CONCLUDING REMARKS: COATED PARTICLE FUELS

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FUELS

KEYWORDS: *coated fuel particles, reviews, fission product release, fabrication, coatings, performance, HTGR-type reactors, pyrolytic carbon, silicon carbides*

Received April 14, 1977
Accepted for Publication April 15, 1977

INTRODUCTION

In this final paper in the special issue of *Nuclear Technology* on Coated Particle Fuels, some of the highlights of the contributed papers are discussed in an attempt to put the current state of the technology in perspective and to indicate directions for future work.

For convenience, this special issue has been structured around five categories of research and development:

1. Coated Particle Fabrication
2. Properties and Characterization of Pyrocarbon (PyC) and Silicon Carbide (SiC) Coatings
3. Fuel Performance and Performance Modeling
4. Fission Product Release
5. Advanced and Improved Fuels and Applications.

However, there is substantial interaction among these various areas. Minimum fission product release consistent with reactor design requirements is the ultimate goal of nearly all coated particle research. Not only high reliability but also a high degree of predictability of coated particle performance in service is essential if this goal is to be met. Accurate and verified fuel performance models provide a vehicle for demonstrating by design that fuel performance and fission product release criteria will be met. However, efficient and reliable fuel fabrication processes, combined with rigid quality inspection procedures and quality assurance programs, and a detailed understanding of the coating materials are required to ensure that the fuel product actually performs as the models predict.

COATED PARTICLE FABRICATION

To ensure the performance of current and future high-temperature gas-cooled reactor (HTR) systems from the standpoint of safety, reliability, and economics, it is necessary to rely not only on proper materials selection and design but also on the production of a consistently high quality product. The fabrication of coated particles involves two distinct production phases:

1. the production of the fissile and fertile kernels
2. the deposition of PyC and SiC coatings.

Several proven large-scale processes are currently available for the production of kernels. The various desired densities of oxide, carbide, and oxycarbide kernels can be produced by powder-metallurgical techniques (Allen et al., p. 246) or by wet chemical processes (Huschka and Vygen, p. 238). An innovative fissile fuel kernel has been developed at Oak Ridge National Laboratory to meet the restrictions of material handling in a remote recycle fuel fabrication facility. Microspheres of weak acid ion-exchange resins (WAR) can be loaded directly with uranyl ions. Weber et al. (p. 217) describe the state of the art and the potential of the WAR process based on their experience with the acrylic acid-divinylbenzene copolymers. They emphasize the versatility the WAR process provides in producing a product of tailored chemical and physical properties.

The PyC and SiC coatings are deposited on the kernels in fluidized-bed coating furnaces. Production coating furnaces up to 25 cm in diameter are in use today in which the fluidizing gas as well as the hydrocarbon gas is introduced into the furnace through cone-shaped, multiple cone, or flat plate distributors at the base of the furnace. Although coating layers can be routinely deposited

that meet the product specifications (Allen et al. and Huschka and Vygen), the deposition mechanisms, as well as the relationships between deposition conditions and the physical properties of the deposit, are not yet fully understood or generally accepted. To improve the quality and to ensure the reproducibility of coatings, extensive investigations are currently under way at various laboratories to further quantify the empirical relationships between deposition conditions and coating properties.

Innovations and new techniques are being employed that require modification to the coating furnaces which, in turn, modify the coating processes. Huschka and Vygen describe the "top reacting" process, which has led to a more homogeneous product. In this technique, the fluidizing gas is injected through the bottom and the hydrocarbon gas through the top of the coating furnace. Lackey et al. (p. 227) describe the improvements in particle sphericity, coating thickness uniformity, PyC isotropy, and lower defective fractions in PyC and SiC layers through the use of a blind hole porous-frit gas distributor system.

The current highly automated, high-throughput fabrication processes represent a considerable advance over the small-scale batch processes used to manufacture fuel for the first prototype HTRs. At the same time, the uniformity and quality of both the kernels and the coatings are being substantially improved.

PROPERTIES AND CHARACTERIZATION OF PyC AND SiC COATINGS

In addition to basic studies concerning deposition mechanisms, the papers in this section deal with the relationship between the properties of coating layers and quality control and quality assurance techniques. Linke et al. (p. 257) developed a mathematical model that describes the deposition process and the structure of the deposited PyC. According to the authors, high molecular weight hydrocarbon species originate in the gas phase and act as nucleation sites for agglomeration. The deposition of the agglomerates results in the PyC layer. The morphology of the basic unit of PyC (the agglomerate), as well as its size and properties, is a function of the deposition parameters. The deposition of individual carbon atoms is also possible, according to the model, under very special conditions.

The simplified deposition model and comparison of agglomerate size with irradiation behavior, described in the paper by Lefevre and Price (p. 263), are a slightly different approach to the subject of modeling PyC deposition. Although the evolution of their model involves many simplifications and the evaluation of agglomerate size is somewhat subjective, the relationship between a measured structural parameter and the coating irradiation performance appears quite promising.

The paper by Wallisch and Koss (p. 279) is an excellent contribution to the subject of quality control and assurance. The use of a rapid optical data collection system permits the determination of particle diameters in the range from 100 to 1500 μm with an accuracy of better than ± 2 μm and a capacity of 100 particles per second. The particle analyzer fulfills the need for a fast and precise routine characterization method to determine whether a batch of particles meets the product specifications for size and sphericity. This type of equipment is currently in use in HTR industrial and research centers.

Transmission electron microscopy (TEM) studies have shown that PyC layers are a composite of several substructures. Pollman et al. (p. 301) report on the state-of-the-art of TEM analysis and the characteristics of the microstructure of PyC. Three different microstructural features—referred to as mosaic, fiber, and layered components—can occur in PyC. The distribution of each of the components determines the shape, size, and microstructure of basic units of PyC. These basic units of PyC, called growth features, are strongly dependent upon the deposition parameters. Interrelationships among the concentration and distribution of these components and many of the physical properties of PyC have been established. The continued use of such sensitive characterization methods should not only improve the understanding of the microstructure, but also should provide more insight into the influence of deposition conditions, the resultant physical properties, and the subsequent irradiation behavior of PyC.

The Note by Morgan and Powell (p. 337) points out an important aspect of PyC behavior that has recently received increased attention, that of permeability to gases. To produce the highly isotropic PyC's that are desirable from the standpoint of irradiation performance, high deposition rates are generally used. However, high deposition rates tend to produce coatings with interconnected porosity, which in turn leads to high permeability. Consequently the deposition conditions for PyC must be carefully controlled to produce the combination of properties required for successful coated particle performance.

Silicon carbide (β-SiC) is used as an intermediate layer in Triso coatings as a barrier to such metallic fission products as strontium, cesium, and silver. Extensive investigations have been performed at various research laboratories

to study the deposition of β-SiC from the thermal decomposition of organo-silane compounds. These studies have encompassed the physical and chemical properties of SiC, before and after irradiation, and the retention properties for various fission products. Price (p. 320) presents a critical discussion and a comprehensive survey of the data that have appeared in literature on SiC.

It is evident from this series of papers that the complexity of PyC and its unique structure and properties continue to make it a prime subject for investigation. The directions of current work are toward improving the understanding of the complex relationships among PyC deposition, structure, properties, and irradiation behavior, and toward the development of improved techniques for characterization of coating quality.

FUEL PERFORMANCE AND PERFORMANCE MODELING

The importance of PyC anisotropy in coated particle performance is graphically illustrated in the paper by Harmon and Scott (p. 343). They show a sharp increase in coating failure above a certain critical value of anisotropy, which in turn they relate to the PyC coating rate. The importance of this work to the development of fuels with improved temperature capability is underscored by the observation that the critical anisotropy value for coating survival decreases with increasing irradiation temperature.

That mechanical integrity is not the only important aspect of the performance of PyC coatings is emphasized in the paper on neutron-induced permeability of Biso coatings by Bradley and Thiele (p. 353). It is pointed out that structural changes that occur during irradiation can lead to increases in the permeability of coatings for fission gases. On the other hand, data reported by Scott and Harmon demonstrate that Biso coatings with PyC properties lying within a narrowly defined band survive irradiation exposures well beyond current HTR design maxima with no increase in permeability. It is clear that the complex relationships among deposition processes, properties, and performance of PyC are not yet completely understood. Even though the properties and deposition conditions of PyC can be specified to ensure adequate irradiation performance, these specifications cannot always be directly transplanted to another laboratory with different equipment, procedures, and analytical techniques. Further work in this area is needed to fully define the materials properties that lead to neutron-induced permeability.

Although the various coated particle stress analysis models have been widely, and quite successfully, used for ~10 years, it has been recognized that they have some significant limitations. Probably the most significant is the assumption that irradiation-induced dimensional changes and creep of PyC are independent of each other. It has been known for some time that irradiation-induced creep strain results in increases in coating anisotropy, and consequently in increases in irradiation-induced dimensional change rates. However, the coated particle stress analysis models were not capable of treating this interaction.

In the first paper of the pair on mechanical behavior of Biso particles, Kaae (p. 359) presents a set of data that, for the first time, allows the inclusion of changes in anisotropy due to irradiation-induced creep in the calculation of stresses in particle coatings. Crystallite averaging techniques are used to approximate the experimental dimensional change data in the calculations. A second significant advance presented in this paper is the application of Weibull analysis to calculate the probability of failure of the particle coatings. Previous performance predictions have used the simplifying assumption of a unique failure stress for the particle coatings.

Although the revisions to the coated particle stress analysis models are physically realistic, the proof of the value of this or any other complex model can only come through experimental verification. Fortunately, although it is not possible to directly measure coating stresses, the irradiation-induced changes in diameter of Biso coatings provide an experimentally convenient way to check the model predictions. In Part II of the paper (p. 368), Kaae and co-workers demonstrate that the form of the dimensional change curve as a function of fast fluence is well predicted by the revised model. The magnitude of the dimensional changes is also very consistent with predictions in most but not all cases. The new model represents a significant advance in the prediction of coated particle performance in that it allows the extrapolation of performance data over fluence. The various models now include all known physical processes that influence fuel performance. With further improvements in input data and further verification of the models with irradiation test results, the goal of coated particle performance predictions from first principles should be achievable.

Although the precise mechanisms controlling the amoeba effect in coated oxide fuel particles are not known, it is widely accepted that the presence of CO is a prerequisite for the process to occur. In the paper by Strigl and Proksch (p. 386), it is shown that the equilibria involving CO are more complex than had previously been

recognized. It is suggested that local equilibria, controlled by kinetic processes involving fission product redistribution, may control the CO pressure in coated particles. Additional work in this area is very desirable as a means of elucidating the mechanism of the amoeba effect in oxide fuels.

The papers on amoeba migration emphasize the behavior of coated oxide particles, which is less well understood than that in carbides. In the paper by Wagner-Löffler (p. 392), the available data and the various proposed mechanisms for amoeba migration in UO_2 are reviewed. Although the mechanism cannot yet be unambiguously determined, it is demonstrated that semi-empirical correlations are adequate to predict fuel performance under reactor conditions.

The mechanism of the amoeba effect in ThO_2 appears to be different than that for UO_2. The microstructural evidence presented by Smith (p. 403) shows that solid-state diffusion is definitely involved in the amoeba effect in ThO_2. The large temperature dependence of the process, comparable to that for the amoeba effect in carbide coated particle fuels, is also suggestive of a solid-state process. On the other hand, the dependence of the process on burnup suggests that the presence of CO is a requirement for the amoeba effect to occur in ThO_2 coated particles. Regardless of the details of the mechanism, the data provided by Smith on the kinetics of the initiation of migration provide a firm basis for reactor design calculations.

The vast range of empirical data on amoeba migration in coated oxide fuel particles provides one of the primary bases for the thermal design of HTR cores. Current design philosophies are to minimize or eliminate failure due to the amoeba effect. As fuel temperatures are increased in advanced HTR designs, detailed understanding of the mechanism and kinetics of amoeba migration in oxide fuels will become even more important. In particular, a better understanding of the controlling mechanisms might reveal ways in which amoeba migration can be reduced or eliminated.

Reactions between fission products and the SiC coating in Triso particles can be a limiting factor in performance under some circumstances. The nature of the reaction and the degree of reaction are highly dependent on the kernel type. In low-enriched oxide and carbide kernels, reactions involving the palladium-group metals (palladium, ruthenium, and rhodium) have been observed. These reactions are only significant when plutonium fission is important. The yield of the palladium-group metals is less from fission of ^{233}U and ^{235}U, so this reaction is not a significant factor in thorium-cycle fuel.

The lanthanide-group fission products (lanthanum, praseodymium, cerium, and neodymium) also have a strong tendency to react with the SiC coating. These elements form relatively stable oxides and tend to be retained in the kernel of coated oxide particles so that reactions with the coatings do not occur. However, these metals are quite mobile in coated carbide particles and can readily react with the coatings at elevated temperatures. This reaction is of particular significance in the fully enriched UC_2 fissile particle in separable thorium-cycle fuel, where it can be the limiting phenomenon under high-temperature accident conditions. Some of the available data on these reactions are discussed in the paper by Grübmeier et al. (p. 413).

The WAR kernel has been adopted for the reference recycle fissile particle in the U.S. program because it is particularly amenable to remote fabrication in a hot-cell facility. The influence of stoichiometry on the performance of fissile kernels derived from WAR beads is discussed in the paper by Homan and co-workers (p. 428). The authors show that oxycarbide kernels with the proper stoichiometry provide many of the best performance features of both oxide and carbide fuels. The oxygen chemical potential is high enough to immobilize the lanthanide-group fission products as oxides in the kernel, thus eliminating fission product-SiC reactions as a limitation on performance. The amoeba effect, which is a limiting factor for oxide fuels under certain conditions, has also not been observed in WAR-derived fissile kernels with a significant fraction of the carbide phase. The absence of the amoeba effect may be due to the high porosity and high carbon content of the kernel and/or to the low oxygen potential relative to oxide kernels. This type of fuel offers considerable promise for improving the temperature capability of the fissile particle for advanced HTR systems, as well as for further improving performance margins for the Steam-Cycle HTR.

The final verification of the fuel performance models, and of fuel specifications, is derived from carefully designed experiments in Materials Test Reactors, and eventually from large-scale tests in operating HTRs. The results of an in-pile verification test of production fuel for the Fort St. Vrain HTR are reported in the final paper in this section by Scott and Harmon (p. 442). Results of the test are compared with fuel performance criteria, and it is demonstrated that in-service fuel performance requirements will be satisfied.

FISSION PRODUCT RELEASE

The release of both metallic and gaseous fission products is well covered in papers in this

special issue. Much of the work on metallic fission product release has concentrated on cesium because its high gamma-ray activity and long half-life give it prime importance in determining exposure to personnel during many maintenance operations. Release of cesium into the primary circuit has a relatively large degree of uncertainty due, to a large extent, to uncertainties in cesium retention in the fuel kernels, diffusion through PyC coatings on Biso particles, and transport through graphite ligaments. (The last is outside the scope of this special issue.) Cesium release is discussed in the first two papers in the section on fission product release.

Diffusion of fission products in the PyC coatings is one of the most important factors affecting metallic fission product release from Biso-coated particles. Diffusion coefficients for PyC have been obtained using standard diffusion couple techniques. However, it is difficult to relate data obtained in this manner to the behavior of coated particles in reactor. Consequently, there has been a tendency to derive diffusion coefficients from fission product release data obtained during annealing studies of irradiated coated particles. In this type of test, in-pile conditions are closely simulated, but the analysis of the data can be quite complex.

Morgan and Malinauskas (p. 457) make the simplifying assumption that cesium release is controlled entirely by the coating in analyzing their postirradiation annealing tests on Biso-coated particles. They show that source depletion and diffusion in the kernel can potentially introduce significant errors in the results. However, the good agreement between their results and previous data obtained from other sources using other techniques indicates that carefully performed experiments of this type can yield very reliable data. The results reported by Morgan and Malinauskas show the now well-established structure dependence for cesium diffusion in PyC, with high-temperature isotropic (HTI) coatings being significantly more retentive than low-temperature isotropic (LTI) carbons.

Cesium diffusion in PyC is now fairly well defined. The role of the fuel kernel, particularly oxide kernels, has become the most uncertain factor influencing cesium release from coated particle fuels. Oxide fuel kernels are known to provide significant retention of cesium at normal HTR operating temperatures and at low burnups. However, the mechanism of retention and the kinetics of release from oxide kernels are not yet well established. The data reported by Stöver and Hecker (p. 465) show very small diffusion coefficients for cesium in $(Th,U)O_2$ kernels at burnups <2.5% FIMA, and much higher diffusivities for burnups >5% FIMA. This abrupt change in kernel retention is perhaps not surprising in view of the structural changes that occur in kernels with increased burnup.

The analysis of postirradiation annealing tests in the regime in which kernel retention is important becomes quite complex. In the paper by Smith et al. (p. 475), a new calculational tool, the COPAR model, is presented. This code allows much more exact analysis of postirradiation annealing tests, as well as more exact reactor release calculations, including the effects of kernel diffusion, source depletion, partition between the various components, and fission recoil effects. The precise use of this type of model requires considerably more basic materials data than are available at the present time. However, with improved data and refinement and experimental verification of the model, the COPAR code should eventually contribute to the precise predictions of fission product release that are desirable for advanced HTR designs. In the meantime, the COPAR code is being used to analyze simplified problems such as metallic fission product release from bare fuel kernels.

Although ^{110m}Ag has a much smaller fission yield and a shorter half-life than ^{134}Cs and ^{137}Cs, it can be a significant contributor to personnel doses in certain maintenance operations. Silver release is of more significance in the low-enriched uranium fuel cycle than in the thorium fuel cycle because of a substantially higher fission yield. Silver is unique in that its oxide is unstable at high temperatures, and it has a very high diffusivity in PyC.

The circulating activity in the helium primary coolant of the HTR is determined primarily by release of fission gases from exposed fuel, including the very small fraction of fuel that is expected to fail in service. The relatively short-lived fission product gases such as ^{88}Kr, ^{133}Xe, and ^{133}I are of particular importance in determining whole-body and thyroid doses during postulated accidents as well as in determining environmental exposures, while the long-lived fission gases such as ^{85}Kr can become important in specialized cases such as rupture of radioactive waste storage tanks.

The state of understanding of gaseous fission product release is well described in the papers by Pointud and Chenebault (p. 494) and by Myers et al. (p. 501). The importance of fission recoil, diffusion, and radioactive decay is emphasized in both papers. In general, the fission gas release values reported in the two papers are in good agreement. However, Pointud and Chenebault show that porosity and burnup tend to degrade fission gas retention for relatively low burnup

oxide fuel kernels (<7% FIMA). In contrast, the paper by Myers et al. shows little burnup dependence for the release of short-lived fission gases up to 63% FIMA for fully enriched UC_2 kernels. This apparent disagreement very likely results from differences in kernel structure. Porosity resulting from the interconnection of fission gas bubbles would be expected to have a significant effect on the surface-to-volume ratio of the fuel kernel and consequently on its fission gas release (primarily through the effect on recoil release). It has also been reported that the highly porous WAR-derived fuel kernels have a substantially higher fission gas release than that of dense kernels for this same reason. Future studies in this area should include kernel structure as a primary variable.

The release paths for both gaseous and metallic fission products are complex, and the uncertainty in release predictions can be large due to compounding of the uncertainties in the various differential release steps. Consequently, verification of the data and methods for fission product release predictions by means of well-designed integral tests and by analysis of reactor operating data is necessary to verify release models and to reduce uncertainty in release predictions. In the papers by Groos et al. (p. 509) and by Röllig (p. 516), the release of gaseous and metallic fission products in irradiation tests of spherical fuel elements is analyzed. Release values were generally quite consistent with what would be predicted from smaller scale differential tests. However, it is noteworthy that the difference in cesium retention for HTI and LTI PyC coatings could not be detected. This is very likely due to the relatively large uncertainties inherent in experiments of this type that are not specifically designed to yield fission product release data. Although these results give added confidence in release predictions, it is difficult to derive quantitative data from them, particularly for metallic fission product release.

Work is currently in progress at a number of laboratories to verify fission product release predictions. This is being done through in-pile loop experiments and through analysis of operating and decommissioned reactors. An essential feature of experiments to verify metallic fission product release predictions is a means of obtaining a complete inventory of fission products to minimize the uncertainty inherent in dealing with small fractional release values.

Differential data on fission product release are, in general, fairly well understood. It is in the area of verification of release predictions that the most important advances are expected to be made in the next few years. This is particularly important for advanced HTR applications where substantial benefits can be gained from reduced or more predictable fission product release.

ADVANCED AND IMPROVED FUELS AND APPLICATIONS

The development of improved coated particle fuels is proceeding along two fronts: improved coatings and improved kernels. The paper by Hollabaugh et al. (p. 527) describes the chemical vapor deposition of ZrC coatings on fuel particles. ZrC as a replacement for SiC in Triso particles offers the potential for increased temperature capability resulting from a reduced tendency for detrimental fission product coating reactions. Zirconium is a high-yield fission product and is present in substantial quantities in all irradiated fuel kernels, but no detrimental reactions involving zirconium have been observed. However, before these coatings can be considered for use in advanced HTR systems, their ability to retain important metallic fission products such as cesium, silver, and strontium must be demonstrated. Irradiation tests currently in progress should answer this important question.

A different approach to improved coatings, the use of co-deposited two-phase mixtures of PyC and SiC, is described in the paper by Kaae et al. (p. 536). With their higher strength, improved dimensional stability under irradiation, and reduced cesium diffusivity (relative to pure PyC), these coatings offer a potentially attractive and considerably simplified substitute for Triso coatings. The area in which they perhaps hold most promise is in the reduction of coating thickness relative to current Biso particle designs. This will allow the use of higher thorium loadings and result in higher conversion ratios in thorium-cycle HTRs. Conversion ratios approaching unity are feasible with current HTR designs if coating thicknesses can be reduced sufficiently.

The ultimate means of improving metallic fission product retention is to tie them up chemically in the kernel. In this way, fission products can be retained in failed particles as well as in intact Biso particles. In the paper by Förthmann et al. (p. 548), it is shown that the addition of alumina and silica is very effective in improving the retention of strontium and barium even in particles with failed coatings. Cesium is also retained in kernels with alumina-silica additives at normal reactor operating temperatures. However, the additives become ineffective at temperatures of ~1400°C (1673 K), apparently due to the limited stability of cesium aluminum silicate compounds.

The ultimate success of this method of improving fission product retention will rest not only on a confirmation of significantly improved retention of cesium relative to undoped oxide kernels, but on demonstration of adequate long-term performance of the coated particles under realistic reactor conditions. However, work to date is encouraging, and it seems clear that the retention of at least some of the important fission products can be improved at the source: the fuel kernel.

The coated particle concept provides great flexibility for future improvement. Although not covered in this special issue, some very promising work on oxygen getters to reduce the amoeba effect in coated oxide particles has been performed under Dragon Project auspices. Limited work has also been performed on nitride kernels and nitride additives to kernels.

With the broad-based development efforts that have been performed, the development of fuels that will have both improved temperature capability and reduced fission product release seems nearly a certainty. This will in turn allow continued improvements in the design of advanced HTRs.