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ABSTRACT

The use of beryllia as the basis of an all-ceramic fuel element for high-temperature reactors cooled by ambient air depends on inhibition of corrosion of beryllium oxide by protecting the surface of the fuel element. Alumina is a promising coating material.

The development of corrosion resistant alumina coatings for BeO spheres is described, and results of corrosion, accelerated corrosion and neutron irradiation tests are presented. The limitations of the coating are discussed in detail. Porous coatings can fail by 'undermining', but dense coatings are probably satisfactory for at least two years' operation out-of-pile at 1200 °C and for much longer times at lower temperatures. Satisfactory operation at 1200 °C for one year has been proved in a long term test. The eventual failure mechanism will probably be associated with the growth of a two layer reaction zone.

Neutron irradiation tests indicate that a dose of 10^{20} nvt and possibly 1.6–2 x 10^{20} nvt should be acceptable for retention of coating-to-BeO bond during simultaneous exposure above 500–700 °C to fast neutrons and moist air.

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1. INTRODUCTION

Beryllium oxide is a promising nuclear material, particularly for high temperature gas cooled reactors. Design of an all-ceramic fuel element which could be cooled in ambient air rather than a highly purified gas might be an attractive possibility for such reactors. However, although BeO is a very stable compound it reacts with moisture at high temperatures to give a volatile hydroxide:

$$BeO(s) + H_2O(g) = Be(OH)_2(g).$$

This reaction becomes significant at about 1,000 °C and its rate increases with increasing temperature. For this reason BeO could not be used in air above 1,000 °C unless the air were dried to very low moisture levels (which may be economically undesirable) or a protective coating were applied to the BeO.

The present study was undertaken to develop a coating for BeO to reduce the rate of reaction with moisture by a factor of 10 to 100 at temperatures up to 1,200 °C. The specification was based on the possible use of a spherical BeO-based fuel element in a small air-cooled gas turbine-operating reactor. The 1–1½ in. diameter fuel elements would be in the reactor core as a fixed ordered array. A target operating time of one year would result in an integrated fast neutron flux of 2×10^{20} nvt. The fuel elements at the cold end of the core would be at 500 °C.

Al_2O_3 was chosen as the most promising coating material for study, as outlined by Reeve (1966). Among reasons for its choice were:

(i) Its thermal expansion coefficient is slightly lower than that of BeO, placing the coating in compression at room temperature.

(ii) Its chemical similarity to BeO, with probably little reaction with BeO or moisture, and none with air.

(iii) Its relatively low thermal neutron absorption cross section.

(iv) Its irradiation behaviour is reasonably compatible with that of BeO at low doses.

This report describes the development of methods of coating BeO spheres with dense alumina, presents results of separate corrosion, accelerated corrosion and neutron irradiation tests, and discusses the limitations of the coating system developed.

2. EXPERIMENTAL

2.1 General Methods

The preliminary assessment proposed three possible types and methods of Al_2O_3 coating in order of preference:

(i) A thick (0.050 in.) layer of Al_2O_3 formed by isostatic pressing and sintering, replacing an 0.050 in. unfuelled BeO layer on prototype fuel elements.

(ii) A thin (0.005 to 0.010 in.) layer of Al_2O_3 applied by dipping or spraying onto an unsintered BeO surface, followed by sintering.

(iii) A thin layer of Al_2O_3 vapour-deposited onto a sintered BeO surface.

Type (i) was preferred initially because it allowed the application of only one coating for the combined task of fission product retention and moisture proofing. However a stress analysis (I.M. Binns, AAEC unpublished) showed that, because of the lower thermal conductivity of Al_2O_3, the tensile thermal stress at the surface of an operating fuel element is increased by adding an alumina coating; although this increase is negligible for a thin coating it is unacceptably high for a coating 0.05 in. thick. Type (ii) was therefore chosen for study.

To simplify the preparation of spheres for coating experiments, unsintered isostatically pressed BeO spheres, rather than BeO coated fuelled BeO spheres, were used throughout the project. The presence of fuel particles in the BeO matrix below the BeO surface (about 0.050 in. away in the standard fuel element concept) would have a negligible effect on the $BeO-Al_2O_3$ interface.

Early attempts to apply an Al_2O_3 coating to unsintered BeO spheres by dipping were discarded because of difficulties in forming a thin, continuous and uniform coating. It was judged that a much better method was to spray-coat a BeO sphere with an Al_2O_3 slip. The difficulty of applying a uniform coating remained but it was thought that this problem could be more readily overcome.

For automatic operation, which would be desirable if large numbers of spheres were to be coated, the sphere would have to be rotated about at least two axes so that all the surface would be exposed to the spray from the nozzle, which might be fixed or travelling (e.g. linearly) with the sphere. Three ideas for this were:

(i) To suspend the sphere on an air jet in the conical section of a flow tube with the spray nozzle in a fixed position and clearances and tapers adjusted to rotate the sphere about a changing axis. Some experimental work was done but the difficulties associated with slurry buildup on the cone, which changed the rotational pattern, were not overcome.

(ii) To arrange that the sphere travels down a winding track with the spray nozzle travel adjusted accordingly. No work was done on this method.

(iii) To rotate the sphere on a set of eccentrically revolving conical rolls to expose all the surface to the spray. The principle of this method was tested with a small laboratory unit. Slurry buildup on the rolls was a problem but the method showed the most promise for successful development of continuous automatic spray-coating.

Although such automatic methods showed promise, batch operation was selected. Up to 20 as-pressed spheres were placed in a square array on absorbent tissue on a porcelain spotting tray. Hand-controlled spraying from eight directions was carried out and then the spheres were inverted and sprayed again. This procedure built up a layer of thickness 0.008 in. For thick layers, the coated spheres were dried at 100 °C before a second 0.008 in. layer was applied as before, and so on. This procedure was highly dependent on operator skill; with experience, a thickness variation of no more than 20 percent on a 0.010 in. sintered coating was possible. An as-sprayed thickness of 0.025 in. gave a thickness of approximately 0.010 in. after sintering.

The sprayed spheres were dried for several hours at 100 °C and then isostatically pressed in rubber latex tubes in a wet bag isostatic press at 45,000 p.s.i. The sintering conditions were optimised for the grade of BeO used. The sintering procedure was to heat in dry N_2 at 200 °C per hour to 1000 °C, 100 °C per hour to 1100 °C, 400 °C per hour to 1450 °C, and then maintain 1450 °C for 6 hours; the furnace was allowed to cool with the power off. Faster heating rates below 1000 °C produced cracks in the coating.

2.2 Adjustment of Shrinkage

The chosen method of 'co-sintering' requires that the shrinkage of the two phases during sintering should be matched sufficiently to preclude shrinkage cracking in either phase. In all cases vibromilled Brush UOX was the grade of BeO used and it sometimes contained 0.1 percent MgO deliberately added during the vibromilling. This pressed to a green density of 1.7 g cm^{-3} and sintered to 2.9 g cm^{-3} under the fixed isopressing and sintering conditions. The volume shrinkage was thus 41 percent, and the linear shrinkage, assumed to be isotropic, was 16 percent.

Early coating experiments used slips made from a grade of alumina (Norton Electronic Grade), which on separate sintering tests had only about 10 volume percent shrinkage. These coatings showed definite signs of having insufficient shrinkage. Although they did not crack they failed to shrink with the BeO and left large blisters or bubbles over most of the surface. Using methods to be detailed later, with different grades of alumina, the shrinkage was increased to near 40 percent; with these coatings it was found that coating shrinkages in the range 35–45 percent were satisfactory in avoiding the formation of bubbles. Thus it was sufficient to match the volume shrinkage to within 6 percent, or linear shrinkage to within 2 percent.

2.3 Thermal Expansion Behaviour

In the assessment which led to the choice of Al_2O_3, the simplifying assumption was made that a sintered coating would remain stress-free during cooling from the sintering temperature until 1000 °C, below which the thermal expansion mismatch, if any, would cause stress to increase to room temperature. It was further assumed that the total thermal expansion between 25 °C and 1000 °C was the important factor. Using figures of 0.94 percent and 0.82 percent for BeO and Al_2O_3 respectively, (J.L. Woolfrey, AAEC unpublished), the tangential compressive stress in the alumina coating was estimated to be 70,000 p.s.i. This stress is not excessive considering the very high strength of alumina in compression (e.g. 420,000 p.s.i. at room temperature (Ryshkewitch 1960)). Also, the presence of an interfacial reaction zone would alter the situation. This point is discussed again in Section 5.

2.4 Course of Development

The first coatings, based on a 24 hour ball-milled aqueous slurry of Norton Electronic Grade Al_2O_3 powder, had two major defects:

(i) Insufficient shrinkage.

(ii) Poor sinterability and low sintered density (< 2.8 g cm^{-3}).

Mixture of Morganite '933' and the Norton aluminas gave a slight improvement in sintered density (to 2.8 g cm^{-3}) and a volume shrinkage of 13 percent. Linde 'A' Al_2O_3 was then introduced, firstly as replacement for the Morganite, with only marginal improvement. Pure Linde 'A', ball-milled for 24 hours in water before use, gave the best result to that time, 3.1 g cm^{-3} with 32 volume percent shrinkage. However, neither density nor shrinkage was quite high enough.

All further coatings were based on Linde 'A', with minor additions to increase density and shrinkage. These additions were:

(i) 'Baymal' colloidal alumina as dry powder; 10 weight percent addition based on dry weight of Linde 'A'.

(ii) MgO powder; 2 weight percent based on Linde 'A' weight.

The addition of Baymal (actually colloidal boehmite, AlOOH) was partly to increase shrinkage and partly to increase sintered density. These effects occur because of the very low packing density of the Baymal coupled with the extremely fine crystallite size of the Al_2O_3 formed by calcining the material. In this case fine alumina is formed in situ during heating of the coating to sintering temperature. The addition of MgO was to increase sintered density, based on the well known effects of MgO on the sintering of Al_2O_3 (see for example Bruch 1962). The amounts of each additive were chosen after very few experiments and were not systematically optimised. Further experimentation was discontinued when the desired result of 3.7 g cm^{-3} with 40–45 volume percent shrinkage was obtained.

The first standard coatings (Type I) were of the following composition:

Linde A	888 g
Baymal	89 g
MgO	18 g
Gum Arabic	6 g
n-Octyl Alcohol	1 g
Water	1,000 g .

The mixture was homogenised by ball-milling for 24 hours in a porcelain mill containing alumina grinding media. Discs made from this material had a shrinkage of 45 volume percent, a density of 3.7 g cm^{-3} and zero open porosity on a simple water impregnation test. The mix was then applied to BeO spheres to give a nominal sintered thickness of 0.005 in. The sintered coatings appeared to have excellent adherence when subjected to simple impact tests and thermal cycling tests between 20 °C and 1000 °C.

Sections of the coated spheres were sectioned and examined by metallography. The definite interface between the BeO and the coating appeared to be reasonably free of pores (Figure 1). The first 0.002 in. (50 μm) of the coating from the interface had a different appearance, suggesting a larger grain size. This layer was suspected to be a reaction product, probably chrysoberyl, although little reaction had been expected at the sintering temperature. In another study (Reeve, Ramm and Buykx 1970a) it was confirmed by electron microprobe and X-ray diffraction techniques that chrysoberyl ($BeO.Al_2O_3$) and a ternary compound ($3BeO.8Al_2O_3.5MgO$) form during sintering, resulting in a two-layer reaction zone. The formation of a reaction zone was not expected to create difficulties, provided the coating was thick enough for the external surface to remain as unreacted Al_2O_3; indeed, the reaction zone should assist in bonding the coating to the core.

Corrosion tests on these coatings (described later), gave promising results which were further improved when the standard nominal sintered thickness was increased to 0.010 in. However, occasional difficulties which arose were:

(i) Springing-off of the coating during final isopressing.

(ii) Springing-off of the coating during sintering.

(iii) Highly porous bond zone in coatings, not obviously associated with (i) or (ii).

In an attempt to overcome (i), the gum arabic was omitted from all further coatings, and the trouble ceased.

Coating failures during sintering still occurred and the cause of variability of behaviour was suspected to be the introduction of a variable amount of impurity during the ball-milling step. Chips from the grinding media would also increase the green density and reduce the shrinkage on sintering, and this behaviour could vary from run to run. The ball-milling time was reduced to 1 hour to reduce these effects. At the same time, with the aim of improving the bond between the coating and the BeO, a pre-mixed equi-molar layer of alumina and BeO powders plus 2 weight percent MgO (prepared by vigorously shaking a BeO-Al_2O_3-MgO-water slurry) was sprayed onto the BeO to give a sintered thickness of 0.001 in. This was followed by the standard Al_2O_3 coating to give a final sintered thickness of 0.010 in. By this means it was expected that a strong graded bond would form more consistently during sintering, with possibly little increase in total thickness of the reaction zone.

The resultant coating, designated Type II (Figure 2), differed from Type I in the following respects:

(i) There were even fewer pores at the interface with BeO and the bond appeared to be very good. The coating could not be detached from the sphere even after an impact test sufficient to fracture the BeO, indicating that the bond was at least as strong as the BeO itself.

(ii) Judged by polishing behaviour the density appeared to vary from 90 percent or higher near the BeO to very porous near the surface. The basic coating mix (that is, without the BeO-Al_2O_3 underlayer) gave on separate sintering tests, a density of 3.1 g cm^{-3} with 21 percent open porosity.

(iii) The denser inner coating was almost certainly a reaction zone; it was approximately 0.002 in. (50 μm) thick, but dendritic growth of this zone extended further in the BeO. No electron microprobe analyses were done, but the reaction zone structure was assumed to be similar to that observed previously.

The low density of the basic coating was surprising, so the effect of ball-milling on coating density and impurity content was studied. The standard Linde 'A'-Baymal-MgO composition was first mixed by vigorous shaking without grinding media for 1 hour; wet ball-milling followed for 24 hours, samples being extracted at 1,4,8 and 24 hours for sintering tests. The results are presented in Table 1. A similar test (0,1,17 and 24 hours) was made on pure Linde 'A' powder (Table 2) and the impurity content was measured spectrographically after 24 hours (Table 3).

It appears from Tables 1–3 that:

(i) The highest density and shrinkage are obtained from unmilled powder and the presence or absence of the MgO and Baymal makes little difference.

(ii) One hour of ball-milling is the worst possible treatment, markedly reducing density and shrinkage. The presence of MgO and Baymal now improves the situation.

(iii) Longer ball-milling increases density and shrinkage, but the density is near that for zero milling only in the presence of MgO and Baymal.

(iv) Long ball-milling in the presence of MgO and Baymal results in a zero open porosity structure.

Coating Type II was thus of low density because it had been ball-milled for 1 hour, but the basic reason for this behaviour is unknown. Since long ball-milling reduces the shrinkage, leads to variable impurity pickup, and gives occasional coating failures during sintering, it was decided to leave out ball-milling altogether. In all further work the basic mix was made by wet shaking. An attempt to leave out the Baymal and MgO, on the grounds that they did not assist densification and shrinkage, resulted in mixes that tended to separate on standing, were difficult to spray, and rubbed off easily during handling. For these reasons the Baymal and MgO additions were retained in all subsequent coatings. Coating Type III now became:

(i) Underlayer of equimolar BeO-Al_2O_3 plus 2 weight percent MgO mixed by shaking without grinding media.

(ii) Overlayer of Linde 'A'-Baymal-MgO mixed as in (i).

The expected coating density was that for zero milling time in Table 1. A typical structure is shown in Figure 3. The coating is generally more porous than that in Figure 1, but less so than that in Figure 2. The bond with the BeO is excellent, and no mechanical failures occurred in impact tests. The reaction zone was still approximately 50 μm thick.

Type III was the final standard coating, although some of the tests to be reported were carried out on the intermediate types. Table 4 summarises the compositions and preparation methods for the three coating types.

3. CORROSION TESTING

3.1 Experimental Method

The high temperature reaction between BeO and water vapour has been the subject of many studies. Stuart and Price (1964) suggested a treatment for relatively low flow rates, where the atmosphere becomes saturated with the volatile $Be(OH)_2$ complex. In this case they showed that the loss rate depends only on the total throughput of water vapour and not on the gas pressure and partial pressure of H_2O. Their equation:

$$\log n_{BeO} = 1.62 - \frac{8.8 \times 10^3}{T} + \log n_{H_2O}$$

thus predicts the maximum possible weight loss from a large mass of BeO over which n moles of water vapour has been passed.

When applied to a proposed reactor case consisting of 33,000 BeO spheres of 1.25 in. diameter in a 3 ft. diameter by 4 ft. high cylindrical array at a temperature of 1200 °C and with a moist air mass flow of 5 lb sec^{-1} (humidity 0.012, equivalent to 50% R.H. at 28 °C), the result was:

$$\omega_{BeO} = 1.4 \times 10^{-9} \text{ g cm}^{-2} \text{ sec}^{-1} \ .$$

In a laboratory test devised to simulate these conditions, a 1 in. diameter BeO sphere of density 97 percent theoretical was placed in a recrystallised alumina furnace tube. The tube was supplied with air saturated with moisture at 70 °C (by bubbling twice through water at 70 °C) at a flow rate of 1500 cm^3 min^{-1}, and the furnace was heated to 1300 °C. (This temperature, rather than 1200 °C, was used to obtain corrosion data in shorter times). After one week the furnace was cooled and the sphere re-weighed. The loss of weight was 0.093 g from the original weight of 20 g, corresponding to a rate of:

$$\omega_{BeO} = 10^{-8} \text{ g cm}^{-2} \text{ sec}^{-1} \ .$$

The estimate of Stuart and Price for this case would be 7.8×10^{-8} g cm^{-2} sec^{-1}. A repetition of the test with three spheres over two weeks gave an average loss rate of 5.2×10^{-9} g cm^{-2} sec^{-1}. It appears that equilibrium was not attained in either test. However, in this test, and in particular in the three sphere case:

(i) The loss rate was within a factor of 4 of that predicted for the reactor case.

(ii) The steam partial pressure (0.3 atmospheres) was very close to that of a typical reactor case (28 °C air with a relative humidity of 50 percent compressed to 20 atmospheres and heated to 1200 °C, giving a steam partial pressure of 0.24 atmospheres).

This test was therefore adopted as standard for coating assessment during the development work. The same test was used for assessment of neutron irradiated coatings. In most cases, the furnace was cooled once per week and all spheres were weighed. Sometimes one or more were replaced for various reasons, so that only in a few cases did the same group of three remain together for a complete test.

3.2 Results of 1300 °C Tests

Results of all standard tests are given in Table 5. Except in a few cases, mainly 0.005 in. thick coatings, the 'improvement factor', that is, the factor by which the average loss rate was reduced by the coating, was in the required range of 10–100. The minimum improvement factor for 0.010 in. Type III coatings, that is, the final standard, was 37. However, the factors given in Table 5 are average values; in practice, the rate of weight loss decreased, and the average improvement factor increased, during a corrosion test.

Cumulative weight loss as a function of time for a particular test is shown in Figure 4. For this test the average improvement factor after 1 week was 15, increasing to 84 after 33 weeks. However, if the comparatively large weight loss during the first week is ignored (the reason for this is not known), and the test is assumed to commence after one week, the first and lowest improvement factor is 30. If the test is assumed to commence at 3 weeks, the improvement factor is virtually constant at 120–130 throughout the remainder of the test. This continuing decrease in weight loss may be associated with continued sintering or pore closure in the coating. Some tests were interrupted for metallographic examination and a typical result is shown in Figure 5. The BeO-coating interface is still sharp.

As shown in Table 5, some coatings cracked or flaked during testing, and such tests were discontinued at that point. These fell into two categories:

(i) Type I coatings which were suspected to be poorly bonded (11–13) or to contain pinholes (16). Also in this category is test 40, in which the original coating was known to contain a small crack.

(ii) Type III coatings tested for 7 weeks or longer in which the coating appeared to be more susceptible to flaking, e.g. on sudden cooling (33–35), on cutting for metallography (39) or even during normal cooling (44–45).

Failures in the first category are suspected to be caused by 'undermining' of the coating, access of water vapour to the BeO substrate having occurred through pinholes or porosity in the coating. It may be significant that average corrosion rates even before failure were generally higher than for similar well-behaved coated spheres, although some which showed high corrosion rates did not fail quickly (23–30, 31).

As regards the second category, there is no doubt that Type III (and probably earlier) coatings do become progressively more susceptible to flaking after about three months' corrosion testing at 1300 °C. This is probably not due to undermining, because similar behaviour has been observed (see Section 5) on annealing at 1300 °C in dry air. The reason for this change is not completely understood. However, the fact remains that six coatings of Type III have been proved to remain protective for periods between 4½ and 8 months and if fast cooling or mechanical shock had been avoided all may have remained so for eight months or longer.

3.3 Results of 1200 °C Tests

Towards the end of coating development work, a long term corrosion test was commenced on Type III coatings at 1200 °C. Humidity and gas flow rate conditions were the same as before, and the aim was to prove successful protective behaviour of four coatings for one year. The test was concluded at 50 weeks and the overall weight losses and improvement factors are given in Table 5. The improvement factors were calculated assuming a weight loss rate for uncoated BeO of 2×10^{-9} g cm^{-2} sec^{-1}. This figure was obtained by applying an activation energy of 42 kcal $mole^{-1}$ (Conway et al. 1964) to the observed rate at 1300 °C.

The results indicate that very good protective behaviour is maintained in standard Type III coatings at 1200 °C in moist air for at least one year. As will be seen, it is predicted that protective behaviour could be maintained for at least 2 years at 1200 °C.

4. IRRADIATION TESTING

The original requirement was that the coating should withstand an integrated fast neutron dose of 2×10^{20} nvt at temperatures between 500 °C and 1200 °C and still remain protective. In irradiation testing as part of this project, emphasis was placed on irradiating selected coatings at temperatures of about 100 °C (to give accelerated damage) and in the range 500 °C to 830 °C. The latter was the highest available without extensive re-design of the irradiation rig.

Results for 38 spheres are available as shown in Table 6. These results may be summarised as follows:

4.1 Irradiation at 100 °C

Twenty coated spheres were irradiated, to doses between 1.4 and 3×10^{20} nvt. All coatings remained intact except the spheres in Tests 1 and 2, which had been corrosion tested for 8 weeks before irradiation (and thus had a large BeO grain size which microcracked at a low fast neutron dose). All were metallographically polished except one from Test 17–32, from which the coating flaked when being sectioned with a diamond slitting wheel. Coating embrittlement was suspected to have occurred at these doses. Subsequently, complete spheres were mounted in resin before careful sectioning and polishing. In no case was there any obvious deterioration of the BeO-to-coating bond and the interface remained sharp but pore-free. One noticeable change was the increased contrast between the interfacial reaction zone and the Al_2O_3 coating proper in the as-polished condition. A representative photomicrograph of an irradiated coating is shown in Figure 6, and the increased contrast can be seen by comparison with Figure 2.

The irradiation doses were in most cases sufficient to cause microcracking of BeO but fortunately this did not occur in the BeO immediately under the coating. The BeO there was much finer-grained than in the 'core' of the sphere and this delayed microcracking. The mechanism for this apparent grain refinement next to the alumina is not known.

No spheres irradiated at 100 °C were subsequently corrosion-tested, because this would have been a rather unreal combination of tests, in view of the actual final use of the coatings. Similarly, no Type III spheres were irradiation tested at 100 °C, emphasis being placed on the more realistic high temperature irradiation as a proving test for these final standard coatings. The significance of the 100 °C irradiation tests was mainly that they could be used as a guide to the probable upper limit of dose at higher temperatures. Tests 33–38 on Type III coatings at 700 °C were thus planned to include doses up to 4.8×20^{20} nvt, because at 700 °C considerably more self-annealing would be expected during irradiation.

4.2 Irradiation at 500–830 °C

Eighteen spheres were irradiated, to doses between 2.6×10^{19} and 4.8×10^{20} nvt. All spheres had intact coatings and several were mounted whole, sectioned carefully, and polished for metallographic examination. Photomicrographs from Tests 13 and 16 are shown in Figures 7 and 8. No deterioration of any kind could be detected metallographically at either dose (0.96 and 3×20^{20} nvt). However, in Tests 35 and 36 (4 and 4.8×10^{20} nvt) radial cracks occurred in the coating, extending only a short distance into the BeO. In some cases smaller cracks appeared to start in the interfacial bond zone region. There was no circumferential failure at any interface. Eventual tensile failure of the Al_2O_3 coating was predicted (Reeve 1966) at a dose between 2 and 5×10^{20} nvt at 100 °C, and this result is therefore not surprising. It also appears that the interfacial reaction zone was being placed in tension, and this is consistent with the reported saturation of chrysoberyl expansion at low neutron doses, at least at 100 °C (Jostsons and Hickman 1968).

Six coated spheres from these tests (7, 8, 14, 15, 33 and 34) were corrosion-tested after irradiation. The results were:

Test 7: Tested for 57 weeks at 1300 °C, with weekly cooling and weighing up to 33 weeks, and thereafter less frequent weighing. The weight loss results are presented in Figure 9. The average improvement factor at the end of the test was 135. Metallographic examination (Figure 10) showed good coating-to-matrix bonding, but some evidence of corrosive attack of BeO at the interface.

Test 8: Tested for 9 weeks at 1300 °C, after which the coating flaked from the BeO. The average improvement factor before flaking was 20.

Test 14: Survived one week at 1300 °C, with an improvement factor of about 10. The coating flaked on cooling after a 2 weeks' test.

Test 15: The coating flaked on cooling after 1 week's test.

Test 33: Tested for 15 weeks at 1200 °C. For this and the following test, improvement factors were calculated assuming a weight loss rate for uncoated BeO of 2×10^{-9} g cm^{-2} sec^{-1}, as for the out-of-pile tests at 1200 °C. The coating remained intact and the average improvement factor over 15 weeks was 30. However, the loss on first weighing at 4 weeks was rather high and may have included absorbed moisture. During the next 11 weeks the improvement factor was 50 which although lower than for Tests 46–49 (Table 5) for unirradiated coatings still indicates good protective behaviour.

Test 34: Tested for 8 weeks at 1200 °C. The improvement factor was only 7, indicating poor protective behaviour.

The number of results is too small for the combined irradiation and corrosion behaviour to be predicted with confidence. However, all three tests above 2.8×10^{20} nvt suggested poorly protective coatings, while two of the three tests up to 1.6×10^{20} nvt gave excellent results. It appears that 2.8×10^{20} nvt is too high a dose at any temperature up to 830 °C for protective behaviour to be retained, but that 10^{20} nvt and, possibly 1.6×10^{20} nvt may be allowable above 500–700 °C.

5. HIGH TEMPERATURE ANNEALING

When it was discovered that a 50 μm thick reaction product zone between BeO and the Al_2O_3 coating formed during sintering, the question arose as to the further rate of growth of this zone during long term elevated temperature testing or usage. If a BeO-containing reaction product grew into the coating and eventually reached the outer surface, corrosive loss of $Be(OH)_2$ would recommence. Accordingly, a study was made of growth rates of Type I coatings at 1500 °C, 1400 °C and 1300 °C. The results discussed in detail in Reeve, Ramm and Buykx (1970a and b) may be summarised as follows:

(i) Two reaction zones of approximately equal thickness form and grow at approximately equal rates. That nearest to BeO is $BeO.Al_2O_3$ and that nearest to the Al_2O_3 is $3BeO.8Al_2O_3.5\,MgO$.

(ii) The growth kinetics are not inconsistent with a diffusion controlled process ($d^2 = d_0^2 + kt$) and the activation energy for the rate-controlling process is 125 kcal mole^{-1}.

(iii) BeO-containing phases would therefore be expected to reach the surface of a 0.010 in. coating after 20 days at 1500 °C, 170 days at 1400 °C, 5 years at 1300 °C, 80 years at 1200 °C, and 1500 years at 1100 °C.

(iv) However, it was observed that after about 3 days at 1500 °C, 16 days at 1400 °C or 90 days at 1300 °C the coating-to-BeO bond began to weaken and after longer times coatings could be easily peeled off from the BeO substrate. A possible mechanism for this effect and its implications on coating lifetime have been discussed in Reeve, Ramm and Buykx (1970b). Briefly, $BeO.Al_2O_3$ has a more open oxygen sub-lattice than either BeO or Al_2O_3, and the largest lattice mismatch thus occurs at the $BeO{-}BeO.Al_2O_3$ interface, which is the one that fails. The higher the temperature the greater is the increase in volume which can be accommodated by pore closure and uniform plastic deformation in the outer alumina coating as chrysoberyl forms. Thus the amount of reaction that can be tolerated before the bond fails falls with decreasing temperature, which is what is observed. The failure mechanism appears to have an 'activation energy' of about 100 kcal mole^{-1} (from the times at 1500 °C, 1400 °C and 1300 °C). Using this value a 2 year lifetime is predicted for 1200 °C and 24 years for 1100 °C. The original target of one year at 1200 °C has already been proved under out-of-pile conditions.

6. DISCUSSION

The work described has shown that alumina coatings can be applied to BeO spheres, and that they reduce the corrosion rate of BeO in moist air at atmospheric pressure at 1300 °C by a factor of between 10 and 130, depending on coating type and corrosion test time. However this coating has certain limitations which have not yet been fully defined. These limitations under relevant headings are now discussed.

6.1 Fabrication

The coating method was developed as a laboratory process only; 24 one-inch diameter spheres constitute a normal batch, and much operator skill is required to apply an even 0.010 in. thick coating. No work was done on the coating of spheres larger than one inch in diameter, but there is no obvious reason why this could not be done. Coating of large numbers of spheres by the present method would require much labour and a more automated spraying process would need to be developed if a large coating requirement arose. There would also be problems of control of coating to avoid occasional poorly bonded batches which still occur in the laboratory process. Finally, the further research and development required to solve these and other problems might result in a more nearly optimised coating system; for example, it is conceivable that the undercoat composition might be changed eventually to ensure a more reliable and even stronger bond. This is discussed again in Section 6.6.

6.2 Corrosion Protection in the Absence of Irradiation

6.2.1 Time and temperature limitations

Time and temperature limitations for the case of dry atmosphere annealing have been discussed above and there is no reason to believe that the interfacial reaction or debonding rates are accelerated by the presence of moisture. The predicted limits of 2 years at 1200 °C and 24 years at 1100 °C therefore still apply.

6.2.2 Applicability of the accelerated corrosion test

Testing was done mainly at 1300 °C, which is 100 °C higher than the maximum temperature at which coatings might be used. Since the coating probably acts simply by restricting the access of moisture to the BeO through a limited number of open pores, it seems very probable that similar corrosion protection would be obtained at 1200 °C. However, in making this prediction the fact that the protective behaviour at 1300 °C improves progressively during a test (Figures 4 and 9) should be considered. This effect might be due to further sintering or pore-closure in the coating, which would take place much more slowly at 1200 °C. If this is so, it may be necessary to use much longer sintering times for coatings to be used at or below 1200 °C. However, the results of tests at 1200 °C, though limited, suggest that good protective behaviour is obtained at 1200 °C after the normal sintering period.

Corrosion testing was done only at atmospheric pressure with a steam partial pressure of approximately 0.3 atmospheres. A possible reactor requirement would be an air atmosphere at up to 20 atmospheres pressure but with a humidity lower by a factor of 25 (that is, air at 28 °C with a relative humidity of 50 percent compressed to 20 atmospheres and heated to 1200 °C). The steam partial pressure used in the accelerated corrosion test is thus quite close to that of conceptual reactor requirements.

The accelerated corrosion test can therefore be used to predict coating behaviour under the target conditions.

6.3 Irradiation Stability

Irradiation testing covered too few temperatures and doses for the practical dose limits of the coating to be stated precisely. However, in summary:

(i) Coating embrittlement was noted after 3 x 10^{20} nvt at 100 °C and 830 °C although coatings did not debond if handled carefully and appeared in excellent condition on metallographic examination. However, this is without doubt too high a dose for an effectively protective coating at temperatures up to 830 °C. At higher temperatures such doses may be allowable.

(ii) One coating remained protective for one year at 1300 °C after a dose of 10^{20} nvt at 500 °C, and another for at least 15 weeks at 1200 °C after 1.6 x 10^{20} nvt at 700 °C. The damage rate would be lower at higher temperatures and therefore 10^{20} nvt should be allowable at all temperatures above 500 °C and below a limit suggested as 1100 °C. At 1200 °C, the debonding mechanism begins to operate and this may be additive with irradiation embrittlement. The promising result from 1.6 x 10^{20} nvt at 700 °C suggests that with further work it may be possible to extend the allowable dose to this figure or even to the target of 2 x 10^{20} nvt, over the range 700–1100 °C or 500–1100 °C. However, no further irradiation testing to define the dose limit in detail is planned.

(iii) The number of results is too small for any possible dependence of irradiation stability on coating type to have been detected. However, irradiation test sphere No. 7 survived a subsequent one year's corrosion test at 1300 °C, and later annealing results on Type III coatings showed that even in the absence of irradiation, debonding commenced after 3 months at 1300 °C. This suggests the possibility that this particular Type I coating was superior in some way, and that it may have also withstood irradiation better than those in later tests. This is discussed again in Section 6.6.

6.4 Corrosion Protection Plus Neutron Irradiation

No in-pile corrosion tests were made or planned. The most nearly applicable results are the corrosion tests on irradiation tests Nos. 7 and 33. To extrapolate these results to in-pile conditions there should be confidence that corrosion tests and irradiation-induced changes are not additive.

There is no obvious reason why moisture should affect in-pile behaviour but as pointed out in Section 6.3, temperature-and neutron-induced changes may be additive in the vicinity of 1200 °C. Below this temperature, temperature induced debonding is very slow already, and above 1200 °C temperature will be the major factor because defects will anneal-out so readily. Therefore the prediction of irradiation stability to at least 10^{20} nvt between 500 °C and 1100 °C should still be valid for corrosion protection in the presence of moisture in-pile.

6.5 Coating Behaviour on an Operating Fuel Element

In addition to the separate and combined effects of neutron irradiation and a moist atmosphere, the effects of thermal stresses in an operating fuel element must be considered. However, as noted earlier, a stress analysis (I.M. Binns, AAEC unpublished) showed that at operating temperatures and power densities the effect of a thin Al_2O_3 coating on the maximum tensile stress (which occurs at or near the surface of the sphere) was negligible. Although the stress in the Al_2O_3 is now tensile, this stress is small (less than 10,000 p.s.i.) and is still slightly compressive with respect to the BeO (by about 1,300 p.s.i.). The conclusion is that if tensile stresses are held low enough to ensure that the BeO does not crack, the Al_2O_3 and the BeO-Al_2O_3 bond should remain intact. However, this conclusion would have to be checked.

6.6 Coating Optimisation

Insufficient work was done to define precisely either the operating limits of the Al_2O_3 coatings or any dependence of these limits on coating type. Three broadly defined types (I, II and III) evolved through the development work, and although development ceased at Type III this is not necessarily the ultimate design in terms of optimisation of bonding, irradiation stability, and other properties. A few results have suggested that temperature-induced debonding may depend on coating type, including the presence and composition of an undercoat such as the BeO.Al_2O_3 deliberately introduced into Types II and III. The presence or absence of MgO in either the undercoat or the Al_2O_3 or both may completely change high temperature or in-pile behaviour. Thus it cannot be said that the concept of an Al_2O_3 coating on BeO has been completely optimised at Type III. Complete optimisation of the coating and its fabrication would require continuation of research and development work in association with continued corrosion and irradiation testing of evolving coating types.

7. CONCLUSIONS

(i) A laboratory method for applying an Al_2O_3 based corrosion-protective coating to BeO spheres was developed. The coating selected is probably not the optimum type to give the best possible corrosion protection in-pile. The method would require development before it could be used to coat spheres in large quantity or sizes greater than one inch in diameter. Definition of an optimised coating for large numbers of reactor fuel elements would require much more work.

(ii) The Al_2O_3 coating at its present stage of development reduces the corrosion rate of BeO in moist air at high temperatures by a factor of 10 to 130 at 1300 °C. To define operating limits precisely, much more work, including continued irradiation, would be needed. One year's corrosion protection out-of-pile has been demonstrated. Predictions of 2 years' corrosion protection out-of-pile at 1200 °C, and of an allowable dose of at least 10^{20} nvt at temperatures between 500 °C and 1100 °C, have been made from the relevant results. With more results, it may be possible to extend this dose to the original target of 2 x 10^{20} nvt. However, behaviour in-pile at 1200 °C cannot be predicted without irradiation testing at this temperature, and no such irradiation testing is planned.

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9. ACKNOWLEDGEMENTS

Much of the earlier laboratory development was carried out by Mr. K.C. Bridgford. Thanks are also due to Dr. D.G. Walker who initiated the irradiation testing, to Mr. R.G. Hemphill for arranging the irradiation, to Mr. E. Meller for the metallography, and to Mr. J.M. Binns for the stress analysis results.

TABLE 1

EFFECT OF BALL-MILLING TIME ON BASIC COATING MIXTURE

Milling Time (hours)	Green Density (g cm^{-3})	Sintered Density (g cm^{-3})	Open Porosity (%)	Measured Volume Shrinkage (%)	Calculated Volume Shrinkage (%)
0	2.10	3.62	6.4	45.0	42.0
1	2.07	3.07	21.2	35.5	32.6
4	2.17	3.21	16.6	36.3	34.0
8	2.16	3.53	3.3	41.0	38.8
24	2.25	3.6	0	39.8	37.5

TABLE 2

EFFECT OF BALL-MILLING TIME ON VARIOUS PROPERTIES OF LINDE 'A' Al_2O_3

Milling Time (hours)	Green Density (g cm^{-3})	Sintered Density (g cm^{-3})	Open Porosity (%)	Volume Shrinkage (%)
0	2.02	3.69	5.4	45.4
1	2.06	2.85	26.0	25.9
17	2.19	3.25	12.7	33.3
24	2.2	3.28	10.0	33.6

TABLE 3

EFFECT OF BALL-MILLING ON THE IMPURITY CONTENT OF PURE LINDE 'A' Al_2O_3

Element Detected	Unmilled Linde 'A' (p.p.m.)	Linde 'A' Ball-milled for 24 hours (p.p.m.)
Mg	10	5,000
Cu	100	5,000
Fe	500	1,000
Si	500	10,000
Na	not detected	500

TABLE 4

SUMMARY OF PREPARATIVE METHODS FOR THE THREE COATING TYPES

	Type I	Type II	Type III
Composition of Main Coating Mixture			
Linde 'A' Al_2O_3, g.	888	888	888
Baymal, g.	89	89	89
MgO, g.	18	18	18
Gum Arabic, g.	6	–	–
n-octyl alcohol, g.	1	1	1
Water, g.	1000	1000	1000
Ball-milling Time, hours	24	1	0
Undercoat Composition			
BeO, g.	–	25	25
Al_2O_3, g.	–	102	102
MgO, g.	–	2.5	2.5
Water, g.	–	200	200

TABLE 5

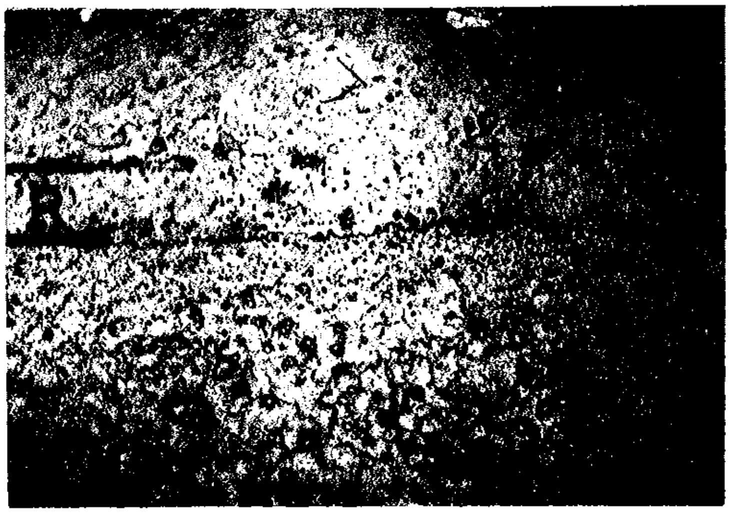
SUMMARY OF CORROSION TEST RESULTS ON UNIRRADIATED Al_2O_3 COATED BeO SPHERES

Test Sphere No.	Coating Type	Nominal Coating Thickness (in.) x 10^3	Test Temperature °C	Test Duration (weeks)	Average Rate of Loss (g cm^{-2} sec^{-1} x 10^9)	Improvement Factor	Reason Removed if other than 'Test Concluded'	Comments
1	None	–	1300	1	10	–	–	–
2–4	"	–	"	2	5.2	1	–	Taken as standard for BeO
5–7	I	5	"	3.3	3.1	1.7	High rate of loss	Coating probably too thin
8–9	I	10	"	8	0.1	52	Irradiation testing	See Section 4.1
10	I	5	"	7	0.24	21	–	–
11	I	10	"	1	0.8	6.5	Coating cracked in following week	Poorly bonded coating?
12	I	10	"	3	0.2	26	" " " "	" " "
13	I	10	"	2	0.2	26	" " " "	" " "
14	I	10	"	13	0.06	86	Metallography	Interface still sharp (Figure 5)
15	I	10	"	14	0.06	86	–	–
16	I	10	"	5	0.3	17	Coating cracked on cooling after 6 weeks	Pinholes in coating?
17	I	10	"	7	0.13	40	–	–
18–22	I	5	"	2	0.47	11	–	Coating probably too thin
23–30	II	10	"	6	0.30	17	–	Coating of low density
31	III	5	"	6	0.80	6.5	–	Coating probably too thin
32	III	5	"	2	0.40	13	–	" " " "
33	III	10	"	7	0.08	65	Coating cracked during cooling in next week's run	Power failure caused sudden shutdown
34	III	10	"	10	0.08	65	" " " " " "	" " "
35	III	10	"	17	0.08	65	" " " " " "	" " "
36	III	10	"	13	0.08	65	–	–
37	III	10	"	6	0.14	37	–	–
38	III	10	"	10	0.08	65	–	–
39	III	10	"	26	0.08	65	Metallography	Coating flaked during cutting
40	III	10	"	23	0.12	42	Coating flaked in one area	The coating was known to contain one small crack at the commencement of corrosion testing
41	III	10	"	30	0.06	84	–	–
42	III	10	"	28	0.04	130	Metallographic examination	Coating flaked during sectioning of sphere
43	III	10	"	33	0.06	84	–	–
44	III	10	"	10	0.08	67	Coating cracked on cooling	Cooling rate possibly too fast
45	III	10	"	19	0.08	65	" " "	" " " " "
46	III	10	1200	50	0.014	140	Test concluded	Coating intact with no tendency to flake
47	III	10	"	50	0.014	140	" "	
48	III	10	"	50	0.010	200	" "	
49	III	10	"	50	0.010	200	"	

TABLE 6

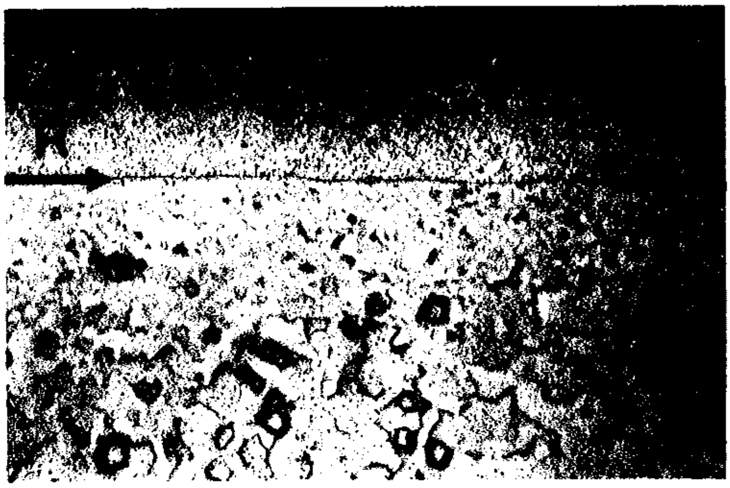
SUMMARY OF IRRADIATION RESULTS ON Al_2O_3 COATED BeO SPHERES

Irradiation Test No.	Coating Type	Temperature of Irradiation (°C)	Integrated Fast Neutron Flux (nvt)	Results and Comments
1–2	Type I, corrosion tested for 8 weeks at 1300 °C prior to test (Table 5, Test 8 – 9).	~ 100	1.4×10^{20}	Coatings flaked badly in some areas, but careful metallography showed that they were still bonded in other areas. The BeO was coarse grained and badly micro- and macro-cracked; this cracking probably caused the coatings to fail.
3–4	Type I	~ 100	1.4×10^{20}	Coatings intact
5	Type I	~ 500	2.9×10^{19}	Coating intact
6	"	"	5.0×10^{19}	Coating intact
7	"	"	9.9×10^{19}	Coating intact – This sphere subsequently corrosion tested. (See Section 4.2).
8	"	~ 750	9.6×10^{19}	Coating intact – This sphere subsequently corrosion tested. (See Section 4.2).
9	"	"	8.0×10^{19}	Coating intact
10	"	"	4.5×10^{19}	Coating intact
11	Type II	~ 500	2.6×10^{19}	Coating intact
12	"	"	4.8×10^{19}	Coating intact
13	"	"	9.6×10^{19}	Coating intact – For metallography, see Figure 7.
14	"	~ 830	3×10^{20}	Coating intact – This sphere subsequently corrosion tested. (See Section 4.2).
15	"	"	3×10^{20}	Coating intact – " " " " "
16	"	"	3×10^{20}	Coating intact – For metallography, see Figure 8.
17–32	"	~ 100	$2.3–3 \times 10^{20}$	All coatings intact, despite BeO microcracking in regions away from the coating in some cases. For representative metallography, see Figure 6.
33	Type III	~ 700	1.6×10^{20}	Coating intact. Corrosion tested. (See Section 4.2)
34	"	"	2.8×10^{20}	Coating intact. Corrosion tested. (See Section 4.2).
35	"	"	4×10^{20}	Coating intact. Not corrosion tested.
36–38	"	"	4.8×10^{20}	Coating intact. Not corrosion tested.



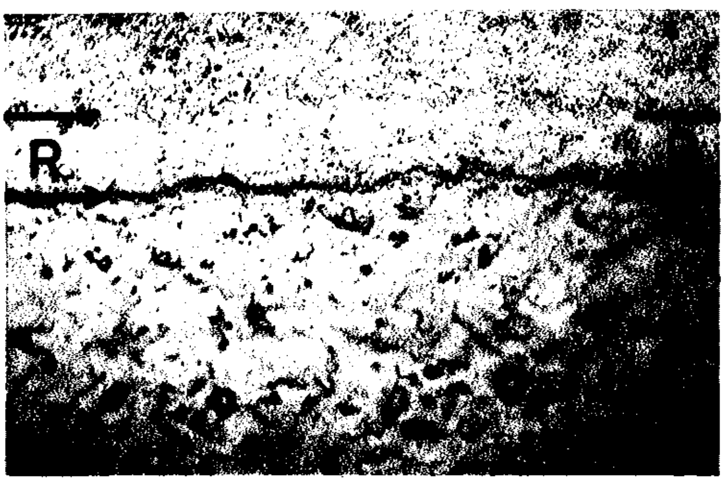
x 250

FIGURE 1 TYPE I Al_2O_3 COATING ON BeO.
INTERFACE BETWEEN COATING (ABOVE)
AND BeO (BELOW) SHOWN BY ARROWS.
REACTION ZONE THICKNESS SHOWN BY R.



x 250

FIGURE 2 TYPE II Al_2O_3 COATING ON BeO.
INTERFACE BETWEEN COATING (ABOVE)
AND BeO (BELOW) SHOWN BY ARROWS.
REACTION ZONE THICKNESS SHOWN BY R.



x 250

FIGURE 3 TYPE III Al_2O_3 COATING ON BeO.
INTERFACE BETWEEN COATING (ABOVE)
AND BeO (BELOW) SHOWN BY ARROWS.
REACTION ZONE THICKNESS SHOWN BY R.

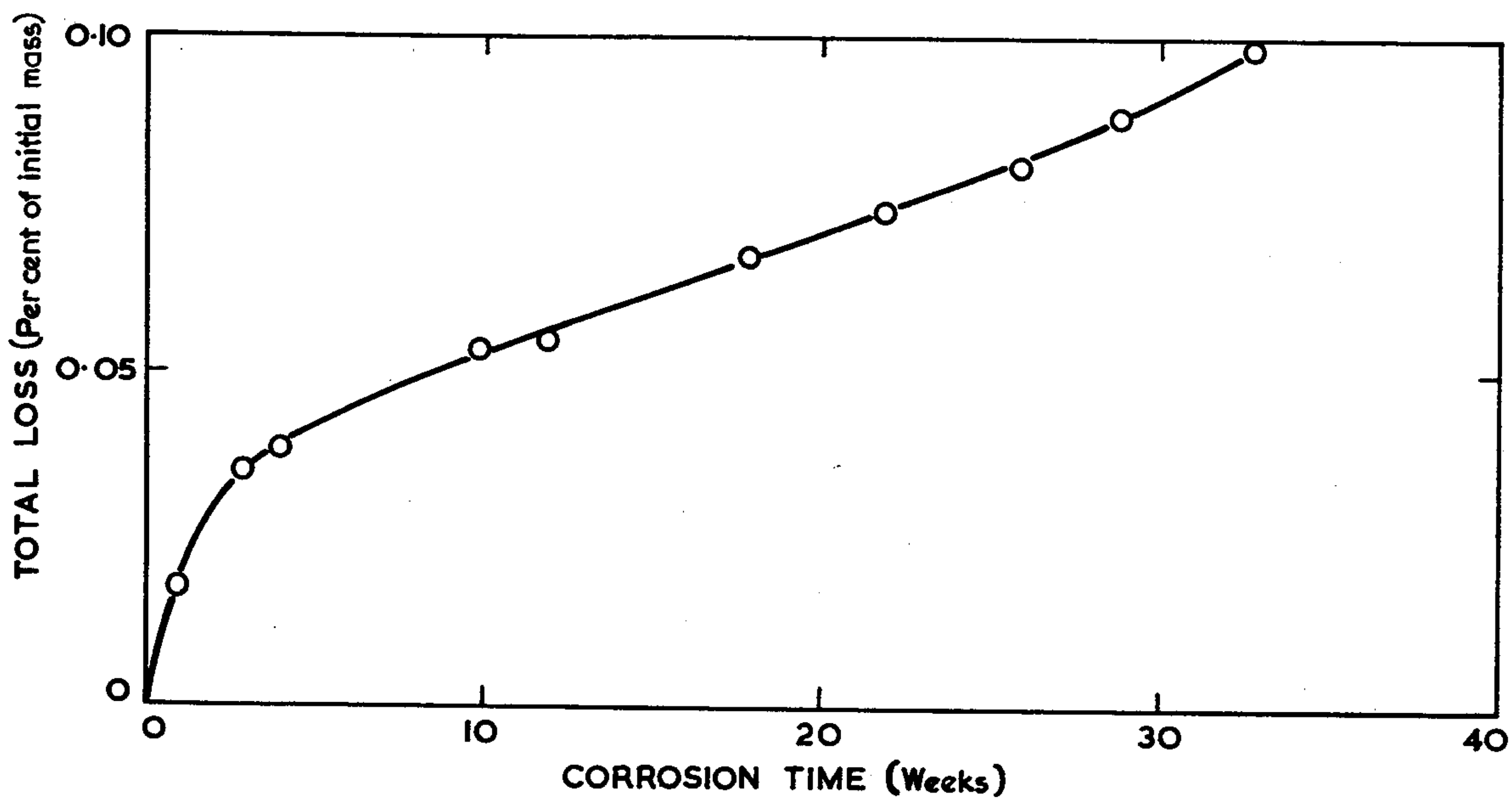
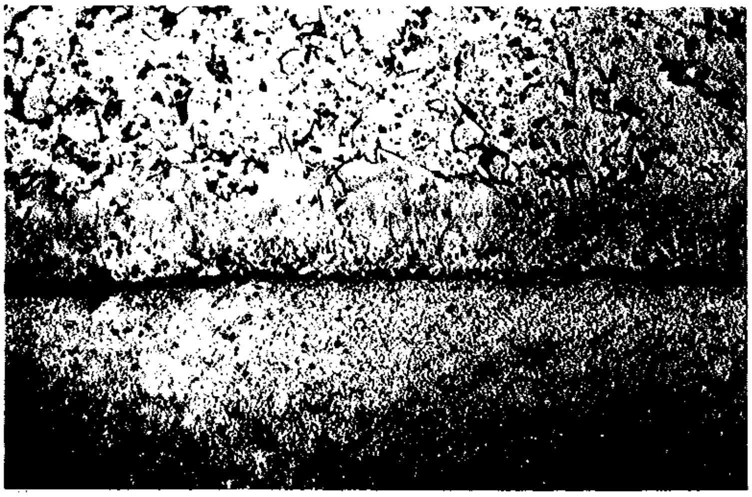
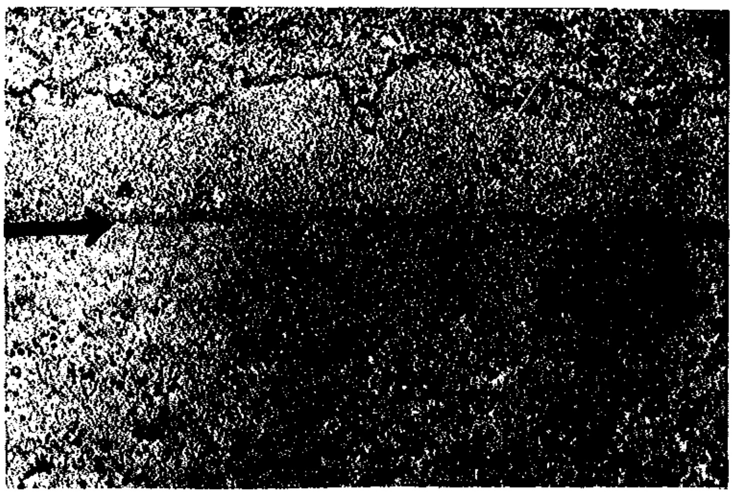


FIGURE 4. CORROSION TEST DATA FOR TEST 43, TABLE 5



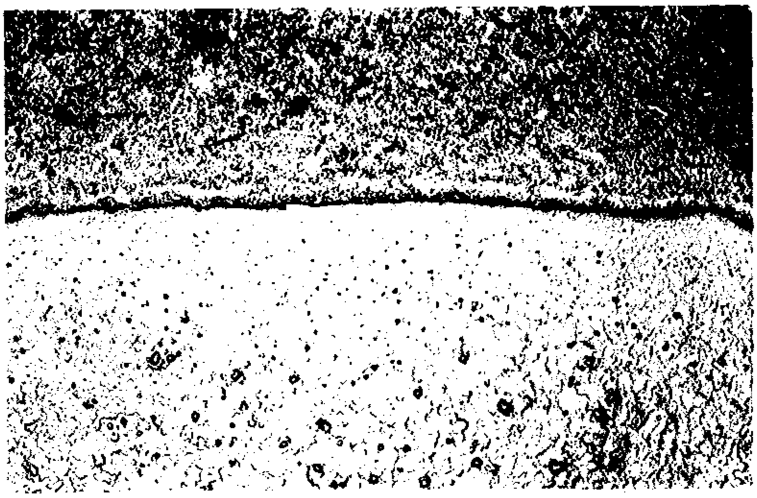
x 250

FIGURE 5 TYPE I Al_2O_3 COATING ON BeO, CORROSION TESTED FOR 13 WEEKS AT 1300°C, (TEST 14, TABLE 5). INTERFACE BETWEEN COATING (ABOVE) AND BeO (BELOW) SHOWN BY ARROWS.



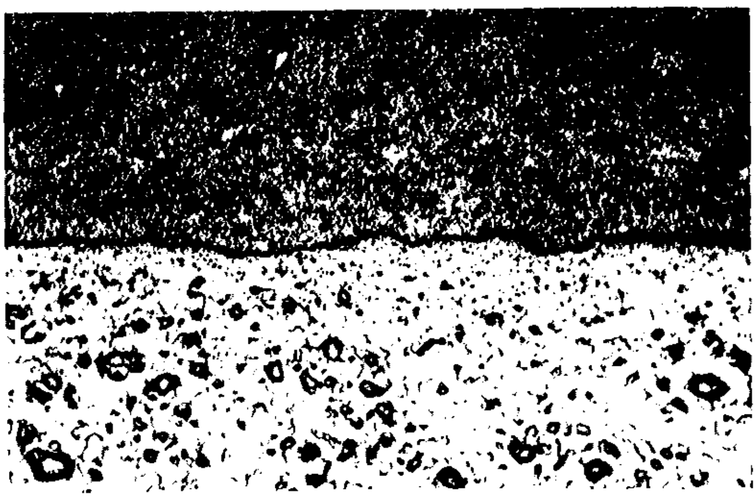
x 100

FIGURE 6 TYPE II Al_2O_3 COATING ON BeO, IRRADIATED TO 2.4×10^{20} nvt AT 100°C, (TEST 21, TABLE 6). INTERFACE BETWEEN COATING (ABOVE) AND BeO (BELOW) SHOWN BY ARROWS.



x 100

FIGURE 7 TYPE II Al_2O_3 COATING ON BeO, IRRADIATED TO 9.6×10^{19} nvt AT 500°C, (TEST 13, TABLE 6). (COATING ABOVE, BeO BELOW).



x 250

FIGURE 8 TYPE II Al_2O_3 COATING ON BeO, IRRADIATED TO 3×10^{20} nvt AT 830°C, (TEST 16, TABLE 6). (COATING ABOVE, BeO BELOW).

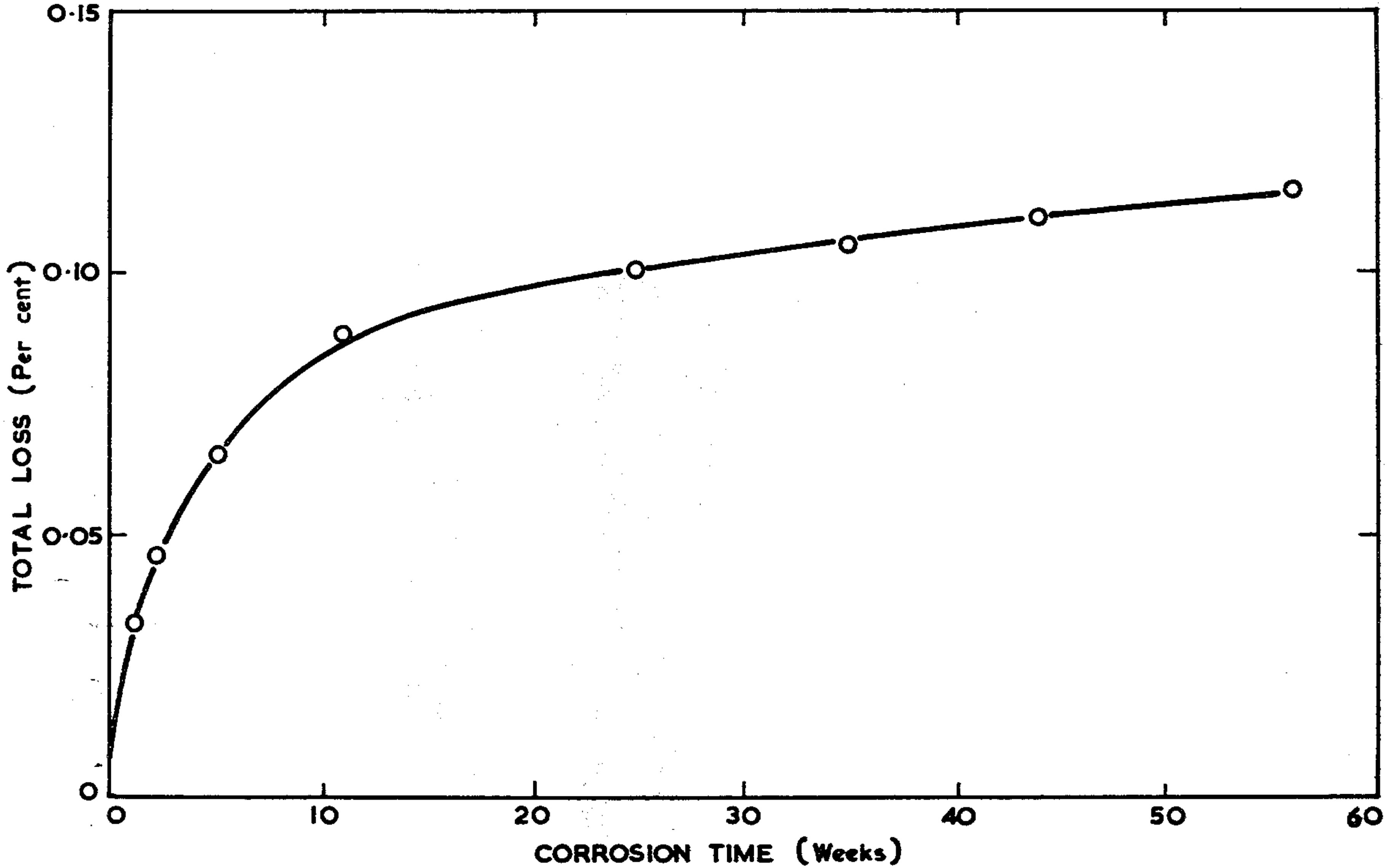
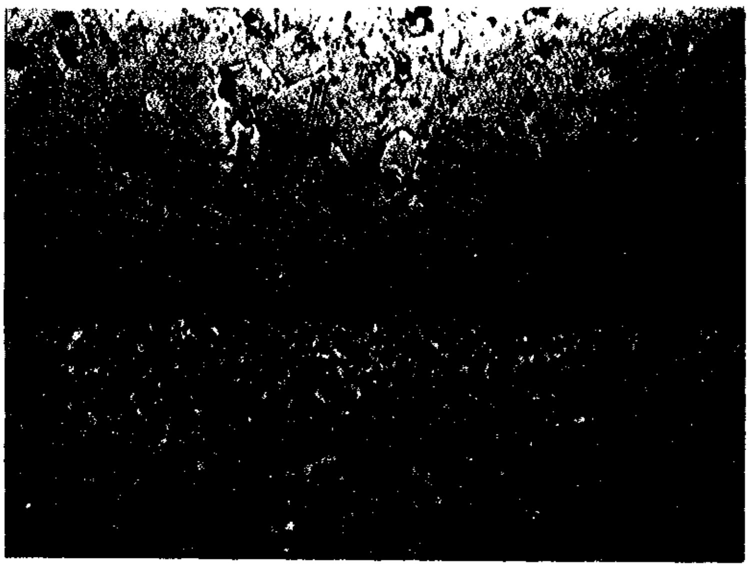


FIGURE 9. CORROSION TEST DATA FOR TEST 7, TABLE 6



x 250

FIGURE 10 TYPE I Al_2O_3 COATING ON BeO, IRRADIATED AND CORROSION TESTED, (TEST 7, TABLE 6). INTERFACE BETWEEN COATING (ABOVE) AND BeO (BELOW) IS NOTICEABLY POROUS.