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Dispersion type zirconium matrix fuels fabricated by capillary impregnation method

A. Savchenko *, I. Konovalov, A. Vatulin, A. Morozov, V. Orlov, O. Uferov, S. Ershov, A. Laushkin, G. Kulakov, S. Maranchak, Z. Petrova

A.A. Bochvar All-Russia Research Institute of Inorganic Materials (VNIINM), P.O. Box 369, Rogova St., 5A, 123060 Moscow, Russia

Abstract

Several novel dispersion fuel compositions with a high uranium content fuel (U9Mo, U5Zr5Nb, U_3Si) and a zirconium alloy matrix with low melting point (1063–1133 K) have been developed at A.A. Bochvar Institute using a capillary impregnation fabrication method. The capillary impregnation method introduces fuel granules and granules of a zirconium alloy into a fuel element followed by a short-term anneal at a temperature above the melting temperature of alloy. The alloy melts down and under capillary forces moves into the joints between the fuel element components to form metallurgical bonds. The volume ratios between the components are: 55–65% fuel, 10–20% matrix, and 15–30% pores. Fuel elements produced by capillary impregnation method have a high uranium content (9–10 g cm^{-3}) and a high thermal conductivity (18–22 W m^{-1} K^{-1}), which, when used as PWR or BWR fuels allow the fuel temperature to be lowered to 723–773 K. They also feature porosity to accommodate swelling. The metallurgical fuel–cladding bond makes the fuel elements serviceable in power transients. The primary advantages for PWR, BWR and CANDU use of these fuels elements, would be the high uranium content, low fuel temperature and serviceability under transient conditions. Consideration is given to their applicability in Floating Nuclear Power Plants (FNPP) as well as for the feasibility of burning civil and weapon grade plutonium.

PACS: 28.41.Bm; 81.05.Zx; 81.05.Rm

1. Introduction

There are several approaches to improve fuels for PWR and BWR reactors including the increase in the uranium content of the fuel, lower temperatures in the fuel element centre, the extension of the burnup and the serviceability of fuel elements operating under transient conditions. High uranium content fuel (U9Mo, U5Nb5Zr, U_3Si alloys or intermetallic) and Zr alloys that meet to a larger extent the above requirements matrices are currently under development at the A.A. Bochvar Institute [1–3]. They are produced by the impregnation with a molten alloy within the inner space of a fuel element with fuel granules arranged inside it [1,2,4]. For this process several classes of novel zirconium matrix alloys with the melting temperatures 1063–1133 K have been designed [2–4].

* Corresponding author. Tel.: +7 495 1908985; fax: +7 495 1964075.
E-mail address: sav@bochvar.ru (A. Savchenko).

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The uranium content in such fuel compositions is 8.5–9.5 g cm^{-3}. The fuel compositions have a high thermal conductivity (22–26 W m^{-1} K^{-1}), are compatible with high uranium content fuel up to 1023 K and are serviceable under transient conditions due to the metallurgical bonding to the cladding [2–4]. Preliminary in-pile tests of these fuel compositions demonstrated their serviceability for the PWR and BWR reactors [6]. The further perfection of this type of dispersion fuel is in progress, both to improve the fuel design (controllable porosity to accommodate swelling) and to modify the fabrication process. Using the capillary properties of the zirconium matrix alloys, a method of capillary impregnation is being developed [3–5]. It consists in co-introducing zirconium matrix alloy and fuel granules into a fuel element. Upon a subsequent anneal of the matrix alloy above its melting temperature it moves into the joints between the fuel element components to form metallurgical bonds.

This paper addresses the properties of the fuel fabricated by the capillary impregnation method and the feasible ways of the application of these fuels.

2. Method of capillary impregnation

The impregnation method has been worked out by taking into account the capillary properties of the melted zirconium alloys. It comprises two stages and is schematically presented in Fig. 1 [2–5].

- *Vibroloading* of mixed fuel and matrix granules into cladding (Fig. 1(a) and (b)). Coarse granules of fuel and fine granules of a zirconium alloy matrix (zirconium brazing alloy) are used. Fuel and matrix granules might be loaded into the fuel element cladding either simultaneously or consecutively, viz., first coarse fuel granules and after that between them fine matrix granules (infiltration route, Fig. 1(b)). The volume ratios of the fuel components are:

The fuel forms a skeleton	55–65%
The matrix within the interstices of the skeleton	10–22%
The pores	16–30%

  The ratios between the diameters of the fuel and matrix granules range from 3:1 to 10:1.
- *Vacuum* anneal above the melting temperature of the matrix alloy (*capillary impregnation* Fig. 1((c) and (d)). While melting down the zirconium matrix alloy fills the joints between fuel particles and the joints between fuel and cladding to form the so-called bridges under the action of capillary forces, which increases the thermal conductivity of the fuel composite.

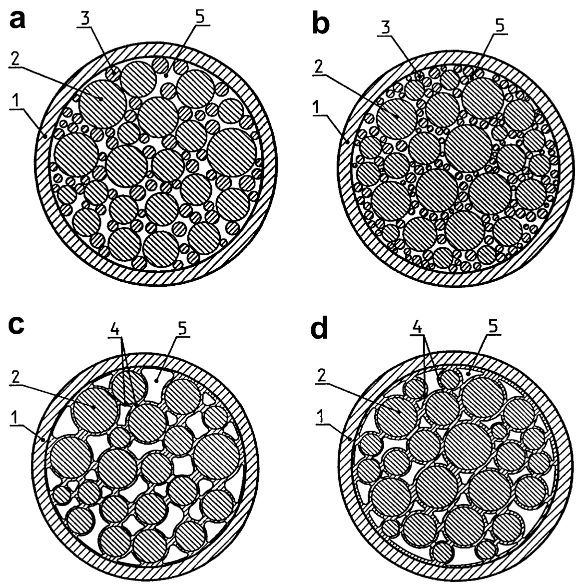

Fig. 1. Schematic cross-section representation of fuel element fabricated by capillary impregnation method [2–4]; (a) and (b) as vibroloaded; (c) and (d) as capillary impregnated, (1) fuel element cladding, (2) fuel granules, (3) Zr alloy matrix granules, (4) 'bridges' and matrix alloy coats on fuel granules after heating and cooling, (5) pores. Conditions: Cladding diameter 5.8 mm, thickness 0.5 mm, fuel granules 0.6–1.2 mm, matrix granules 0.15–0.5 mm in (a) and 0.06–0.2 mm in (b).

Although it is easier to use fuel in the form of granules the capillary impregnation method might also be used for fuel particles produced by grinding (UO_2 and U_3Si in Fig. 2).

Fig. 3 illustrates the appearance of the fuel composition (without cladding) and the macrostructure of the fuel. Fig. 4(a)–(d) show micrographs of a fuel element fracture and cross section as well as the fuel microstructure.

Figs. 3 and 4 clearly reveal the occurrence of metallurgical bonding via the alloy between individual fuel granules and between the fuel granules and the cladding. The fuel granules at the inner surface of the cladding are coated with a zirconium matrix alloy layer 3–10 μm thick.

The process flow sheet used to fabricate fuel elements for BWR, PWR, CANDU and FNPP is presented in Fig. 5.

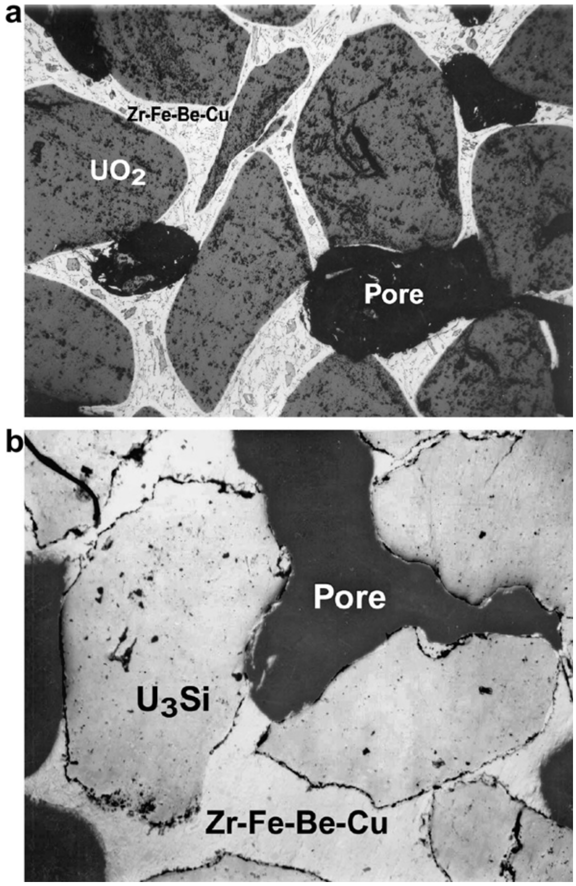

Fig. 2. Microstructure of fuel compositions comprising alloy (Zr, Fe, Be, Cu) and fuel produced by grinding; (a) UO_2, (b) U_3Si.

Both the uranium and zirconium alloys were melted in induction furnaces. Fuel granules 0.6–1.0 mm in size and alloy granules 0.06–0.2 mm in size were produced by the centrifugal sputtering method [2]. The volume content of pores was controlled by the fuel and matrix sizes. The larger the difference between the granule sizes of the fuel and the matrix the higher, the denser was the granule packing in the fuel element cladding and, consequently, the lower was the porosity. The vibratory loaded fuel granules form a skeleton which inhibits the fuel column shrinkage during subsequent annealing. It promotes the uniform fuel distribution along the fuel element length. The coefficient of the fuel distribution nonuniformity does not exceed 1.04 [2,3].

The capillary impregnation process was carried out under both static conditions in the resistance furnace and also by pulling the container with the fuel pins through a heating device. In the latter case the fuel was arranged horizontally, which did not affect the impregnation quality since the process is driven by capillary forces and depends only weakly on the gravity. In future the capillary impregnation will be implemented by a high frequency heating current, while pulling fuels through an induction heater. This method will diminish the influence of the anneal temperature on the structure of the fuel element cladding. The appearance of the specimens of the fuel to be tested out-of-pile is shown in Fig. 6.

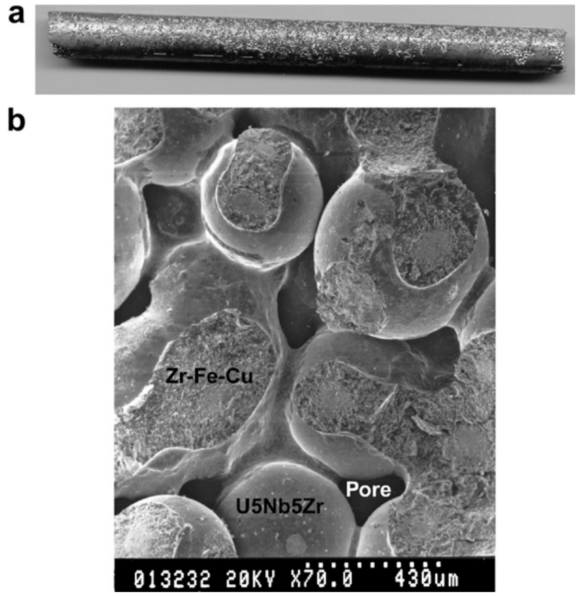

Fig. 3. Appearance of uncladded fuel composition with 25% porosity (U–9Mo + Zr–Fe–Cu; outer diameter 7.7 mm) (a) and macrostructure of U5Nb5Zr fuel meat with 30% porosity (b).

The anneal carried out in the capillary impregnation process results in some structural changes of the zirconium alloy cladding, i.e. the formation of elongated α-zirconium grains separated by β-zirconium interlayers. After a stabilization anneal at 853 K for 3 h the structure of the alloys recovers its initial phase state. The accelerated corrosion tests carried out in steam at 673 K did not reveal any difference in the corrosion behaviour of the zirconium cladding after the capillary impregnation [2]. After a 5 year in-pile test to a burnup of 40 MW d kg^{-1} no changes in the cladding corrosion behaviour of the RBMK type fuels with UO_2–Zr6.4Fe2.5Be dispersion composition were observed indicating that the fuel element had operated at low temperatures.

3. Properties of fuel compositions

In the fuel pins fabricated by the capillary impregnation method the volume fraction of the

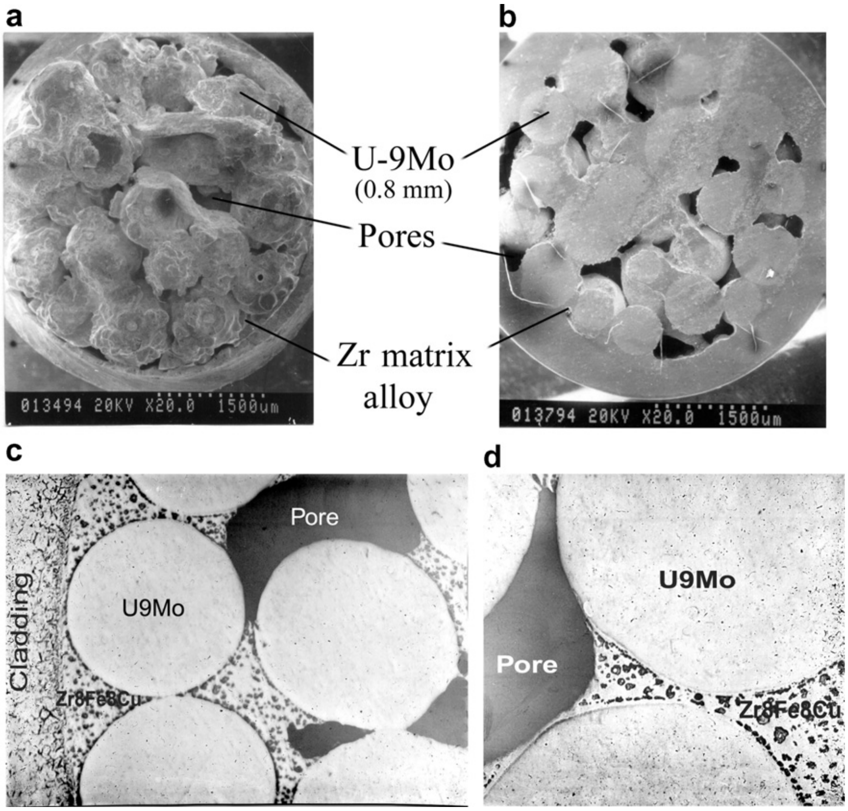

Fig. 4. Structure of (U9Mo + Zr8Fe8Cu) fuel composition fabricated by capillary impregnation; (a) fractogram of fuel element fracture 18% porosity, (b) macrostructure of fuel composition 22% porosity, (c) and (d) microstructure of fuel composition [2,4,5]. Conditions: cladding diameter 5.8 mm, thickness 0.5 mm, fuel granules 0.5–0.8 mm.

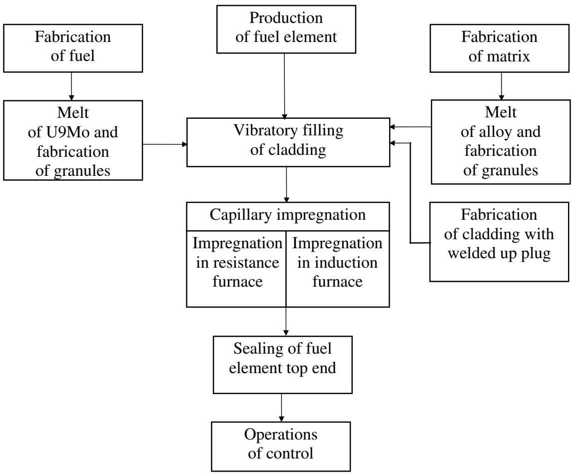

Fig. 5. Process flow sheet of fuel element fabrication by capillary impregnation method [2].

fuel is 62–64%. Consequently, using high uranium content fuel, e.g. U9Mo, the uranium density reaches 9.5–10.0 g cm^{-3}.

The thermal conductivity of the fuel as determined by flow heat method was 18–22 W m^{-1} K^{-1} for 773 K and for its 25% porosity. This ensures the low operating temperature in the fuel element centre. The volume–mass characteristics of the fuels are summarized in Table 1 and the individual properties of the fuel compositions are presented in Table 2 [2,3].

The long-term isothermal anneals (~1000 h) of the fuel compositions at 973 K (below the melting temperatures of the alloys) did not reveal any noticeable interaction between the fuel element components. At higher temperatures, i.e. above the melting temperature of the matrix zirconium alloy, the composition alters due to the intake of zirconium from the fuel element cladding. Since the zirconium matrix alloys are deep ternary and quaternary eutectics any change in the alloy composition leads to a drastic rise of its melting temperature. As a result the alloy melting temperature increases, the alloy solidifies and further interaction stops. Consequently, at the initial stage of heating

Fig. 6. Appearance of fuel elements 9.15 mm in the diameter produced by capillary impregnation method [2].

Table 1
Volume–mass characterization of fuel meat [2,3]

Code	Fuel composition (wt%)	Fuel element diameter (mm)	Volume fraction of fuel (%)	Volume fraction of matrix (%)	Porosity of meat (%)	Density of loaded granules (%)	Uranium content ($g\,cm^{-3}$)
C-17	U5Nb5Zr + Zr10Fe10Cu	5.8	59.31	15.07	25.62	74.38	8.35
C-18	U2Mo1Si + Zr10Fe10Cu	5.8	58.72	14.97	26.30	73.69	9.29
C-19	U9Mo + Zr10Fe10Cu	5.8	58.40	14.87	26.3	73.27	8.96
C-13	U5Nb5Zr + Zr10Fe10Cu	9.15	63.05	15.23	21.72	78.28	8.88
C-14	U2Mo1Si + Zr10Fe10Cu	9.15	62.46	14.85	22.70	77.31	9.90
C-15	U9Mo + Zr10Fe10Cu	9.15	62.08	15.18	22.75	77.26	9.53
C-16	U5Nb5Zr + Zr10Fe10Cu	9.15	63.49	9.06	25.43	72.55	8.94
C-24	U5Nb5Zr + Zr10Fe10Cu	9.15	64.27	18.20	17.53	82.47	9.05
C-25	U2Mo1Si + Zr8Fe8Cu	9.15	63.72	19.96	16.31	83.68	10.10
C-26	U9Mo + Zr8Fe8Cu	9.15	64.56	18.04	17.39	82.6	9.91
C-27	U9Mo + Zr8Fe8Cu	9.15	64.21	20.10	15.69	84.31	9.85

Table 2
Some properties of fuel compositions [2,3]

Code	Fuel composition	Phases of fuel	Axial thermal conductivity, κ_{fuel} ($W\,m^{-1}\,\kappa^{-1}$) Temperature of measurement			
			603 K	713 K	793 K	873 K
C-17	U5Nb5Zr + Zr10Fe10Cu	α'', $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	14.0	17.3	19.3	23.1
C-13	U5Nb5Zr + Zr10Fe10Cu	α'', $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	15.2	18.1	21.4	23.8
C-14	U2Mo1Si + Zr10Fe10Cu	α', γ, $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	15.9	18.3	22.0	24.1
C-15	U9Mo + Zr10Fe10Cu	γ, $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	13.8	17.9	20.8	23.1
C-16	U5Nb5Zr + Zr10Fe10Cu	α'', $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	14.8	17.9	21.0	23.3
C-24	U5Nb5Zr + Zr10Fe10Cu	α'', $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	16.1	19.3	22.6	24.6
C-25	U2Mo1Si + Zr8Fe8Cu	α', γ, $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	17.3	19.7	22.9	25.0
C-26	U9Mo + Zr8Fe8Cu	γ, $Zr_2(Fe,Cu)$, Zr_2Cu, α_{Zr}	15.8	18.5	22.3	24.1

capillary forces inhibit the matrix alloy migration within the fuel element.

Fig. 7 illustrates the microstructure of a specimen of the U9Mo + Zr8Fe8Cu fuel pin after an anneal at 1273 K for 30 min, simulating accidental conditions [2]. It appears from Fig. 7 that there was little change (from about 10 to 15–30 μm) in the interaction layer on the fuel granules and the zirconium cladding. No changes in the geometrical sizes or the shape of the fuel pin specimen took place, the cladding–fuel spallation was not observed. The thermal conductivity of the fuel element measured after the accident conditions simulation decreased insignificantly by approximately 8%.

4. Application of fuels fabricated by capillary impregnation process

The application of fuel elements produced by the capillary impregnation method is schematically presented in Table 3.

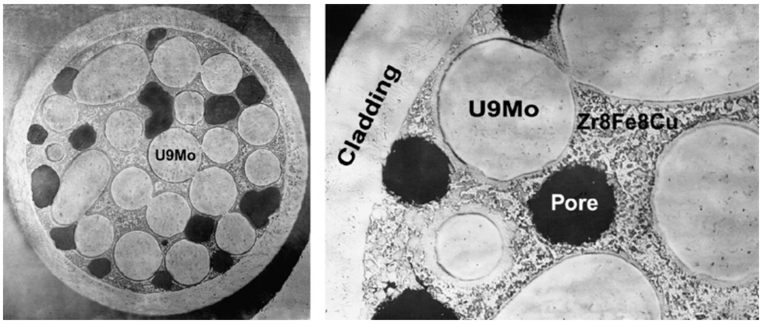

Fig. 7. Microstructure of U9Mo + Zr8Fe8Cu fuel element specimen 30 min annealed at 1273 K [2]. Conditions: cladding diameter 5.8 mm, thickness 0.5 mm.

Table 3
Feasible application of fuels fabricated by capillary Impregnation

Reactor type	Used design temperature in fuel element centre Uranium content	Advantages of capillary impregnated fuel elements
PWR, BWR, VVER-1000	UO_2 pellets 1773–2273 K 7.8 g cm^{-3}	20–25% increased uranium content Maximal fuel temperature of 723–773 K Serviceability in transients
FNPP	UO_2 in aluminium matrix 673–723 K 4.0–5.0 g cm^{-3}	A factor of 2 increased content of uranium Serviceability under accident conditions
CANDU	UO_2 pellets 1573–1873 K 8.2 g cm^{-3}	20–40% increased uranium content Maximal fuel temperature of 673–723 K Serviceability in transients
PWR to burn Pu within inert matrix fuel (IMF)	Pellets of $(Er, Y, Zr, Pu)O_2$ 2073–2273 K	Extended burnup Maximal fuel temperature of 873–1073 K Serviceability in transients

Fuel elements fabricated by the capillary impregnation method are dispersion type fuels having specific features, i.e., high serviceability, transient conditions included, reliability, feasibility of extending burnup and high thermal conductivity. Some extra specific properties of this type of fuel elements include compatibility with high uranium content fuel provided by the application of zirconium alloy matrices as well as available pores to accommodate swelling.

Fuel elements of this type are promising for reactors of the PWR, BWR or FNPP types. For instance, the uranium density of a capillary impregnated fuel element reaches levels of 9–10 g cm^{-3}. This is 20–25% higher that the uranium content of the standard VVER-1000 fuel rods, which permits the U-235 enrichment of the fuel to be reduced. The maximum temperature in the fuel centre should not exceed 723–773 K. The porosity of the fuel meat allows the accommodation of swelling up to the burnup (in g-fiss) of 0.8–1.0 cm^{-3}, which in term of the standard VVER-1000 fuel rod corresponds to 100–130 MW d kg^{-1}. A further advantage is a metallurgical bond between the fuel and the cladding which enables fuel elements to be serviceable under transient conditions.

Of particular interest is the use of the novel fuel compositions in CANDU fuel elements. Currently its fuel is uranium dioxide with a natural enrichment. The uranium content of the fuel is 8.3 g cm^{-3}. Hence, the fuel burnup is usually not high, i.e., 10–15 MW d kg^{-1}. An increase in the uranium content of the fuel fabricated by the capillary impregnation method may substantially prolong the cycle and reduce the specific consumption of uranium per unit of generated electric power. It is possible to further increase the fuel uranium content up to 11 g cm^{-3} by increasing the volume fraction of fuel granules

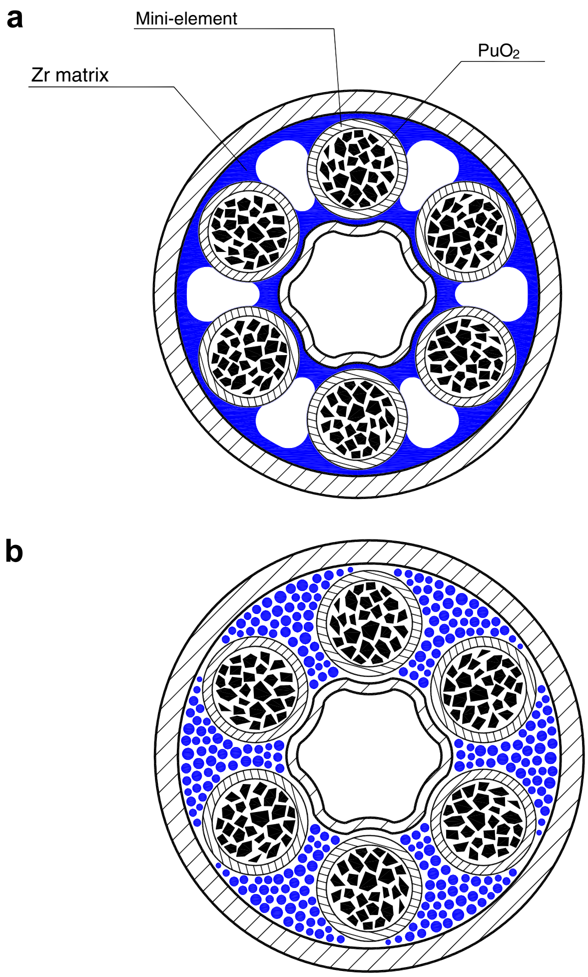

Fig. 8. Schematic presentation of IMF versions; (a) proposed IMF with fuel mini-elements and zirconium matrix, (b) its fabrication via capillary impregnation [5]. Conditions: cladding diameter 9.1 mm thickness 0.7 mm.

introduced into a fuel element and decreasing the volume fraction of the matrix and pores. This is achievable through a partial substitution of matrix granules by fuel ones and a decrease in the fuel porosity.

For CANDU fuel elements it is advisable to use U7Mo alloy as fuel, since its uranium content is higher than that of U9Mo and the content of molybdenum is lower. The use of Zr6.4Fe2.5Be alloy instead of Zr8Fe8Cu is also more expedient because of the lower of thermal neutron capture. The optimized volume ratio between the components in the CANDU fuel element is 70% fuel, 15% matrix and 15% pores.

These fuel elements are also usable in FNPP reactors under development; that are based on the reactors of atomic ice-breakers [7,8]. A dispersion fuel with a UO_2 base in a matrix of aluminium alloys is currently under consideration for this purpose [2,8]. The uranium density in this fuel is 4–5 g cm^{-3}, which tolerates the use of 20% ^{235}U, and meets the IAEA proliferation requirements. However, to prolong the fuel element cycle or to increase the power density the uranium content of the fuel need to be increased, which is not feasible with UO_2. In addition, the application of the low melting aluminium matrix limits the serviceability of fuels under accident conditions.

An additional application of the capillary impregnation method, in particular, for the use of novel zirconium matrix alloys, is the application of capillary impregnation to inert matrix fuel (IMF) foreseen to burn weapon and fuel-grade plutonium. For this purpose (Er, Y, Pu, Zr)O_2 pelletized fuel elements are considered e.g. [9]. A design, where PuO_2 base fuel is isolated in fuel minielements that are placed inside a fuel element is proposed, see Fig. 8(a) and (b) [5]. Inner space is filled with Zr matrix granules (Fig. 8(b)). After heating (capillary impregnation) zirconium matrix alloy moves into the joints and provides the fuel minielement-cladding contact (Fig. 8(a)).

This design for the use as IMF in comparison with YSZ (Er, Y, Pu, Zr)O_2 pelletized fuel element could extend the burnup, lower the fuel temperature, accommodate swelling and make a fuel element serviceable under transient conditions.

5. Conclusion

Several novel dispersion fuel compositions with high uranium content fuel (U9Mo, U5Zr5Nb, U_3Si) and a matrix based on a low melting point (963–1133 K) zirconium alloys as well as the method of fabrication by capillary impregnation have been developed at A.A. Bochvar Institute.

The capillary impregnation method involves introducing fuel granules and granules of zirconium alloy matrix into a fuel element which then undergo a short-term anneal at a temperature above the melting temperature of alloy. The matrix alloy melts down and under capillary forces moves into joints between the fuel element components to form metallurgical bonds. The volume ratio between the fuel components are: 55–65% fuel, 10–20% matrix, 15–30% pores.

Fuel elements produced by this method have high uranium content (9–10 g cm^{-3}), high thermal conductivity (18–22 W m^{-1} K^{-1}), which when used in PWR or BWR reactors allow the fuel temperature to be lowered to 723–773 K; they also feature porosity to accommodate swelling. The metallurgical fuel–cladding bond makes fuel elements serviceable in power transients.

For the PWR, BWR and CANDU, their primary advantages are high uranium content, low temperature of the fuel and serviceability under transient conditions. Consideration is given to their applicability in Floating Nuclear Power Plants (FNPP) as well as to the feasibility of burning civil and weapon's grade plutonium.

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