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**IMPROVEMENT OF NUCLEAR GRADE GRAPHITE BASED ON ISOTROPIC AND HIGHLY  
CRYSTALLINE NATURAL GRAPHITE BY GENERATION OF  
SILICON - OR ZIRCONIUM – CARBIDE IN SITU**

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**ABSTRACT**

Following the fabrication technique originally developed for HTR-molded block fuel elements a process was introduced to fabricate nuclear graphite with the aim to attain the improved irradiation stability above  $3 \times 10^{22} \text{n/cm}^2$ ,  $E > 0,1 \text{ MeV}$  and to increase corrosion resistance. Nuclear highly crystalline natural graphite is used. A phenol formaldehyde resin with additives of silicon or zirconium oxide powder serves as binder. The mixture thus obtained is isostatically consolidated into spheres and spheres are crushed to granules from which the 0.3 - 3 mm fraction is obtained. The granulate is hot molded into graphite bodies. The green bodies are heated to about  $800 \text{ }^\circ\text{C}$  to carbonise the resin and subsequently annealed at  $1900^\circ\text{C}$  in vacuum.

The key feature of the proposed process is based on the chemical affinity of binder coke with the structure obtained by carbonisation of green bodies. Consequently it reacts selectively in situ with the added  $\text{SiO}_2$ , or  $\text{ZrO}_2$  to carbides in vacuum at  $1900^\circ\text{C}$ . Silicon carbides and zirconium carbides are characterised by high mechanical strength and very good resistance to corrosion. The properties of reactor graphite, such as density, mechanical properties and in particular stability to fast neutron irradiation are considerably improved.

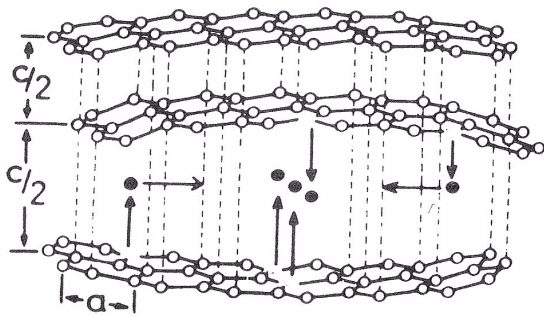
Keywords: HTR, VHTR, Molded Block Fuel Elements, Fuel Spheres, Reflector Graphite, Natural Graphite, Hot Molding, Carbonising, High Temperature Annealing, In Situ Formating of SiC, ZrC, Silicon Carbide/Zirconium Carbide, Oxidation Behaviour, High Isotropy

**DESCRIPTION**

The phrase reactor graphite began to be used at the end of 1942 when the first nuclear fission occurred in a graphite moderated nuclear reactor. The importance of graphite in nuclear technology is based on its outstanding nuclear physical properties i.e. nuclear low capture cross section, a relatively low mass number and good moderating and reflecting efficiency.

By designing and building of gas-cooled nuclear reactors, in particular the Mk II advanced gas-cooled reactors, (AGR) and helium cooled high temperature reactors (HTR) nuclear grade graphite became one of the most important reactor materials. The reactor graphite is used to produce fuel elements as well as for the fabrication of stationary assemblies such as the reflector. The reflector should minimise the neutron escape from the reactor core. To achieve this the reactor core is closely surrounded by a graphite reflector at the top, bottom and sides. The following example illustrates the importance of reactor graphite in more detail. Thus for the thorium-high-temperature-reactor (THTR) with a power of 300 MWe 600 kg uranium-235 and with 7000 kg thorium as fertile material about 400.000 kg nuclear grade graphite have been required - a mass ratio of about 1:50.

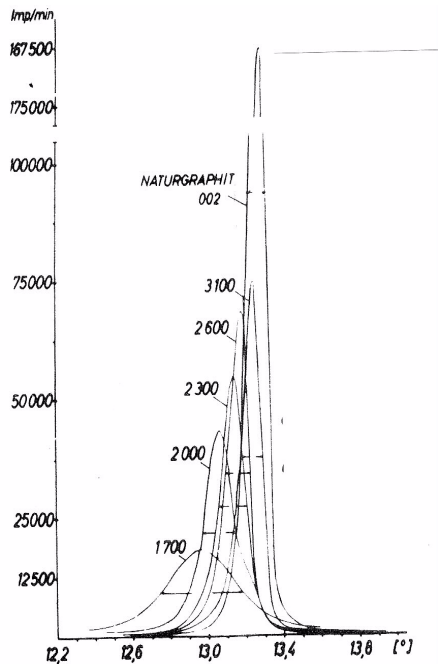
During the operation of nuclear reactors the graphite is exposed to high fast neutrons doses (or fluences). The neutrons may significantly damage the graphite (see figure 1).



**Fig. 1 Diagram illustrating the structure of Irradiated Graphite**

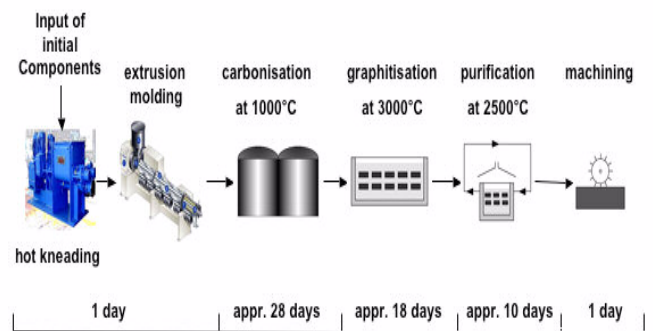
Since the physical, mechanical and chemical properties of graphite can be influenced negatively by radiation induced damage, the reactor graphite must be sufficiently radiation stable in accordance with the respective criteria of the reactor design. Additionally, the reactor graphite must be of nuclear purity. This means that the neutron capture cross section must be less than 4 mbarn. This is required in particular for reflector graphite because it should have a life time of at least 30 years. During this time the reflector graphite would be subjected to a very high integrated fluence of fast neutrons of about  $3 \times 10^{22} \text{ n/cm}^2 E > 0,1 \text{ MeV}$ .

The results from literature reveals that nuclear graphite maintains the dimensional and mechanical integrity when irradiated with fast neutrons with temperatures above  $1000^\circ\text{C}$  only when it is highly graphitised and arranged to be isotropic<sup>1,2,3</sup> (see figure 2).



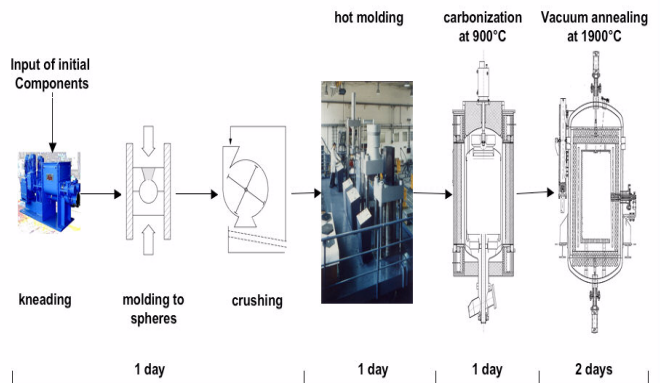
**Fig. 2 X-Ray Diffraction pattern of Petroleum Coke graphitised at temperatures between  $1700^\circ\text{C}$  and  $3100^\circ\text{C}$  compared with Natural Graphite**

The process used for the production of nuclear graphite is similar to that used to produce conventional graphite, the raw materials being petroleum coke and pitch. The initial mixing involves melting the pitch and forming blocks by molding or extrusion. The raw materials are chosen such that they graphitise easily. To carbonise the binder the molded or extruded body is heat treated in an inert atmosphere at up to about  $1000^\circ\text{C}$ . As a second stage the baked carbon is graphitised at about  $3000^\circ\text{C}$ . The process may also involve a high temperature gaseous purification treatment to bring the concentration of neutron absorbers down to acceptable levels. The production cycle takes about two months. Figure 3 illustrates schematically the process for the production of synthetic reactor graphite.<sup>4</sup>



**Fig. 3 Flow Diagram Illustrating Reactor Graphite Fabrication**

A new method for producing reactor graphite is now described (see figure 4).

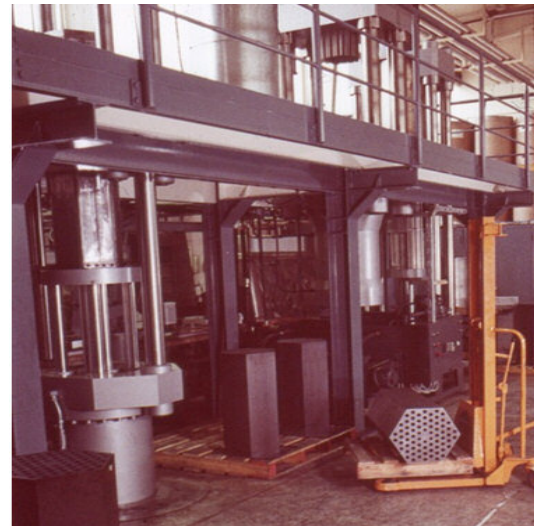


**Fig. 4 Flow Diagram Illustrating Proposed Reactor Graphite Fabrication**

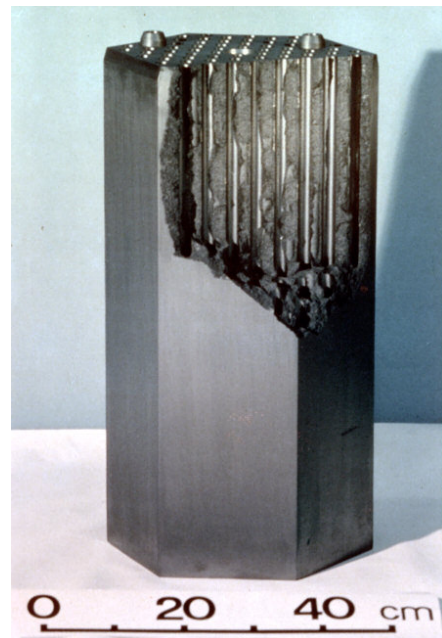
Nuclear purity highly crystalline natural graphite powder, FP of company Kropfmühl, is used as a primary starting material. A phenol formaldehyde resin dissolved in alcohol serves as binder. The components are first mixed at room temperature and then either silicon or zirconium oxide powder is added to the graphite resin premix. This mixture is then molded in a two stage process.

In the first step spheres are molded semi isostatically in a rubber die at a relatively high pressure of about 100 MN/m<sup>2</sup>. Afterwards the spheres are crushed to form granules with an average diameter of about 1 mm. The average granule contains about 1 million (10<sup>6</sup>) isotropically arranged graphite particles of the original graphite powder. For further improvement of isotropic behaviour of molded bodies the company Kropfmühl has developed a natural graphite powder of the same origin however with almost spherical grain size. For the second step the isotropic granulate is hot molded into graphite bodies in the plastic temperature range of the binder resin at relatively low pressures of about 12 MN/m<sup>2</sup>. To enhance the molding a lubricant and air displacement agent is incorporated into the granulate.

To carbonise the resin the “green” graphite bodies are heated to about 800°C in an inert gas atmosphere. A hot-gas ventilator creating an internal convection sucks off the argon top down and blows it up again in between the guide tube and the heated furnace lining. The composition products formed during the carbonisation condense in the lower furnace region and are removed from the carbonisation process immediately after their formation. The heating and cooling cycle takes 24 h and is therefore very short as compared to the established processes. Figure 4 shows a schematic illustration of the proposed process. The process has been developed for the production of HTR molded block fuel elements (see figure 5,6 and 7).<sup>5</sup>



**Fig. 6 Pilot Plant for Fabrication of HTR Moulded Block Fuel Elements (lower working level)**



**Fig. 7 HTR Molded Block Fuel Element after Heat Treatment**



**Fig. 5 Pilot Plant for Fabrication of HTR Moulded Block Fuel Elements (upper working level)**

The key feature of the proposed process is based on the chemical affinity of binder coke with the structure obtained by carbonisation of molded graphite bodies. Consequently it reacts selectively in situ with the added SiO<sub>2</sub> or ZrO<sub>2</sub> to carbides during the annealing of the carbonised graphite bodies in vacuum at 1900°C.<sup>6</sup> Both carbides, SiC and ZrC, are suitable reactor materials having cubic crystalline structure (Syngonie) and are inherently isotropic. Silicon carbides and zirconium carbides are characterised by high hardness, high mechanical strength and very good resistance to corrosion. Combined with the large crystals of the natural graphite it will lead to an improved oxidation behaviour of HTR fuel elements (fuel spheres and prismatic fuel elements) and

structural components of an HTR like reflectors or supporting elements<sup>7</sup> compared to A3 matrix graphite and V483T nuclear grade graphite. The properties of reactor graphite, such as density, mechanical properties and in particular stability to fast neutron irradiation are considerably improved. The proof tests are in progress.

The reactor grade graphite can also be used in non-nuclear applications, such as chlorine alkali electrolysis or for thermal electrodes, i.e. as current supplying parts in high-temperature electric furnaces.

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