Warm-Moulded Graphitic Matrix for Spherical HTR Fuel Elements

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1. Introduction

The development and irradiation testing of graphitic matrix materials for cold-moulded HTR fuel elements have been completed successfully with the use of two approved materials for the fuel elements of the reactors AVR (matrices A3-3 and A3-27) and THTR (matrix A3-3).

In order to enable the manufacture of fuel elements with high heavy-metal loading, as well as to improve the fabrication technology, the NUKEM/HOBEG company developed a process for the warm-moulding of the elements[1]. Furthermore, pitch coke graphite was used as a filler raw material instead of the mixture of natural graphite and petroleum coke graphite used before. On this basis, structural materials for warm-moulded fuel elements were developed and two optimized matrices (W2-1 and W2-2) were tested under fast neutron exposure at 700, 900 and 1100°C in the High Flux Reactor Petten, The Netherlands. Measurements of the sample dimensions and the physical properties were performed at KFA Jülich.

The present paper deals with some comparisons between the warm-moulded and the cold-moulded fuel matrices as far as the material composition, fabrication parameters, material properties and two of irradiation results are concerned.

2. Warm-moulded graphitic matrices compared to cold-moulded matrices

2.1 Material composition and fabrication parameters

Table 1 shows the compositions of the warm-moulded matrices W2-1 and W2-2 as well as those of the cold-moulded fuel matrices A3-3 and A3-27.

The material W2-1 represents the standard quality of the first matrix category. Its variant W2-2 serves as a reference material and is especially intended to provide a better understanding of irradiation behaviour. The materials differ only by their composition whereas the raw material and fabrication parameters are equal. The filler component consists of pitch coke graphite and the binder component has been made of phenolic resin binder to which 5 wt % of the hardener hexamethylenetetramine was added. As a moulding method, the warm-moulding in a steel die was used in contrast to the isostatic cold-moulding in rubber dies used before. Final heat treatment was carried out at 1950°C to achieve a favourable corrosion rate.

The two cold-moulded fuel matrices A3-3 and A3-27 are based on the same filler mixture consisting of natural graphite and petroleum coke graphite. They differ in the binder and its processing or synthesis. Whereas prefabricated phenolic resin binder is processed together with the filler components for fabricating the standard matrix A3-3, synthesis of the binder only takes place during the matrix formation for producing the material A3-27. The two phenolic resin binders differ in binder type and crosslinking; consequently, the binder cokes are of different structures[2]. The process step of isostatic cold-moulding was the same for both materials. Final high-temperature treatment took place at different temperatures. Earlier fuel element reload batches for the AVR reactor, which had been produced with A3-3, as well as matrix spheres for machining irradiation specimens were subjected to a heat treatment at 1800°C. For later AVR reload batches and for the THTR production, the temperature was increased to 1950°C in order to improve the corrosion resistance.

Table 1. Composition of warm-moulded and cold-moulded matrices

Material		Filler	(wt.%)	Binder	(wt.%)	Hardener	* (wt.%)	Binder coke (wt.%)
Warm-moulded matrices	W2-1**	pitch coke graphite	84	phenol form-aldehyde	16	hexa-methy-lenete-tramine	5	9.8
	W2-2		82		18		5	11.0
Cold-moulded matrices	A3-3	natural graphite + petroleum coke graphite	80		20	–	–	10.0
	A3-27		78	phenol*** hexamethylene-tetramine	22	–	–	11.0

*related to the binder content **standard quality
***synthesized during matrix formation

2.2 Material properties

In Table 2, material properties of the warm-moulded and the cold-moulded matrices are summarized.

A comparison of the warm-moulded matrices W2-1 and W2-2 shows that the standard quality W2-1 exhibits a better strength behaviour than the matrix W2-2. Furthermore, the thermal conductivity determined at 1000°C and the Young's modulus are also somewhat more favourable for this material; only the higher corrosion rate points to a slightly more unfavour-

Table 2. Material Properties of Warm-Moulded and Cold-Moulded Matrices.

Material		High-temp. treatment (°C)	Application	Property												
				Young's modulus ($kN \cdot cm^{-2}$) ∥	⊥	Density ($g \cdot cm^{-3}$)	Coeff. of lin. therm. expansion 20-500 °C ($10^{-6}K^{-1}$) ∥	⊥	Quotient of coeff. of therm. expansion $\alpha_\perp/\alpha_\parallel$	Therm. conductivity at 1000 °C ($W \cdot cm^{-1}K^{-1}$) ∥	⊥	Compressive strength ($daN \cdot cm^{-2}$) ∥	⊥	Tensile strength ($daN \cdot cm^{-2}$) ∥	⊥	Corrosion rate at 1000 °C in He of 1 bar with 1 vol. % H_2O (10h) ($mg \cdot cm^{-2}h^{-1}$)
Warm-moulded matrices	W2-1	1950	Development of warm-moulded fuel elements	1095	882	1.73	2.94	3.73	1.27	0.30	0.27	844	832	225	200	1.14
	W2-2	1950		1110	980	1.74	2.97	3.70	1.25	0.28	0.26	775	740	132	164	1.01
Cold-moulded matrices	A3-3	1950	AVR fuel elements, THTR Production	1000	970	1.73	2.89	3.45	1.19	0.32	0.29	435	426	135	126	0.97
		1800	Previous AVR fuel elements	1020	991	1.70	2.80	2.92	1.07	0.28	0.27	382	376	104	105	1.19
	A3-27	1950	AVR fuel elements	1070	1020	1.74	2.43	2.69	1.11	0.34	0.32	469	464	135	130	0.73

able corrosion behaviour. The coefficients of linear thermal expansion (α) determined between 20 and 500°C and, consequently, also their quotients $\alpha_\perp/\alpha_\parallel$ are similar for both materials. Comparing the material properties of the standard quality of the warm-moulded matrix (W2-1) with those of the cold-moulded fuel matrices A3-3 (1950°C), A3-3 (1800°C) and A3-27, the first shows a substantially better strength behaviour. On the other hand, the corrosion rate of W2-1 is more unfavourable than that of A3-3 (1950°C) and A3-27 (1950°C), although heat treated at the same temperature[3]. Moreover, moulding in a die, causes a higher quotient of thermal expansion coefficients ($\alpha_\perp/\alpha_\parallel$) for W2-1 and W2-2.

2.3 Irradiation behaviour

In Figures 1 and 2 irradiation results concerning the dimensional behaviour and the thermal conductivity, resp. of the warm-moulded as well as the cold-moulded matrices are demonstrated.

Fig. 1 shows higher dimensional changes versus fluence for both warm-moulded materials W2-1 and W2-2 compared to those of cold-moulded matrices A3-3 and A3-27. This different irradiation behaviour can be attributed to the different filler

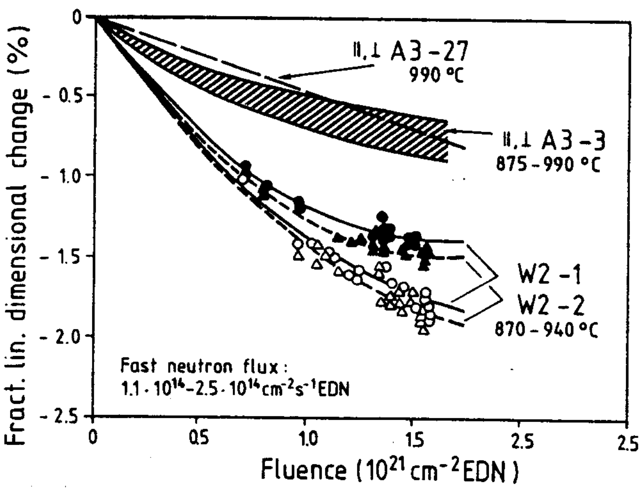

Fig. 1. Dimensional change of warm-moulded and cold-moulded matrices versus fluence.

materials as well as to the differences in structure[1,2]. Furthermore W2-1 and W2-2 show slightly anisotropic dimensional behaviour analogous to their quotients of thermal expansion (Tab. 2), and they differ in skrinkage due to the different binder coke contents[4,5] (Tab. 1).

The thermal conductivity (λ) of all four matrices generally decreases under irradiation, at temperatures of about 900°C approximating a saturation value of about 60 % of the pre-irradiation value (Fig. 2).

3. References

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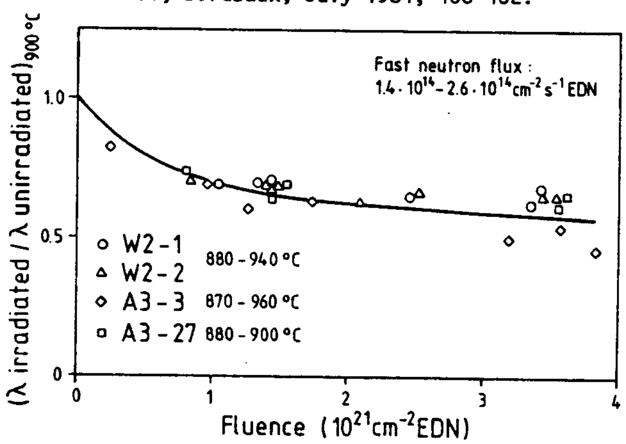

Fig. 2. Fractional change of thermal conductivity of warm-moulded and cold-moulded matrices versus fluence.