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UMACS Process and its Application to MABB Fuel Fabrication

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Abstract

In the framework of minor actinide, and especially americium, transmutation, a new fabrication process was developed to produce highly dense $U_{1-x}Am_xO_{2+\phi}$ fuels. This process, called UMACS, is based on the dissociation of the solid solution formation and its densification, by means of a conventional sintering. The competition that occurs during a reactive sintering between these two phenomena – which is known to limit the densification – is thus avoided. Several pellets ($x = 0.075; 0.15; 0.20$) were produced using the UMACS process and characterized in the ATALANTE facility (CEA Marcoule). Pellets with high densities and no significant open porosity were obtained.

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Keywords: UMACS; MABB fuels; minor actinides; americium; transmutation; sintering.

1. Introduction

Minor actinides (MA = neptunium, americium, curium) are generated in UOX (uranium oxide) and MOX (mixed oxide) fuels during irradiation in nuclear reactors. Transmutation in fast neutron reactors is a promising way to recycle these long-lived and highly radiotoxic elements. In this field, MABB (minor actinide-bearing blanket) fuels, and more specifically $U_{1-x}Am_xO_{2+\phi}$ fuels, are currently being studied by the LEMA (*Laboratory of studies of actinide-based materials*, CEA Marcoule).

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Similarly to MOX fuels produced using the MIMAS (micronized masterblend) process [1], MABB fuels can be fabricated via a method implying a reactive sintering [2-4]. In the latter, a powder mixture of single oxide precursors (such as $\text{UO}_{2+\delta}$ and $\text{AmO}_{2-\epsilon}$) is first prepared, then directly sintered through a thermal treatment in which both solid solution formation and its densification occur. In the case of $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\phi}$, the sintering conditions have to be adapted to take into account the high oxygen potential of americium oxides (compared to those of plutonium or uranium oxides) [5], and thus to avoid americium sublimation at high temperature. Usually, a sintering thermal treatment of 4 h at 2023 K with heating and cooling rates of $3 \text{ K}\cdot\text{min}^{-1}$ are used, under an atmosphere composed of Ar/H_2 (4%) – Ar/O_2 (100 ppm) gas mixture or of moistened Ar/H_2 (4%). A reactive sintering in these conditions allows monophasic pellets to be obtained, without significant americium loss by sublimation during sintering. Their density, however, barely reaches 93% TD (of the theoretical density) with a few percent of undesired open porosity. This limitation is directly caused by the reactive sintering.

In this type of sintering, solid solution formation and densification are in competition, which can delay or even preclude the latter, as was notably observed in the case of $\text{UO}_2\text{-Gd}_2\text{O}_3$ systems [6,7]. The creation of a new phase, here due to Gd_2O_3 presence, also leads to the emergence of an additional porosity which is nearly impossible to resorb during sintering. Densification cannot be complete as long as the solid solution is not fully formed. The difference in interdiffusion coefficients between uranium and gadolinium is furthermore responsible for the generation of an additional porosity through the Kirkendall effect [6-9]. Americium's particularities in terms of thermodynamic properties seem to lead to a similar situation. An unexpected charge distribution in $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\phi}$ ($x = 0.10; 0.15; 0.20$) materials was observed by XAS (X-ray absorption spectroscopy) [10]: americium is fully reduced to the (+III) state, whereas uranium exhibits a mixed (+IV/+V) valence, which compensates for americium reduction and leads to an O/M (oxygen to metal) ratio close to 2.0. HT-XRD (high temperature X-ray diffraction) studies completed these results, by showing that, under the considered conditions, $\text{AmO}_{2-\epsilon}$ is reduced to hexagonal Am_2O_3 starting at a relatively low temperature, i.e. 1200 K [11,12]. The solid solution is then formed by a reaction between Am_2O_3 and UO_2 at higher temperature, i.e. 1900 K [12]. Concerning Kirkendall-generated porosity, its occurrence was also reported during reactive sintering between uranium and americium oxides [9].

Consequently, a reactive sintering, which might be appropriate for some systems, should be avoided in the case of the $\text{UO}_{2+\delta}\text{-AmO}_{2-\epsilon}$ system, as it does not allow the fabrication of highly dense pellets exhibiting no trace of open porosity. Based on this assessment a new process, called UMACS (uranium-minor actinide conventional sintering), was developed by the *LEMA*. Its principle and first applications are presented here below.

2. UMACS process

2.1. Principle

UMACS is a two-step process that allows the separation of the two main phenomena of the above-mentioned reactive sintering, i.e. the solid solution formation and its densification, as can be seen in the flow chart presented in Fig. 1. The first step is fully dedicated to $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\phi}$ synthesis, which is performed by a solid-state route under controlled atmosphere. The obtained $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\phi}$ powder is then used for a conventional sintering during a dedicated thermal treatment.

2.2. Solid solution synthesis

The first step consists of preparing a $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm\phi}$ solid solution suitable for pelletizing and sintering. A mixture of the considered dioxides (in this case $\text{UO}_{2+\delta}$ and $\text{AmO}_{2-\epsilon}$) is prepared. This mixture must be homogeneous to facilitate the reaction between the precursors. Moreover, this homogeneity guarantees the absence of any U- or Am-rich spots in the final compounds, which is important to prevent anchored defects

(during the conventional sintering step) or hot points (under self- or in pile irradiation). This homogeneous mixture is obtained via ball-milling. Ball-milling cycles typically last 30 min, at an oscillation frequency of 15 Hz, which proved to give a homogeneous repartition of americium [2-4].

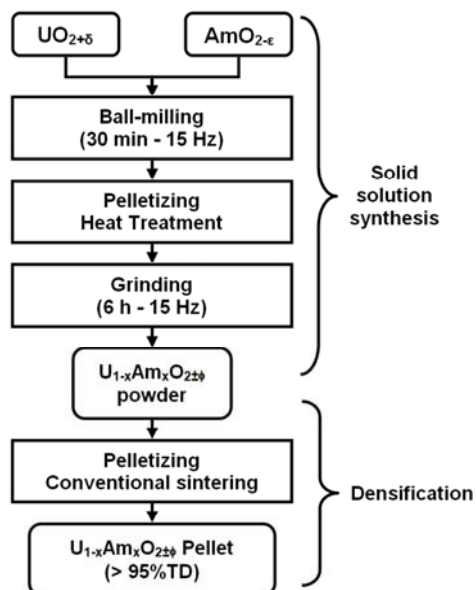


Fig. 1. UMACS process flow chart.

Before the heat treatment, the mixture is pressed into pellets. This step is used to create as much interaction surface between the precursors as possible. It may not be mandatory to obtain the solid solution, but it surely helps its formation by reducing the temperature or the time required. Furthermore, as the work with americium-bearing compounds is mostly achieved in shielded boxes using remote manipulators, the handling of pellets instead of powders represents a significant advantage. The solid solution is synthesized during a single heat treatment. The conditions of this heat treatment can be chosen taking into account both uranium and americium oxides' specific thermodynamic properties. It was notably shown that, after heat treatments in overstoichiometric conditions (i.e. under a neutral Ar atmosphere) for 4 h at an intermediate temperature (i.e. between 1300 and 1500 K), biphasic compounds are obtained, which means that the $U_{1-x}Am_xO_{2\pm\phi}$ solid solution formation is not complete [9]. Thus, reducing atmospheric conditions and higher temperatures are preferred, as all the monophasic $U_{1-x}Am_xO_{2\pm\phi}$ materials reported in the literature were fabricated in these conditions [2-4,10,13]. More precisely, HT-XRD measurements notably proved that 4 h at 1773 K are sufficient to create a fully-formed solid solution from a powdered sample [12]. After the heat treatment, the $U_{1-x}Am_xO_{2\pm\phi}$ pellets can be ground in order to obtain a powder suitable for pelletizing. This milling also allows the removal of all microstructural defects, mainly porosity induced by the Kirkendall effect [8].

2.3. Conventional sintering

As-obtained solid solution powder is then used to prepare green pellets for sintering. As these pellets are composed of a single and stable phase, the sintering process will be simplified to a conventional sintering, which allows the final sintering steps to be reached. Pellets exhibiting very high density (> 95% TD) and almost no open porosity can thus be obtained. Moreover, as the americium is integrated in a stable oxide structure since the beginning of the thermal treatment, the risks of its reduction (to Am^0 or Am^{II}) or sublimation are significantly

decreased. A wider range of oxygen potential can thus be used than in the case of a reactive sintering, which allows a more accurate control of the final O/M ratio of the pellet. Furthermore, if any sintered waste, size adjustment scraps or fractured pellets are obtained, it is possible to recycle these, directly into the $U_{1-x}Am_xO_{2\pm\phi}$ powder, or with the first $U_{1-x}Am_xO_{2\pm\phi}$ pellets produced just before the milling step. This represents a simple way to decrease waste production.

3. Application to $U_{1-x}Am_xO_{2\pm\phi}$ fuels

This part gives a brief description of pellets obtained using the UMACS process in the ATALANTE facility, in order to present its characteristics and advantages. Until now, pellets exhibiting three compositions were prepared using the UMACS process ($x = 0.075; 0.15; 0.20$).

3.1. Sample preparation

The pellets were fabricated from $UO_{2+\delta}$ and $AmO_{2-\epsilon}$ powders whose characteristics are given in Table 1. The raw pellets, exhibiting a density around 60% TD, were heat treated for 4 h at around 1900 K under an Ar/H₂ (4%) - Ar/O₂ (100 ppm) gas mixture to form a solid solution. After a grinding step, XRD was used to check the complete formation of the compound. For each compound, only one fluorite-type phase is observed, with no trace of any additional Am₂O₃ or U₄O₉ phase. This suggests that the solid solution is completely formed and that the americium is homogeneously dispersed within it. The other characteristics of one of obtained materials, $U_{0.85}Am_{0.15}O_{2\pm\phi}$, are compared to those of the precursors in Table 1. This powder was then used to prepare green pellets that present a high density, i.e. nearly 70% TD. The sintering cycle was composed of a 4 h plateau at 2023 K, and cooling and heating rates of 3 K.min⁻¹. A flow of Ar/H₂ (4%) was maintained during the whole cycle. XAS studies on a $U_{0.85}Am_{0.15}O_{2\pm\phi}$ sample prepared by reactive sintering under the same atmosphere show, through measurements of U and Am valences, that this atmosphere gives an O/M ratio close to 2.0 [10]. It is worth saying that this method is, up to now, the only one available to estimate O/M ratios of $U_{1-x}Am_xO_{2\pm\phi}$ materials.

Table 1. Precursor ($UO_{2+\delta}$ and $AmO_{2-\epsilon}$) and solid solution ($U_{0.85}Am_{0.15}O_{2\pm\phi}$) powder characteristics.

Characteristics	Powder		
	$UO_{2+\delta}$	$AmO_{2-\epsilon}$	$U_{0.85}Am_{0.15}O_{2\pm\phi}$
Morphology	Spherical and porous agglomerates		-
Granulometric factors (μm)	d_{10} *	0.46 (3)	1.8 (1)
	d_{50} *	0.71 (5)	7.5 (5)
	d_{90} *	7.2 (5)	45 (2)
Actinide content (wt.%)	U	87.8 (4)	0.17 (2)
	Am	-	78 (2)
	Np	-	2.6 (2)
Am/(U+Am) ratio (wt.%)	-	-	15.4 (6)

* Respectively, 10, 50 and 90 vol.% of particles have a size inferior to d_{10} , d_{50} and d_{90} factors.

3.2. Characterization

Sintered pellets present rectilinear shapes and no visible macroscopic defects. Their mean densities, calculated using pellet weight, diameter and height, are equal to 97, 96 and 95% TD, respectively, for $U_{0.925}Am_{0.075}O_{2\pm\phi}$, $U_{0.85}Am_{0.15}O_{2\pm\phi}$ and $U_{0.80}Am_{0.20}O_{2\pm\phi}$ pellets. Hydrometric weight measurements were taken to analyze the open porosity ratio. No significant amount of open porosity was detected in the ($x = 0.075$; 0.15) samples, as the results were under the detection limit. This is coherent with the high relative densities obtained, as it can be considered that, above 93-94% TD, no open porosity should remain. In the case of similar samples fabricated by reactive sintering, such a result was not achievable. Sintered pellets always contained a few percent of undesired open porosity, and densities barely reached 93% TD [2]. The UMACS process thus overcomes the densification limitations inherent in a reactive sintering.

SEM (scanning electron microscopy) observations reported in Fig. 2 were made in the ATALANTE facility on both polished and fracture surface. The polished surface (Fig. 2 (a)) shows a homogeneous sample, whose porosity is mostly submicronic, the larger visible “holes” being attributed to sample preparation. Fracture surface observations (Fig. 2 (b)) reveal the grains, which allows a more detailed microstructure characterization. Both micrographs certify that a majority of submicronic pores are intergranular. Intragranular pores are also found. Both inter- and intragranular pores have similar sizes and shapes, i.e. spherical pores with diameter comprised between 0.1 and 1 μm . Well-faceted polyhedral grains of several microns in width are observed on the fracture surface, which confirms that the final stage of sintering was reached and complete. Thus, size reduction of the porosity is achieved through the UMACS process, when compared to a reactive sintering. This is notably due to the use of a conventional sintering that enhances the densification process, but also to the milling step, which is useful to remove the defects (mainly non-resorbable porosity) created during solid solution formation.

XRD patterns of the samples confirm the presence of a only one fluorite-type phase with lattice parameters close to those previously reported [2,10], i.e. 5.469 \AA for $x = 0.075$ and 5.468 \AA for $x = 0.15$. No secondary phases, such as Am_2O_3 or U_4O_9 , were reported. This indicates a homogeneous repartition of americium in the sample, and the absence of U- or Am-rich spots. This homogeneity is not surprising, as it was achieved after the first thermal treatment, or after a reactive sintering in similar conditions [2-4,10].

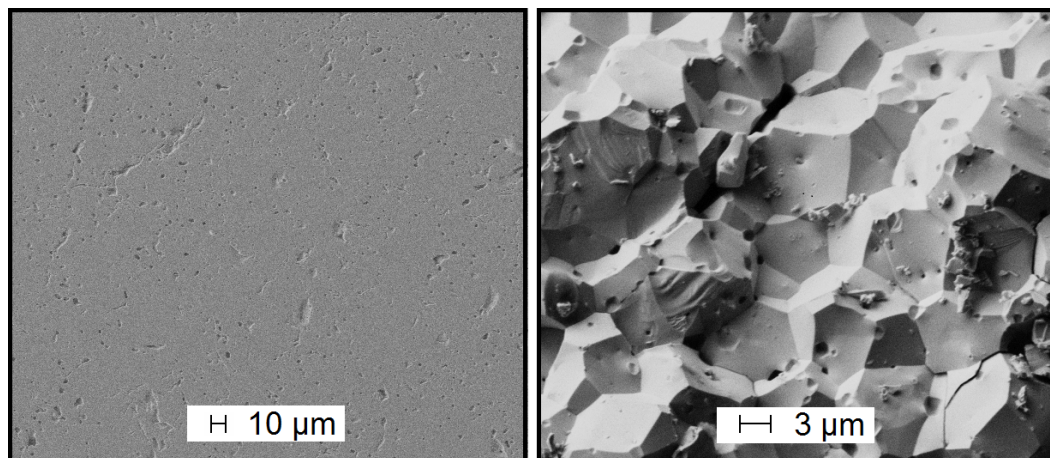


Fig. 2. SEM observations of $U_{0.85}Am_{0.15}O_{2\pm}$ pellet fabricated using the UMACS process on (a) a polished surface and (b) a fracture surface.

4. Conclusion

To overcome the limitation of densification caused by the use of a reactive sintering of $U_{1-x}Am_xO_{2\pm\phi}$ MABB fuels, a new process has recently been developed by the LEMA (CEA Marcoule). The latter, called UMACS, is based on the dissociation of solid solution formation and its densification. A solid-solution powder is firstly produced by a solid state route at high temperature, and then used to prepare green pellets sintered conventionally. Using the UMACS process, various $U_{1-x}Am_xO_{2\pm\phi}$ samples ($x = 0.075, 0.15; 0.20$) were fabricated. High densities, i.e., $> 94\%$ TD, are achieved without a significant amount of open porosity. This process thus represents a convenient and suitable way to produce $U_{1-x}Am_xO_{2\pm\delta}$ or other MABB fuels, notably for experimental irradiation [14].

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