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RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

AN ASSESSMENT OF POSSIBLE PROTECTIVE COATINGS FOR BeO AND BeO BASED REACTOR FUEL ELEMENTS

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ABSTRACT

Beryllium oxide based reactor fuel elements may be required to operate in moist air at temperatures in the range 1000 – 1200 °C. In this environment, unprotected fuel elements would lose excessive amounts of BeO as $Be(OH)_2$. Methods of preventing this loss by means of non–reactive coatings are considered. By application of established coating principles and also criteria specific to this requirement, the most promising materials are found to be Al_2O_3 and $MgAl_2O_4$. $MgAl_2O_4$ would be difficult to apply to form a dense crack–free coating; Al_2O_3 could be applied by various methods, the best of which appear to be isostatic pressing, slip casting or spraying, and vapour deposition. It is recommended that a detailed thermal stress analysis be carried out on an Al_2O_3–coated fuelled BeO sphere, and that experimental work should be concentrated on isostatic coating

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1. INTRODUCTION

In some high temperature gas-cooled reactor designs, an all-ceramic fuel element which could be operated in air rather than a highly purified gas might be an attractive possibility. Such a fuel element would be based on oxide-type materials, and would probably include beryllium oxide, which has the outstanding advantages of high thermal conductivity and low thermal neutron absorption cross section, and is also a good moderator. BeO is generally a highly stable compound, but reacts with moisture above 1000°C to give a volatile hydroxide according to the reaction:

$$BeO(s) + H_2O(g) \longrightarrow Be(OH)_2(g)$$

The rate of loss increases with temperature, and in moist air in a reactor would become excessive between 1000°C and 1200°C (Stuart and Price 1964). The gaseous $Be(OH)_2$ would deposit in cooler areas as BeO and cause toxicity and heat transfer problems.

Either of two general approaches can be taken to reduce or eliminate this loss. In the first, the BeO activity is reduced chemically, for example by use of a bulk additive or surface-active adsorbed layer, and the equilibrium in the above equation is thereby pushed far to the left. In the second, access of moisture to BeO is prevented by interposing a physical barrier between the gas and the BeO. This takes the form of a coating of some non-reactive material on the BeO. It should preferably be completely impermeable to moisture and may be many microns thick.

This report considers only the second general method, that is, coating, and various possible coating materials and systems are critically assessed. The main fuel element shape considered is a sphere of about one inch in diameter with an outer surface of fuel-free BeO; the core of this sphere contains particles of uranium oxide — thorium oxide solid solution dispersed in BeO. This fuel element forms the basis of the Commission's High Temperature Gas Cooled Reactor Feasibility Study (Roberts 1964). Protection of shapes other than spheres is considered briefly.

2. COATING PRINCIPLES AND REQUIREMENTS

Coating principles and practices have been discussed in detail by various authors in "High Temperature Inorganic Coatings" (Huminik 1963).

Most of the coatings discussed, for example ceramic glazes, porcelain enamels, oxidation-resistant coatings on oxidisable metals, and emittance control coatings on space vehicles, could be classified as "thin", being less than 0.010 inch thick. Much of the following discussion concerns coatings in this range of thickness.

The most important requirements for the coating on a BeO-based fuel element are:

(i) The coating should protect BeO from reaction with water vapour.

(ii) The coating material should be stable with respect to oxidation, reaction with water vapour, reaction with BeO, and should have no phase changes at least over the range ambient to 1200°C.

(iii) Adherence between matrix and coating should be good under all conditions, for example in the presence of an applied thermal stress and after neutron irradiation.

(iv) Neither matrix nor coating should be under excessive stress at the interface. This necessitates close matching of thermal expansion coefficients.

(v) Resistance of the coating to abrasion, thermal stress, thermal shock, and neutron irradiation should be at least as good as that of BeO.

(vi) Neutron absorption cross section should be low.

An initial selection of possible coating materials is first made using requirements (ii), (iv), and (vi). It is assumed that any coating satisfying (ii) will also satisfy (i). Then conditions (iii) and (v) are discussed for a small number of selected materials.

3. SELECTION OF MATERIALS

3.1 Chemical Stability

3.1.1 Oxidation resistance and reaction with water vapour

Of all the refractory compounds, the oxides and complex oxides alone are generally stable at high temperatures in air. The "hard metals", including carbides, borides, nitrides, silicides, etc., and the refractory metals (W, Mo etc.) can all reduce free energy by forming an oxide. Of these groups the silicides (including SiC and Si_3N_4) are unique in forming protective or semi-protective silica films which reduce the rate of further oxidation. The silicides therefore are the only non-oxide group considered in later sections of this assessment. All other hard metals and refractory metals are excluded from further discussion.

Of the oxides, CaO, BaO, and SrO hydrate readily in moist air and must also be excluded.

3.1.2 Phase changes and metastability

The following materials are excluded at this stage for the reasons given:

All crystalline forms of SiO_2 (all have α-β phase inversions below 600°C).

Vitreous SiO_2 (metastability; shows strong tendency to devitrify above 1000°C).

ZrO_2 (unstabilised) (Phase change 1000-1200°C).

FeO, Fe_3O_4 (can oxidise to Fe_2O_3).

Fe_2O_3 (can lose oxygen to give Fe_3O_4 at 1400°C).

All glasses are metastable, but since they are widely used in the form of glazes and in enamels as protective coatings, they are not excluded at this stage.

3.1.3 Reaction with BeO

BeO forms compounds with Al_2O_3, SiO_2 and CaO among the common oxides but of these only CaO would be likely to react at appreciable rates below 1400°C. CaO forms a compound 3 BeO.2 CaO which can form a liquid phase with BeO at about 1360°C. Eutectics between BeO and other common oxides occur at 1835° (Al_2O_3), 1670° (SiO_2), 1855° (MgO), and 2145°C (ZrO_2). Fe_2O_3, MgO, and CaO promote sintering and grain growth in BeO at temperatures as low as 1300°C. This consideration would probably limit the use of MgO, MgO-stabilised ZrO_2, and CaO-stabilised ZrO_2, although these materials are not excluded at this stage.

3.2 Neutron Absorption Cross Section and Other Reasons for Exclusion

The following are excluded for the reasons shown:

Borates, borate based glasses
Rare earth oxides (except CeO_2 and Y_2O_3)
Lithium compounds
(High neutron absorption cross section)

UO_2
ThO_2
(Fissile, fertile)

Complex silicates (except mullite and zircon
Aluminates (except spinel)
Titanates
Zirconates
(See below)

The last four are excluded at present on two grounds:

(i) That simple, well-characterised materials should first be considered.

(ii) That property data on the complex materials is not reliable and any argument, based for example on published thermal expansion coefficient data, may later be invalidated.

Returning to neutron absorption cross section, if we assume that a cross section below 1 barn (1000 mb) is desirable in the metal oxide, the only single oxides which could be considered are: Al_2O_3, MgO, CaO (already excluded), ZrO_2, SiO_2 (already excluded), and CeO_2. This list is based on an arbitrary assumption and is therefore not completely exclusive, but it does serve as a guide to materials likely to be of great interest in later discussions.

3.3 Thermal Expansion Co-efficients

It is assumed that matching of total expansion between coating and BeO over the range 25-1000°C is sufficient to produce a stress-free, crack-free, adherent coating. Exact matching at all points within this range is desirable but is probably unattainable. Above 1000°C, BeO can relax at appreciable rates, and this probably also applies to most coatings. Glasses, for example can probably relax at appreciable rates to lower temperatures even than 1000°C.

If complete matching of total expansion is not possible, the coating should be in compression at room temperature rather than in tension. This means that a higher total expansion than that of BeO is unallowable, but a slightly lower value may be allowable. Pentecost (1963) lists such total expansion for a wide variety of materials. His figure 0.88 per cent. for BeO from 25-1000°C compares reasonably well with the figure 0.90 per cent. of Rotsey (private communication).

Cole and Inge (1961) have discussed calculation of "mismatch stresses" at interfaces. In the absence of any vertical stress component, the stress S_x parallel to the interface is given by:

$$S_x = \frac{\epsilon_x E_c}{1-\mu_c}$$

where ϵ_x is the stress in the coating at the interface,
E_c is the elastic modulus of the coating material, and
μ_c is the Poisson's ratio of the coating material.

ϵ_x will be less than the thermal expansion mismatch because the substrate is also deformed elastically. In the present simple treatment, the stress in the coating is first calculated assuming that ϵ_x is the thermal expansion difference between the unbonded materials, and that $\mu_c = 0.3$. This stress value is then corrected for substrate strain by applying the factor $(1 + E_c/E_s)^{-1}$ where E_s is the elastic modulus of the substrate. In this treatment, elastic modulus and μ values are assumed to be constant over the range 25-1000°C.

Data and results of simple calculations on oxides and silicides which have not been excluded up to this point are given in Table 1.

3.4 Discussion

From Table 1, it appears that only the last nine materials, plus stabilised zirconia (> 8 w/o CaO) are worth further consideration.

3.4.1 ZrO_2

Information in the literature on stabilised zirconia is meagre and conflicting, since behaviour depends on the type and content of stabilising additive, but it is known that ZrO_2 fully stabilised with CaO expands somewhat more than BeO. Partially stabilised ZrO_2, containing about 4 w/o of CaO, has a lower total expansion, but shows expansion hysteresis due to a small content of residual monoclinic phase. It is likely that a partially stabilised zirconia with total expansion equal to that of BeO could be prepared. However, it would not satisfy the requirement of complete absence of phase changes. Fully stabilised ZrO_2 would probably fail in tension; also it contains the additive CaO which may cause growth in BeO grain. In addition any form of stabilised ZrO_2 may be unattractive because of uncertainty about its long term stability at high temperatures.

3.4.2 Systems Containing Glass

Glasses and glass-ceramics, such as porcelain enamels and glass-bonded ceramics containing only a few volume per cent. of glass, form a very large group of materials. It is probable that many different compositions with satisfactory adherence to BeO could be formulated. Successful work along these lines has already been reported (Ramm, Smith, and Reeve 1966). However, any systems containing glass have the following disadvantages:

(i) Metastability of the glass phase; danger of devitrification if overheated.

(ii) Difficulty of support during firing without pinhole formation (applies mainly to high glass content).

(iii) Danger of adherence under load at temperatures of 1000-1200°C.

(iv) Uncertain irradiation stability.

(v) A glass usually contains two or more oxides and thus lacks simplicity.

Systems containing glass are therefore not considered further at present.

3.4.3 Other materials

Of the other eight promising materials from Table 1, others are now provisionally excluded for the reasons given:

WSi_2 $MoSi_2$	Potential instability in air, particularly under conditions where the integrity of the protective SiO_2 film may not be maintained e.g. combined neutron irradiation and abrasion; also thermal neutron absorption cross sections are high.
TiO_2, Cr_2O_3, CeO_2, Y_2O_3	Medium-high thermal neutron absorption cross sections; all except Y_2O_3 have variable oxidation states. (The latter may be no great problem in air operation where the fully oxidised state should be easy to maintain).

This leaves Al_2O_3 and $MgAl_2O_4$. These are single-component, well-known, low cross section materials and should be examined in detail before any materials previously excluded are reconsidered. Their properties are now summarised.

4. PROPERTIES OF Al_2O_3 AND $MgAl_2O_4$

4.1 Thermal and Mechanical Properties (see Bibliography)

Thermal conductivity data for Al_2O_3, $MgAl_2O_4$, and BeO are summarised in Table 2.

Mechanical properties of Al_2O_3 and BeO have been measured by various investigators but a survey of data from the literature would be of little value since properties depend critically on density, grain size, preferred orientation, and purity. In the absence of data on Al_2O_3 of fixed structure, density, and purity, use of the corresponding values of bend strength, elastic modulus, and shear modulus to those of BeO is justifiable since published figures for BeO and Al_2O_3 fall within almost the same ranges in each case.

There is little corresponding information on spinel but measured values of strength appear to be lower (by approximately 50 per cent.) than those of BeO and Al_2O_3. However, it is not certain that these measurements were made on an optimum or even near-optimum structure. The elastic modulus of 97 per cent. dense spinel has been measured as 38×10^6 p.s.i., which is about 25 per cent. lower than the values for BeO and Al_2O_3.

4.2 Phase Relations (see Bibliography)

The stable form of alumina at all temperatures up to the melting point (2050°C) is hexagonal α-Al_2O_3. $MgAl_2O_4$ is a stable compound with a cubic spinel-type structure and a melting point of 2135°C. It can take excess Al_2O_3, but not MgO, into solid solution up to a mole ratio (MgO : Al_2O_3) of 1 : 4. Phase relations relevant to the coating of BeO and BeO-(UTh)O_2

are as follows:

BeO-Al_2O_3: The phase diagram shows three compounds, 3 BeO . Al_2O_3, $BeAl_2O_4$, and BeO . 3Al_2O_3. The eutectics are at 1835°C, 1850°C, and 1890°C. Available phase diagrams show no solid solution in this system. These compounds do not form in BeO-Al_2O_3 mixtures at an appreciable rate below 1500°C (Beaver and others 1964).

BeO-Al_2O_3-ThO_2: The phase diagram shows only the BeO-Al_2O_3 binary compounds. The lowest eutectic in the system is at 1795°C.

BeO-Al_2O_3-ThO_2-UO_2: There is no published phase diagram for this system. If the UO_2 : ThO_2 (or PuO_2 : ThO_2) ratio is low the eutectic temperature should not be very different from the value 1795°C given above. If all the ThO_2 were to be replaced by UO_2 the eutectic temperature may fall, possibly to 1700°C.

$MgAl_2O_4$-BeO: This system probably behaves as a simple binary system with an estimated eutectic of 1720°C.

$MgAl_2O_4$-BeO-ThO_2: This system has not been reported. However, the lowest eutectic will certainly be below 1720°C and it may be in the range 1600-1650°C. The corresponding system containing UO_2 may not behave very differently.

4.2.1 Comments on phase relations

(i) Al_2O_3 coatings on BeO or BeO-$(UTh)O_2$ could be sintered at least up to 1700°C with no danger of liquid formation but chrysoberyl will form above 1550°C.

(ii) $MgAl_2O_4$ coatings on BeO could be sintered at least up to 1600°C with no danger of liquid phase formation.

(iii) $MgAl_2O_4$ coatings on BeO-$(UTh)O_2$ may have to be sintered as low as 1500°C to avoid the danger of liquid phase formation.

4.3 Sintering Behaviour

Al_2O_3: The subject of sintering of Al_2O_3 is too large to be reviewed here. Alumina and beryllia have very similar sintering behaviour which depends more on the crystallite size, pressing characteristics, and green density than on the composition of the material. Although alumina is often sintered commercially at temperatures over 1600°C, Coble (1962) has shown that a 0.3μ powder containing 0.25 w/o of MgO can be sintered to at least 95 per cent. theoretical density in 1 to 2 hours at 1480°C. The function of the MgO is to increase the Al_2O_3 sintering rate and to inhibit discontinuous grain growth. It thus seems quite feasible for BeO and Al_2O_3 to be matched in sintering behaviour, since powder properties and additive content can be varied independently in each material. Sintering at 1550°C or above will result in a reaction zone of chrysoberyl. This may assist bond formation but may be detrimental to irradiation stability. (See Section 4.4).

$MgAl_2O_4$: There is little information on the sintering of spinel, but if powders with similar characteristics to sinterable BeO and Al_2O_3 were available, it is almost certain that $MgAl_2O_4$ could be sintered in the same way as BeO. The difficulty is that spinel powders are obtained by reacting MgO and Al_2O_3 and then ball-milling the reaction product. This is not likely to yield the 0.1-0.3μ crystallite size characteristic of sinterable alumina and beryllia powders formed by low temperature calcination of salts of the metals. Temperatures well above 1500°C would be required for ball-milled $MgAl_2O_4$ prepared by reaction of MgO and Al_2O_3, but it has been shown (Section 4.2) that a liquid phase between $MgAl_2O_4$ and BeO will form at 1720°C. Thus, since the sintering of $MgAl_2O_4$ onto BeO would require considerable work to develop a sinterable $MgAl_2O_4$ with shrinkage matched to that of BeO, this material is not attractive for this application.

4.4 Irradiation Damage

Al_2O_3: The effects of neutron irradiation on BeO and Al_2O_3 have been studied by Hickman and Walker, who summarised and compared the behaviour of these materials in two recent papers (1966a and b).

On irradiation at pile temperature (75-100°C), polycrystalline alumina showed density decreases of 0.13 per cent. at 2×10^{19}nvt (>1MeV), 0.28 per cent. at 5×10^{19}, 0.4 per cent. at 10^{20}, 0.63 per cent. at 2×10^{20}nvt, and 1.05 per cent. at 5×10^{20}nvt. Typical corresponding figures for polycrystalline BeO were 0.07 per cent. at 2×10^{19}, 0.17 per cent. at 5×10^{19}, 0.35 per cent. at 10^{20}, 0.65 per cent. at 2×10^{20}, and 2.7 per cent. at 5×10^{20} nvt. At higher doses, volume changes in BeO continue to exceed those in Al_2O_3. However, at doses up to 2×10^{20} nvt there is a maximum of 0.1 per cent. difference in volume changes, or 0.033 per cent. difference in length changes. On the above figures, at 5 x 10^{19} nvt the alumina could be in compression at room temperature by 12,000 p.s.i. in addition to the 18,000 p.s.i. arising from thermal shrinkage in fabrication, while at 2 x 10^{20} nvt, the total compressive stress at room temperature in the alumina would have been reduced to about 16,000 p.s.i. At 5 x 10^{20} nvt, the difference in linear expansion is 0.55 per cent. and alumina bonded to BeO would certainly fail in tension (calculated stress 192,000 p.s.i.).

The behaviour of alumina under irradiation at 1000-1200°C is more difficult to predict, and will depend on neutron flux (damage rate), integrated flux, temperature, and also on stress relaxation rates which will probably depend on impurity content and grain size. At doses up to 2 x 10^{20} nvt the total growth in each material, and the disparity between their length changes, should be smaller, and the irradiation-induced stresses will also be smaller. At higher doses, the tensile stress in the Al_2O_3 caused by the larger expansion in the BeO to which it is bonded may be progressively relieved by creep in the alumina if its grain size and diffusion rates allow this. The coating will be most likely to fail in tension at doses above 2 x 10^{20} nvt at temperatures below 1000°C.

In the above discussion, no account is taken of the possible existence of a thin layer of chrysoberyl, $BeAl_2O_4$, between the BeO and Al_2O_3; this is most likely to be present where the coating-matrix bond is strong. At pile temperature, chrysoberyl expands at a much faster rate than BeO or Al_2O_3 and its presence would probably limit the allowable dose much more than discussed above (Walker, private communication). The position may be again much more favourable at temperatures of 1000°C and above. Every effort, however, should be made to avoid the formation of chrysoberyl, for example by keeping fabricatio temperatures to 1500°C or below. (See Section 4.2.1).

Spinel: No detailed irradiation study of spinel has been reported. Crawford (1965) quoted an isolated result from fast neutron irradiation, presumably at < 100°C, in which density had not changed after a dose of 4 x 10^{20} nvt. At the same time, he reported a density decrease of 1 per cent. for Al_2O_3 at 6 x 10^{20} nvt, which agrees with Hickman and Walker's results.

5. COATING METHODS

Coating methods may be summarised (after Withers 1963) as follows:

Electro Deposition
- Aqueous Solution
- Fused Salts
- Organic Solvents
- Electrophoresis

Spraying
- Oxyfuel Flame
- Arc Plasma

Cladding
- Roll Cladding
- Gas Pressure Bonding
- Isostatic Coating*
- Co-extrusion*

Vapour Deposition
- Pack Cementation
- Chemical and Pyrolytic Reaction (vapour phase or fluidised bed)

Enamelling

Vacuum Metallising

Hot Dipping
- Molten Metals
- Selective Freezing

Slurry
- Painting
- Trowelling
- Spraying*

Exothermic Reaction

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* Withers did not include these methods in his tabulation.

Of these only the following five could be used for applying coatings of Al_2O_3 or $MgAl_2O_4$:

- Flame or Plasma Spraying
- Isostatic Coating
- Co-extrusion (not for spheres)
- Vapour Deposition
- Slurry Methods.

5.1 Flame or Plasma Spraying

Thin Al_2O_3 or $MgAl_2O_4$ coatings could be applied to sintered BeO surfaces by flame and plasma spraying. These processes however have several intrinsic disadvantages:

(i) Coatings are usually porous with a fairly open microstructure.
(ii) They are weaker than the same material in bulk.

(iii) They often have quenched-in strains or are in a metastable state.

Flame-sprayed alumina usually exists in the gamma rather than the normal alpha form; its strength in bend has been quoted as 4000-6000 p.s.i. compared with 40,000 p.s.i. for bulk Al_2O_3.

Of the flame-sprayed coating systems which have achieved recognition, the Norton "Rokide" process has the best reputation. In this process, which uses sintered rods of the material being sprayed, all particles which pass through the flame become molten. "Rokide A" coating consists of γ-Al_2O_3 of density 3.3 g/cm^3, with 7 per cent. open porosity. The compressive strength at room temperature is quoted as 37,000 p.s.i., and its adherence to steel as 600-1000 p.s.i.

A difficulty also arises in applying coatings to such shapes as spheres, particularly in large numbers and by automatic or semi-automatic methods. A possible solution would be to spin each sphere rapidly around a rapidly precessing axis; this could be done by supporting the sphere on a suitably designed air jet. Flame-spraying could then be carried out in (optimistically) 5-10 seconds per sphere. This type of support will be mentioned again for other spraying methods.

Thus, although the difficulty of application could probably be solved, flame spraying does not appear promising for the present application because of porosity, weakness, metastability (of Al_2O_3) and quenched-in strains in the sprayed coating. Plasma spraying has not been as widely used or reported but the same general remarks apply. Neither process could be used for coating the bore of long tubes, but, with the above limitations, could be used to coat rods.

5.2 Isostatic Coating

This method has been developed at Lucas Heights for applying unfuelled BeO coatings to fuelled BeO cores. The core is first pressed at a pressure less than that finally required, and rounded by hand-machining or centreless grinding. The green core is then suspended in a "Duralon" (polyurethane) die containing a spherical cavity while BeO powder is formed into a spherical shell around the core. The die is closed and the final isostatic pressure is applied. The coated sphere is finally rounded and sintered. As the tolerance on coating thickness which can be achieved by this method is probably ± 0.005 inch, the method is not suitable for application of coatings much thinner than 0.050 inch, which is the reference thickness for the BeO coating on a standard fuelled BeO sphere.

If Al_2O_3 or $MgAl_2O_4$ were to be applied to a spherical fuel element by this method, it would be logical, although not essential, to replace the present 0.050 inch BeO coating with a "thick" Al_2O_3 or $MgAl_2O_4$ coating applied by the same method. This solution would be simple in that no techniques in addition to these used at present would be required, and the fuel element sphere would still have only one unfuelled coating. There is no reason to believe that the Al_2O_3 coating could not be made as dense as the BeO coating. In what follows, it is assumed that at equal densities (per cent. theoretical) BeO and Al_2O_3 will be equally fission product retentive.

Difficulties with this system would be:

(i) The little-known sintering behaviour of $MgAl_2O_4$ and the lack of a commercially available sinterable $MgAl_2O_4$ powder, (see Section 4.3).

(ii) Maintenance of a good bond during sintering of the coating onto the BeO. This could be overcome by ensuring that at sintering temperature the coating shrinks slightly more than the BeO and perhaps reacts to form a very thin incipient intermediate layer of $BeAl_2O_4$; the green densities and powder characteristics, the type and extent of sintering enhancing additives, and the sintering time and temperature, could be adjusted to ensure this. If the differential sintering shrinkage is not too high, the coating should be able to accommodate this strain plastically at sintering temperatures. During cooling, BeO shrinks more than Al_2O_3 or $MgAl_2O_4$ and provided that a good bond has been formed this should remain during cooling.

(iii) Thermal stress behaviour of the composite spheres during internal heat generation. This is not considered here, but the composite system should be analysed. An alumina coating could possibly be made stronger than the BeO matrix, but in any analysis the same strength as for BeO should be assumed. The lower thermal conductivity of the coating will of course be detrimental.

(iv) The Al_2O_3 or $MgAl_2O_4$ may cause grain growth in the BeO, or inhib sintering in the BeO. It may also react with exposed $(UTh)O_2$ or $(PuTh)O_2$ fuel particles. From available phase diagrams (Section 4.2), it seems unlikely that the eutectic in either of the systems Al_2O_3-UO_2-ThO_2-BeO or MgO-Al_2O_3-UO_2-ThO_2-BeO would be below 1600°C. It is therefore unlikely that UO_2, PuO_2 or ThO_2 would completely traverse a 0.050 inch coating during sintering. These possible difficulties should not prevent further consideration of this type of coating.

(v) A considerable volume (1 per cent.) of a 1 inch diameter sphere is taken up by a 0.050 inch thick coating. If this is Al_2O_3, there may be objections on reactor physics grounds because of replacement of some of the BeO by materials which have little moderating power and a higher neutron absorption cross section.

(vi) The behaviour of Al_2O_3 on neutron irradiation at doses above 2×10^{20}nvt (see Section 4.4) may be a problem; the behaviour of spinel is not well known.

(vii) Possible invalidity of the assumption that at equivalent densities BeO and Al_2O_3 will be equally fission product retentive.

5.3 Co-extrusion

This can be considered as an alternative to isostatic coating with the differences that:

(i) It can only be used on shapes such as rods or tubes which are normally extruded and sintered.

(ii) There remains a problem of sealing the ends of the extrusion if this is required.

(iii) Much thinner coatings, for example 0.010 inch, can be applied than by isostatic coating.

(iv) The coating would preferably be directly on a fuelled BeO surface and hence should be thick enough to retain fission products. Application of two coatings (BeO and Al_2O_3) simultaneously would necessitate a very refined technique and may be costly.

5.4 Vapour Deposition

Sintered fuel element spheres could be coated with Al_2O_3 by a vapour deposition process, for example hydroloysis of $AlCl_3$ vapour; the spherical shape would be suitable for fluidised bed operation. Thin coatings (for example up to 0.005 inch or 125μ) could probably be built up within reasonable times. This type of process could be used for rods, but would not be suitable for the bore of long tubes.

$MgAl_2O_4$ could not be applied directly by vapour deposition. Nolting and others (1961) have however made brief reference to forming $BeAl_2O_4$ on BeO and then converting to $MgAl_2O_4$. A 0.001 inch coating was said to protect BeO from reaction with water vapour at 1400°C. The method of achieving this was not stated, but could have involved formation of an Al_2O_3 layer by vapour deposition, conversion to $BeAl_2O_4$ by heating to 1600-1700°C, then reacting the coating with a volatile magnesium compound. If the coating is only to be used to 1200°C, reaction to $BeAl_2O_4$ may not be necessary since this would not occur appreciably during use. The Al_2O_3 coating could in this case be directly converted to $MgAl_2O_4$.

A vapour deposited coating could probably readily be made as dense as the present BeO coating and thus should retain fission products equally well. It could thus replace the present BeO coating on fuel element spheres.

5.5 Slurry Methods

Enamels and glazes which develop a glassy phase during firing can be applied to already densified materials; during firing, the glassy phase allows flow and material redistribution in the coating. A material such as Al_2O_3 applied as a slurry to dense BeO would be of low green density and would crack badly due to high shrinkage during sintering, since no flow can take place. However, a thin Al_2O_3 (or $MgAl_2O_4$) coating could be applied in slurry form to an unsintered BeO surface (for example by spraying a rotating sphere), and provided that only a very thin layer (for example 0.001 inch) was applied, this may remain intact during sintering. It could be envisaged that the BeO surface would partially react with the coating sufficiently to draw the coating inwards during sintering whereas a layer thick enough to have some identity (for example > 0.005 inch) would probably crack. While the thin layer may remain crack-free it may not be completely protective. A very much thicker layer (> 0.020 inch) could be isostatically pressed onto the sphere, but the method then becomes similar to isostatic coating which is the preferred method for thick coatings on spheres.

A thin layer applied by the slurry method could not be relied upon for fission product retention and hence would not replace the present BeO coating on a fuelled sphere. Rods could be coated by this method but the coating of the bore of long tubes would be difficult.

6. CONCLUSIONS AND RECOMMENDATIONS

1. The following systems appear to show most promise for spheres at present and are worth further consideration:

(i) Isostatically-pressed thick Al_2O_3 coating, probably replacing the unfuelled BeO layer in the present fuel element spheres.

(ii) Thin slip-cast or sprayed Al_2O_3 coating on the present unfuelled BeO surface.

(iii) Vapour deposited thin Al_2O_3 coating.

(iv) As in (iii), then converted to $BeAl_2O_4$, and then to $MgAl_2O_4$ by reaction with vapour-deposited MgO.

2. If none of the above methods and materials prove satisfactory, TiO_2, CeO_2, Y_2O_3 and Cr_2O_3 could be considered as alternatives to Al_2O_3 in systems (i), (ii), and (iii). Stabilised ZrO_2 could also be reconsidered, but probably only in systems (i) and (ii).

3. For coating rods and tubes, the same materials applied by co-extrusion would be of most interest.

4. Flame-sprayed coatings, coatings containing glass, and systems based on materials which are potentially unstable in moist air should be avoided if possible. Materials which show phase changes over the range 20-1200°C should be definitely excluded, while metastability in this range is very undesirable.

5. A coating system which appears completely satisfactory out-of-pile may fail under irradiation; a system which is completely matched out-of-pile will in fact be unlikely to be matched in in-pile behaviour. However, BeO and Al_2O_3 may be sufficiently close in irradiation expansion behaviour at low doses (2×10^{20}nvt.).

6. It is recommended that the starting points for a project to prove the feasibility of moisture protection of BeO-based fuel element spheres should be:

(i) A detailed thermal stress analysis of a fuel element sphere in which the BeO coating is replaced by Al_2O_3. A bonded structure which is stress free at 1000°C before irradiation should be assumed.

(ii) An experimental fabrication programme to determine the feasibility of isostatically coating fuelled BeO cores with Al_2O_3 and then sintering.

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TABLE 1.

THERMAL EXPANSION AND "MISMATCH STRESS" DATA ON OXIDES AND SILICIDES WITH BeO SUBSTRATE

Material	Total Expansion (25-1000°C) %	Approx. Value of E (25-1000°C) p.s.i. x 10^6	Stress in Coating at Interface (p.s.i) + Tension - Compression	Comments
BeO	0.88	50	Not applicable	
MgO	1.33	30	+120,000	Would fail in tension
Stabilised ZrO_2 (> 8 w/o CaO)	0.95	30	+ 19,000	Possibly satisfactory.
$3\ Al_2O_3 \cdot 2\ SiO_2$ (mullite)	0.50	20	- 77,000	Compressive stress too high
ZrO_2-SiO_2 (zircon)	0.45	30	-112,000	
SiC	0.50	50	-135,000	
Si_3N_4	0.28	13	- 89,000	
Cr_3Si	1.08	Assume 50	+ 70,000	Would fail in tension
Mo_3Si	0.68	Assume 40	- 63,000	Compressive stress too high
WSi_2	0.81	Assume 40	- 22,000	$MoSi_2$ preferred
$MoSi_2$	0.83	50	- 18,000	
Y_2O_3	0.88-0.93	Not known	Small	(Warshaw and Roy 1961)
TiO_2	0.86	Assume 20	- 4,000	
CeO_2	0.87	20	- 2,000	
Al_2O_3	0.83	50	- 18,000	
Cr_2O_3	0.84	Assume 50	- 14,000	
$MgAl_2O_4$ (spinel)	0.82	35	- 18,000	
Glasses, glass-ceramics	Variable	Variable	Variable	

TABLE 2

THERMAL CONDUCTIVITY OF Al_2O_3, $MgAl_2O_4$, AND BeO

(Data of Kingery and others 1954)

Temperature	K(cal sec^{-1} cm^{-1} deg C^{-1}) (Corrected to zero porosity)		
	Al_2O_3	$MgAl_2O_4$	BeO
100	0.072	0.036	0.525
200	0.054	0.031	0.417
400	0.031	0.024	0.222
600	0.022	0.019	0.112
800	0.017	0.016	0.065
1000	0.015	0.014	0.049
1200	0.013	0.013	0.041

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