Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Nuclear Materials 352 (2006) 165–173
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Fabrication, characterization and property evaluation of mixed carbide fuels for a test Fast Breeder Reactor

S. Majumdar, A.K. Sengupta *, H.S. Kamath

Nuclear Fuels Group, Bhabha Atomic Research Centre, Head Fuel Property Evaluation Section, Mumbai 400085, India

Abstract

The Fast Breeder Test Reactor (FBTR) at Kalpakkam, India is operating successfully since October 1985 with high plutonium content hyperstoichiometic mixed carbide as driver fuel. The reactor was first made critical with a small core containing $(Pu_{0.7}U_{0.3})C$ fuel (MKI) and the core is now being progressively enlarged with addition of fuel containing $(Pu_{0.55}U_{0.45})C$ (MKII). Comparison of out-of-pile experimental data generated on thermal expansion, hot hardness, thermal conductivity, solidus temperature and fuel clad coolant chemical compatibility predicts similar in pile behaviour for both the fuels. Progressive post irradiation examination carried out on MKI fuel estimates a conservative burn up capability of 150 GW d t^{-1} for the fuel.

1. Introduction

The Fast Breeder Test Reactor (FBTR) at Kalpakkam, India is successfully operating since October 1985 with a high plutonium containing hyperstoichiometic mixed carbide fuel. Initial criticality was achieved with a small core containing $(Pu_{0.7}U_{0.3})C$ fuel (MKI fuel) and the reactor was operated for several campaigns at low power levels mainly to gain operational experience and to carry out various reactor physics and safety experiments. The small core is now being progressively expanded with $(Pu_{0.55}U_{0.45})C$ fuel (MKII fuel) to increase the electrical power level of the reactor for fuel and material irradiation of prototype fast breeder reactor (PFBR) – a 500 MW fast reactor to be commissioned by the year 2010. As no reported information were available for these unique fuel compositions, establishment of fuel fabrication flow sheet and parameters, fuel pellet specification, process control and characterization techniques, generation of thermo-physical and thermo-mechanical properties data and out-of-pile fuel-clad-coolant compatibility tests had to be carried out indigenously. A very conservative performance was envisaged for the initial fuel; a burn up of 25 GW d t^{-1} and linear power of only 250 W cm^{-1}.

However, periodic post irradiation examination (PIE) and performance assessment carried out on irradiated sub-assemblies gave confidence in progressive enhancement of the fuel performance and till date the fuel has seen a burn up of 140 GW d t^{-1} at a linear heat rating of 400 W cm^{-1}.

* Corresponding author. Tel.: +91 22 25593933; fax: +91 22 25505151.
E-mail address: arghya@apsara.barc.ernet.in (A.K. Sengupta).

0022-3115/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2006.02.050

Mixed uranium plutonium carbide fuel is considered an advanced liquid metal cooled fast breeder reactor (LMFBR) fuel compared to mixed oxide fuel due to higher fissile atom density, lower non-fissile atom fraction, better thermal conductivity and better compatibility with liquid sodium coolant [1]. This permits higher specific power operation and leads to a higher breeding ratio [2]. However, as described in the subsequent sections of this paper, compared to oxide fuels, carbide fuel fabrication is much more difficult and challenging task. This may be one of the reasons why no country has yet ventured to run a fast reactor with mixed carbide fuel. In fact, India is the only country in the world to operate a fast reactor with mixed carbide as driver fuel. The paper describes our experience of mixed carbide fuel fabrication for the last two decades and predicts in pile behaviour of the fuels based on the out-of-pile data of some of the properties of mixed carbide fuel generated by us and post irradiation examination (PIE) carried out on MKI fuel.

2. Fuel fabrication

Table 1 gives some of the important specifications of the mixed carbide fuel pellets for FBTR and Fig. 1 gives the general flow sheet developed for the fabrication of mixed carbide (MC) pellets meeting all the required specifications. The main steps in the fabrication of MC fuel pellets are:

Table 1
Specifications of (Pu, U)C fuel pellets for MKI and MKII cores of FBTR

Specification	$(Pu_{0.7}U_{0.3})C$	$(Pu_{0.55}U_{0.45})C$
Chemical		
Plutonium (wt%)	66 ± 1	51.9 ± 1
Plutonium and Uranium (wt%)	$\geqslant 94$	$\geqslant 94$
Americium (wt%)	Not specified	0.3 Maximum
Oxygen (ppm)	$\leqslant 6000$	$\leqslant 5000$
Oxygen + nitrogen (ppm)	$\leqslant 7500$	$\leqslant 6000$
M_2C_3 (wt%)	5 to 20	5 to 15
Tungsten (ppm)	$\leqslant 200$	$\leqslant 200$
Total impurities (ppm) (excluding oxygen, nitrogen, americium)	$\leqslant 3000$	$\leqslant 3000$
Physical		
Diameter (mm)	4.18 ± 0.04	4.18 ± 0.05
Height (mm) (nominal)	7.00 ± 0.04	7.00 ± 0.05
Density (%TD)	90 ± 1	86 ± 2
Linear mass (g/cm)	1.67 ± 0.04	1.60 ± 0.04

- Vacuum carbothermic synthesis of MC from UO_2, PuO_2 and graphite powder.
- Crushing and milling of MC clinkers.
- Consolidation of MC powders into fuel pellets by cold pressing and sintering.

2.1. Carbothermic reduction of oxides

The feed materials for the vacuum carbothermic reduction are UO_2, PuO_2 and graphite powders in required weight proportion. While fixing the carbon content in the oxide–graphite powder mixture, the initial UO_2 stoichiometry, expected increase of carbon content through binder – lubricant used during pressing of MC powder and expected oxygen pick up during further processing of the material has to be taken into account. The characteristics of the powders, their thorough homogeneous mixing and consolidation play an important role in achieving faster reaction rates during carbothermic reduction and complete conversion of oxides to carbide at a relatively low temperature so as to keep plutonium votalization loss at reasonably low level. The reduction reaction proceeds towards the forward direction with the evolution of CO, control of whose partial pressure is very important. Before reaching the final stage, the reaction

$$x\mathrm{PuO_2} + (1-x)\mathrm{UO_2} + 3\mathrm{C} = (\mathrm{Pu}_x\mathrm{U}_{1-x})\mathrm{C} + 2\mathrm{CO}\uparrow, \quad (1)$$

traverses through various intermediate paths and in one stage forms a mixed uranium–plutonium monoxy carbide solid solution [3]. Oxygen can be substantially removed from this solid solution only at temperatures over 1900 K at the cost of high plutonium votalization loss. Hence, the specification of MC fuel allows presence of some oxygen depending on the Pu content in the fuel; higher the Pu content, higher is the allowable oxygen content. However, as some Pu loss is unavoidable, proper stoichiometric adjustment of Pu content has to be done at the beginning to compensate for the subsequent loss.

2.2. Preparation of carbide powder

The MC product available after carbothermic reduction of oxides is in the form of clinkers and need to be crushed and milled to fine powder of required surface area for obtaining the feed material

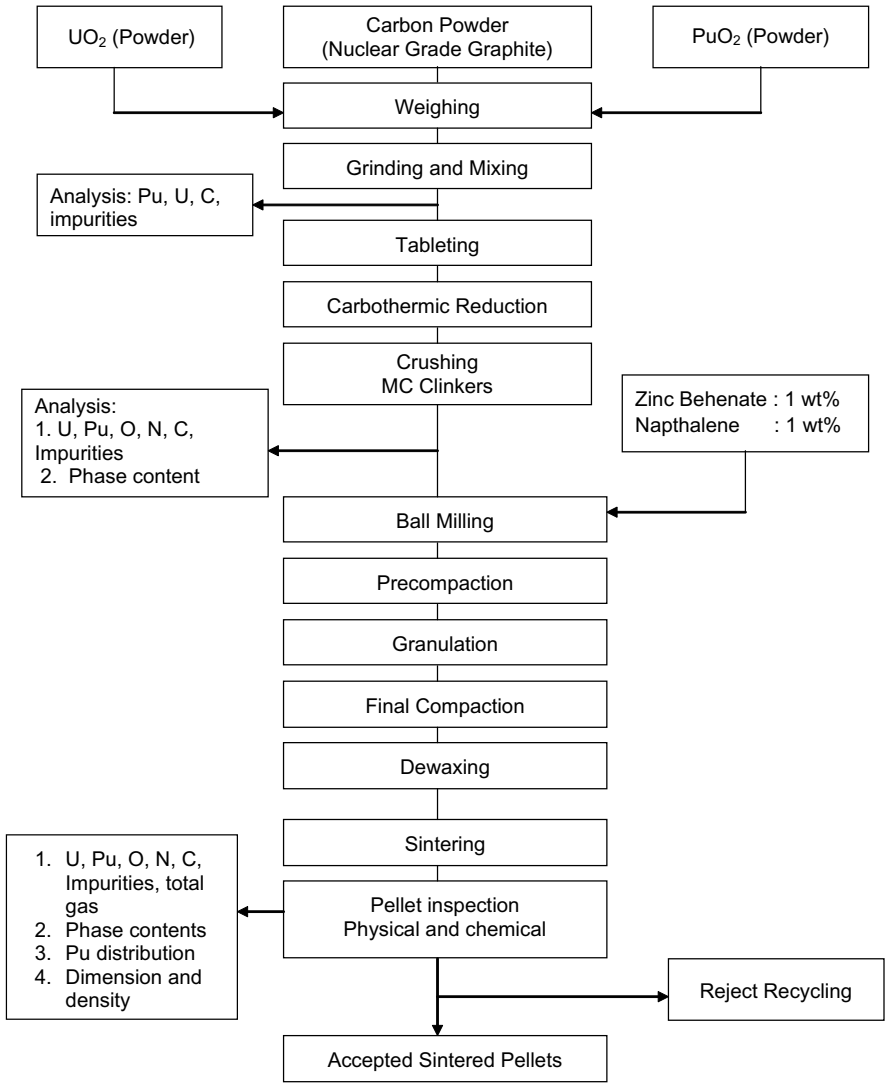

Fig. 1. Flow sheet for fabrication of (Pu, U)C pellets from UO_2, PuO_2 and graphite powder.

for pellet fabrication. From the time carbide clinkers are formed, further processing of the material is difficult as they are highly susceptible to oxidation and hydrolysis with oxygen and moisture even at room temperature. Fine powders of carbide are highly pyrophoric too. Hence, all processing of this material has to be carried out inside leak tight glove boxes maintained under dynamic flow of high purity (oxygen and moisture, each less than 25 vpm) inert gas both from the view point of product purity and safety. As oxygen impurity in MC act as carbon equivalent, the carbon content has to be properly adjusted in advance depending on the expected oxygen pick up during further processing of this material. Large oxygen pick up during processing of clinkers to the final sintered pellet cannot be compensated by keeping a very low carbon stoichiometry at the beginning because, in that case, a large amount of unreduced oxide will remain in the MC clinker after carbothermic reduction. High equivalent carbon content will increase the sesquicarbide content beyond acceptable limit and too low an equivalent carbon may lead to formation of unwanted metal phase, which needs to be totally avoided.

However, plutonium-rich mixed carbide has some advantages over its uranium-rich counter parts. First, PuC- and Pu-rich MC have some range

of carbon stoichiometry, unlike UC- and Uranium-rich MC which are line compounds [4]. So control of carbon stoichiometry is somewhat relaxed. Second, higher quantities of sesqui carbide phase and oxygen impurity can be tolerated in MC without risk of significant carburization of SS-316 cladding. In the two-phase field of MC and M_2C_3, M_2C_3 is richer in plutonium [5] and for Pu-rich MC, M_2C_3 is virtually Pu_2C_3. Pu_2C_3 phase has carbon potential lower than that of U_2C_3 at all temperatures and SS-316 up to 978 K [6]. Theoretical calculations have also shown that for fuel composition of hyperstoichiometric $(Pu_{0.7}U_{0.3})C$ and $(Pu_{0.55}U_{0.45})C$ containing 6400 ppm. oxygen, the P_{CO} values are too low to cause any significant gas-phase carburization of the cladding [7]. Thus no cladding carburization is anticipated if the interface temperature of the cladding is kept below 1000 K.

2.3. Pressing and sintering

The carbide clinkers were milled to make powders of surface areas 1.0–1.2 $m^2\,g^{-1}$ for MKI and 0.3–0.5 $m^2\,g^{-1}$ for MKII. They were pre-compacted, granulated and finally pressed to a density of 65% TD using zinc behenate and naphthalene as lubricant and binder respectively. The pellets were dewaxed by heating at a temperature in the range 623–723 K and the dewaxed pellets were sintered in the temperature range 1848–1923 K in $Ar + 8\%\ H_2$ gas. The furnaces were cooled under vacuum from 1073 K to room temperature to degas the pellet. An all-metal furnace was used for sintering to reduce oxygen pick up on the pellets.

2.4. Process control

In order to obtain the final product conforming to fuel specification, the quality of the intermediate products was checked in terms of U/Pu ratio, C, O, N and M_2C_3 content. The type of tests carried out is shown in Fig. 1. The equipment used for these tests are given below:

(a) Combined and sequential 'O' and 'N' determinators by inert gas fusion method.
(b) Carbon analyzer based on combustion technique.
(c) BET surface area analyzer.
(d) Automatic combined and sequential XRF/XRD system for U/Pu analysis.

3. Fuel property evaluation

Knowledge of the out-of-pile thermo-physical and thermo-mechanical properties of MC fuel is very important and essential for evaluating the usefulness of the fuel in the reactor, predicting the in-pile performance of the fuel, fission gas release, fuel-clad mechanical interaction, whole core accident analysis, etc. The reported literature [2,8–12] on these properties is limited to a composition up to 40% Pu. Some of the properties of interest are coefficient of thermal expansion, thermal conductivity, hot hardness and solidus temperature. It is also important to know the out-of-pile chemical compatibility of the fuel, clad and coolant. These properties for both MKI and MKII fuel have been generated as a function of temperature and their out-of-pile chemical compatibility with SS-316 cladding and liquid Na coolant has been established experimentally.

3.1. The following equipment were used for evaluation of thermo-physical and thermo-mechanical properties

(i) For thermal expansion and solidus temperature: horizontal push rod type dilatometer. Make: Netzsch, Germany with graphite sample holder and push rod from ambient to 1773 K at Argon atmosphere.
(ii) For measurement of thermal diffusivity: transient laser flash method. Make: Ulvac Sinku Riko Inc., Japan from ambient to 1773 K at 0.133 Pa vacuum.
(iii) For hot hardness: high temperature microhardness tester. Make: Nikon, Japan with Vickers pyramid indenters made of diamond and cubic boron nitride [13,19].

3.2. Thermal expansion

The thermal expansion was measured from room temperature to 873 K for MKI fuel under vacuum of 4.65×10^{-3} Pa. The details of the procedure have been reported in Ref. [13]. The relation between $(\Delta L/L_0)$ and T can be expressed by the following equation:

$$(\Delta L/L_o) = -16.59 \times 10^{-4} + 4.17 \times 10^{-6} T + 4.60 \times 10^{-9} T^2, \quad (2)$$

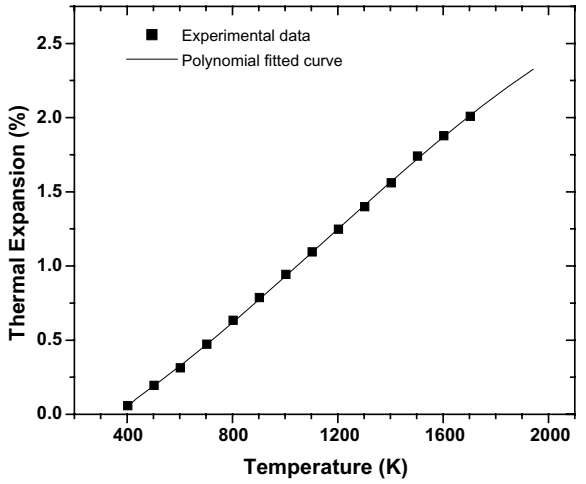

Fig. 2. Thermal expansion as a function of temperature for hyperstoichiometric sintered $(Pu_{0.55}U_{0.45})C$.

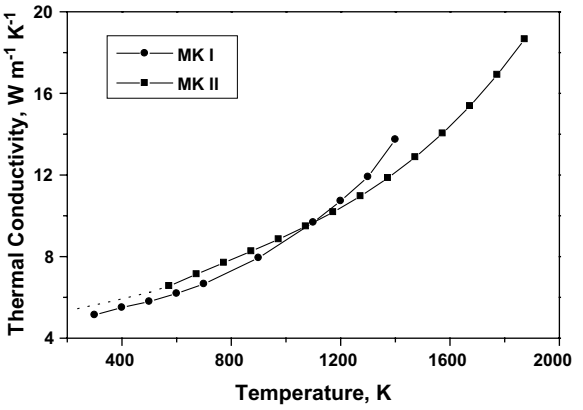

Fig. 3. Thermal conductivity of MKI $[(Pu_{0.70}U_{0.30})C]$ and MKII $[(Pu_{0.55}U_{0.45})C]$ fuels as a function of temperature.

where ΔL is the net expansion and L_o is the original length at ambient temperature.

The details of the experimental procedures followed for measurements of thermal expansion of MKII fuel are given in Refs. [14,15]. The percentage thermal expansion $[(\Delta L/L_o) \times 100]$ at any temperature between 300 and 1800 K can be expressed by

$$[(\Delta L/L_o) \times 100]_T = -0.3333 + 7.1528 \times 10^{-4} T + 7.6889 \times 10^{-7} T^2 - 2.249 \times 10^{-10} T^3. \quad (3)$$

The plot of thermal expansion coefficient (α) versus temperature for MKII [15] is shown in Fig. 2. An average value of coefficient of thermal expansion between 300 and 1800 K has been calculated as $11.6 \times 10^{-6}\ K^{-1}$ for MKII fuel where as the same for MKI fuel in the same temperature range is $13.8 \times 10^{-6}\ K^{-1}$. So, MKI fuel has higher coefficient of thermal expansion than MKII fuel which is expected due to higher Pu content in the MKI fuel.

3.3. Thermal conductivity

The thermal conductivity, κ, at any given temperature was calculated using the relation

$$\kappa = D \times \rho \times C_\rho, \quad (4)$$

where D, ρ and C_ρ are thermal diffusivity, density and specific heat respectively at the measurement temperature.

Thermal diffusivity (α) was measured by transient laser flash method from ambient to 1773 K in vacuum of 0.133 Pa. The details of the experimental procedure are given in Ref. [13]. The density (ρ) of both MKI and MKII fuels were corrected for temperature using the measured average coefficient of linear thermal expansion data, to calculate thermal conductivity at each temperature using the relation (4) above. Specific heat capacity C_ρ of both MKI and MKII fuels were determined by adding the specific heat data available in literature [16] for UC and PuC proportional to the weight fraction present in MC fuels.

Thermal conductivity of MKI and MKII fuels are plotted as a function of temperature and shown in Fig. 3. It may be mentioned that fuel specification of MKI and MKII specifies a density of $91 \pm 1\%$ and $85 \pm 1\%$ TD respectively. Fig. 3 indicates that for both the fuel, thermal conductivity increases with increase in temperature and thermal conductivity of MKI fuel is lower than that of MKII up to about 1100 K although density of MKI is higher than that of MKII. Thermal conductivity of mixed carbide fuel decreases with increase in PuC content and increase with increase in temperature and density. The effect of PuC appears more prominent which explains why MKI fuel has lower thermal conductivity (up to a temperature of 1100 K). Beyond a temperature of 1100 K thermal conductivity of MKI is more than that of MKII. This could be attributed to the fact that in MC, PuC is present as a defect structure (PuC_{1-x}) and contributes to electronic transfer of heat which is a function of temperature. This contribution appears to be more for MKI containing 70% PuC than that of MKII containing 55% PuC beyond 1100 K. However, at the average working temperature, both MKI and

MKII fuels have almost similar thermal conductivity.

3.4. Hot hardness

Hot hardness for MKI and MKII fuels was measured using a high temperature micro hardness tester with Vickers pyramid indenters made of cubic boron nitride. The accuracy and reproducibility of the equipment was tested at room temperature using standard test pieces JIS – B 7725 and NB5 SRM 1894. The details of the equipment and the procedure are given in Refs. [13,17].

The relation between the hardness (H_v) and temperature (T) is given by the Ito–Shishokin [18,19] relation

$$H_v = A\exp(-BT), \tag{5}$$

where A is the intrinsic hardness of the material at absolute zero and B is the softening coefficient. The plot of Log$H$ vs. T for MKI and MKII fuels are shown in Fig. 4. For MKI fuel the plot clearly shows a change in slope at around 1123 K (~0.52 T_m; where T_m is the melting point of the material). The change in slope indicates change in deformation mechanism from simple slip to diffusion-controlled processes. For MKII fuel also, hardness decreases with increase in temperature; the decrease being less at lower temperature range (<973 K) than the same at higher temperature. No sharp transition could however be observed in this fuel. The data generated have been compared with that of Tokar [11] who had reported data from experimental measurements for mixed carbide containing 21% and 69% PuC.

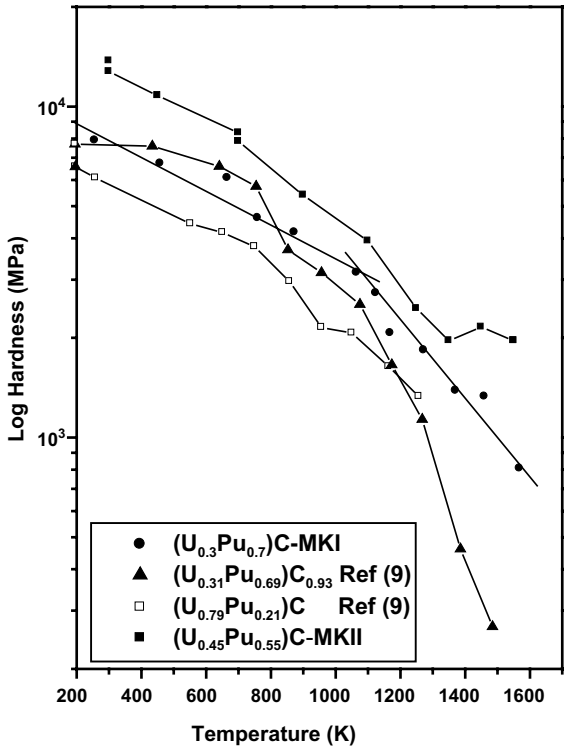

Fig. 4. Variation of hardness with temperature for MKI [($Pu_{0.70}$-$U_{0.30}$)C] and MKII [($Pu_{0.55}U_{0.45}$)C] fuels as a function of temperature.

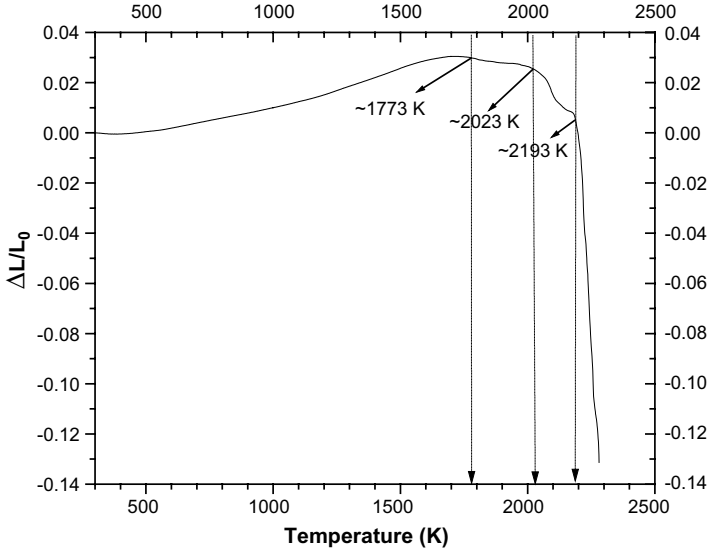

Fig. 5a. Shrinkage rate versus temperature for ($Pu_{0.55}U_{0.45}$)C.

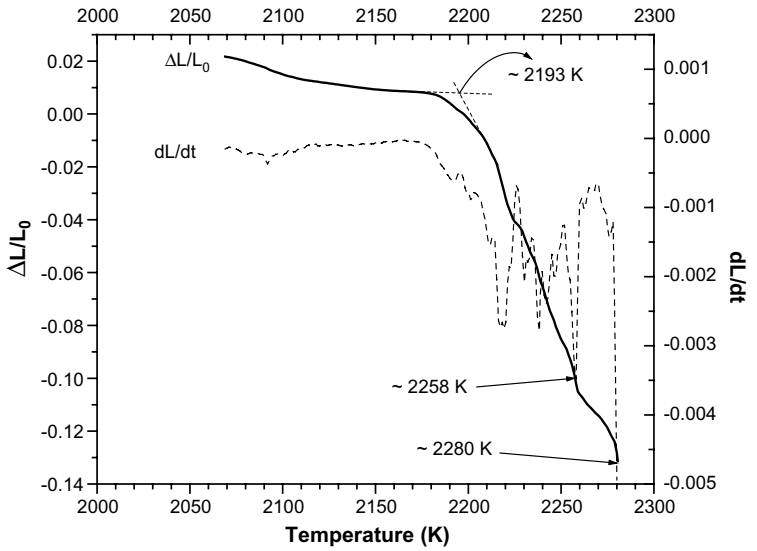

Fig. 5b. Magnified high temperature end of the plot.

The data generated by Tokar for 69% PuC are in close agreement with those of the present data containing 70% PuC (MKI) up to 1100 K. The small variation in the hardness could be attributed to difference in composition, second phase sesquicarbide and porosity between the samples.

Hardness data of MKII fuel is higher than that of MKI fuel at all temperatures. This could be attributed to higher melting point of MKII fuel compare to MKI, which has a direct bearing on hardness. Higher hardness of MKII fuel than either MKI containing 70% PuC or that containing 20% PuC could also be due to solid solution hardening. An increase in hardness beyond 1300 K could be due to microstructural changes or due to oxidation at higher temperature.

3.5. Solidus temperature

The solidus temperature for MKII fuel was determined in a horizontal dilatometer by heating

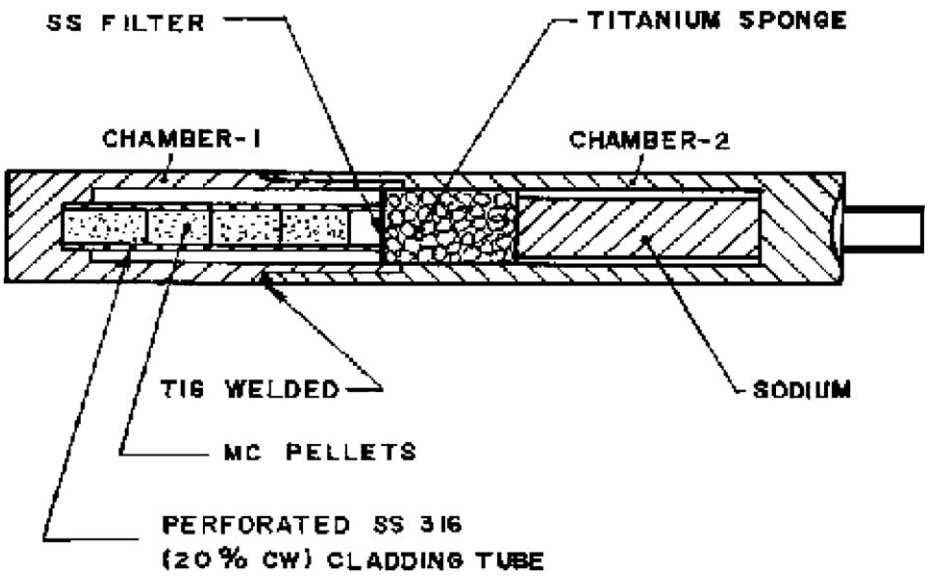

Fig. 6. Schematic diagram of fuel-clad-coolant compatibility capsule.

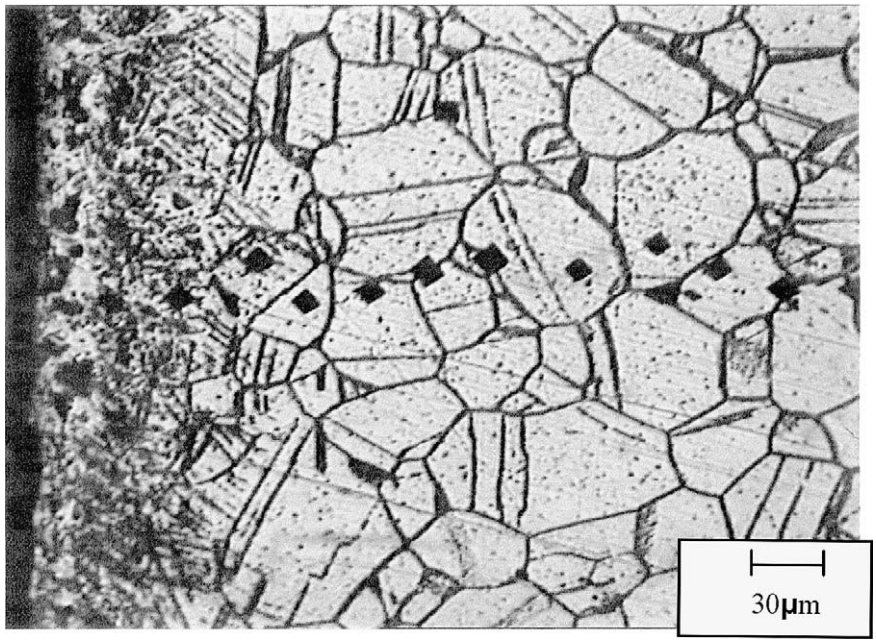

Fig. 7. Photomicrograph of SS-316 (20% cold worked) showing Vickers indentation after fuel-clad-coolant compatibility experiment.

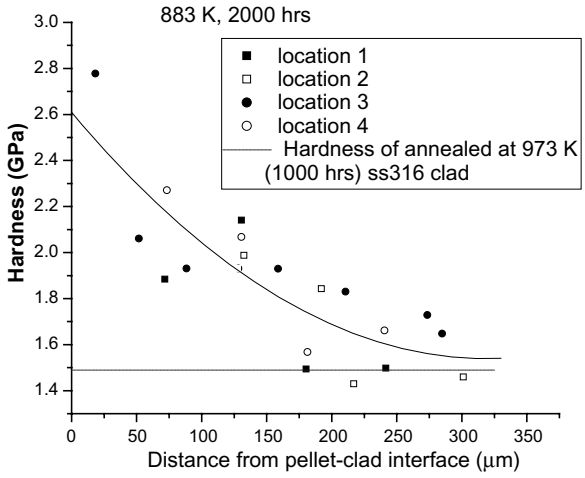

Fig. 8. Hardness profile of SS316 (20% cold worked) cladding from fuel-clad interface.

a pellet up to 2283 K in flowing Argon gas and monitoring the change in length as a function of temperature (Figs. 5a and 5b). A sudden/abrupt change is slope at 2193 K was observed. Beyond this temperature a high rate of shrinkage was observed which could be attributed to gradual melting of the pellet. This was confirmed by visual and metallographic examination of the sample after cooling to room temperature.

4. Out-of-pile chemical compatibility

The fuel-clad-coolant compatibility capsule design is shown in Fig. 6. The capsules have two chambers, separated by a SS filter. Chamber 1 contains a perforated SS-316 cladding tube, in which four numbers of sintered MKI and MKII pellets are loaded. Chamber 2 contains titanium sponge (Oxygen getter) and sodium rod. Sodium is allowed to come in chamber 1 after melting. Capsules were heated in this condition at 883 K up to 2000 h. After the experiments, sodium was leached out both from the pellet and the cladding material. The clad and the fuel were observed to be in good physical condition. Metallographic examination revealed very narrow reaction layer near clad-coolant interface (Fig. 7). Hardness profile of SS-316 (20% cold worked) cladding material from the fuel-clad interface is shown in Fig. 8.

5. Post irradiation examination (PIE) of MKI fuel sub-assembly and pins

PIE of MKI fuel sub-assembly (FSA) and pins after 100 GW d t^{-1} burn up have recently been taken up at Indira Gandhi Centre for Atomic Research (IGCAR), the site for FBTR. The PIE results indicate [20] that, in general the fuel has

performed very well. The clad tubes still have residual ductility of the order of 3% at 703 K, the estimated nominal mid wall operating temperature of the fuel pin clad. The maximum increase in fuel pin diameter is 1.6% due to combined effect of creep and swelling of clad tube. The maximum increase in fuel pin length is 0.4% and the average increase in fuel pellet stack length is 1.73%. The maximum fission gas release is only 14%. A maximum increase of about 0.7% was observed in the width-across flat and 0.5% in the corner to corner distance of wrapper. Head-to-foot misalignment of the FSA was found to be 4.3 mm. The fuel-clad gap was seen closed at the centre of the fuel column. The pattern of fuel cracking was found to change from radial to circumferential after 100 GW d t^{-1} burn up, indicating annealing of radial cracks due to fuel-clad mechanical interaction (FCM1). No significant clad carbonization was observed. It has been predicted that the fuel will be able to withstand a burn up of about 150 MW d t^{-1} before the limit is reached.

6. Conclusion

Fast Breeder Test Reactor has been operating for the last two decades with a high plutonium content hyperstoichiometric mixed carbide as driver fuel. The initial MKI fuel has already seen a burn up of 140 GW d t^{-1} without any fuel pin failure. From PIE of MKI fuel at different burn ups, it has been estimated that the fuel is capable of reaching a burn up of 150 GW d t^{-1} without any failure. As the out-of-pile properties of both MKI and MKII fuels at the average working temperature of the fuels are not very different, it is expected that even MKII fuel will behave in a similar way. Indigenous development of MC fuels, and operation of FBTR with these fuels for the last twenty years has helped us mastering the fast reactor technology, which has culminated in launching a 500 MW Prototype Fast Breeder Reactor programme in India.

Acknowledgements

The authors gratefully acknowledge the important role played by Dr C. Ganguly, former Head, Radiometallurgy Division, BARC, (presently in IAEA) in developing the mixed carbide fuel for FBTR and its initial production. The authors are also thankful to Post Irradiation and Remote Handling Division, IGCAR, for making available the PIE results on the Fuel Sub-Assembly.

References

[1] R. Farmakes (Ed.), Proceedings of Fast Reactor Fuel Element Technology, New Orleans, April 13–15, 1971, American Nuclear Society, 1971.
[2] R.B. Mathews, R.I. Herbst, Nucl. Technol. 63 (1983) 9.
[3] M. Theodore, T. Besmann, B. Lindemer, J. Nucl. Mater. 67 (1977) 77.
[4] E.K. Storms, R.J. Ackermann, IAEA Technical Panel on Assessment of the Thermodynamic Properties of UC, PuC and (U, Pu)C Systems, Grenoble, France, May 6–8, 1974.
[5] P. Browning, B.A. Phillips, P.E. Potter, M.H. Rand, in: Proceedings of International Conference Plutonium and other Actinides, Baden Baden, September 10, 1975, p. 257.
[6] O. Goetzmann, R.W. Ohse, Fuel cladding compatibility of stainless steels with gas and sodium bonded Uranium–Plutonium Carbide Fuels, EUR-4892 e, European-American Nuclear Data Committee, 1972.
[7] S.V. Iyer, C.K. Mathews, Calculation of carbon potential of the mixed carbide fuel containing oxygen as impurity, Private communication, Reactor Research Centre, India, 1982.
[8] D. Stahl, A. Strasser, in: Proceedings of Symposium Carbides in Nuclear Energy, Harwell, UK, 1963, p. 373.
[9] A.E. Ogard, C.C. Land, J.A. LeenThe Thermal Expansion of PuC and PuC–UC Solid Solution, LA-2768, Los Alamos Scientific Laboratory, 1962.
[10] M.A. Tokar, A.W. Nutt, J.A. LearyMechnical properties of Carbide and Nitride Reactor Fuels, LA-4452, Los Alamos Scientific Laboratory, 1970.
[11] M. TokarHigh Temperature Compression Creep and Hot-hardness of Uranium–Plutonium Carbides, LA-4704, Los Alamos Scientific Laboratory, 1971.
[12] J.A. Leary, K.W.R. Johnson, Nuclear Metallurgy, vol. 13, in: Proceedings of International Symposium Plutonium Fuels Technology, 1967, p. 309.
[13] A.K. Sengupta, S. Majumdar, C. Ganguly, D.S.C. Purushotham, P.R. Roy, Am. Ceram. Soc. Bull. 65 (1986) 1057.
[14] A.K. Sengupta, J. Banerjee, R.K. Bhagat, R. Ramachandran, S. Majumdar, D.S.C. Purushotham, Thermal Expansion Data of (Th, U)O_2 Fuel, BARC/2000/E/008, Bhabha Atomic Research Centre, India, 2000.
[15] A.K. Sengupta, J. Banerjee, T. Jarvis, T.R.G. Kutty, K. Ravi, S. Majumdar, Nucl. Technol. 12 (2003) 260.
[16] C.E. Holley Jr., M.H. Rand, E.K. Storms, The Chemical Thermodynamics of Actinide Elements: The Actinide Carbid International Atomic Energy Agency, International Atomic Energy Agency, 1984, p. 6.
[17] A.K. Sengupta, U. Basak, C. Ganguly, J. Mater. Sci. Lett. 6 (1987) 20.
[18] K. Ito, Sci. Rep. Tohoku Imp. University Ser. 1 (1923) 137.
[19] V.P. Shishokin, Z. Anorg. Allg. Chem. 189 (1930) 263.
[20] B. Raj (Ed.), Annual Report 2003, vol. 60, Indira Gandhi Centre for Atomic Research, 2004, p. 63.