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Detection of Gas-Permeable Fuel Particles for High-Temperature Gas-Cooled Reactors

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METALS AND CERAMICS DIVISION

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DETECTION OF GAS-PERMEABLE FUEL PARTICLES FOR HIGH-TEMPERATURE
GAS-COOLED REACTORS

B. A. Thiele, D. P. Stinton, and D. A. Costanzo

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DETECTION OF GAS-PERMEABLE FUEL PARTICLES FOR HIGH-TEMPERATURE GAS-COOLED REACTORS

B. A. Thiele,* D. P. Stinton, and D. A. Costanzo†

ABSTRACT

Fuel for High-Temperature Gas-Cooled Reactors consists of uranium oxide-carbide and thorium microspheres coated with layers of pyrolytic carbon and silicon carbide. The pyrolytic carbon coatings must be gastight to perform properly during irradiation. Therefore, particles must be carefully characterized to determine the number of defective particles (i.e., bare kernels, cracked or permeable coatings). Although techniques are available to determine the number of bare kernels or cracked coatings, no reliable technique has been available to measure coating permeability. This work describes a technique recently developed to determine whether coatings for a batch of particles are gastight or permeable. Although most of this study was performed on Biso-particles, the technique applies equally well to Triso-particles.

About 150 randomly selected Biso-particle batches were studied in this work. These batches were first subjected to an 18-h chlorination at 1500°C, and the volatile thorium tetrachloride released was measured versus chlorination time. Chlorinated batches were also radiographed to detect any thorium that had migrated from the kernel into the coatings.

From this work a technique was developed to determine coating permeability. This technique consists of an 18-h chlorination of multiple samples without measurement of the heavy metal released. Each batch is then radiographed and the heavy metal migration within each particle is examined. From this examination one can determine if a particle batch is permeable, slightly permeable, or gastight.

INTRODUCTION

The two-particle concept of coated fissile and coated fertile fuel particles is the reference design^{1,2} for High-Temperature Gas-Cooled Reactors. Fertile ThO₂ kernels are coated with low-density pyrocarbon (buffer) and a high-density low-temperature isotropic (LTI) pyrocarbon

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and are referred to as Biso-particles. The LTI layer of Biso-particles is the main barrier to gaseous fission products. To improve its fission product retention the fissile uranium-bearing particle is coated with a buffer and an inner LTI layer similar to Biso-particles and also with a silicon carbide layer and an outer LTI layer. This is referred to as a Triso-particle. In both types of fuel particles it is essential that the pyrocarbon layer be gastight. In a Bisco-particle the high-density LTI coating serves primarily as a pressure vessel for the gaseous fission products. Therefore, gastightness of the pyrocarbon to short- and long-lived xenon and krypton isotopes is vital for satisfactory irradiation performance of the Biso-particle. In a Triso-coated particle the inner pyrocarbon layer must be gastight because a permeable pyrocarbon would allow gaseous chlorine from subsequent processing to pass through the buffer layer and react with the fuel kernel. Gaseous chlorine is generated from the thermal decomposition of methyltrichlorosilane during the deposition of the silicon carbide layer. Chlorine will react with the kernel material³ and, during reactor operation, with the rare earth fission products, causing their migration into the coatings and corrosion⁴ of the silicon carbide layer. These reactions could be eliminated by an inner pyrocarbon that is gastight to chlorine at the high silicon carbide deposition temperature (1500–1650°C).

As shown previously, the LTI of Biso-particles and the inner LTI of Triso-particles must be gastight for adequate performance. Before this work a technique using a hot gaseous chlorine leach was used to determine the fraction of defective particles (i.e., bare kernels or cracked coatings) in a batch.^{5,6} The kernel material of broken fuel particles or particles with microcracks in the coating is quantitatively converted to volatile chlorides within a 2-h chlorination at 1500°C. A similar chlorine leach technique is being used for the quantitative determination of uranium and thorium contents in oxide or carbide samples.⁷ Neither of these techniques yielded significant information about the permeability of pyrocarbon coatings. The technique described in this

paper uses a variation of the chlorine leach procedure plus a thorough examination by microradiography to determine pyrocarbon permeability of both Bisco- and Triso-coated particles.

DESCRIPTION OF THE TECHNIQUE

Pyrocarbon gas permeability of as-produced loose Bisco-particles was studied with a chlorine leach apparatus previously described.⁵ The inner LTI of Triso-particles was examined for gastightness before the SiC and outer LTI were applied or after burning off the outer LTI of a fully coated particle. Chlorine will react with the SiC during chlorination and leave only a very porous carbon structure. We do not recommend determining the gas permeability of bonded fuel because of the observed sealing effect of the binder. The sample is heated in a vertical, water-jacketed, quartz tube furnace (Fig. 1) with heating provided by a 7.5-kW induction-heating unit of 500 kHz nominal frequency. Loose particles lay open in a porous graphite tray exposed to the chlorine. The system is purged with argon before heating to 1000°C. Chlorine at 75 ml/min then replaces the argon flow inside the graphite sample holder. Fumes of chloro-organic compounds, which may evolve at this temperature, are allowed to disperse and are swept out of the apparatus before the temperature is raised to 1500°C for the designated period of time. At the termination of the chlorination, the system is purged with argon and allowed to cool for 15 min.

At 1500°C gas-permeable coatings allow chlorine to diffuse through the pyrocarbon and react with the heavy metal of the kernel. The heavy metal chlorides migrate into the buffer and, depending on the degree of pyrocarbon permeability, through the LTI layer. The highly volatile uranium chlorides (sublimation point about 500°C), which are released from cracked or permeable particles, are trapped in a coarse frit. For chlorination of the ThO₂ fertile fuel the coarse frit is not required because the ThCl₄ condenses at 750°C in a very restricted area of the upper part of the quartz furnace.

Fig. 1. Apparatus for Chlorine Leach at 1500°C.

RESULTS

Nearly 150 batches of Biso-coated thoria have been chlorinated for 18 h by the previously described technique. These batches were developmental coating runs, where in some instances the coating conditions were deliberately varied over wide ranges. From these examinations it became clear that batches with widely varying permeabilities had been produced. Initially each batch was chlorinated for intervals of 2, 3, 4, or 6 h, and the ThCl_4 was collected and quantitatively analyzed after each interval. From the amount of thorium collected at each interval the fractional release of heavy metal was determined. Batches with very permeable coatings could easily be identified because the heavy metal release increased rapidly with

chlorination time (Fig. 2). It was very difficult or nearly impossible to distinguish between gastight coatings and slightly permeable ones because of random variation in the analytical results between particle batches. To help distinguish between slightly permeable coatings and gastight coatings, x-microradiographs⁸ were made after each leaching interval. It was discovered that, in the case of permeable particles, the heavy metal gradually migrated from the kernel into the coatings. It was quite surprising to see that thorium had migrated into the coatings of several batches that had been thought to be gastight. All the batches chlorinated for 18 h were examined by x-microradiography. It became clear that microradiography after an 18-h chlorination was a much more sensitive determination of permeability. The microradiographs of very permeable coatings showed that thorium had migrated from the kernel, completely saturated the buffer layer of most particles, and diffused

Fig. 2. Batches with Particles Having Permeable Coatings Show Increased Release of Heavy Metal with Chlorination Time.

through the LTI layer [Fig. 3(a)]. Occasionally coatings were so permeable that the kernel had been completely removed [Fig. 3(b)]. Batches that were only slightly permeable showed thorium migration into the buffer but not enough to saturate the buffer (Fig. 4). Thorium from these particles diffused through the LTI but not in significant quantities. Quite often only a fraction of the particles within the batch were permeable and the remainder were gastight. Chlorinations were extended up to 72 h to monitor these partially permeable batches. Some fraction of permeable particles continued to release thorium for 72 h, but the remainder of the particles were completely gastight, as indicated by microradiography. The variation in coating permeability from particle to particle can be explained as a consequence of variations in coating characteristics. Apparently, when a certain property (i.e., density, porosity, microstructure, etc.) varied significantly from the mean, the coating became gas permeable. The microradiographs of gastight particles that were leached with chlorine for 18 h appeared completely normal (Fig. 5). No thorium had migrated into the buffer.

The examination of many microradiographs of chlorinated particles had demonstrated that microradiography is more informative about coating permeability than chemical analysis for the quantity of thorium released. Examination of radiographs simplified the technique considerably because the sample could be chlorinated continuously for 18 h without stopping to analyze for thorium. It further simplified the technique because multiple samples could be chlorinated in a single apparatus since no chemical analysis was required. Presently about ten samples in individual graphite holders are chlorinated simultaneously, making the analysis rapid and very simple.

Several batches of highly anisotropic particles (Bacon Anisotropy Factor > 1.10) were chlorinated and showed an unusual behavior. The chlorine damaged the LTI coating and caused portions of the coating to spall away from the underlying material (Fig. 6). The spalled coatings, of course, became permeable after a short chlorination. Attack of the

Fig. 3. Radiographs of Permeable Particles. (a) Typical permeable particles. Note the presence of high-density thorium in the buffer layer. The buffer layer of particles with gastight LTI coatings would be free of thorium. (b) Extremely permeable particles. Some kernels were completely removed.

Fig. 4. Typical Radiograph of Slightly Permeable Particles Showing Slight Migration into the Buffer.

Fig. 5. Radiograph of Gastight Particles. Note that no thorium is present in the buffer.

Fig. 6. Typical Radiograph of Highly Anisotropic Particles Showing Spalling Behavior.

coatings was unusual since detailed examination (scanning electron microscopy, strength measurements, etc.) of normal coatings showed that chlorine did not react with the pyrocarbon coating.

CONCLUSIONS

The technique of an 18-h chlorination followed by microradiography has proven very successful in determining the gas permeability of both Bisco- and Triso-coated particles. Particles can be classified very easily into categories of permeable, impermeable, or only slightly permeable. Several modifications have allowed numerous batches to be chlorinated simultaneously, with no need for an analytical determination of the heavy metal released.

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