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Fabrication of mixed uranium–plutonium carbide fuel pellets with a low oxygen content and an open-pore microstructure

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ABSTRACT

Mixed uranium–plutonium carbides are considered as potential fuels for Generation IV fast reactors. Compared to that of oxide fuels, their fabrication with regard to required specifications is more difficult. Carbides are obtained by a two-step procedure from the mixture of UO_2, PuO_2 and graphite powders. Due to their extreme reactivity with oxygen and moisture, fabrication and handling of carbide fuels are performed in glove boxes maintained under a dynamic flow of nitrogen providing operational safety. Nevertheless, oxygen pickup during processing of the material seems unavoidable and thus must be limited by suitable procedures. The oxygen content in the carbides can vary over a wide range of values, which can affect the green density and hence the sintered density. The addition of zinc stearate in a suitable amount to the fuel powder leads to an open-pore microstructure. A high open porosity contributes to minimizing the residual oxygen content in the sintered pellets.

1. Introduction

Mixed uranium–plutonium carbide has been for many years an advanced and alternative fuel to the mixed oxide being developed for the next generation nuclear energy systems, Gas-cooled Fast Reactors (GFR) and Sodium-cooled Fast Reactors (SFR), known as "Generation IV".

Their high metal atom density (12.9 g cm^{-3} vs 9.8 g cm^{-3}) and their high thermal conductivity (about eight times higher than the oxide one), the latter compensating for their lower melting point (Table 1), are among the advantages of mixed carbide fuels over the widely used oxide fuels for current nuclear power generation [1]. Moreover, their compatibility with the coolant allows them to be safely used in liquid metal (Na) or gas cooled (He) reactors.

But, despite these advantages, compared to oxide fuel manufacturing, carbide fuel fabrication process is a much more difficult and challenging task [2].

Owing to their extreme reactivity with oxygen and moisture, there is always the possibility of residual oxygen content in mixed carbide fuel materials (the oxygen maximum solubility has been estimated at around 12,400 ppm at 1850 K from thermodynamic calculations [3]). The form in which oxygen is present, as oxide or in solution in the carbide, may affect the performance of the fuel material and also the compatibility of the fuel with cladding materials.

In this work, mixed carbide pellets were obtained by a carboreduction process. Emphasis was put on the optimization of the fabrication parameters in order to manufacture fuels that meet pellet requirements, and in particular a low oxygen level specification.

The use of a pore former to adjust the sintered density of carbide pellets was investigated, as well as the effect of such an addition on the fraction of open porosity and the oxygen content in the sintered pellets.

2. Mixed carbide pellet requirements

The specifications set for mixed carbide pellets result from irradiation feedback (NIMPHE 2 experiment in the Phénix reactor in France [4,5]). A two-phase fuel (i.e. containing a main (U,Pu)C monocarbide phase and a secondary $(U,Pu)_2C_3$ sesquicarbide phase) with a plutonium content of 15% is specified, with:

- A sintered density of 80 to 85%TD, to partially accommodate the fuel swelling and limit the cladding mechanical interaction to yield decent burnup without breaking.
- A predominant open porosity P_{open} which promotes the release of fission gases: $P_{open}/P_{total} > 50\%$.
- An oxygen content lower than 1000 ppm, to limit the degradation of the irradiation behavior of the mixed carbide fuel.

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Table 1
Properties of mixed uranium–plutonium oxide and carbide fuels [1].

Properties	$(U_{0.8}Pu_{0.2})O_2$	$(U_{0.8}Pu_{0.2})C$
Theoretical density ($g\,cm^{-3}$)	11.04	13.58
Melting point (°K)	3083	2750
Thermal conductivity ($W\,m^{-1}\,K$)		
1000 K	2.6	18.8
2000 K	2.4	21.2
Crystal structure	Fluorite	NaCl
Breeding ratio	1.1	1.2–1.3
Swelling	Moderate	High
Handling	In air	Inert atmosphere
Compatibility		
Clad	Average	Carburization
Coolant	Average	Good
Dissolution and reprocessing amenability	Demonstrated on industrial scale for aqueous and pilot scale for pyro-processes	Dissolution not simple. Process not yet demonstrated on industrial scale.
Fabrication/irradiation experience	Large/good	Limited

- A $(U,Pu)_2C_3$ sesquicarbide content between 5 and 10 wt.% to avoid the presence of a metallic phase with a low melting point, while reducing the risk of clad failure by carburization.
- And, finally, an impurities (Na, Si, Cl, F) content as low as possible.

These requirements are globally comparable to those specified for previous fuels produced for out-of-pile studies and irradiation programs in the early 1960s in France and in the 1980–1990s in Japan, Germany, United States... [6–9]. But a much higher oxygen content, up to 3000 ppm, used to be accepted. Nowadays, the recommended oxygen content (less than 1000 ppm) is a more stringent requirement.

Whereas most of the studies carried out in different laboratories have been confined to uranium-rich compositions, the Indian carbide fuel is a high plutonium hyperstoichiometric mixed carbide. A plutonium-rich fuel can accommodate more oxygen than a uranium-rich fuel. This is in agreement with the fact that the oxygen solubility in PuC_{1-x} is almost double of that in UC [10]. So, the higher the Pu content, the higher the allowable oxygen content. Hence, for Indian fuels with a plutonium content ranging from 55 to 70% [1], an oxygen content up to 6000 ppm is specified.

3. Experimental procedures

3.1. Carbide fabrication

Mixed carbides were obtained by a powder metallurgy route. As they react easily with oxygen and moisture, all processing of the materials was carried out in nitrogen-filled glove boxes with moisture and oxygen levels below 50 ppm each. These operating conditions are less severe than those practiced in India where the carbide fuel fabrication facility consists of chains of interconnected gloves boxes with moisture and oxygen levels below 25 ppm each [1]. But, even these levels are too high to avoid some oxygen pickup, particularly when handling finely milled carbides. Therefore, special care has to be taken. For example, in storage conditions and during all transfer operations, carbides were stored in specific sealed containers.

The flowsheet in Fig. 1 shows the process used for the fabrication of mixed carbide pellets, which involves two main steps. The first step consists in synthesizing carbide as a species by carboreduction and the second stage deals with the densification of the carbide crude, after milling and shaping by pelletizing of the powder obtained.

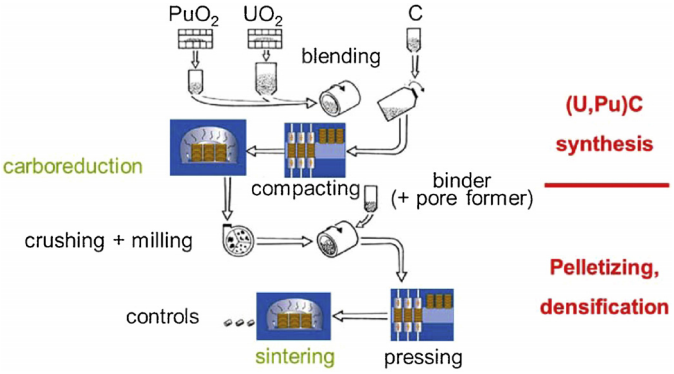

Fig. 1. Fabrication process of uranium–plutonium mixed carbide pellets.

A significant loss of plutonium may be caused by vaporization during the heating steps of the fabrication process, at high temperatures. An increase in the temperature or a hypostoichiometric composition (carbon to metal ratio C/M < 1, M = U + Pu) will contribute to increasing the partial pressure of plutonium [11] (Fig. 2).

The Pu loss is also influenced by the vacuum conditions. Under unfavourable conditions (after a 10^{-3} Pa vacuum reduction of oxides performed at 1570 °C for 4 h), the plutonium loss can amount to 10% [12]. The predominant gas phases have been assumed to be Pu and PuO [13]. Such a plutonium loss affects the carbide composition and must be thus limited.

3.1.1. First step of fabrication: Carbide synthesis

The feed materials were UO_2, PuO_2 and an excess amount of graphite powders, which were blended mechanically. The oxide–carbon blend containing 15% Pu was pressed at 190 MPa into compacts 10 mm in diameter. The compacts were then submitted to a thermal treatment in the temperature range of 1500–1750 °C under a primary vacuum for 15 h. Special attention was paid to the evolution of the weight losses and densities of as-reacted carbides measured after the treatment.

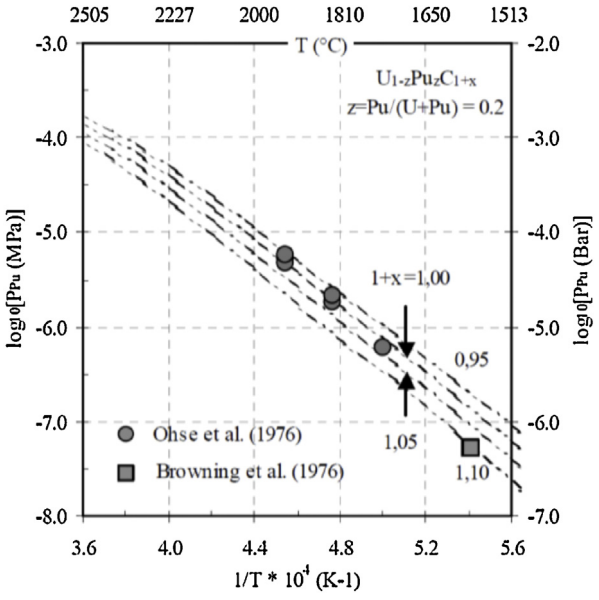

Fig. 2. Evolution of the partial pressure of plutonium as a function of the temperature for a range of carbide compositions ($0.95 \le C/M \le 1.10$ and Pu/M = 0.2, M = U + Pu) [11].