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MANUFACTURE OF HIGH CORROSION RESISTANT FUEL SPHERES (FS) FOR HIGH TEMPERATURE PEBBLE BED MODULAR REACTORS (PBMR)

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ABSTRACT

The standard FS for PBRs are spherical balls with a diameter of 60 mm, made from A3-graphite matrix, containing the fuel as coated particles.

The coated particles, embedded in the graphite matrix are homogeneously distributed in the core of the ball, surrounded by a 5 mm thick, fuel-free shell. The shell and the core are connected to form one single unit.

The A3-graphite of the core and the shell is identical, containing 72,7 % natural graphite, 18,2 % graphite petroleum coke and 9,1 % binder coke.

In the invented new FS ball, the binder coke of the outer shell is converted into silicon carbide (SiC) and / or zirconium carbide (ZrC) and the thickness of the shell is approx. 3 mm.

This prevents a selective corrosion of the binder coke out of the A3-matrix and the integral corrosion resistance of the matrix against oxygen and water vapor is increased by the factor of three.

Based on this, the requirements on the FS-balls are fulfilled, even if a hypothetical failure, e.g. complete shut-down of the cooling system and / or an uncontrolled introduction of water or water vapor under full capacity of the reactor occurs.

In addition, the reduction of the shell thickness reduces the temperature of the fuels in the ball core and therefore the retention of the gaseous and solid fission products is increased.

INTRODUCTION

The fuel element of high temperature pebble bed modular reactors is a graphite sphere with a diameter of 60 mm, manufactured by molding of A 3 special graphite. The sphere consists of a fuel containing core, 50 mm in diameter, surrounded by a 5 mm thick fuel-free shell.

The core of the fuel sphere is seamlessly connected with the shell and thus forms one single unit. The fuel, in form of coated particles, is distributed homogeneously in the sphere's core. Fig. 1 shows the schematic diagram of the fuel spheres.

Graph of Molded Fuel Element Sphere

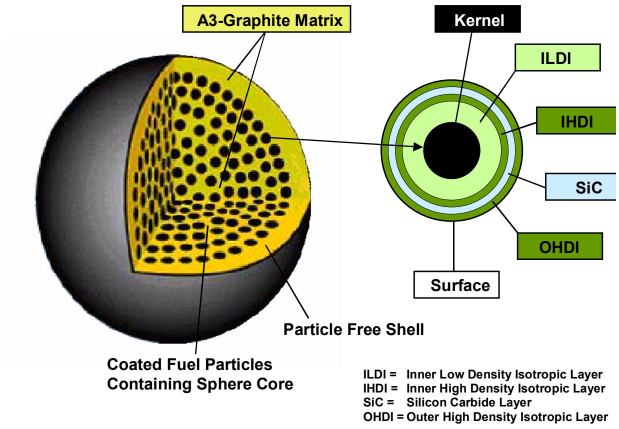

Figure 1

PRESENT PRODUCTION OF FUEL SPHERES

The fuel spheres of the PBM reactor contain 14 g heavy metal in form of UO_2-coated particles. The number of coated particles per sphere is 23.300.

The uranium is enriched on U-235 to 7,8 %. The fuel spheres are produced by molding of resinated graphite matrix powder and coated particles followed by heat treatment. In order to obtain the required quality, the carbon compacts usually pass through a graphitization process in temperatures ranging from 2700 °C to 3000 °C. However, after molding the fuel spheres contain coated fuel particles in the core. Therefore a graphitization process in temperatures above 2700 °C can not be performed due to the following reasons:

At temperatures above 2100 °C the uranium from the fuel kernels diffuses into the coating layers of the particles and then into the graphite matrix of the fuel spheres. The uranium which has diffused into the fuel sphere's porous graphite matrix outside of the coating would lead to an inadmissibly high contamination of the cooling gas with released fission products (1)

Furthermore, the pyrocarbon layers change their structures at temperatures above 2100 °C while the anisotropy of the crystallographic orientation of the pyrolytic carbon rises sharply. As a consequence the coated particles in the reactor may lose their mechanical integrity very early and therefore spontaneously release radioactive fission products (2).

Further, the relevant literature states that graphite will only maintain its dimensional stability and mechanical integrity under radiation with fast neutrons and temperatures above 1000 °C, if the structure is isotropic and highly crystalline.

In order to attain the dimensional stability and mechanical integrity of the molded fuel sphere during the entire residence time in the reactor in spite of heat treatment at a limited temperature of approx. 2000 °C, a special graphite was developed. The special graphite is described in the technical literature as A 3-graphite matrix. The A 3- graphite matrix is based on natural graphite. Natural graphite is distinguished by an extremely high crystallinity. However, its primary grain is platelet-like with a hexagonal crystalline order (syngony) and is therefore highly anisotropic.

To obtain the required isotropy of the matrix' physical properties the fuel spheres are molded in a rubber die, preferably silicone rubber. The cylindrical rubber die comprises several pieces. It is equipped with an ellipsoid-shaped cavity in the center for reception of resinated molding powder-fuel-mixture. The cavity is dimensioned to form a sphere when pressure of more than 5 Mpa is applied. The rubber die is inserted in a steel die of the hydraulic press and compressed between upper and lower punchies.

Fig. 2 shows the rubber die

The Silicon Rubber Die

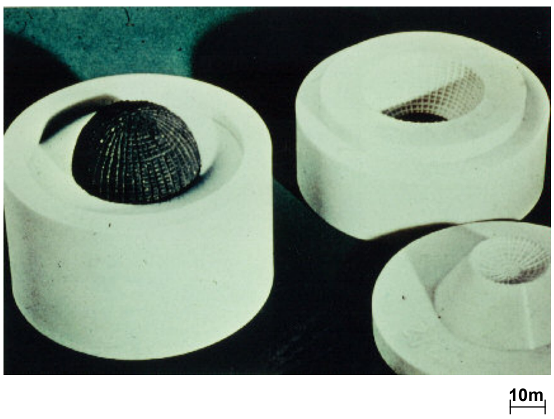

Figure 2

For the manufacture of the fuel spheres, first of all, a mixture of resinated graphite molding powder and coated fuel particles are premolded into a manageable sphere core which is then embedded in resinated graphite molding powder in a second rubber die and molded with increased pressure to form a permeable sphere. Finally, the permeable sphere is molded in vacuum in a third rubber die to its final density.

To carbonize the resin, the fuel spheres are heated to 800 °C within 18 hours and subsequently annealed at approx. 2000 °C. Fig. 3 shows a metallographic cross section.

Metallographic Cross Section through Fuel Sphere and Microphotograph of Embedded Coated Particle

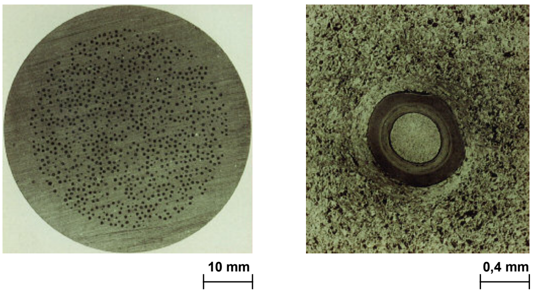

Figure 3

and Fig. 4 shows an x-ray photograph of a molded fuel sphere.

X-Ray Photograph of Molded Fuel Element Sphere

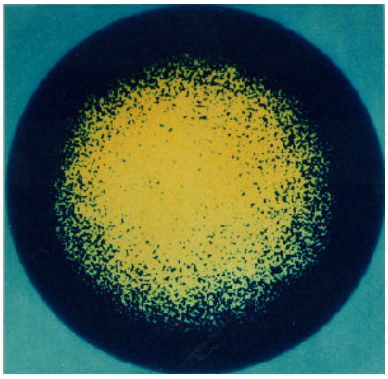

Figure 4

After heat treatment, the A 3-matrix consists of 71 weight % natural graphite, 18 weight % petroleum coke graphitized at 3000 °C and 11 weight % binder coke (5, 6, 7).

In order to manufacture not only isotropic fuel spheres but also fuel spheres without almost any property gradient, they are molded in a final third step at a high mold pressure of 300 Mpa to 1,92 g/cm^3 which corresponds to approx. 99 % of the theoretic density. When pressure is released at first the density is reduced to 1,8 g/cm^3, it further decreases during subsequent heat treatment and reaches its minimum value of 1,6 g/cm^3 at 280 °C. At this temperature the binder resin starts to carbonize while developing crack-gases.

The required porosity is obtained through the addition of synthetic graphite powder, thus ensuring a nearly pressureless degassing of the matrix and preventing crack formation. As the decomposition of the resin the graphite matrix begins to shrink and finally reaches a relatively high density of 1,73 g/cm^3 at 850 °C. The weight loss of the sphere matrix due to resin carbonizing amounts to approx. 9 weight %. (s. Fig. 5)

Composition of A3 Graphite Matrix and Principle of Molding

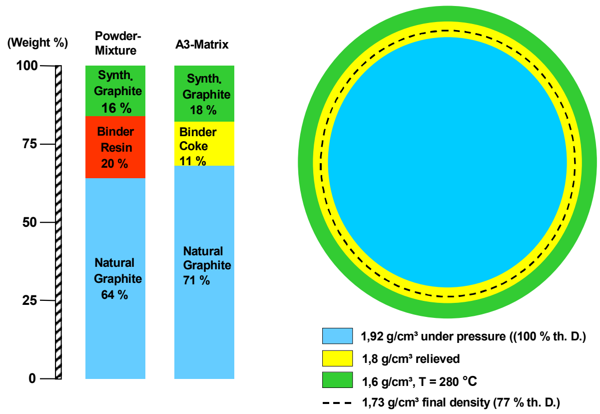

Figure 5

In the Seventies and Eighties over one million molded A 3-fuel spheres were used in the pebble bed reactor AVR in Jülich and in the thorium-high temperature reactor in Schmehausen/Uentrop. The fuel spheres have performed well in continuous operation and showed perfect behavior.

HOW TO IMPROVE THE STABILITY OF FUEL SPHERES

Additionally, the fuel spheres must meet further requirements in the next generation of nuclear reactors. The fuel spheres must remain intact during maximum reactor operation and may not release inadmissible fission products in case of an hypothetical accident such as complete failure of the cooling and/or uncontrollable intrusion of air, water or steam into the reactor core. Therefore, high corrosion resistance of A 3-molded fuel spheres against oxygen resp. steam is required.

A standard test is performed to evaluate the corrosion resistance. In this test the fuel spheres are heated up to 1000 °C in inert gas atmosphere, containing steam, and weight loss is determined. A 1 vol. % steam-argon mixture is used as reaction gas. This mixture is produced in a humidification container filled with water. The argon bubbles through the water and is saturated with the steam. The flow velocity of the reaction gas is 150 l/hour. It is selected in a way where only approx. 20 % of the supplied oxygen reacts with the graphite matrix of the sphere.

The corrosion rate represents the graphite burn-up per hour in milligram, relating to one 1 cm^2 of sphere surface. The value determined on the A 3-fuel spheres in 1000 °C ranges at 1 to 1,25 mg/cm^2 per hour. Hereby, a **SELECTIVE** burn-up of the binder coke was observed.

The comparative value of 0,7 mg/cm^2 per hour for the nuclear grade ATJ reactor graphite of Union Carbone Corporation (UCC), graphitized at 3000 °C, is distinctly lower.

The fuel spheres for the first core of the AVR were manufactured by UCC, using the spherical shell of ATJ graphite. The main approach to improve corrosion-resistance of the A 3-graphite matrix lies in the use of the high chemical affinity of the binder coke, which up until now has proven to be a disadvantage in corrosion tests, whereas however, the high chemical affinity of the binder coke can be used by adding a Si and/or Zr-chemical compound during the preparation of resinated molding powder production for the fuel sphere shells. Analog to the oxidation with steam the added Si and/or Zr-compound also reacts selectively with the carbon of the binder coke during the annealing of the fuel spheres in vacuum at a maximum temperature of 2000 °C. Hereby, only the binder coke content which is responsible for the corrosion of the A-3-graphite matrix is transferred to the corrosion-resistant SiC or ZrC. Both carbides, SiC and ZrC are proven reactor materials with a cubical crystalline order (syngony) and are therefore inherently isotropic. SiC and ZrC are distinguished by their high degree of hardness, mechanical strength properties and very good corrosion-resistance. Through the use of SiC and ZrC in the production of the A 3-graphite matrix the quality of the fuel spheres such as density, breaking load and especially corrosion-resistance for example, is improved considerably and the requirements on the fuel spheres for the next generation of pebble bed modular reactors are met.

FURTHER ADVANTAGES

Because of the increased corrosion- and strength properties, the nominal thickness of the fuel-free shell of fuel spheres can be reduced from 5 mm to 3 mm. Hereby, the volume of the sphere core containing fuel is increased and the fuel temperature is decreased accordingly. The lower fuel temperature considerably increases the retention of the coated particles for fission products.

The SiC-content in the 3 mm thick fuel sphere shell amounts to 5,32 g if the binder coke is completely transformed into SiC. This value is relatively small and corresponds to the nominal value of 5,28 g SiC coating of a fuel sphere, containing 23.300 coated particles.

SUMMARY

Today's way of producing fuel spheres is a proven and reliable process. The only insufficient issue is the weakness of these spheres against corrosion because of a non-uniform structure of the graphite and binder material. This weak point is eliminated by the described process where the binder material is transferred into SiC or ZrC during thermal treatments. The SiC / ZrC increases the corrosion-resistance dramatically, but does not substantially influence the nuclear activity.

Additionally, the spheres produced this way allow to use a thinner protective shell which lowers the inner temperature and therefore increases the retention for fission products.

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