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Journal of Nuclear Materials 300 (2002) 273–276

journal of nuclear materials

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Letter to the Editors

Fission product precipitates in irradiated uranium carbonitride fuel

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Received 23 July 2001; accepted 19 October 2001

Abstract

Austenitic steel-cladded uranium carbonitride fuel pins were irradiated in the BR2 up to 6.4% burnup. A cross-section of the pin RV 24 with the fuel composition $UC_{0.86}N_{0.09}O_{0.05}$ was prepared for X-ray microanalysis of the fission product precipitates. Rare-earth oxide and $U(Mo,Tc)C_2$ phases were observed in the whole fuel region. Bright phases present in annular rings of the outer fuel zone were identified as $U_2(Tc, Ru, Rh)C_2$. Alkaline-earth oxide and U–Pd–Ni phases were shown in the fuel-cladding gap. The rare-earth and alkaline-earth fission products extracted the oxygen from the fuel matrix which became nearly oxygen free. The formation of nitrides could not be detected. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Nuclear carbide and nitride fuels are anew of increasing interest in the context of the selection of optimised compositions of plutonium and higher actinide compounds within the actinide transmutation programme [1]. Disadvantages of carbide fuels are impediments to the processing due to their pyrophoricity, the non-stoichiometry and possibly the limited mutual solubility of the higher actinide carbide phases, and the carburisation of the steel claddings at high temperatures. The use of nitride fuels results in the formation of β-active ^{14}C by the nuclear reaction $^{14}N(n,p)^{14}C$. The carbonitrides U(C, N), Pu(C, N), etc. forming a continuous series of solid solutions may unify the advantages and minimise the disadvantages of the boundary phases. The thermodynamic activity of carbon is reduced compared to that of pure carbides with respect to the pyrophoric behaviour of the carbides. U(C, N) and UN are more compatible with austenitic steels than UC [2] for similar reasons. The same may hold for the respective plutonium and higher actinides compounds.

2. Literature survey

Post-irradiation studies on carbonitrides are very scarce. Walker has investigated hyperstoichiometric $U_{0.8}Pu_{0.2}C_{0.82}N_{0.22}O_{0.02}$ fuel (atom ratio $(C + N + O)/(U + Pu) > 1$) after 3.9% burnup by X-ray microanalysis, measured the fraction of the fission products dissolved in the carbonitride matrix and analysed semi-quantitatively the following families of fuel–fission product precipitates: $U(Tc, Ru, Rh, Pd)_3$, Pu–RE–Sn–Pd phases, (RE, Te)C and RE_2O_3, RE are rare earths [3]. Nitride fuel of the composition $U_{0.8}Pu_{0.2}N_{0.94}C_{0.03}O_{0.03}$ has been analysed after 1.3% burnup in a preceding paper by Giacchetti et al. [4]. The phases $U(Mo, Ru, Rh, Pd)_3$, $(U, Pu)O_2$ and Mo–Tc–W, where W is an impurity of the fuel, were observed. Both experiments were irradiated in fast reactors and evidenced radial plutonium migration to lower temperature regions.

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PII: S0022-3115(01)00741-3

The X-ray microprobe analysis at Forschungszentrum Karlsruhe was started on irradiated UC and (U, Pu)C in 1973 with emphasis of radial fuel component redistributions, solubility and precipitation behaviour of condensed fission products in the fuel, fission gas content, clad carburisation, influence of the oxygen impurities, etc. [5–8]. From the observations it followed that the type and composition of the fission product precipitates depend on the stoichiometry $(C+N+O)/(U+Pu)$ and particularly on the oxygen content of the carbide fuel. The latter controls the stoichiometry shift of the fuel matrix. The complex carbides $(U, Pu)\cdot(Mo, Tc)C_2$ and $(U, Pu)_2\cdot(Tc, Ru, Rh)C_2$ are the dominant phases in hyperstoichiometric fuel. The rare earths are dissolved in the carbide matrix if it is oxygen poor. Higher oxygen contaminations result in the formation of oxicarbide and oxide precipitates. The alkaline earths are precipitated as dicarbides in oxygen-free fuel and at higher oxygen impurity contents as monoxides. (U, Pu)C and $(U, Pu)\cdot(C, N)$ fuel matrices are nearly oxygen-free already at medium burnups due to the oxygen getter effect of the alkaline-earth- and rare earth-fission products.

The findings of the post-irradiation examinations [5–8] and unpublished results of the more recent mixed carbide irradiations DFR-330 and DIDO-03 give more precise information on the fission product behaviour of carbonitride fuel which is discussed in the following sections.

3. Experimental

Uranium carbonitride was prepared by carbothermic reduction of a mixture of UO_2 and graphite under a nitrogen atmosphere up to 2300 °C [2]. The AISI 304 steel cladded pins with 8 mm outer diameter and 150 mm length were filled with the solid U(C, N) pellets and ZrC isolation pellets on both ends of the fuel column. Helium was used for the fuel-gap bonding. The pins of different fuel compositions were irradiated in Na–K capsules in the unshielded neutron flux of the BR2 reactor at Mol, Belgium, up to 6.4% burnup with maximum heat ratings of 90 kW/m. The fuel and irradiation data of the investigated pin RV 24 within this MNK 07 experiment are listed in Table 1 [9]. The pin cross-section was prepared by cutting a 10 mm thick specimen from the middle of the fuel length in the hot cells. The section was embedded in araldite resin under nitrogen atmosphere and was polished with diamond paste down to 0.5 µm grain size. A γ-shielded wavelength dispersive X-ray microanalyser was used for the quantitative element analysis in the range between carbon and the actinides.

Table 1
Fuel and irradiation data of pin RV 24 of the MNK 07 experiment

Composition (in wt%)	95.06% U, 4.12% C, 0.50% N, 0.32% O($UC_{0.86}N_{0.09}O_{0.05}$), C-equivalent: 4.79%[a]
Uranium enrichment	13.3% U-235/U-tot
Fuel density (volumetric)	11.9 Mg/m^3 (≈84% th.d.)
Solid pellet diameter	6.62 mm
Diametral gap	190 µm
Fuel length	80 mm
Cladding	Austenitic steel 1.4301 (AISI 304)
Cladding thickness	0.52 mm
Linear heat rating	70–80 kW/m
Outer cladding temperature	$\leqslant$ 520 °C
Maximum burnup at max. linear heat rating	6.4%

[a] C-equivalent = 4.12 + 0.50(12/14) + 0.32(12/16) = 4.79 wt%.

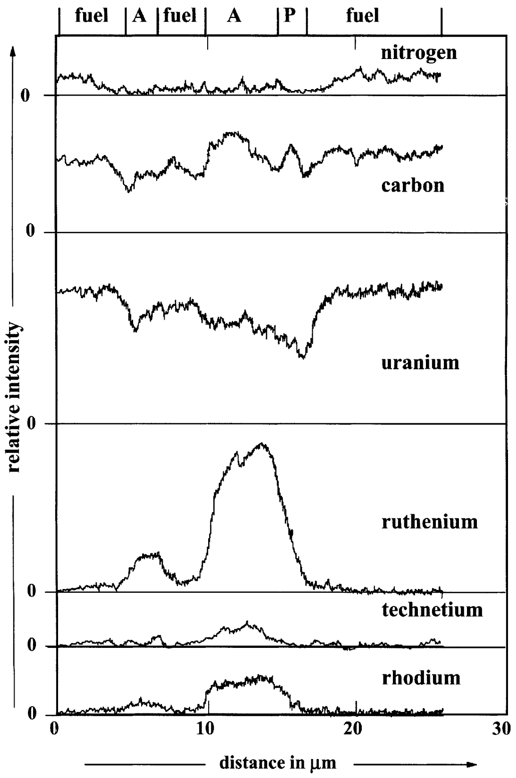

Fig. 1. Relative concentration profiles across the fission product precipitates $U_2(Ru, Rh, Tc)C_2$ (A) within the U(C, N) fuel adjacent to a pore (P).

4. Results

Irregularly shaped fission product precipitates up to 7 µm diameter and with metallic shine were observed in the outer fuel region near the pellet surface. They contained the elements U, Ru, Rh, Tc and C, but essentially no palladium, nitrogen and oxygen (see Figs. 1 (phase A), and 2). The quantitative analysis gave (in wt%) 81.4% U,

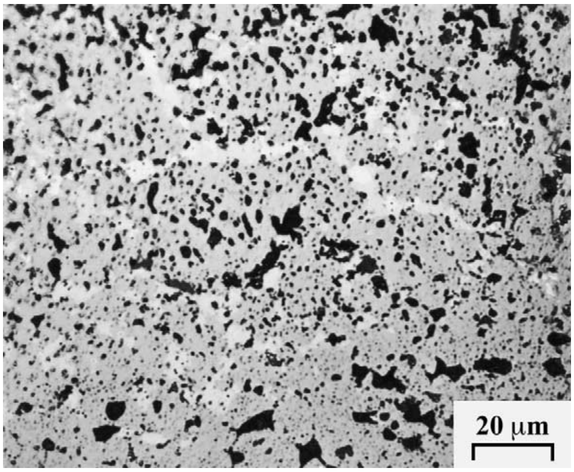

Fig. 2. Light-optical microstructure of the $U_2(Ru, Rh, Tc)C_2$ precipitates (bright) in the outer U(C, N) fuel region.

11% Ru, 3% Rh, 1% Tc and 3.6% C which corresponds approximately to the formula $U_2(Ru_{0.73}\text{-}Rh_{0.20}Tc_{0.07})C_2$. This composition is in agreement with the ternary carbides U_2RuC_2 and U_2RhC_2 which crystallise in a tetragonal structure of the U_2IrC_2-type [10]. These phases are formed peritectically at about 1700 °C by the reaction U carbides + liquid U–Ru(Rh) = U_2RuC_2-(U_2RhC_2) [11]. The liquid in-pile precipitates should have been transported to lower temperature regions due to the high vapour pressure.

A second type of carbide precipitates was found in the inner and outer fuel pellet regions with diameters <2 μm. A quantitative analysis was not possible. However, the relative concentration profiles across these fission product precipitates evidenced the presence of U, Mo, Tc, C and smaller amounts of Zr and N (see Fig. 3, phase B). The existence of the ternary carbides $UMoC_2$ [12] and $UTcC_2$ [13] crystallising in the orthorhombic $CrUC_2$-type structure suggests the composition U(Mo, Tc)C_2 of this phase.

A third type of lustreless precipitates was observed in the entire fuel pellet range with the larger phases up to 10 μm diameter in the fuel centre. The relative concentration profiles in Fig. 3 point to a solid solution of rare-earth sesquioxides, phase D. The quantitative analysis results in (in wt%) 13% La, 13% Ce, 8% Pr, 31% Nd, 5% Pm, 8% Sm and 18% O, close to the RE_2O_3 sesquioxide composition. The phase is free of nitrogen and contains small amounts of yttrium and zirconium.

Palladium is not component of the complex carbide precipitates because a ternary carbide does not exist in the U–Pd–C system [14]. This fission product was observed in the fuel-clad gap and on the inner clad surface in the form of U–Pd–Ni–Fe solid solutions in different compositions.

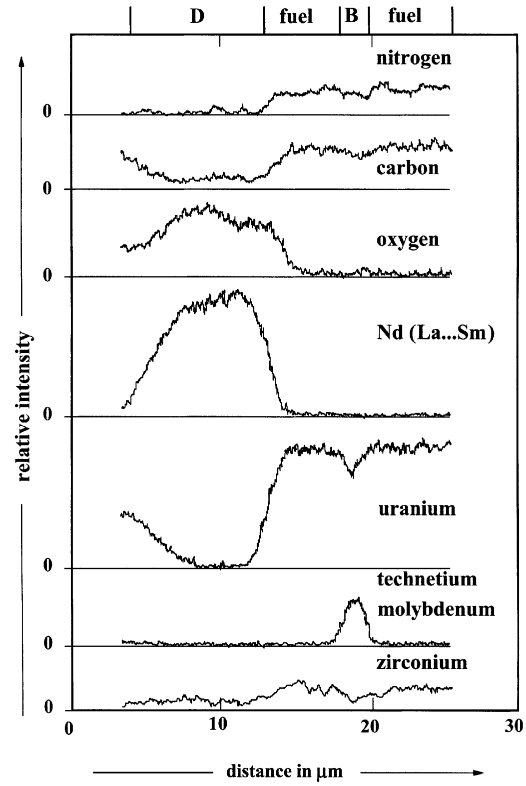

Fig. 3. Relative concentration profiles across the fission product precipitates U(Mo, Tc)C_2 (B) and RE_2O_3 (D) within the U(C, N) fuel.

The flux depression is reflected by the fuel radius dependent concentrations of the fission products dissolved in the U(C, N) fuel matrix. Fuel section averaged concentrations of 0.3% Mo and 0.6% Zr have been detected. The fuel matrix is nearly oxygen free and therefore, the composition has approached a pure carbonitride fuel at the end of life. The rare earths in the fuel and the alkaline earths in the fuel-clad gap have gettered the oxygen from the U(C, N, O) matrix to form oxide precipitates. The Vickers hardness was measured near the inner clad surface to be 500 HV (0.5 N) which decreases steeply to 250 HV in the inner clad region [9].

5. Conclusions

No significant differences of the fission product precipitates were observed between pure carbide fuel [8] and carbonitride fuel of the present investigation. The start-of-life fuel stoichiometry is slightly hypostoichiometric due to the carbon equivalent of 4.79 wt% and decreases further with increasing burnup. Despite the decreased thermodynamic activity of carbon in $UC_{0.86}N_{0.09}O_{0.05}$ by about 10% compared to UC, the formation of the fuel–fission product complex carbides is exemplified. The clad carburisation is reduced which will become important for the use of advanced carbonitride fuels. Oxygen is almost completely removed from the fuel by formation of rare-earth oxide and alkaline-earth oxide precipitates acting as oxygen sinks. Oxycarbides and carbides of these fission products will be formed with decreasing oxygen impurity content in the fuel [8]. The end-of-life fuel matrix is nearly free of oxygen. The shift of the carbon-(+nitrogen)-to-actinide ratio with burnup in oxygen containing fuels is difficult to predict because the chemical state of the rare earths, alkaline earths and alkalines is dependent on the amount of the oxygen impurities.

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