STRUCTURE OF PYROCARBON COATINGS FOR NUCLEAR FUEL AND IMPLICATIONS FOR QUALITY ASSURANCE

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The High Temperature Gas-Cooled Reactor (HTR) is a second generation nuclear reactor with the ability to stretch uranium resources(1,2) and unique potential to achieve high efficiency in converting fission energy into useable forms (up to 90% for a combined electricity and district heating plant(3,4)). It depends for its success, inter alia, on several areas of carbon technology. In particular the basic unit of fuel is the coated particle which consists of a spheroidal ceramic kernel (such as uranium oxide) surrounded by a series of coatings. The coatings may be composed wholly of pyrolytic carbon (termed BISO), include an interlayer of silicon carbide (termed TRISO) or the pyrolytic carbon and silicon carbide may be co-deposited. They must in combination constitute a barrier to the escape of actinides and fission products.

From the several deposition processes (eg fluidisation, tumbling bed, vibrating bed) considered in the early 1960's, high temperature fluidised bed coating has emerged as the standard manufacturing process and batch sizes up to 35kg have been coated. The problems of coating these small nuclear fuel particles (200-800 μm diameter plus $\sim$200 μm total coating thickness) have first been solved empirically. The result has been a strong linkage between small-scale manufacture and irradiation performance.

Initially coatings were laid down at high temperature (typically $>$ 1600°C) using methane as the source gas. As irradiations proceeded, it emerged that the outer pyrocarbon layer on large TRISO particles was failing at fast neutron doses of about $3.10^{21} n.cm^{-2}$ Dido Nickel Equivalent. More recently it was observed that pyrolytic carbons deposited at lower temperatures ($<$1500°C) were able to withstand much higher fast neutron doses. During this phase the irradiation effects were generally assessed by measuring the change in properties of small strips of carbon deposited on discs coated at the same time as the particles. The validity of measuring the properties of deposits on discs was always in doubt because of the different hydrodynamic behaviour of particles and discs, as well as strong interactions between layers in service.

Using a material which is as structurally sensitive as pyrolytic carbon in an application where the consequences of poor performance are financially serious it is important to establish the loop manufacture - quality - performance so that an adequate Quality Assurance (QA) programme can be defined. With commercialisation imminent it was considered to be the time to launch a concerted effort to try to improve the understanding of the factors controlling the process of coating with pyrolytic carbon. It was also hoped that this might help provide a basis for a QA programme. An important step was the formulation by Lefevre (5) of a process model which postulates that the structure of pyrocarbon is made up of spherical growth features (SGF's). The model has the merit that it predicts the relative size of the SGF's as a function of various input parameters such as carbon : hydrogen atom ratio in the coating gas and can therefore be used to design experiments. An approximate check of the model was made by asking 30 operators to classify photomicrographs of ceramographic sections of 24 different coatings according to the coarseness of the deposits. The average ranking which resulted is compared with prediction in Figure 1.

These encouraging results led to a systematic programme but this first required standardisation of input parameters (eg the method of obtaining the same deposition temperature irrespective of gas composition, specific heat and heat of decomposition (6)). A series of 15 coating runs was then undertaken to check the model and details are given in (7). Only the structure of the outer pyrocarbon layers of TRISO particles was varied and the morphology of these layers was examined by scanning electron microscopy of a fracture surface or by optical microscopy after electrochemical oxidation of a polished section. The photomicrographs were first measured by 3 operators and a good correlation obtained (8) but detailed examination of the data showed that it was obviously necessary to standardise the method of measurement. The structure was therefore quantified for both the size distribution of agglomerates and the number per unit area by the use of a simple linen gauge consisting of a magnifying glass and graticule. The test method was proven using an Analysis of Variance technique (9). Nine of the previous 15 batches chosen to be representative of the spread of results, were then remeasured by 2 previously validated operators. The results obtained from Polaroid photographs of SEM images (mag. x13000) and wet oxidation photomicrographs (mag. x1000) are compared with predictions in Figure 2. A strong correlation is indicated with an identical slope for the two test methods but a different Y-intercept. The presence of SGF's has also been confirmed qualitatively by transmission electron microscopy.

The 15 coating batches have been irradiated in the Colibri HTR 5 experiment but post-irradiation examination results are not yet available. The opportunity has therefore been taken to apply the linen gauge measurement method to SEM fractographs of 5 coating batches from the immediately previous irradiation experiment (HTR 4). The results obtained are plotted against survival of the outer pyrocarbon layer in Figure 3.

It is concluded therefore that low temperature isotropic pyrocarbons consist essentially of spherical growth features whose relative size can be predicted from the Lefevre model and controlled by appropriate input parameters. The method of measurement of SGF is somewhat tedious but is at present the only validated method of measuring pyrocarbon structure. At a later stage an

automatic image analyser or automatic optical anisotropy measurement may be more suited to routine quality control. But the former has not been developed and there is considerable debate about the validity of the latter. Workers disagree as to the importance or not of the polishing method for the preparation of specimens prior to measurement of optical anisotropy and there has been little benefit from attempts to provide inter-laboratory comparisons and standards. Since the size of packed spheres controls the size of the cusps between the spheres, porosity measurement could also be considered as a control method.

Turning to the question of QA for pyrocarbon it is useful to take advantage of the approach taken by Delle et al (10) to deduce test methods by working backwards through the coated particle failure modes, the parameters affecting reliability and the testing parameters. Such a technique leads to the hypothesis that adequate QA for pyrocarbon coatings on nuclear fuel particles can be achieved with only -

i a validated automically controlled coating process;

ii a weighing balance;

iii a validated optical particle size analyser;

iv a validated method of measuring structure.

The work outlined here has shown that structure (expressed as the size of spherical growth features), is a controllable parameter related to particle endurance but more work is necessary to achieve an automatic measuring method.

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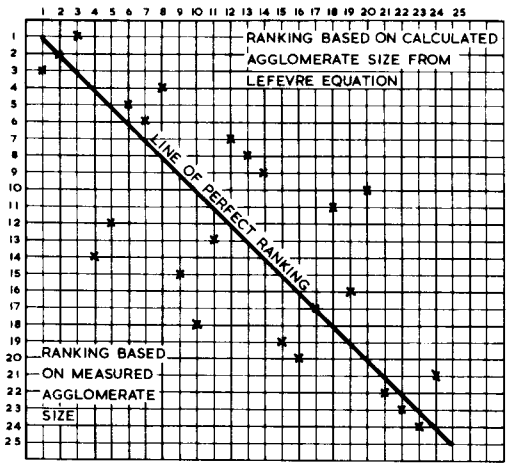

Fig. 1 - Comparison of Ranking Between Calculated SGF Size and Observed Coarseness of Structure in a Photomicrograph of a Polished Section.

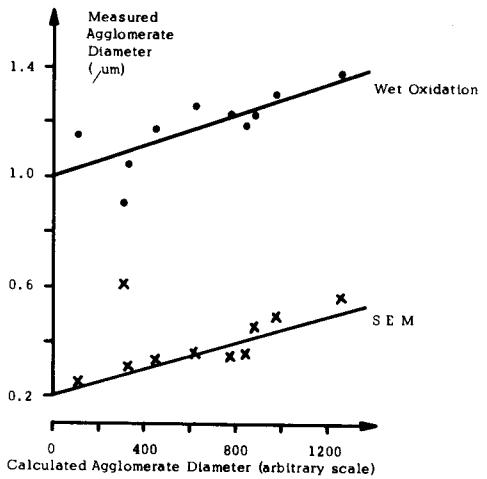

Fig. 2 - Regression of the Mean SGF Size Measured on 'Wet Oxidation' and SEM Photomicrographs on the Predicted Values.

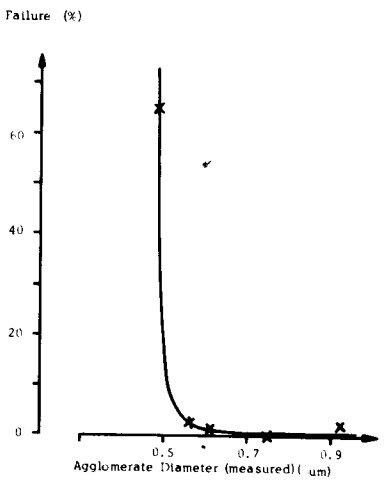

Fig. 3 Particle Failure in HTR 4 Experiment Versus Measured SGF Diameter.