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FABRICATION OF BERYLLIA–COATED, FUELLED BERYLLIA SPHERES

FOR IN–PILE FISSION PRODUCT RELEASE TESTS

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ABSTRACT

Three sets of beryllia–coated fuelled beryllia spheres were made for fission product release testing in a sweep capsule irradiation rig. Results of various pre–irradiation tests are presented and discussed, and a summary of fission gas release results is included. Gas release rates were expected to vary inversely as the beryllia density. However, the release rate was lowest for the loading with an intermediate density and was highest for that with the highest density. One or more of several structural factors may have changed the behaviour from that expected.

CONTENTS

CONTENTS (Continued)

INTRODUCTION

This report describes the fabrication and pre-irradiation examination of BeO-coated, (UTh)O_2-fuelled BeO spheres prepared for irradiation in a sweep capsule fission product release rig (X124). The rig operates at temperatures between 500°C and 900°C and the activity of the CO_2 sweep gas for each sphere loading is analysed continuously for two to three months. The burnup reached depends on the enrichment of the uranium (so far, 0.7-20 per cent. U235), but has not been above 6×10^{19} fissions/cm^3 in the fuel particles.

It was intended that the main material variable of the three sets of specimens whose fabrication and properties are to be described would be BeO density. It was expected that at constant temperature, burnup, etc., the fission gas release rate from all fuel particles would be the same, with a lower but variable release rate from the spheres because of hold-up by the matrix and coating. The magnitude of this "matrix effect" would depend on the permeability of the BeO. The relationship between permeability coefficient and density for one grade of BeO has been determined (Clare 1966). Briefly, the total permeability coefficient K falls sharply from 10^{-8} cm^2/sec at a BeO density of 95 per cent. theoretical to 10^{-12} cm^2/sec at 97 per cent. theoretical, and cannot be measured with available apparatus at higher densities (Figure 1). The fission product release experiments covered BeO densities in the range 96.5 - 98.5 per cent. theoretical, that is, an expected permeability coefficient range of 10^{-12} to about 10^{-15} cm^2/sec.

However, between the first two and the third loadings the fuel particles differed in enrichment, fabrication method, grain size and density. The higher density of loading-3 fuel particles was expected to be beneficial in reducing the release rate from the spheres. It now appears that this assumption may not have been justified (Hanna, private communication, Table 6) and that the difference in fuel particle density and fabrication method between loading 3 and the earlier ones may have been an important material variable with an effect not fully understood.

The general specifications are given in Table 1. The specified BeO density increased with each loading, and in the third, the 20 per cent uranium enrichment was introduced to improve counting sensitivity. This enrichment

also increased the fission rate, burnup achieved, release rate from the spheres, and fission product concentration in the spheres, but it was expected that the effects of these changes would either be small or be readily accounted for.

2. FABRICATION AND TESTING OF FUEL PARTICLES

The fuel particles were prepared from a fine, intimate mixture of ammonium diuranate $(NH_4)_2 U_2O_7$ and thorium hydroxide $Th(OH)_4$, obtained by co-precipitation from uranyl nitrate-thorium nitrate solution using concentrated ammonia. An analysis of this material as used for X124-3 is given in Table 2. X124-1 and 2 material was analysed in the form of sintered particles only.

2.1 X124-1 and X124-2

Fuel particles for these two loadings were prepared as one batch. The precipitate was wet ground for 2 hours in a rotary mill with BeO grinding cylinders to reduce the mean crystallite size to < 10μ. The ground precipitate was then air dried at 85°C for 24 hours. The dried powder was calcined in hydrogen at 700°C for 2 hours, wet ground with alcohol and BeO grinding cylinders in a Turbula mill and air-dried at 85°C for 12 hours. The powder was isostatically pressed at 45,000 p.s.i., crushed, and sieved to collect the -60 + 85 (B.S.S.) mesh fraction. The particles were sintered in hydrogen for 2 hours at 1700°C.

2.2 X124-3

For X124-3 the precipitate was vacuum dried at 85°C for 24 hours and then dry ground for 4 hours with BeO grinding media in a polythene jar on a Turbula mixer to give a mean crystallite size in the precipitate of approximately 5μ. The ground powder was isostatically pressed at 45,000 p.s.i., crushed, and sieved to collect the -52 + 60 mesh fraction. This size range was larger than for X124-1 and X124-2 because the green density was lower and the sintering shrinkage higher. The particle yield was 12-15 per cent. Sufficient material was processed to produce the required weight of particles without recycling the -60 mesh fraction. The particles were sintered in hydrogen for $3\frac{1}{2}$ hours at 1650-1700°C.

2.3 Tests on Sintered Fuel Particles

Bulk densities of sintered fuel particles were measured by setting a measured weight of particles in Araldite and measuring the bulk density of

the composite specimen by water displacement. Measured densities were 9.3 - 9.5 g/cm^3 for X124-1 and X124-2 and 9.87 g/cm^3 for X124-3.

Photomicrographs of as-polished and as-etched fuel particles are shown in Figures 2 and 3. Measured grain sizes are given in Table 4.

X-ray diffraction lattice parameter measurements were made on sintered fuel particles, with the following results :

$$\text{X124-1 and X124-2} \quad : \quad a_o = 5.5863 \pm 0.0001 \text{ Å}$$
$$\text{X124-3} \quad : \quad a_o = 5.5859 \pm 0.0001 \text{ Å}$$

The X-ray patterns of both sets of particles were otherwise identical, showing only $(UTh)O_2$ lines. The implications of the slight a_o differences are discussed later.

3. FABRICATION OF BeO COATED FUELLED SPHERES

3.1 Sources of BeO

The beryllia powder used for X124-1 and X124-2 spheres was Brush UOX grade (-200 mesh) Lot 269. The beryllia used for X124-3 spheres was NGK-CF grade (-20 mesh) Lot 907-21. The properties of these two powders are significantly different and are given in Table 3.

3.2 Formation of Fuelled Core

The BeO powder was pre-compacted at 30,000 p.s.i. and granulated to -44 mesh before use. The required weights of fuel particles and beryllia for one fuelled "core" were shaken together in a plastic container and then placed in a latex tube, the ends being tied. The powder was lightly compacted by hand, the compact crushed, and the fragments re-mixed in the sealed tube. This compaction, crushing, and mixing was repeated up to eight times to ensure a uniform dispersion.

The mixture was then formed into a near spherical shape either in a steel die with concave-faced plungers (for X124-1 and X124-2, using approximately 100 p.s.i. forming pressure) or in the Duralon (polyurethane) container of a dry-bag isostatic press (for X124-3, using 3000 p.s.i. forming pressure). In each case the formed sphere was then sealed into an evacuated latex tube and pressed isostatically at 11,000 p.s.i.

The cores (at this stage approximately 1 inch in diameter) were machined to the required size and sphericity by hand machining. The spheres

were rotated by hand against a rotating diamond-impregnated trepanning drill (for roughing) or a sintered alumina tube (for finishing), held in a lathe or drill chuck.

3.3 Coating of Fuelled Core

The coating technique used for these and other irradiation specimens involved the use of a three-part Duralon die which contained a spherical cavity when fully assembled (Figure 4). A measured quantity of 30,000 p.s.i., -44 mesh BeO powder was placed in the hemispherical cavity of the mould base and formed into a shell with a hemispherical-faced tool, so that the internal radius of the shell conformed to that of the fuelled core. The core was placed in the shell and the upper hemispherical cavity of the mould was located around the core. BeO powder was then poured through the filler hole and vibrated to form the upper portion of the BeO shell around the fuelled core. The third section of the die (a plug) was then inserted and the complete die enveloped in a latex tube which was evacuated and sealed. The assembly was isostatically pressed at 45,000 p.s.i. The coated sphere was strong enough to be handled without damage.

3.4 Machining and Radiography

The coating technique did not accurately centralise the core within the sphere, nor was the pressed compact a perfect sphere. To improve concentricity and diametric tolerance, the pressed compact was first radiographed in two directions at right angles to show coating thickness variations. Using the radiograph as a guide the sphere was machined against an abrasive ring as before, and, after about 20 per cent. of the required material had been removed, was radiographed again. Machining followed by radiography was continued until the final size (allowing for sintering shrinkage) had been reached. The sphere was then re-pressed at 45,000 p.s.i. before sintering.

3.5 Sintering

Spheres for X124-1 and X124-2 were sintered in a Super-Kanthal muffle furnace. A flow of dry nitrogen was directed over the specimens which were placed in a large alumina crucible lying on its edge. X124-3 spheres were sintered in a platinum-rhodium wound tube furnace with a flow of dry nitrogen through the alumina tube. Other details are given in Table 4.

4. TESTS ON SINTERED SPHERES

The density, open porosity, concentricity, and microstructure of all spheres were examined before irradiation.

4.1 Density

The bulk densities (Table 5) were measured in two ways

(i) by water displacement, using the formula :

$$\text{Bulk Density} = \frac{W_a}{W_{sat} - W_{sus}} \quad ,$$

where W_a = weight of sample in air,

W_{sat} = weight of saturated sample in air, after vacuum "boiling", and

W_{sus} = weight of saturated sample suspended in water.

(ii) by accurately measuring and weighing, bulk density being the ratio of weight to volume.

There is a small discrepancy between the two values, the first method of measurement giving a higher value than the second. Method (i) was considered least accurate and was used only for in-process control. Only method (ii) densities are used in later discussion sections of this report.

The "impregnated" density was determined by vacuum-impregnation with, and suspension in, n-octanol. The formula :

$$\text{Impregnated density} = \frac{W_a \, d_e}{W_a - W_{sus}} \quad ,$$

where d_e is the density of the liquid, was used.

4.2 Open Porosity

The difference between the true density and bulk density (from (ii) above) was used to determine the open porosity of the spheres (Table 5). The occurrence of some negative values casts doubt on the significance of these porosity measurements. Sphericity of some spheres was poor and this could lead to small errors in bulk density measurement by method (ii) and hence errors in open porosity.

4.3 Concentricity

Each sphere was radiographed and the coating thickness was estimated at four points on each radiograph using a Nikon Shadowgraph. A typical radio-

graph is shown in Figure 5, and maximum and minimum measured values of coating thickness are given in Table 5.

4.4 Metallography

One sintered sphere from each series was cut across a diameter, mounted, polished, and etched to show the BeO grain size. Representative photomicrographs are shown in Figures 6 - 8.

Linear intercept grain sizes of fuel particles (determined from Figures 2 and 3 and assumed not to change during sintering in BeO) and of the BeO matrix and coating, are given in Table 4.

5. DISCUSSION

5.1 Fuel Particles

The higher density and larger grain size of X124-3 fuel particles compared with X124-1 and X124-2 was evident from the photomicrographs (Figures 2 and 3). In both materials, the grain size varied more widely between than within particles. Mean grain sizes within particles varied from 13 to 100μ for X124-3 and from 4 to 7μ for X124-1 and X124-2. BeO inclusions were present in X124-1 and X124-2 only (Figures 6a and 7a); these inclusions arose from abrasion of the BeO grinding media during wet milling.

Another feature of X124-3 was the more angular and less equiaxed particle shape. From Figures 2a and 3a, average values of the radio of perimeter to area were determined for all particles in each field. This ratio was higher for X124-3 by a factor of only 1.2. The surface area per unit volume would also be higher, probably in about the same ratio. This difference would have a very small effect on fission product release rates.

According to Cohen and Berman (1966) the lattice parameter of a ThO_2-rich solid solution $(U_y Th_{1-y})O_{2+x}$ varies with uranium and excess oxygen content according to the equation :

$$a_o = 5.5975 - 0.090\ x - 0.127\ y - 0.1\ xy .$$

Inserting observed values of a_o and y into this equation the following values are obtained:

For X124-1 and X124-2 $x = 0.002$.

For X124-3 $x = -0.002$.

Since these values are very close to zero, and since a negative value of x is meaningless, it must be concluded that both batches of fuel particles were stoichiometric in oxygen content within very close limits.

5.2 Microstructure of Fuelled Spheres

X124-1: The grain size of the BeO matrix was very variable $(4-100\mu)$ and much larger than that of the coating (3μ); high iron content in the fuel particles was at first thought to be the cause, but chemical analysis showed that the iron content was low. This feature is at present unexplained. The core-coating interface could be distinguished only by a change in grain size and by the absence of fuel particles in the coating. Both core and coating showed evidence of the commonly-observed needles, characteristic of Brush UOX powders. In the coating they appeared as grains up to 100μ long x 15μ wide; in the core there was evidence of residual needle outline inside much larger grains which had grown discontinuously. There was considerable intragranular porosity in the core BeO but in the coating the porosity was mainly intergranular.

X124-2: Grain sizes of the BeO in both core and coating $(8-100\mu)$ had probably been influenced by some impurity, possibly Al, in the fuel particles; the higher sintering temperature would allow the impurity to have a wider influence. Residual needles could be seen inside large BeO grains, and the porosity was mainly intragranular.

X124-3: The mean BeO grain size varied from about 4μ in some areas to 7μ in others with a mean of 5μ. This variation occurred in both core and coating which had the same BeO microstructure with no observable discontinuity. Porosity was mainly intergranular.

5.3 Density of Fuelled Spheres

The specification of progressively increasing BeO density from X124-1 to X124-3 with constant fuel particle density and microstructure was not achieved (Table 4). The change in fuel particle characteristics from the second to the third loading has already been discussed.

BeO matrix and coating densities could only be assessed by making the following assumptions :

(i) The BeO density was the same throughout

(ii) The fuel particle content of the core was exactly to specification.

(iii) The fuel particle density was known.

Fuel particle density was known most accurately for X124-3, where it measured as 9.87 g/cm^3.   Using the figure of 7.43 w/o of fuel particles in the core and an assumed BeO matrix and coating density of 98 per cent. theoretical (2.95 g/cm^3), a sphere density of 3.032 g/cm^3 was obtained, which was identical with the mean density (Table 4), and corresponds with a volume per centage of fuel particles of 2.34.

For X124-2, assuming a fuel particle density of 9.3 g/cm^3, the sphere density corresponding to a BeO density of 98 per cent. is 3.028 g/cm^3, and for 97 per cent., 2.997 g/cm^3, which was the mean density observed.   If the fuel particle density were higher than 9.3 g/cm^3, the BeO would be correspondingly less dense.

It is therefore certain that the BeO matrix and coating of X124-3 was about 1 per cent. more dense than that of X124-2.   X124-3 spheres also had the lowest measured open porosities, although the presence of "negative" values indicates that these measurements were of limited accuracy.

The coating and matrix were of different grain size and probably different density in X124-1.   The mean BeO matrix density was 0.4 per cent. higher than X124-2, and 0.6 per cent. lower than X124-3.

5.4 Concentricity of Core and Coating

The concentricity of core and coating, as shown for X124-3 in Table 4, was not good.   The difficulty in achieving concentricity arose from the small size of the spheres and the hand method of manufacture.   While the observed variation in coating thickness from 0.024 in. to 0.089 in. was undesirable, the minimum thickness was still much larger than required to prevent fission product escape by recoil, and if the permeability model is valid, these deviations should change the release rate from that expected for a 0.050 in. coating by a factor of 2 or less.   Since orders of magnitude differences in release rates between different types of spheres were expected, the variation in coating thickness was considered to be unimportant.

5.5 Expected and Actual Order of Fission Product Release

If (i) the permeability-density relationship determined for the batch of Brush UOX BeO is assumed to hold for NGK-CF BeO, (ii) fuel particle characteristics are assumed to be identical in the three loadings, and (iii) only mean

BeO densities are considered, the expected order of gas release rates would be :

$$X124-2 \quad > \quad X124-1 \quad > \quad X124-3 .$$

Actual results for each loading, expressed as $^R/B$ ratios for three to four Kr-Xe isotopes, are given in Table 6. (Hanna private communication). The observed order of release rates was :

$$X124-3 \quad > \quad X124-2 \quad > \quad X124-1 .$$

The structural factors which may have changed the simple picture presented above, in which X124-3 would be expected to have the lowest release rate, are :

(1) The effect of fuel particle density and grain size (X124-3 had the highest density and largest grain size).

(2) The high proportion of grain boundary porosity in the matrix and coating of X124-3, and in the coating of X124-1.

(3) Possible microcracking in the coarse-grained areas of X124-1 and X124-2.

(4) Permeabilities of the BeO matrix and coating may not be the rate-controlling factors under these conditions.

Further work is required to increase our understanding of factors affecting fission gas release rates from BeO-coated fuelled spheres, and so allow specification of fabrication conditions for spheres with greatly improved fission product retention properties.   This work will include short-term post-irradiation diffusion annealing experiments on $(U,Th)O_2$ particles and coated spheres covering a range of material variables, together with further X124-type in-pile experiments on promising materials.

7.   REFERENCES

Clare, T.E. (1966). - Gaseous flow through sintered beryllia. J. Aus.
        Ceram. Soc., in course of publication.

Cohen, I., and Berman, R.M. (1966). - J. Nucl. Mat. 18 : 77

TABLE 1

SPECIFICATION OF BeO COATED FUELLED BeO SPHERES

FOR

FISSION PRODUCT RELEASE EXPERIMENTS (X124)

	X124-1	X124-2	X124-3
Overall sphere diameter (in)	0.50	0.50	0.50
Thickness of unfuelled coating (in)	0.05	0.05	0.05
UO_2:ThO_2 mole ratio in fuel particles	1:10	1:10	1:10
Fuel particle diameter (μ)	150-200	150-200	150-200
Enrichment of uranium	Natural	Natural	20%
Volume per cent. of fuel particles in core (approx)	2.3	2.3	2.3
Weight per cent. of fuel particles in core (actual)	7.43	7.43	7.43
Density of BeO matrix and coating (% theoretical)	96-97	Higher than X124-1	98 (higher than X124-2)
Grain size of matrix and coating (μ)	< 5	No limit specified	< 10
Number of spheres for irradiation	4	4	4
Total number of spheres	9	6	6

TABLE 2

ANALYSIS OF FUEL MATERIAL

	X124-1 and 2 (Sintered Fuel Particles)	X124-3 (Co-precipitated Powder
UO_2 : ThO_2 mole ratio	1:10.5	1:9.8
Fe (p.p.m.)	20	35
Al	100	140
Ca	< 20	n.d
Mg	40	n.d
Total cations	n.d	210
Total halogens	n.d	< 40
Sulphur	n.d	300

TABLE 3

PHYSICAL PROPERTIES, ANALYSIS, AND SINTERABILITY OF BRUSH UOX AND NGK-CF GRADES OF BERYLLIA

A. Physical Properties

Powder	Surface Area (m^2/g)	Density (g/cm^3) Pour	Tap	Green (Pressed 20 ton/in^2)	Shape, Size and Agglomeration of Powder
UOX Lot 269	9.7	0.30	0.53	1.82	Loose aggregates of sub-micron crystallites plus acicular grains up to 200 microns long x 40 microns wide
CF Lot 907-21	20.0	0.74	0.94	1.70	5-500 micron aggregates of sub-micron crystallites; some aggregates were very loose, others denser and less deformable

B. Analyses

Impurity (p.p.m.)	UOX Lot 269	NGK-CF Lot 907-21
Al	55	10
Fe	20	< 10
Si	45	85
Mg	50	15
Mn	5	< 5
Cr	4	< 5
Ni	< 3	< 4
Na	10	36
Ca	< 30	90
C	600	-
S	938	830

C. Sinterability
(After iso-pressing at 20 ton/in^2)

Sintered in N_2 for	UOX Lot 269 Density (g/cm^3)	Grain Size (micron)	CF Lot 907-21 Density g/cm^3	Grain Size (micron)
3 hr at 1350°C	2.83	1.5	2.96	5
3 hr at 1400°C	2.90	2.0	2.96	6
6 hr at 1400°C	2.93	3.0	2.97	7
3 hr at 1450°C	2.93	3.0	2.97	7
1 hr at 1500°C	2.93	2.5	2.97	10

TABLE 4

SINTERING, DENSITY, AND GRAIN SIZE DATA

FOR X124 SPHERES

Loading	Sintering Time and Temp. (hr. °C)	Mean Bulk Density by Method (ii)* (g/cm³)	Grain Sizes (μ)		
			Particles	BeO in core	Coating
X124-1	3 - 1450	3.005	4 - 7	4 - 100	3
X124-2	2 - 1525	2.997	4 - 7	8 - 100	8 - 100
X124-3	3 - 1450	3.032	13 - 100	5	5

* See Section 4.1

TABLE 5

DENSITY, OPEN POROSITY, AND CONCENTRICITY

OF X124 SPHERES

Sphere No.	Density (g/cm³)			Open Porosity %	Coating Thickness in. x 1000	
	Impreg-nated	Bulk Method (i)*	Bulk Method (ii)*		Max.	Min.
X124-1 Sphere 1	3.010	3.01	N.D.	N.D.	72	38
2	3.011	2.99	3.010	0.03	57	43
3	3.005	3.04	3.002	0.10	65	43
4	3.005	2.99	3.005	0.00	55	46
5	3.001	3.00	N.D.	N.D.	62	48
6	3.005	3.04	3.005	0.00	55	48
X124-2 Sphere 1	2.990	2.98	2.986	0.13	55	46
2	3.001	3.03	2.997	0.13	73	34
3	2.995	3.00	2.994	0.03	79	35
4	2.998	3.03	2.997	0.03	57	44
5	2.996	3.04	2.994	0.07	59	45
6	3.011	3.03	3.014	Negative	54	46
X124-3 Sphere 1	3.030	3.04	3.029	0.03	61	41
2	3.028	3.04	3.037	Negative	89	24
3	3.028	3.04	3.019	0.30	74	29
4	3.030	3.04	3.030	0.00	66	35
5	3.043	3.05	3.048	Negative	58	42
6	3.033	3.05	3.039	Negative	68	46
7	3.017	3.03	3.012	0.17	64	39
8	3.039	3.05	3.039	0.00	76	28

* See Section 4.1

TABLE 6

SUMMARY OF X124 FISSION GAS RELEASE RESULTS

(Hanna, Private Communication)

Rig Loading	Irradiation Temperature (°C)	$R/B \times 10^6$ for each Isotope				Burnup (10^{18} fissions/ cm^3)
		Kr85m	Kr87	Xe133	X135	
X124-1	850	1	–	1	0.7	1.5
	900	1	–	1	1	1.1
	910	3.8	–	2.4	1.7	1.8
X124-2	750	5	–	50	1	4.7
	850	1	–	100 } *	2	1.05
	900	5	–	4 }	4	3.1
X124-3	700	300	40	460	16	21
	800	250	70	200	200	43
	900	650	80	320	500	52

* Unexplained Inconsistency
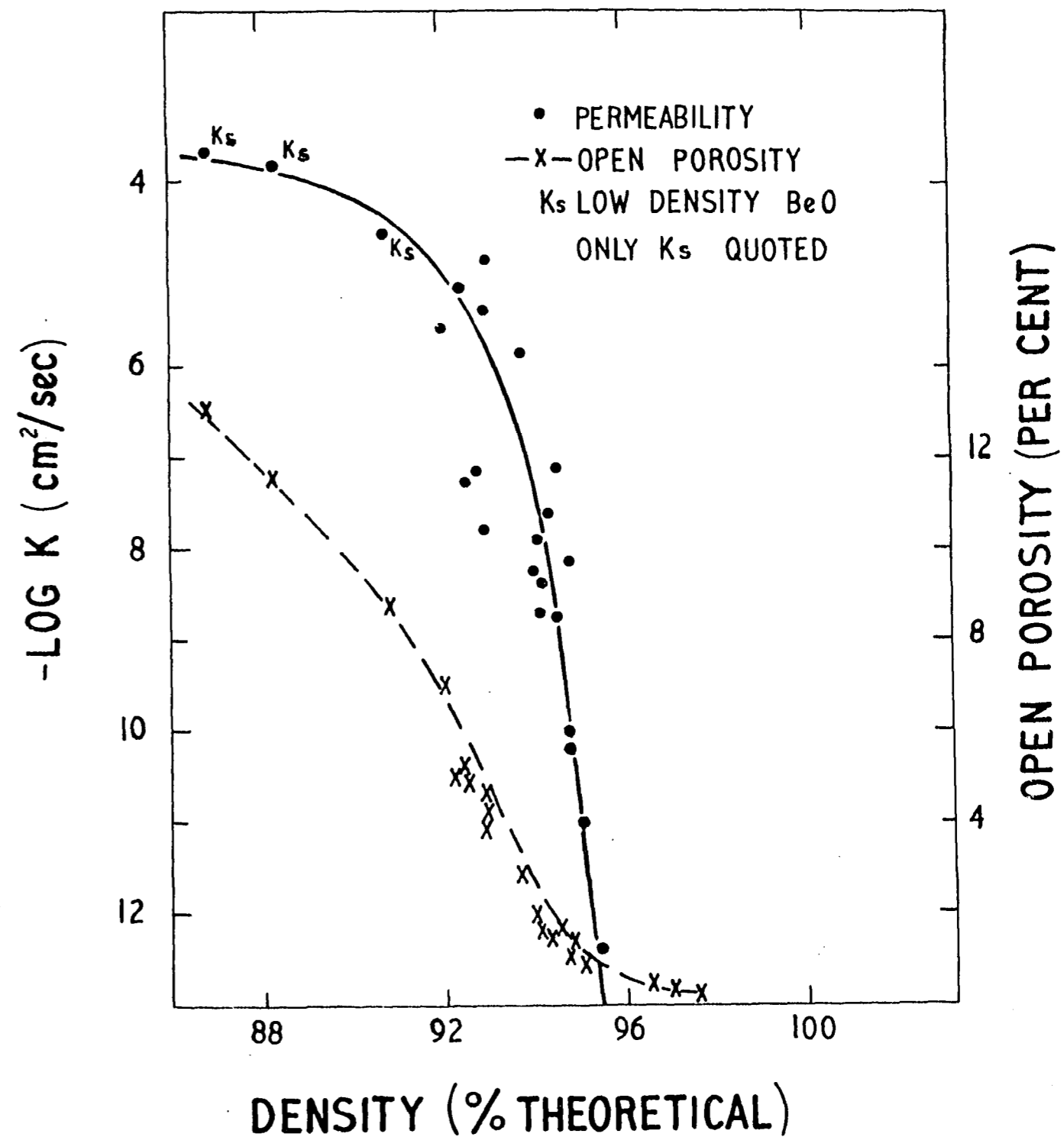
FIGURE 1. TOTAL PERMEABILITY COEFFICIENT AND OPEN POROSITY V. DENSITY FOR SINTERED UOX BeO (Lot 266)

P946
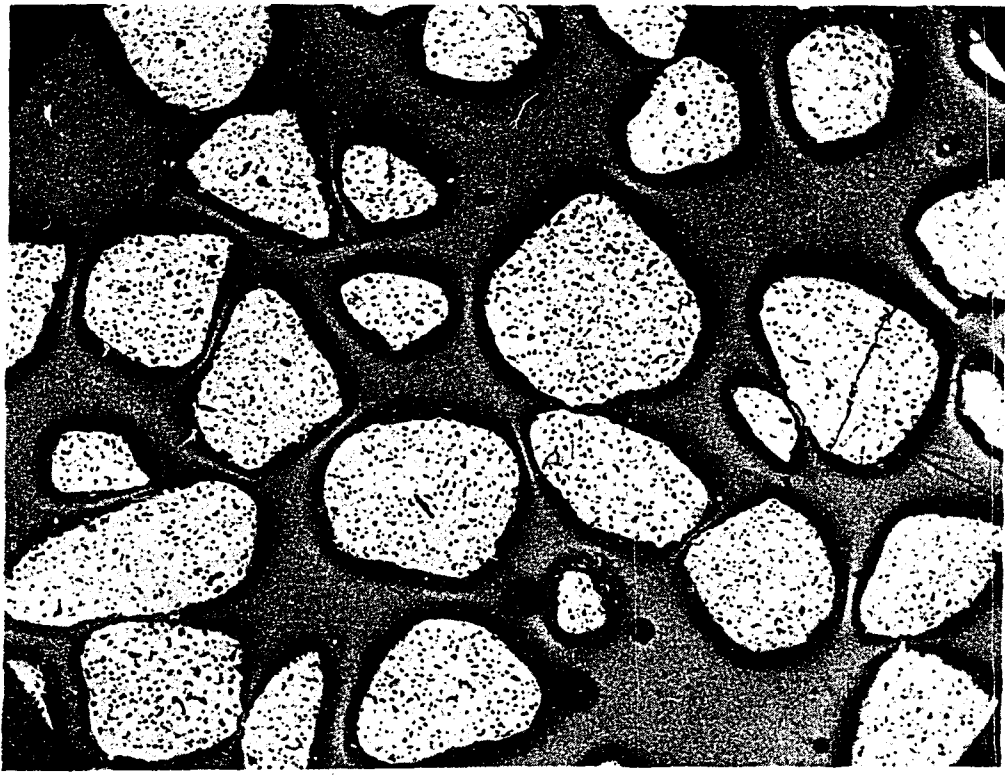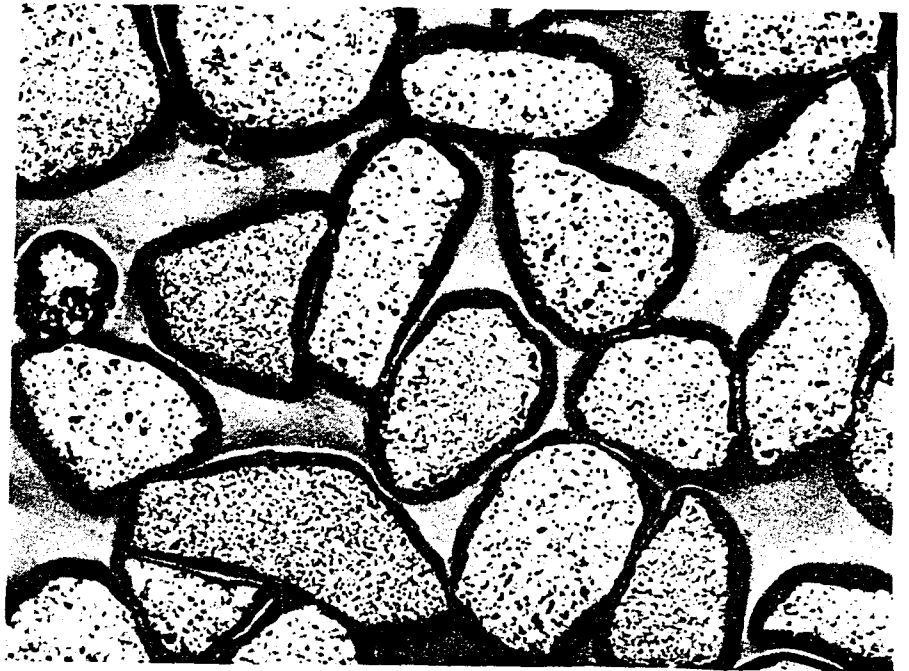
(a) AS - POLISHED   ×100   (b) ETCHED   ×100

FIGURE 2. SINTERED FUEL PARTICLES FOR X124-1 AND X124-2

(a) AS - POLISHED   ×100   (b) ETCHED   ×100

FIGURE 4. 'DURALON' (POLYURETHANE) COATING DIE
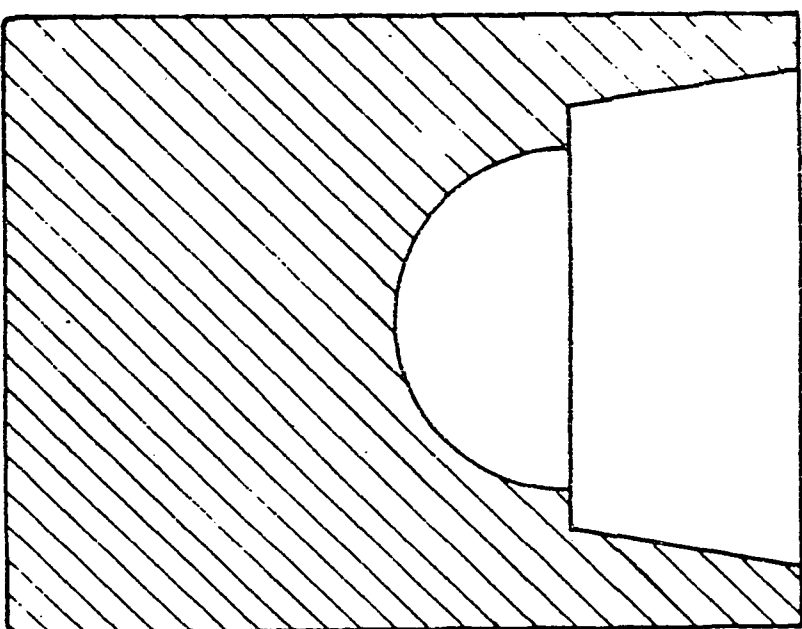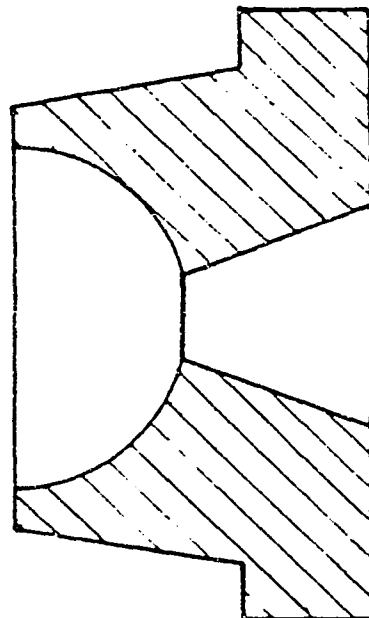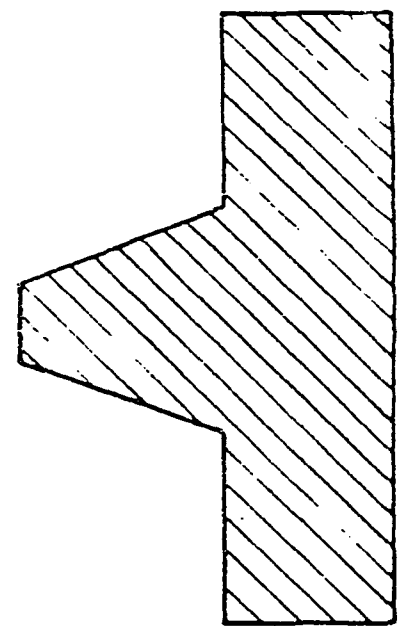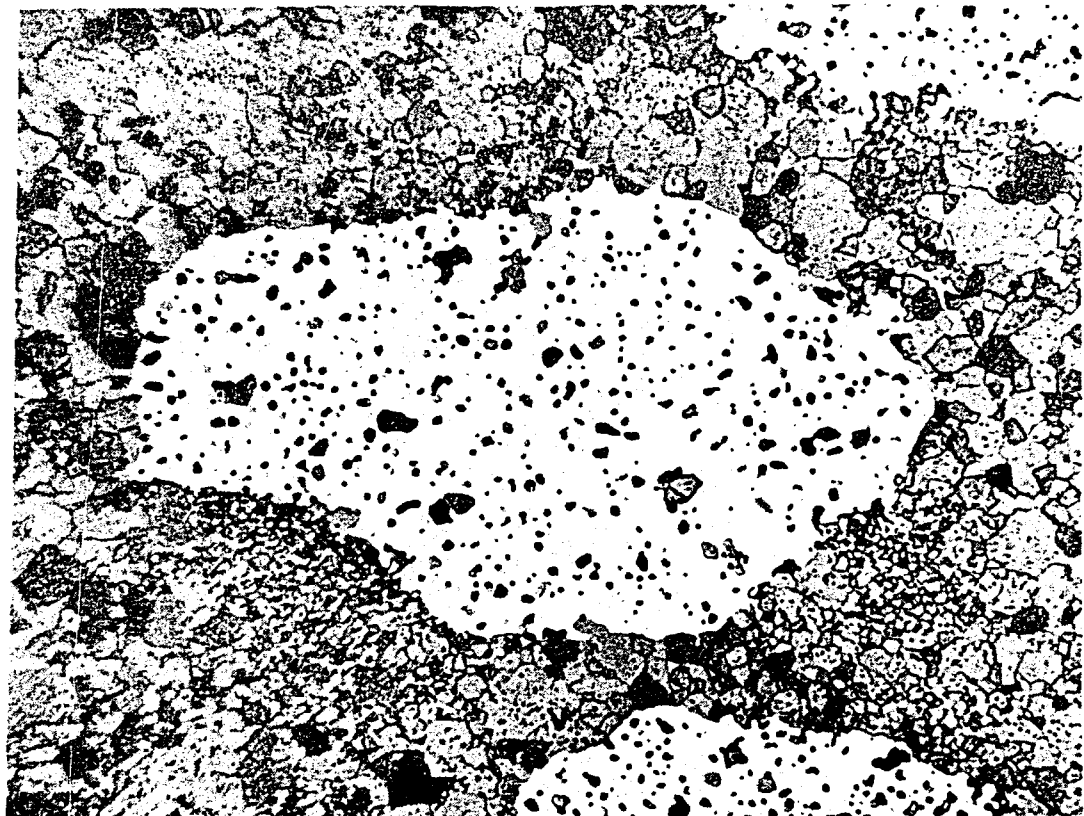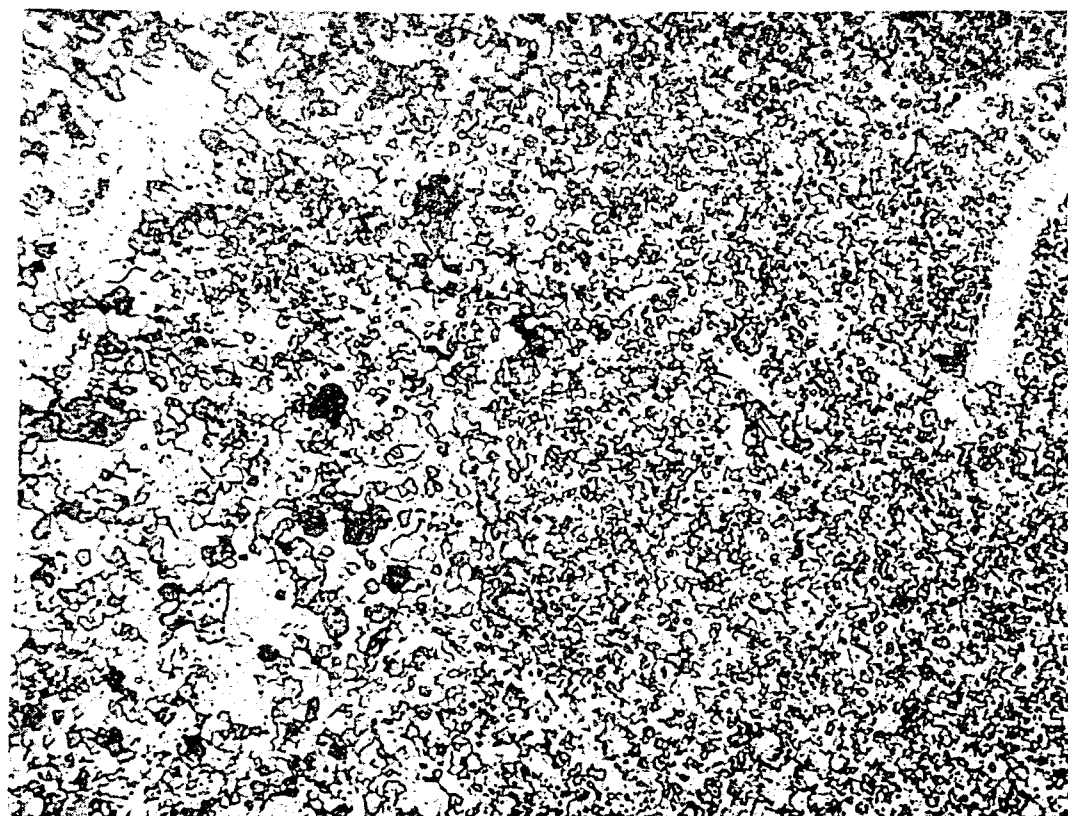

BASE   CLOSURE   PLUG
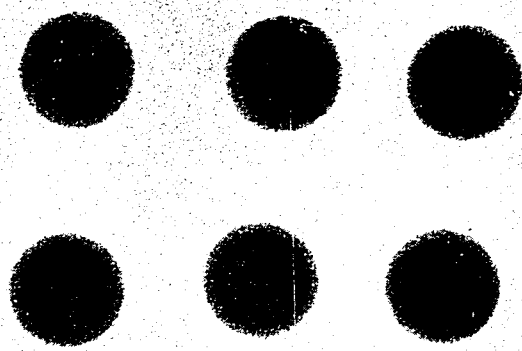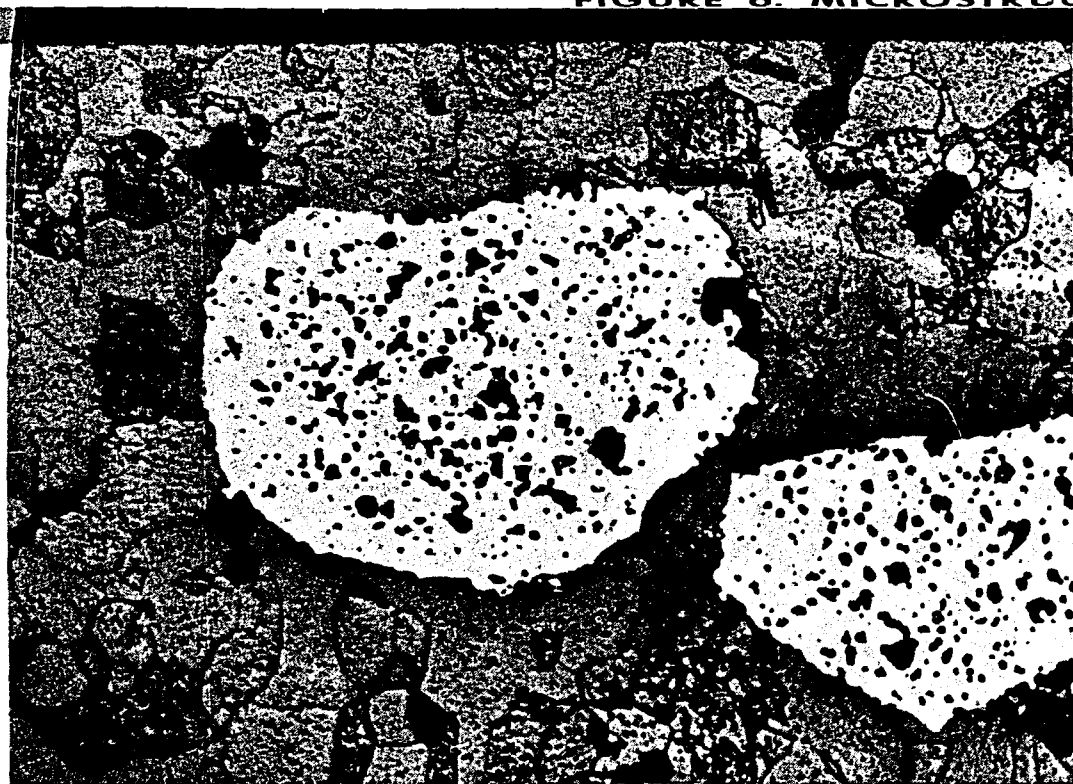
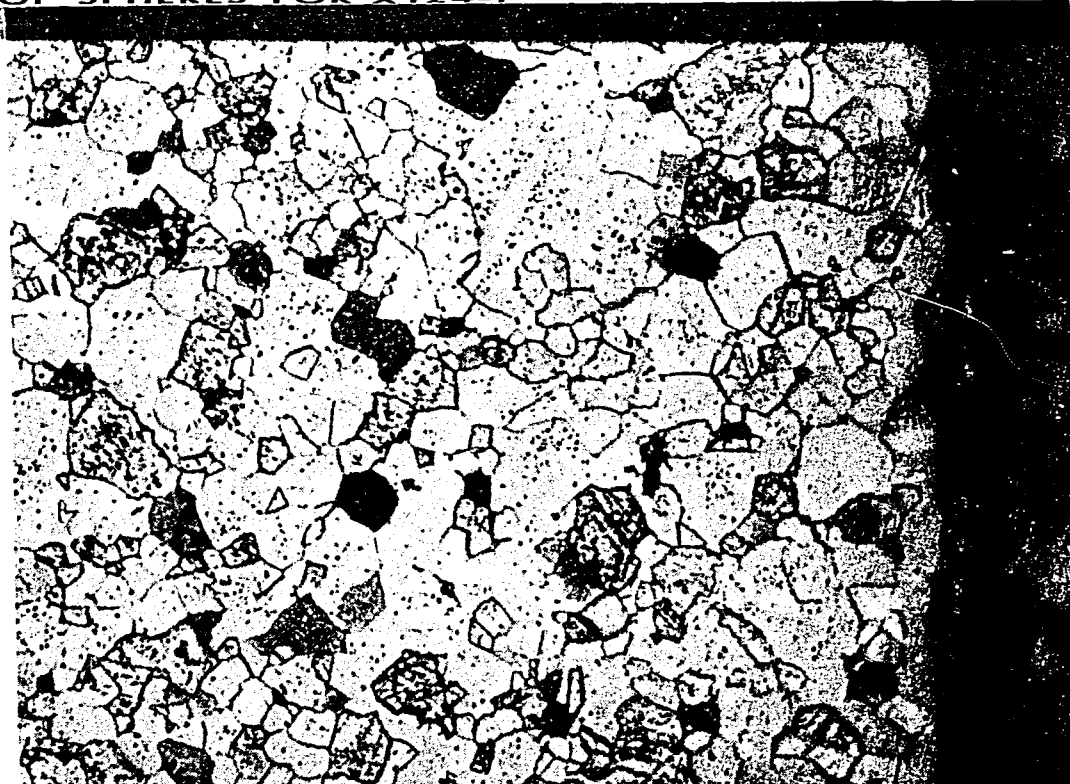FIGURE 5. RADIOGRAPH OF SINTERED SPHERES FOR X124-3
(actual size)

(a) CORE ×250

(b) CORE-COATING INTERFACE ×250

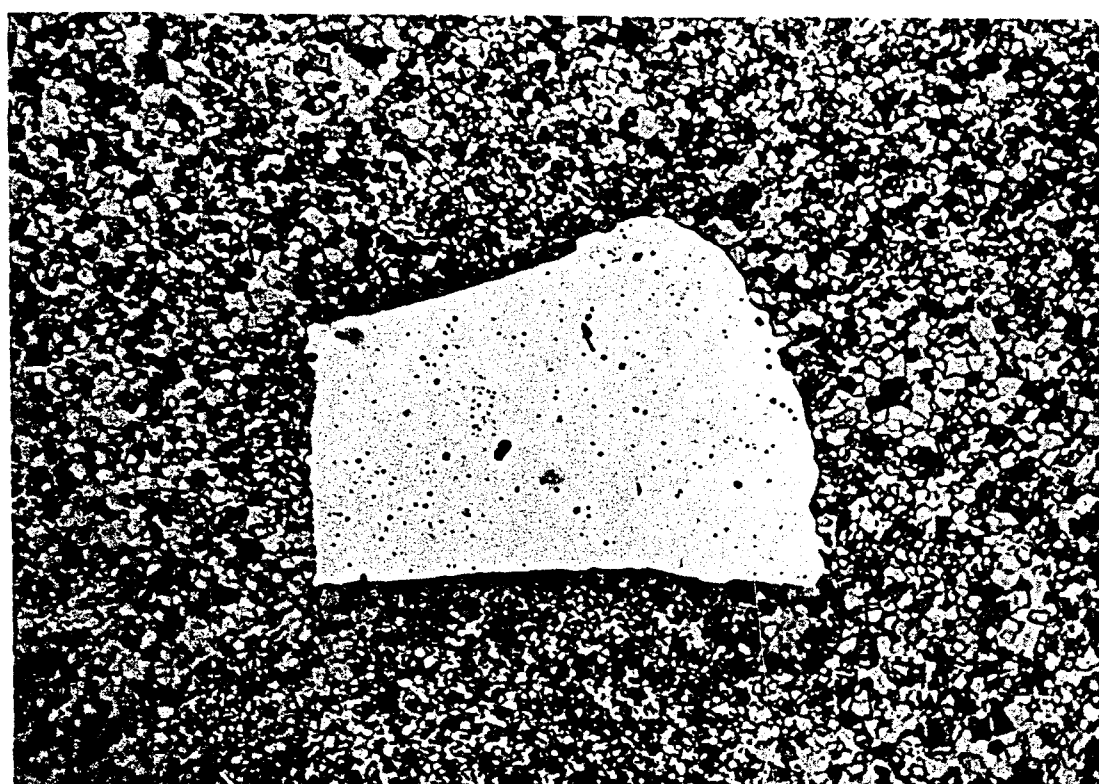FIGURE 6. MICROSTRUCTURE OF SPHERES FOR X124-1
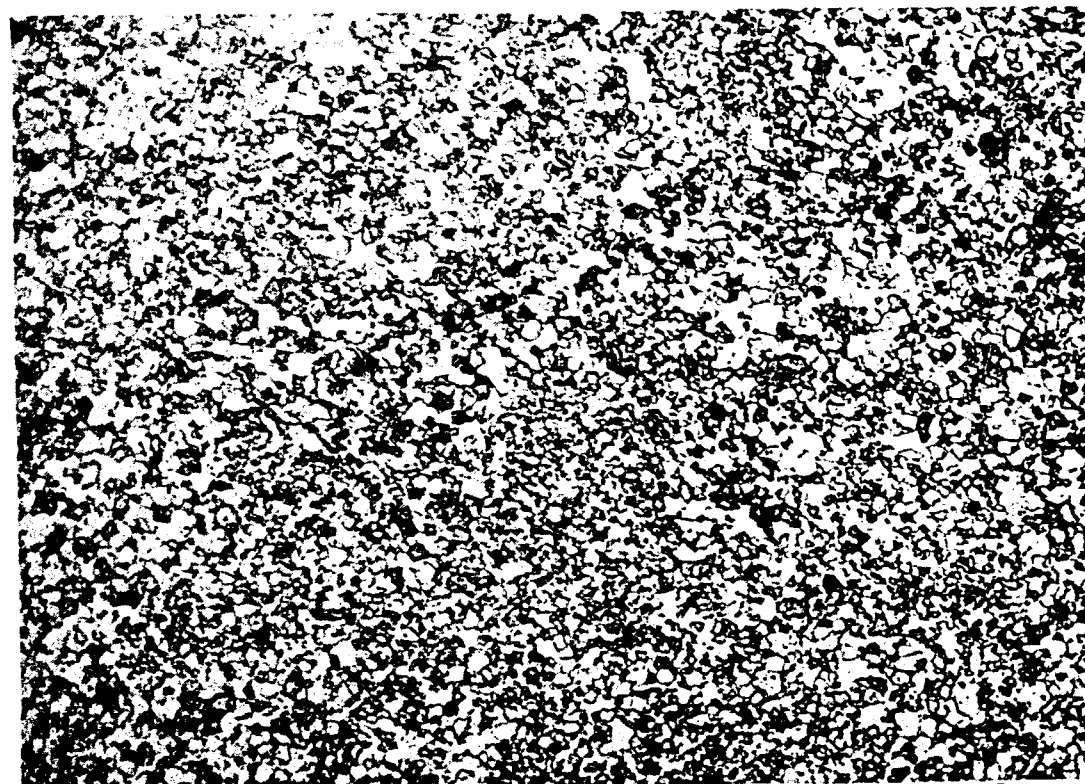

(a) CORE ×250

(b) COATING ×250

FIGURE 7. MICROSTRUCTURE OF SPHERES FOR X124-2

(a) CORE ×250

(b) COATING ×250

FIGURE 8. MICROSTRUCTURE OF SPHERES FOR X124-3