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# Experience on mixed carbide fuels with high 'Pu' content for Indian fast breeder reactor – An overview

A.K. Sengupta *, U. Basak, Arun Kumar, H.S. Kamath, S. Banerjee

*Bhabha Atomic Research Centre, Mumbai, Maharashtra 400 085, India*

A B S T R A C T

Hyperstoichiometric Plutonium rich (70%) mixed Uranium Plutonium carbide fuel was proposed as the driver fuel for Indian Fast Breeder Test Reactor (FBTR) after some deliberations. The issues of mixed carbide fuel and of plutonium rich (70%) carbide fuel, in particular, are: presence of 'O' impurity, clad carburization, lower solidus temperature, lower thermal conductivity and pyrophorocity. The paper highlights the extensive research and development carried out to address the above issues. The modification incorporated in the different process steps of fabrication flow sheet is also presented. The performance of the fuel has been assessed by periodic Post Irradiation Examination (PIE) of the fuel sub-assemblies for extension of life. Till date the fuel has seen a burn up of 155 Gwd/t without any pin failure.



## 1. Introduction

The Fast Breeder Reactor Programme in India was initiated in the early eighties with the construction of an experimental breeder test reactor of 40 MWth (13.2 MWe) capacity. The small core size warranted high fissile inventory which, probably could be met with the use of Plutonium rich (76%) mixed Urania–Plutonia oxide fuels. However, this was not considered as reported literature [1] indicated sodium fuel incompatibility. Uranium (85% enriched) Plutonium mixed oxide (30% $PuO_2$) was also not a possible solution because of non-availability of enriched Uranium. The ultimate choice was on Plutonium rich (70%) mixed Uranium–Plutonium carbide fuel (MKI). The in-pile and out-of-pile properties of this fuel composition were unknown in literature which led to serious soul searching of the different issues and challenges of this fuel. Extensive research and development work were carried out to generate sufficient out-of-pile data to overcome these issues and gain confidence to use it as a fuel. The results of these studies have been reported in Refs. [2–8].

FBTR has been in operation since 1985 and seen a burn-up of 155 GWd/t. Initially it was made critical with a small core of 23 sub-assemblies (MKI) followed by use of additional fuel subassemblies of MKI and MKII (55% PuC). Periodic PIE was carried out for extension of the life of the fuel pin.

Mixed carbide fuels have many advantages [9] namely higher breeding ratio and thermal conductivity; excellent chemical compatibility with sodium coolant and satisfactory irradiation behavior. However, 'Pu' rich mixed carbide fuels had several issues which need elaborate studies: both experimental measurements and theoretical calculation. The issues of high 'Pu' carbide fuel when compared with that of 'U' rich carbide are: lower solidus temperature and thermal conductivity, presence of 'O' and 'N' (impurities) and 'Pu' loss during fabrication.

Apart from this, 'C' stoichiometry plays a very important role in determining the extent of Fuel–Clad Chemical Interaction (FCCI) and Fuel–Clad Mechanical Interaction (FCMI). A hyperstoichiometric fuel is preferred as the metal phase M (Pu + U) present in hypostoichoimetric fuel causes formation of low melting eutectic with 'Fe' and 'Ni' of SS316 cladding. Moreover, carbon to metal ratio decreases with burn-up and in extreme case may lead to metal phase formation at fuel–clad interface; bonding the fuel to the clad resulting severe FCMI. Agarwal and Venugopal [10] however concluded from theoretical calculation using SOLGASMIX-PV code that for an initial (C/M) of 1.03, metal phase will not form even at 150 GWd/t burn up. A hyperstoichiometric fuel on the other hand may cause clad carburization due to high 'C' potential. This could however be controlled by optimizing the sesquicarbide ($M_2C_3$) and 'O' content. Again $M_2C_3$, a hard and brittle phase may, act as an obstacle for dislocation glide and climb hindering creep deformation and accommodation of restrained swelling. Carbides being pyrophoric and prone to oxidation and hydrolysis need high purity inert cover gas (oxygen and moisture < 25 vpm) to minimize 'O' pick up and prevent pyrophorocity.

The experience gained over the years in the operation of FBTR helped in relaxing the fuel specification which was rather conservative. Introduction of some novel processing techniques, optimization of process parameters, modified end plug design and use

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

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**Table 1**
Thermo physical properties of mixed carbide fuels.

| Properties | MKI $(U_{0.3}Pu_{0.7})C$ | MKII $(U_{0.45}Pu_{0.55})C$ | $(U_{0.8}Pu_{0.2})C$ |
|---|---|---|---|
| Solidus temperature (K) | 2148 | 2193 | 3023 |
| Thermal conductivity (W/m K) at 1273 K | 12.0 | 10.7 | 19.0 |
| Coefficient of thermal expansion (300–1800 K) | $13.8 \times 10^{-6}$ | $11.6 \times 10^{-6}$ | $10.9 \times 10^{-6}$ |
| Hardness (MPa) at 1273 K | 1800 | 2100 | 1500 |

(Density – MKI: 91%TD; MKII: 86%TD).

of pulsed TIG welding have resulted in higher yield. The present investigation highlights the research and development work carried out from the inception of this fuel till date, to get an insight into the fuel behaviour and add to the confidence level of fuel designer to extend the fuel burn up without encountering any failure.

## 2. Fuel production

### 2.1. Pellet fabrication

The process flow sheet for fabrication of mixed carbide fuel pellets has been described in Ref. [11,12]. There are two steps e.g. carbothermic reduction of oxide to make carbide powder and compaction of powders and sintering to make pellets. The carbothermic reduction reaction is given by

$$0.3UO_2 + 0.7PuO_2 + 3C = (U_{0.3}Pu_{0.7})C + 2CO\uparrow \quad (1)$$

The performance of the fuel up to a burn up of 155 GWd/t without failure helped in reviewing fuel specification with respect to 'O' and 'N' content, classification of pellets into Class 'A' and 'B' based on $M_2C_3$ content and surface defects. The end plug weld acceptance specification was also moderated to accept criteria of minimum leak path (MLP) in the weld region instead of defect free weld. Repair of top end plug welds was also introduced. Further, earlier classification of pins as Class 'A' and 'B' is no more practiced instead all pins are allowed to have 70 mm (maximum) of fuel column with class 'B' pellets in the bottom side. These changes led to higher acceptance of both fuel pellets and pins. Also, the loading of fuel sub assemblies in the core has become simpler.

### 2.2. New process developments in fuel production

A high energy stirred ball mill 'Attritor' was introduced in place of planetary ball mill to reduce processing time from powder to pellet thus increasing productivity and lowering energy consumption [13]. The weld reject due to 'root pocket' in the top end plug was almost eliminated by adopting pulsed TIG instead of continuous TIG welding. Additionally, FEM analysis of top end plug weld indicated that root pocket up to 60 μm radius can be accepted [14]. The end plug design was also changed from interference fit to straight face sliding fit. Recently, a fully automated pellet inspection machine based on laser is being installed for dimensional, surface inspection and computation of linear mass.

There are two types of pellet rejects namely physically defective and chemically unacceptable. Sintered pellets rejected due to non-conformation of chemical specification ('O', 'N', 'C' and $M_2C_3$) are crushed into powder followed by controlled oxidation to obtain oxide powder with (O/M) ratio of 2.17–2.20 [15]. After adjusting the Pu/U ratio, oxide powders are co-milled with graphite powder followed by carbothermic reduction and sintering. Physically reject sintered pellets not conforming to dimensions and physical defect criteria (cracks, chips, surface defects etc.) are crushed and milled to obtain sinterable grade carbide powders to make pellets of required density and dimension.

## 3. Out-of-pile properties

Some of the important thermo physical properties like solidus temperature, thermal expansion, thermal conductivity and thermal toughness (hot hardness) were measured in house. These properties play a very important role in predicting the in-pile fuel performance. Table 1 briefly presents the data generated on the properties of MKI and MKII fuels and that of conventional uranium rich mixed carbide fuel.

### 3.1. Solidus temperature

Solidus temperature was estimated from the heating/cooling curve or by measuring linear thermal expansion in a dilatometer. For MKI, it was estimated from the cooling curve. This was supported by metallographic examination. For MKII it was obtained by dilatometric studies where an abrupt shrinkage of the pellet at a particular temperature indicates the solidus temperature. The details of the measurement procedures and the apparatus used are given in Ref. [7,8]. The solidus temperature of MKI and MKII fuels were 2148 K and 2193 K respectively. Fee and Johnson [16] reported the solidus and liquidus curve for UC–PuC solid solution. With increase in PuC, solidus temperature decreases which is in agreement with the data of Dalton [17] explaining lower value of MKI compared to MKII. The solidus temperature data had been useful to the designer in estimating the maximum permissible LHR of these fuels.

### 3.2. Thermal expansion

Thermal expansion was measured using a dilatometer. The average value of the coefficient of linear thermal expansion for MKI and MKII fuel between 300 and 1800 K were $13.8 \times 10^{-6}$ [2] and $11.6 \times 10^{-6}\,K^{-1}$ [4] respectively. MKI fuel has higher coefficient of thermal expansion than that of MKII fuel. This was attributed to higher Pu content in the MKI fuel [8].

### 3.3. Thermal conductivity

Thermal conductivity was determined from the experimentally measured thermal diffusivity data by laser flash method and subsequently multiplying it with the heat capacity [18] of UC–PuC solid solution and density. The details of the procedure have been given in ref. [2,4]. The result indicated that thermal conductivity increases with increase in temperature but decreases with PuC content [19,5] resulting in lower thermal conductivity of MKI (up to about 1100 K) but higher beyond this temperature. The higher conductivity of MKI beyond 1100 K is attributed to the contribution from electronic heat transfer by PuC which is inherently a defect structure ($PuC_{1-x}$). However, at the average working temperature, both MKI and MKII fuels have almost similar thermal conductivity. Hence, the thermal performance of these fuels in terms of LHR etc. may not be much different even considering the marginal difference in the solidus temperatures of the two fuels.

### 3.4. Thermal toughness (hot hardness)/creep

Hot hardness data can predict the FCMI behaviour of fuels. Carbide being more closed packed, swells more than the oxide and retains more fission gases. Swelling of carbide occurs by creep resulting in fuel–clad gap closure. Further swelling results in development of back stress which help in restrained swelling i.e. creeping of the fuel within the available pores. Generation of creep data for 'Pu' bearing fuel is a very elaborate and expensive proposition requiring number of samples and battery of creep machines under different time, temperature and stress conditions. Alternately, this can be determined qualitatively by hot hardness data which is much simpler needing small sample size.

Hot hardness of MK I and II fuels were measured using a high temperature micro hardness tester with Vickers pyramid indenters [3]. The result showed hardness of both MKI and MKII decreases with increase in temperature with MKII having higher hardness at all temperatures. MKI indicate sharp decrease in hardness at 1123 K (~0.52 $T_m$; where $T_m$ is the solidus temperature,) indicating onset of creep deformation. For MKII fuel no such sharp transition was observed. The data generated for MKI were in close agreement with that of Tokar et al. [20,21] up to 1100 K. The $M_2C_3$ phase is harder than that of MC and is uniformly distributed in the MC phase. This may hinder creep deformation. Hence, the content of this hard phase should be optimized. Though, 'Pu' rich carbide fuel is harder than 'U' rich fuel; beyond a temperature of 1553 K (Average volumetric temperature) this fuel behaves the same way as that of 'U' rich carbide for which in reactor performance indicated no failure due to FCMI. Hence from extrapolation it could be presumed that this fuel will also behave in a similar manner.

### 3.5. Fuel–clad chemical interaction

Fuel–Clad Chemical interaction is a key issue limiting the life of a fuel pin in a reactor. For carbide fuel this occurs by clad carburization by solid state (direct contact) 'C' transfer or gas phase carburization by CO. The extent of clad carburization depends on the 'Carbon Potential' of the fuel and partial pressure $P_{co}$ generated by the reaction of dissolved 'O' with MC. However, 'Pu' rich 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 'U' rich MC which are line compounds [22]. Secondly, higher quantities of $M_2C_3$ phase and 'O' impurity can be accommodated in MC without the risk of significant clad carburization. In the two phase field of MC/ $M_2C_3$, $M_2C_3$ is richer in plutonium [23] and for 'Pu' rich MC, $M_2C_3$ is virtually $Pu_2C_3$. $Pu_2C_3$ phase has lower carbon potential than that of $U_2C_3$ at all temperatures and with SS-316 up to 978 K [24]. Saibaba et al. [25] carried out some theoretical calculation based on thermodynamic data of free energies of formation of PuC, PuO and $Pu_2C_3$ and predicted that both 'C' potential and $P_{CO}$ pressure decreases with increase in 'Pu'. Hence MK I and II are less carburizing than 'U' rich fuel [26]. They also indicated that an uncertainty of ±2 kcal in the free energies of formation data may lead to an error in $P_{co}$ of 2–3 orders of magnitude and 3–4 kcal for 'C' potential. These uncertainties led to carry out actual out-of-pile experiments. Theoretical calculations [27] have shown that for MKI and MKII fuels containing 6400 ppm 'O', the $P_{CO}$ values are too low to cause any significant gas-phase carburization of the cladding up to clad temperature of 1000 K. Experiments were carried out to generate thermodynamic data of MKI fuel. e.g. activity of carbon in SS316, 'C' potential, chemical compatibility with

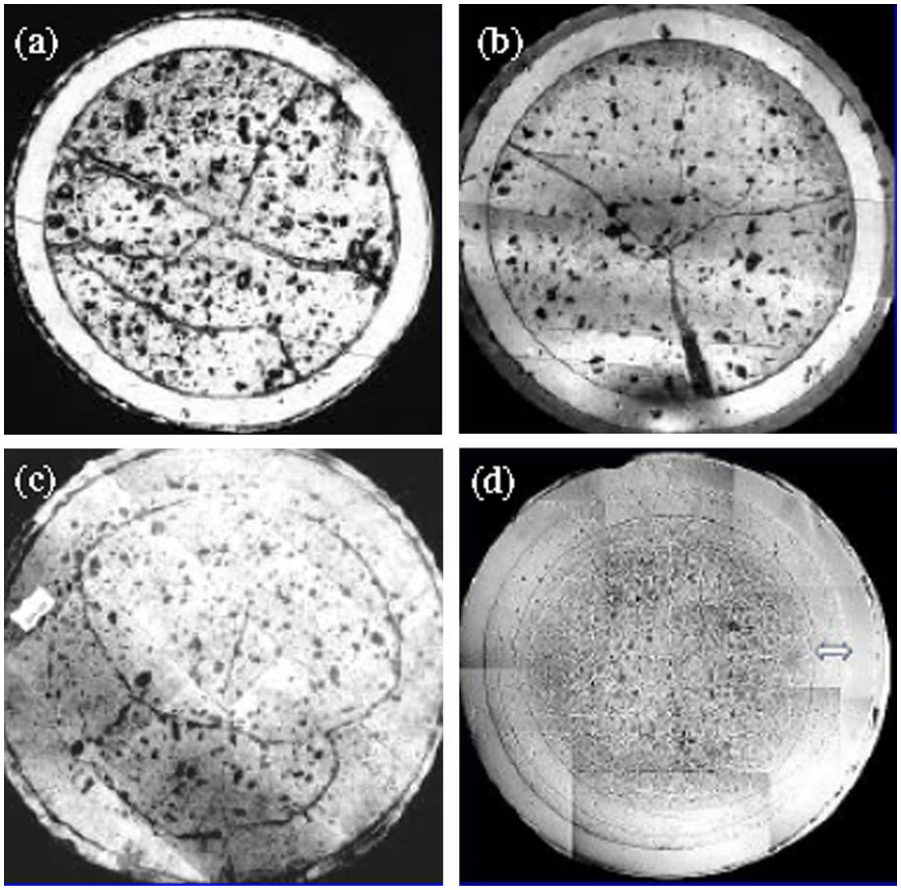


**Fig. 1.** Photomicrographs of MKI fuel pin at the centre of the fuel column at different burn ups; (a) 25 GWd/t, (b) 50 GWd/t, (c) 100 Gwd/t and (d)155 GWd/t (Refs. [28,29]).

SS316 under abnormal condition and equilibrium $P_{CO}$ over U–Pu–C–O. The results of these studies have been summarized in Ref. [23–26]. These data were helpful to substantiate the compatibility experiments.

The results of out-of-pile experiments carried out are summarized [6,7] below. Chemical compatibility of hyperstoichiometric fuel containing 0.7 w/o 'O' and up to 20 wt.% $M_2C_3$ was excellent with sodium coolant and SS316 cladding at 973 K for 1000 h. The depth of clad carburization was insignificant (<12 μm).This observation provided a valuable support to the fuel designer in specifying the allowable 'O' and $M_2C_3$ content. Tests were also carried out for fuel containing higher 'O' (1 wt.%) and $M_2C_3$ (60 wt.%) which showed carburization of the cladding up to a depth of 25% of the cladding thickness (370 μm). This is much lower than the clad carburization reported for Uranium rich mixed carbide containing 15% $M_2C_3$ and less than 0.2 wt.% 'O' when 70% of clad wall thickness was affected. The experimental result tend to confirm the reported theoretical prediction that relatively high 'O' and $M_2C_3$ content could be tolerated in hyperstoichiometric MKI fuel because of its low 'C' potential activity and $P_{co}$ even at the operating fuel center temperature of 1550 K.

## 4. Post irradiation examination (PIE)

Assessment of fuel and core structural material behaviour were carried out after bum ups of 25 GWd/t, 50 GWd/t, 100 GWd/t and 155 GWd/t [27,28]. PIE on 25 GWd/t & 50 GWd/t revealed low swelling rate of fuel leaving sufficient fuel–clad gap for further burn up. After 100 GWd/t bum-up, significant increase in the dimensions of hexagonal wrapper and fuel pins were observed. However, they were within the limits of fuel handling and coolant flow considerations. No fuel–clad gap was observed at the center of fuel column indicating onset of FCMI. The analysis of the PIE data with respect to fission gas release, the residual ductility of the clad, cladding strains, porosities available in the fuel etc. gave immense confidence to increase the bum up. After 155 GWd/t, visual examination of the subassembly and the fuel pins indicated no gross abnormalities. The maximum diametral strain of fuel pin was around 5% compared to 1.6% estimated at 100 GWd/t. Maximum internal pressure in the fuel pin due to fission gas release was 2.09 MPa. Metallographic examination of the fuel–clad cross section at the centre of the fuel (Fig. 1) revealed a distinct zone with no porosity near the periphery due to creep of the fuel. Fuel–clad gap closure and circumferential cracking at the centre as well as at the end of the fuel column indicates that the fuel column is under the restrained swelling regime. Swelling and porosity exhaustion in the fuel, high void swelling of the cladding, loss of tensile strength, ductility and dilation of the wrapper tube and its impact on the fuel handling operations will be the limiting factors in increasing the burn-up beyond 155 GWd/t.

## 5. Conclusions

Indian Fast Breeder Reactor Program started on a very conservative but distinctive note with the commissioning of its first ever tried Plutonium rich (70%) mixed uranium plutonium carbide fuelled fast breeder test reactor (FBTR) in the year 1985. The unique feature of this fuel prompted extensive out-of-pile studies both by experimental measurements and theoretical calculations to understand fuel behavior and address various issues. The experience gained on the performance of this fuel over the years helped in optimizing the fuel specifications in terms of 'O', 'N' and $M_2C_3$ content. Reduction of milling time with the use of 'attritor' and recycling the physically defective pellets resulted in increasing productivity. PIE of the fuel at different stages of burn up played a key role in deciding the life of the fuel. As of now the fuel has seen a burn up of 155 GWd/t without any problem.

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