	----	----	[10]
5-10	----	Th : 1 %	[9]

These transition metals (for example Ta) are able to reduce the actinide carbides into metals (Table II) according to the reaction



Starting materials and tantalum carbide have such low vapour pressures that no vapour phase contamination is to be feared at temperatures as high as 2 500 °C.

Stoichiometric mixtures of finely divided oxide and graphite powder are pressed into pellets and heated in vacuum according to the reaction



The pellets are radiofrequency heated at 2 000 °C in a graphite crucible. The partial pressure of CO is maintained below 10⁻⁴ torr during the carboreduction. The carbide is mixed with 50 % excess of tantalum powder with respect to equation (1). The mixture is pressed at 5 t/cm² and the pellets are radiofrequency heated in a tantalum crucible under a pressure of 10⁻⁶ torr. The actinide metal vapour is condensed in quartz domes. Rate and yield of the reduction of UC and PuC by tantalum powder are shown in figure 6. They compare favourably with those of the metallothermic reduction of the oxides [3, 6].

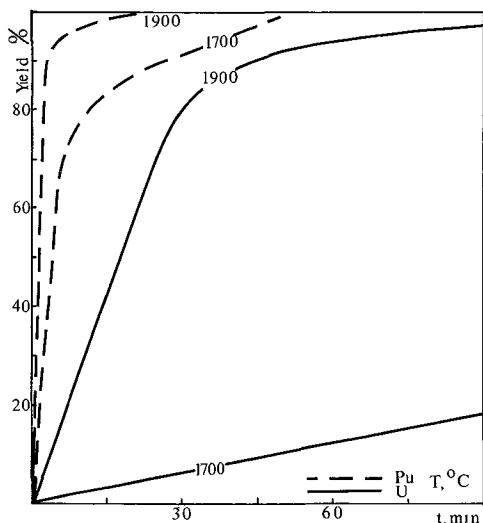


Fig. 6. — Distillation yield of uranium and plutonium during tantalothermic reduction of the carbides in vacuum.

This new method of preparation of the actinide metals is very promising since :

- it is a universal method for preparation of the actinide metals *via* the vapour phase with optimum reaction rate and yield,
- it might allow high purity material production starting from very impure material (waste). High

decontamination factors result from the selectivity at each step :

- a) evaporation of the volatile oxides and metals during the carboreduction (RuO_x, SiO, TiO, B₂O₃, Hg, Cd, Zn, Cs, Mg, Li, Tl, Bi, Ag, In, Sr, Mn, Cu, Ca, Al, Fe, Cr, Ni, Co, Be),
- b) stability of the carbides of impurities (Nb, Hf, W, Zr, Re),
- c) selective evaporation and condensation of the actinide metal.

2.5 REFINING OF ACTINIDE METALS BY SELECTIVE EVAPORATION AND CONDENSATION. — The evaporation of metals in high vacuum is described by the molecular evaporation law of Langmuir

$$w_i = 0.058 \ 33 \ P_i^0 \sqrt{\frac{M}{T}}$$

where w_i is the evaporation rate (g/s.cm²), P_i the vapour pressure (torr), T the temperature (K) and M the molecular mass. The selectivity of the separation of the constituents of a binary mixture (A, B) by molecular evaporation is given by the relative evaporation coefficient $\alpha(A, B)$

$$\alpha(A, B) = \frac{\gamma_A \cdot P_A}{\gamma_B \cdot P_B} \sqrt{\frac{M_B}{M_A}}$$

with γ being the activity coefficient of the element in the mixture. The efficiency of the refinement

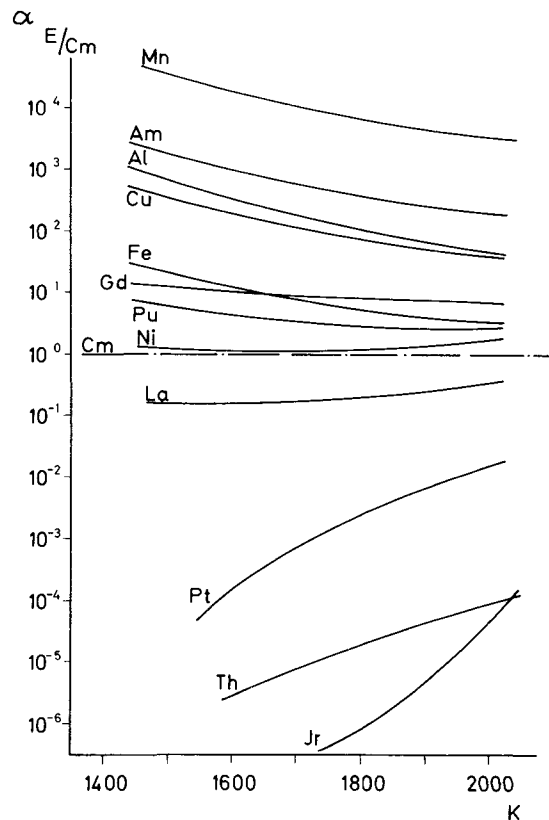


Fig. 7. — Simplified relative evaporation coefficient of various metals with respect to curium as a function of the temperature.

process depends on the vapour pressure ratio of the components.

The simplified relative evaporation coefficient ($\gamma_A/\gamma_B = 1$) of some common impurities with respect to Am, Cm, U are presented in the figure 7 as a function of the temperature.

Very good decontamination efficiency can be reached for all impurities with exception of Ag in Am, and Fe, Cr, Ni, Si, Gd in Cm or Pu.

It follows from figure 7 ($\alpha(A, B) \rightarrow 1$ with increasing temperature) that a selective evaporation has to be realised at the lowest possible temperature to minimize the coevaporation of the elements with low vapour pressure ($\alpha < 1$). A selective condensation occurs at the highest possible temperature to allow the reevaporation of the elements with higher vapour pressure ($\alpha > 1$). Choice of experimental conditions requires a compromise between good separation efficiency on one side and high evaporation rate and good yield on the other. The refining of the actinide metals is performed in RF heated tantalum distillation columns in a vacuum of 10^{-6} torr. The condenser with the metal obtained after the metallothermic reduction is introduced into the crucible.

With americium, evaporation rates of 100 mg/min were obtained at 1 100 °C. Cm was evaporated at 1 600 °C with a rate of 2 g/h. Condensation temperatures are for americium and curium 800 and 1 300 °C, respectively. The operation is repeated 2 or 3 times. For the last run, the condenser is replaced by a tantalum disk. The metal is condensed on the disk in the solid state and grows in the form of a button. At low evaporation rate, physical vapour transport and annealing yield single crystals. Figure 8 shows single crystals of dhcp Am metal. The small hexagonal prisms are 0.1 mm in diameter and 2 mm in length. A Cm metal single crystal weighing 600 mg was also prepared by this method [6].

2.6 CHEMICAL VAPOUR DEPOSITION ; THE IODIDE PROCESS. — Because of the low vapour pressure of Th and Pa (evaporation rate of 1 mg/h . cm² at 2 100 K, Fig. 3), their preparation by the metallothermic reduction in vacuum is a very slow process. Temperatures as high as 2 500 K are required

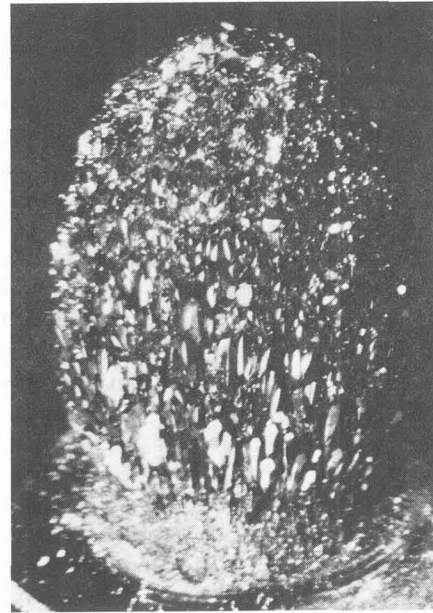


Fig. 8. — Americium metal deposited by physical vapour transport showing single crystals in the form of hexagonal pyramids.

to obtain satisfactory preparation rates in the laboratory scale. For these metals, the application of another process was necessary. The van Arkel process (iodide process) is usually applied to the final purification of crude metals obtained by different procedures. The crude metal is transported as volatile iodide *via* the gas phase to a zone, hot enough (generally a resistively heated tungsten wire) to decompose the iodide into pure metal and gaseous iodine. The liberated iodine diffuses back to the crude metal and reacts to form new iodide sustaining the chemical transport process (transfer of the metal as volatile iodide from the feed material to the metal deposit).

The van Arkel process can be used for the direct preparation of metals if the starting materials react easily with the transporting agent at the process temperature. This is the case for thorium and protactinium carbide which can easily be produced by carbothermic reduction of the oxides and react easily with iodine at 300 °C to give volatile iodides.

Finely ground oxides (ThO₂ or Pa₂O₃) are mixed with graphite powder and are pelletized at 10 t/cm².

Table II. — Summary of preparation conditions and results.

	Th				Pa						
	Hot wire [11]		RF heating		Hot wire [11]		RF heating				
Mass of metal in the starting oxide (g)	0.4	0.3	2.5	8				1.8	1.8	2.2	
Cell temperature (°C)	475	460	475	475	420	475	420	420	475	475	475
Deposition temperature (°C)	1 300	1 200	1 200	1 300	1 200	1 200	1 200	1 250	1 400	1 150	1 300
Mass of deposited metal (g)	0.36	0.26	2	5.9	0.06	0.03	0.15	0.03	1.2	0.8	1.4
Deposition time (h)			40	56					10	35	14
Metal yield (%)	91.9	86.4	80	73	95.2	53.4	86.9	91.5	66	44	64
Average rate (mg/h)	14.7	8.6	50	105	5.1	3.4	5.3	5.1	120	25	100

The carboreduction is carried out in a RF heated graphite crucible under dynamic vacuum (10^{-4} torr) until the end of the CO evolution.

The carbide pellets (PaC or ThC) are sealed under a vacuum of 10^{-6} torr in the van Arkel bulb (pyrex) with a quartz capillary containing the iodine. The van Arkel bulb is heated between 420 and 470 °C and the tungsten wire is maintained between 1 200 and 1 400 °C, dissociation temperature of the iodides. The hot wire technique allowed the preparation of very pure thorium and protactinium metal samples in quantities of the order of 200 mg. The wire is covered with very pure metal with pronounced crystalline appearance. Preparation conditions and results are summarized in table II [10, 11].

Attempts to deposit larger quantities of metal by the hot wire method were not successful and resulted in the appearance of hot spots and breaking the wire after melting of the deposited metal. In addition, the very low growth rate does not make the process very attractive for the production of large samples. To obtain large samples of compact material it was necessary to modify the experimental set up. The new van Arkel bulb and its assembly are shown in figure 9. The decomposition of the iodide occurs on a small radiofrequency heated tungsten sphere. The absence of electrodes allows the fabrication of quartz ampoules which can be heated, if necessary, at higher temperatures with a quartz resistance furnace. Results obtained with this as-

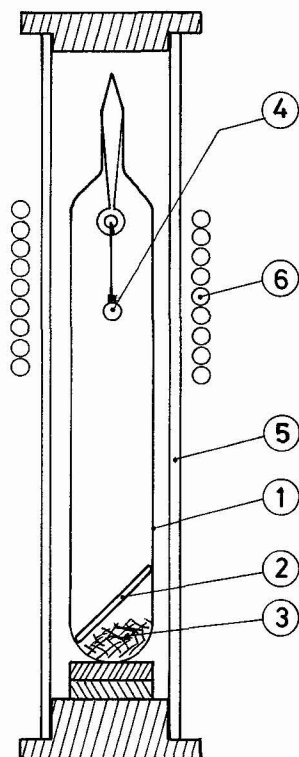


Fig. 9. — RF heated van Arkel deposition assembly. 1. Quartz bulb, 2. Iodine capsule, 3. Feed of metal or carbide, 4. Tungsten sphere, 5. Resistance furnace, 6. RF coil.

sembly are summarized in table II. Samples of 6 g of thorium and 1.4 g of protactinium with large, well formed single crystal faces (Fig. 10) were grown with a rate of 100 mg/h. Large samples of compact material without tungsten nucleus are prepared by cutting the protactinium deposit with a low speed diamond saw, by vacuum melting of the metal or repeating the transport process using a small piece of heated protactinium metal to start the deposition.

The thorium and protactinium produced by the carbide-iodide process show a very high degree of purity resulting from the multiple purification steps :

- evaporation of volatile materials during the carboreduction (metals and oxides),
- difference of stabilities of the carbides in iodine vapour,
- difference of stabilities of the iodides at the deposition temperature,
- volatilization of the metals at the deposition temperature.

Metallic impurities contained in the starting oxide which could contaminate the final product are U, Hf, Zr.

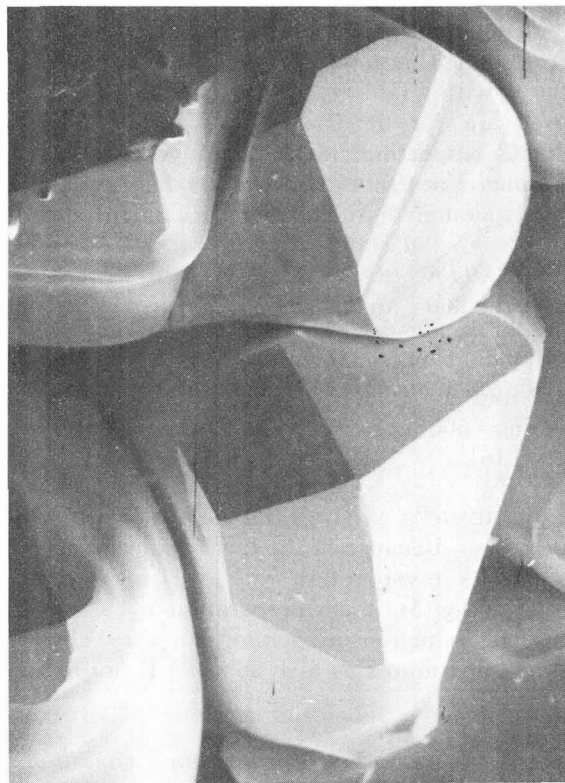


Fig. 10. — Scanning electron micrograph of van Arkel protactinium single crystals.

3. Synthesis and crystal growth of actinide compounds. — Pure actinide compounds in powder form are easily prepared by direct synthesis from the metals. The actinide metals react with the vapour of

most of the metalloid elements. Composition and structure of the compounds can be controlled by the reaction conditions and subsequent annealing at an appropriate temperature. Intermetallic compounds are obtained by direct reaction between the elements at high temperature in protective atmosphere. Due to the high reactivity of the actinide metals and compounds care has to be taken to avoid attacks by components of the environment during preparation, handling and storage.

3.1 PREPARATION OF ACTINIDE COMPOUNDS. — The following techniques are used in our laboratory to prepare actinide compounds :

— reaction of the metal at elevated temperature in a stream of O_2 , N_2 , H_2 , to prepare the oxides, nitrides and hydrides,

— reaction of the metals with pnictogen or chalcogen vapours, with I_2 or mercuric halides in vacuum sealed quartz bulbs to obtain pnictides, chalcogenides or halides,

— RF heating of the metals in a cooled crucible to prepare intermetallic compounds.

3.2 CRYSTAL GROWTH OF ACTINIDE COMPOUNDS. — To perform measurements of solid state properties, powder samples are not always suitable and good quality single crystals with high purity level and convenient dimensions are frequently required.

Different techniques of crystal growth were developed with respect to the application to radioactive material :

- high temperature solution growth,
- chemical vapour transport,
- pulling from the melt.

The first two methods produce small single crystals (0.1 to 500 mm^3) presenting well developed natural faces. By pulling from the melt large cylindrical crystals can be obtained.

Crystals of dioxide (CeO_2 , TiO_2) and of ternary oxides ($PbTiO_3$) — as stand in for actinide compounds — were prepared by solvent evaporation and temperature gradient methods from solutions of dioxide in lead fluoride melts. Single crystals of uranium and thorium dichalcogenides (US_2 , USe_2 , ThS_2 , $ThSe_2$, $ThOS$) were grown by chemical vapour transport using iodine as transporting agent. The feed material is introduced into a quartz capsule with the iodine. The capsule is evacuated and sealed under a pressure of 10^{-6} torr. The transport of the dichalcogenides occurs in a temperature gradient of $50\text{ }^\circ\text{C}/10\text{ cm}$. The feed material is held at $900\text{ }^\circ\text{C}$, the crystals grow at $850\text{ }^\circ\text{C}$. A crystal of ThS_2 is shown in figure 11.

Uranium and neptunium dioxide single crystals were grown with $TeCl_4$ as transporting agent, prepared in quartz ampoules. The oxide feed pellets are

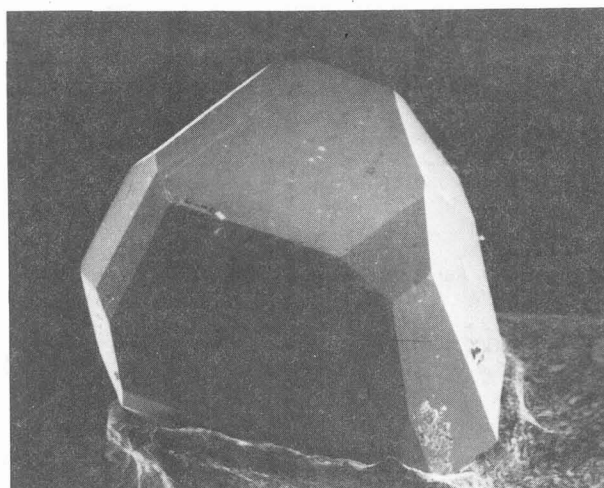


Fig. 11. — Single crystals of chalcogenides prepared by chemical vapour transport with iodine : ThS_2 .

heated at $1075\text{ }^\circ\text{C}$ and the crystals are grown at $975\text{ }^\circ\text{C}$ [12].

Attempts to prepare crystals of ThO_2 and PuO_2 by this process resulted in the strong corrosion of the quartz bulb. Attempts to prepare thorium pnictide single crystals by chemical vapour transport with I_2 and to prepare the monopnictides of uranium, thorium and protactinium by direct synthesis resulted in the attack of the walls of the quartz bulbs. The van Arkel procedure, however, permitted direct synthesis and crystal growth of actinide (U, Th, Pa) pnictides starting from the elements : films and small crystals of U_3As_4 , UAs , USb_2 , U_3Sb_4 , USb , Th_3As_4 , $ThAs$, $ThSb_2$, Th_2Sb_3 , $ThSb$, $PaAs_2$, Pa_3As_4 , $PaSb_2$, Pa_3Sb_4 were grown on an induction heated tungsten support [13].

4. Characterization of samples. — The samples are characterized for composition and stoichiometry by standard analytical methods like gravimetry, coulometry, potentiometry, spectrophotometry.

The crystal structures and phase compositions are determined by X-ray diffraction methods (Debye-Scherrer, Weissenberg).

The orientation of the crystals is given by the Laue diagram. Large contamination and crystal inhomogeneities are detected by scanning electron microscopy and by X-ray fluorescence (electron microprobe). Typical analyses of impurities at trace levels are obtained by emission spectroscopy and spark source mass spectroscopy. The acquisition of a plasma induced emission spectrometer and a secondary ion mass spectrometer will complete the spectrum of analytical facilities in the near future to permit a more complete characterization of each sample.

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DISCUSSION

Dr. R. A. HAIRE. — Have you had any problems with tantalum in your metal products, due to reaction between the product and the tantalum receivers ?

In our work, we have observed that tantalum will dissolve in the actinide metals, up to several percent of tantalum.

J. C. SPIRLET. — The metal is condensed on the receiver in the solid state so that the contamination is limited to the first metal layers and is not detectable.

Pr. J. R. PETERSON. — What is the practical lower limit of operation (mass of actinide) for the preparation of an actinide metal *via* the carboreduction process ? Each vaporization-deposition step must involve some loss of material. What are the typical efficiencies for this procedure ?

J. C. SPIRLET. — The process yield is 95 to 99 %. The problem of preparation of actinide metals in the submilligram scale is given more from the recovery of the condensed metal from the receiver than from the limitations introduced by the metallothermic process itself.

Pr. F. WEIGEL. — Did you determine the stoichiometry of your single crystal actinide dioxides, and if so, how ?

J. C. SPIRLET. — The stoichiometry was checked by determining the lattice parameter as measured by X-ray diffraction.

Pr. F. WEIGEL. — If you prepare uranium by the de Boer-van Arkel method, you have only a small temperature margin, because, if your temperature is too low, the iodide does not decompose, if it is too high, the molten metal goes off the wire.

J. C. SPIRLET. — The preparation of uranium metal by the hot wire technique is not to be recommended. But, in the RF heated support method, the deposition of molten metal should not be disturbing.

Dr. R. TROC. — What size were your single crystals of uranium monoarsenide ? Did you try to obtain larger single crystals ?

J. C. SPIRLET. — The largest dimension of the single crystals is between 0.1 and 0.5 mm. We did not try to obtain larger crystals.

COMMENT

Pr. MÜLLER. — There are political considerations that might, at least for the near future, prevent the application of the metallothermic reduction of carbides for reprocessing advanced nuclear fuel.

Pr. R. PETERSON. — I want to comment on one of the problems you mentioned in connection with the preparation of actinide metals *via* the reduction of the corresponding fluorides. We have solved the problem of preparing pure, anhydrous fluorides by

using fluorine to ensure that any oxygen present in the sample is replaced by fluoride. Of course the α , n problem still remains, and it limits the amount of actinide we use in an individual preparation.

COMMENT TO THE COMMENT BY J. C. SPIRLET TO Pr. J. R. PETERSON. — The handling of fluorine in glove boxes is very dangerous and the halide is hygroscopic so that the problem of handling and storage persists.