INERT GAS PERMEABILITY OF PYROCARBON COATINGS*

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Pyrocarbon coatings are used to retain fission products produced in thorium- or uranium-containing kernels during irradiation of fuel particles in gas-cooled reactors. The extent of inert gas permeability of pyrocarbon coatings, which can be varied extensively by adjusting deposition parameters, is important for this purpose. Permeability values may bear a correlation with other pyrocarbon properties such as strength, density, crystal structure, or growth feature size. Thus, inert gas permeability measurements can be useful in evaluating pyrocarbon coating techniques.

Gas contents of fuel particles have been measured by cracking the particle in a chamber connected to a mass spectrometer by Bildstein and Strigl[1] and Clough *et al.*[2] This method afforded a measure of internal pressure when the volume occupied by the gas was estimated from geometrical measurements. Lindemer and Pearson have obtained similar results without use of a mass spectrometer.[3] In the present work the high-temperature inert gas permeabilities of the pryocarbon coatings of HTGR Biso fuel particles have been measured. Fuel particles were annealed in an atmosphere of the inert gas or gases, then broken individually in a dynamically pumped chamber containing a mass spectrometer and the inert gas pressure transient was monitored and integrated. The mass spectrometer was calibrated using known amounts of gas and was sensitive to 1×10^{-14} mol of an inert gas. The composition of gas evolving from the fuel particle could be determined qualitatively by operating the mass spectrometer in a scanning mode or an individual gas could be determined quantitatively by monitoring a single mass number. The particle crushing gas measurement technique and data on helium permeability of Biso fuel particles have been previously reported.[4]

Extensive measurements of helium permeability of the pyrocarbon coating were made on one fairly typical batch of fuel particles (OR 2261-T). Process helium was first removed from these fuel particles by a vacuum anneal for 1 hr at 1800°C.[4] Lots of fuel particles were then annealed under isothermal and isobaric conditions for fixed time intervals. Twenty samples from each lot were analyzed individually to determine the average helium content. Results for samples exposed to 98 kPa He under isothermal conditions at either 450, 550, 650, 750, 850, 1000, 1200, or 1425°C for various time intervals were used to construct permeation isotherms. An inflection in the permeation curve at early times characteristic of a nonsteady state diffusion process was observed.[5] At long times the helium content data approach a saturation value at a rate that is first order. Empirically, the asymptotic gas content, n_∞, is dependent on the absolute temperature according to

$$n_\infty = 3.95 \times 10^{-7}/T \text{ mol He/particle} \qquad (1)$$

in agreement with the perfect gas law. The coefficient in Eq. (1) yields a standard deviation of 4% indicating that samples of 20 particles are adequate. The helium permeation curves had essentially the same shape at all temperatures. All isotherms were well fitted by first-order kinetic equations beyond the point of inflection. The inverse of the calculated characteristic time (*i.e.*, the permeation coefficient) was found to obey

$$k_{He} = 43.6 \exp\{-14175/T\} \text{ sec}^{-1} \qquad (2)$$

where the standard deviation of the pre-exponential term is 5.5 sec^{-1} and 122 K for the activation temperature. Equation (2) indicates an activation energy for permeation of 118 kJ mol^{-1} (28 kcal mol^{-1})

A solution to the mathematical aspects of the problem of transient diffusion through a spherical shell into a finite reservoir has been developed by Reeves and Tolliver[6] and will be used for a more rigorous evaluation of the permeation isotherm data.[5]

Pyrocarbon coatings are permeable to neon and the preliminary rate constant data from permeation isotherms at 850 to 1500°C for batch OR 2261-T could be expressed as Eq. (3)

$$k_{Ne} = 21.8 \exp\{-20264/T\} \text{ sec}^{-1} \qquad (3)$$

indicating an activation energy for permeation of 166 kJ mol^{-1} (40 kcal mol^{-1}). At 1000°C the neon content was a linear function of neon pressure for 48-hr anneals. Insufficient data were available to give a reliable standard deviation, but the saturation neon content at 1000 and 1200°C agrees well with Eq. (1). As $T \to \infty$, $k_{He}/k_{Ne} = 2.0$. If the permeation rates were inversely related to the square root of the molecular weights of the permeating species, k_{He}/k_{Ne} would have the value 2.2.

Inert gas permeabilities of the pyrocarbon coatings of many fuel particle preparations were screened using a dual-gas technique. The fuel particles were annealed at 1375°C for 1 hr in a 96 kPa atmosphere composed of He–50% Ne. The gas content of the particles was determined individually, one gas at a time. Usually 15 particles were broken for the determination of each gas and the results averaged. The ratio of moles neon:helium in the fuel particle represents a measure of the permeability which is relatively independent of particle size. Also, the use of two gases enables differentiation between a very impermeable compact and one which is so highly permeable that the gases leak out before the particle is broken. The permeability values obtained for selected fuel particle batches are given in Table I along with standard deviations determined from the measurements. Table I also contains deposition conditions and geometric parameters of the pyrocarbon coatings. The results show that pyrocarbon coating permeability

*Research sponsored by the U.S. Energy Research and Development Administration under contract with the Union Carbide Corporation.

Table I. Pyrocarbon Coating Permeabilities

Batch Number	Gas Content[a] (moles·particle^{-1} × 10^{10})		Ratio Ne/He	Particle Geometry, μm		Deposition Conditions		
	Helium	Neon		Diameter	LTI Thickness	Temperature (°C)	Gas[b] Composition (mol %)	Coating Rate (μm·sec^{-1})
OR-1978-T	0.66±0.03	0.02±0.003	0.03	819	84	1240	50 propylene	0.013
OR-2263-T	1.51±0.17	0.19±0.03	0.13	874	91	1325	25 MAPP[c]	0.060
OR-2276-T	1.95±0.39	0.25±0.02	0.13	865	85	1275	15 MAPP	0.052
OR-2262-T	1.66±0.38	0.33±0.04	0.20	872	85	1275	50 MAPP	0.108
OR-2261-T	1.62±0.39	0.38±0.04	0.23	875	89	1325	50 MAPP	0.123
OR-2265-T	1.67±0.24	0.54±0.10	0.32	888	94	1325	100 MAPP	0.262
OR-2269-T	1.81±0.32	0.74±0.10	0.41	847	81	1325	50 MAPP	0.208
OR-2274-T	2.03±0.31	1.02±0.16	0.50	889	91	1325	100 MAPP	0.465

[a]Immersed 1 hr at 1375°C in Ne–50% He at 720 torr. [b]Remaining gas component argon.

[c]MAPP gas is marketed by Airco, Inc., and consists primarily of methylacetylene and propadiene with alkanes as stabilizers.

increases with increasing rate of deposition and, to a lesser extent, with increasing deposition temperature.

Void volumes obtained from helium content data are in good agreement with values obtained by mercury porosimetry at a pressure of 103 MPa on cracked fuel particles, *e.g.*,

Batch Number	Volume, m^3 per fuel particle	
	By Helium Content	By Mercury Porosimetry
	× 10^{-11}	× 10^{-11}
OR-2013-T	1.70	1.77
OR-1972-T	1.54	1.59
OR-2010-T	4.25	4.14

The extent of void volume present in small pores not opened when the pyrocarbon coating is cracked has not been determined.

Tests of the permeability of pyrocarbon coatings for higher molecular weight inert gases were initiated using argon. Significant argon permeability at 1800°C was evident only in more permeable pyrocarbon coatings such as in batch OR-2274-T. Argon permeability was unmeasurably low in pyrocarbon coatings with typical Ne/He ratios. In these fuel particles process argon remaining from preparation was not removed by 4-hr vacuum anneal at 1800°C. The decrease in permeability in the He, Ne, Ar series indicates that typical, unirradiated, uncracked pyrocarbon coatings have no measurable permeability to krypton or xenon at 1800°C.

The permeability of irradiated fuel particles with inert kernels measured on two batches is shown in Table II. The permeability decreases with small doses of radiation but increases sharply with fluence approaching HTGR design. The significance of irradiation temperature is not clearly defined from this limited number of tests.

The extensive variation of permeability with pyrocarbon preparation may indicate that defects in the coating are important rather than lattice spacing. The sharp increase of permeability with higher fluences shows that structural defects resulting from the neutron bombardment increase permeability.

Table II. Permeability of Irradiated Inert Fuel Particles

Batch Number	Fluence (neutrons/m^2) (E > 0.18 MeV)	Design Temperature (°C)	Ne/He
	× 10^{25}		
OR-2294-T	0		0.22
OR-2294-T	4.0	950	0.12
OR-2291-T	0		0.27
OR-2291-T	3.5	900	0.23
OR-2291-T	7.5	1250	0.89
OR-2291-T	8.6	1250	1.26

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