

## *Beryllium—Ceramic Compatibility Tests*

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*Robert J. Hanrahan, Jr.*

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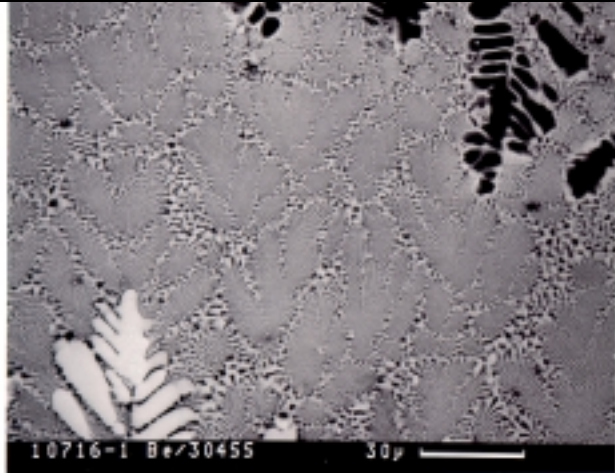
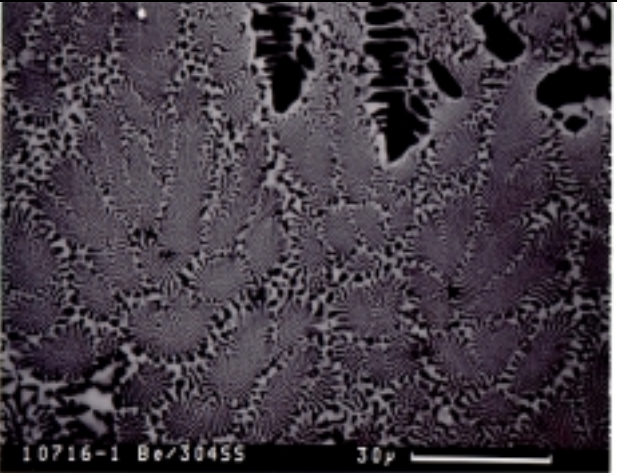
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### **Abstract**

We are interested in the possibility of using induction melting in order to recycle beryllium components. This process will require the use of a container for the molten Be. Although BeO is the obvious choice of materials based on compatibility, engineering considerations dictated that other materials be considered. Therefore, a series of experiments was performed in order to test the compatibility of molten beryllium with various ceramic crucible materials. The materials tested include  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{SiC}$  and  $\text{SiO}_2$  (fused silica). Alumina exhibited the best compatibility among the materials tested, based on the relatively trivial observation that the molten beryllium did not stick to alumina. We have evaluated the reaction products and to some extent the mechanism of reaction of beryllium with each of these materials. In the case of alumina for example, the compatibility may be attributed to the formation of a layer of an intermediate BeO- $\text{Al}_2\text{O}_3$  phase or phases. In the magnesia, yttria, and zirconia-Be systems ternary oxides are not observed but the oxides may be reduced by beryllium resulting in formation of intermetallic phases and beryllium oxide. The silicon based compounds are reduced to form BeO and free silicon. The significance of these results with regard to the published thermodynamic data (particularly phase diagrams) will be discussed. Additional tests were conducted to evaluate the products of the reaction between molten beryllium and stainless steel. This report also discusses the results of these tests.

### **Be – SS Alloy Tests**

These tests were conducted in order to experimentally evaluate the possibility of lowering the melting point of the resulting mix. Elemental beryllium was melted (using DC arc) with samples of 304 stainless steel. Ingots were cross sectioned to evaluate microstructure and determine composition using x-ray diffraction. The resulting microstructures revealed a mixture of intermetallic compounds such as  $\text{CrBe}_2$  ( $T_{\text{mp}}$  1840° C)  $\text{NiBe}$  ( $T_{\text{mp}}$  1605° c) and  $\text{FeBe}_2$  ( $T_{\text{mp}}$  1463° C). The true liquidus temperature of the resulting alloy is above the allowed temperature limit of the DTA system available for beryllium work (1400° C) therefore precise melting points could not be determined. Although eutectics exist in all of these systems the lowest melting points are only marginally below that of Be (1289° C). In a crucible experiment these intermetallic compounds can be expected to form at the interface between the molten Be and SS, resulting in a reaction rate that is limited by diffusion across the intermetallic layer. In the case of solid-solid reactions Flament et al. have calculated the rate of interdiffusion across the reaction zone.<sup>1</sup> Although the rates may be expected to be much higher in the case of molten Be-SS reaction complete reaction is unlikely to be achieved in a reasonable time without stirring and the use of the maximum available furnace temperatures.

	
<p>SEM micrograph (backscatter mode) of Be alloyed with 304 SS. The microstructure is predominantly primary dendrites of <math>\text{FeBe}_2</math> and <math>\text{CrBe}_2</math> with a ternary eutectic of unknown composition containing at least two, possibly three phases.</p>	<p>Higher magnification image of the eutectic region in the area at left.</p>

### **Beryllium – Crucible Compatibility Tests**

The objective of this series of experiments was to determine the compatibility and (if compatible) optimum heating and cooling rates for ceramic crucibles used to melt beryllium metal. Compatibility was evaluated based on the condition of the crucible (no cracks or holes) and the extent of interaction between the crucible and the beryllium (if the beryllium stuck to the crucible, what and how much reaction product formed). Crucible materials were chosen based on available thermodynamic information, previous experience, and availability.

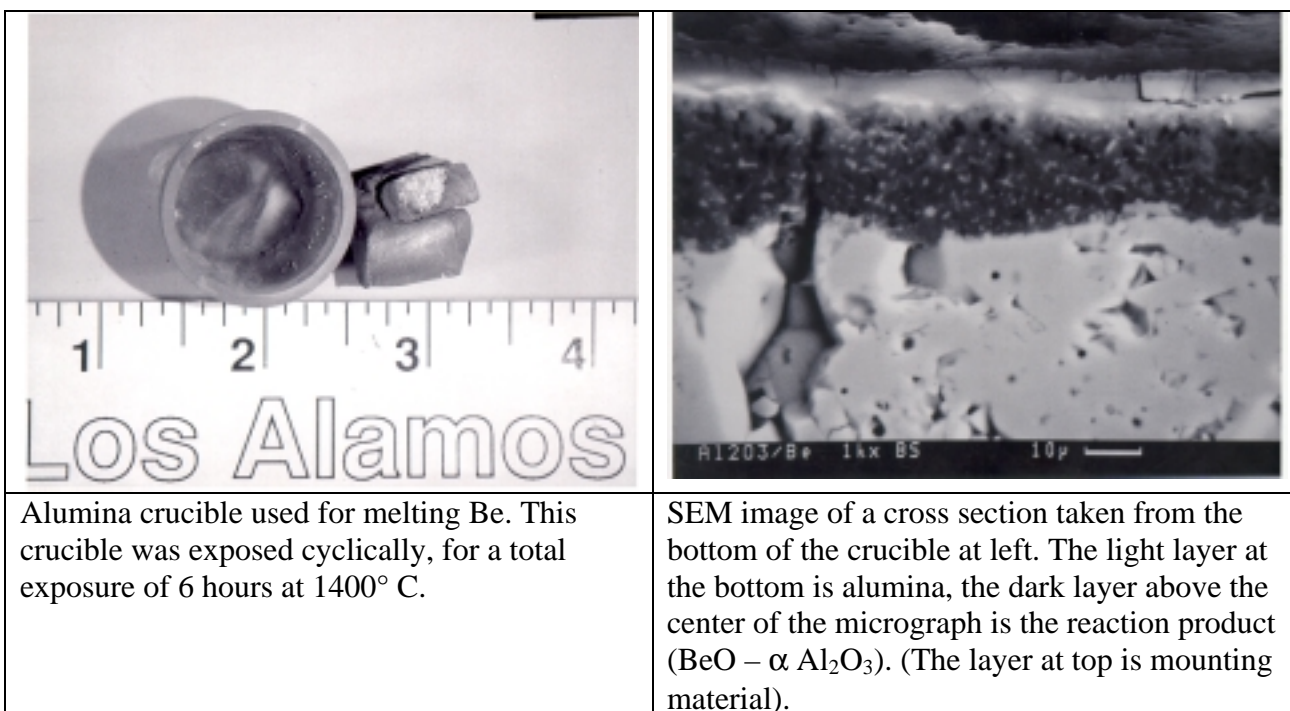
Materials are listed in alphabetical order rather than the order in which they were tested. All experiments were conducted at furnace temperatures of 1350° or 1400° C in a 2" i.d. Lindberg tube furnace unless otherwise noted.

### **Alumina**

Early experience in using  $\text{Al}_2\text{O}_3$  crucibles for melting Be in the DTA had revealed that the Be stuck to the crucible indicating some reaction. Furthermore, discussions with personnel in the beryllium team indicated that alumina had been observed (by workers at Brush–Wellman) to result in Al contamination of the resulting Be melt. Therefore this material was initially eliminated from consideration. Only after all of the other materials evaluated had failed to produce completely satisfactory results was it tested.

Commercially available crucibles produced by Coors Ceramics Co. were used in these tests. The results of these tests revealed that alumina was sufficiently compatible with molten Be to allow its use as a crucible for melting Be (as long as slight amounts of Al contamination are not a concern). The beryllium did not stick to the crucible but fell out as a smooth ball. It appears that the surprisingly good compatibility of alumina and beryllium is attributable to the formation of the thin barrier layer visible in the

micrograph below. X-ray diffraction indicated that this layer consisted of BeO and Al<sub>2</sub>O<sub>3</sub>. The layer is thick enough that we cannot rule out the presence of additional ternary phases within the layer. There are three identified ternary compounds in the BeO-Al<sub>2</sub>O<sub>3</sub> system.<sup>2</sup> These intermediate compounds may act as barriers to further reaction. In any case this reaction product also explains the apparent reaction in the much smaller and narrower DTA crucibles. No intermetallic compounds exist in the Be – Al system which may also contribute to the relatively high compatibility observed in these tests. (Examples of systems where intermetallic compound formation is observed are discussed below.)


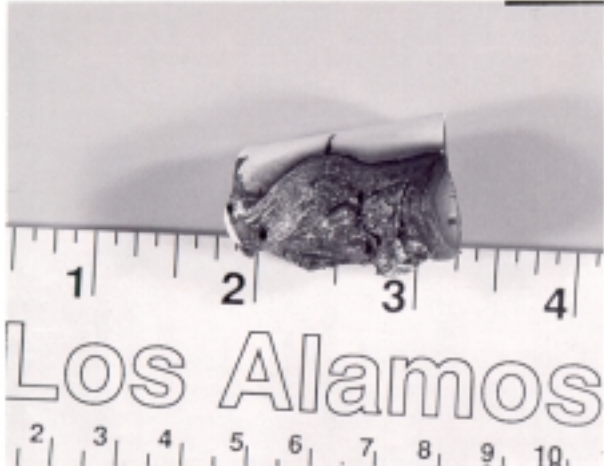


## Boron Nitride

Boron nitride is often recommended for molten metal handling as it is generally considered resistant to metal wetting. For optimum strength and hardness compositions containing other inorganic compounds (ceramic alloys) are often specified (see ZSBN below).

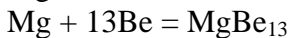
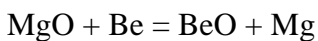
Pure self bonded boron nitride crucibles, grade AX05 were obtained from Carborundum Corp.

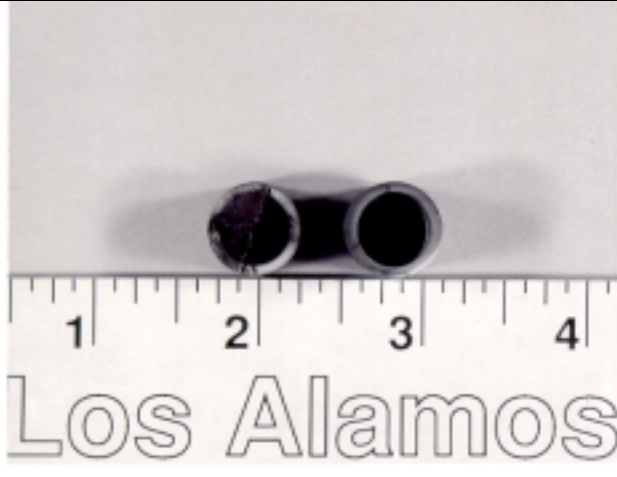
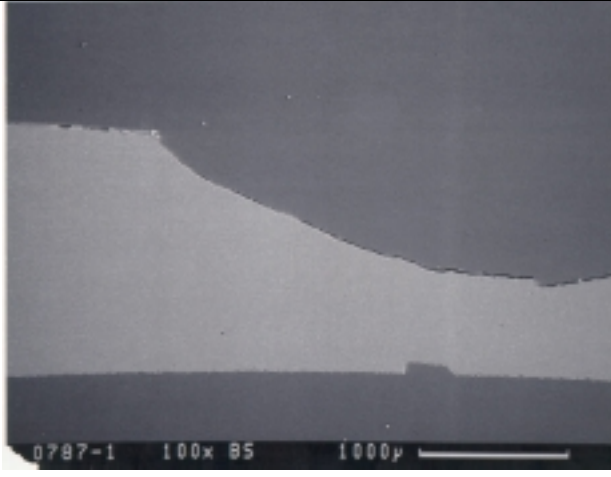
Inconsistent results were obtained in these tests. In the first test no obvious reaction was noted, although the crucible cracked (at left below). In later tests the Be was observed variously to stick to the sides of the crucible, while in some tests apparently localized reactions resulted in cracking and escape of the molten Be from the crucible. The reaction products have not been completely identified at this time. In any case BN is apparently not appropriate as a crucible material for melting Be.

	
<p>Boron nitride crucible with melted beryllium pellet at right. Exposed for 30 minutes at 1350° C. The crucible survived largely intact except for the crack visible at the bottom.</p>	<p>Boron nitride crucible exposed for 30 minutes at 1350° C. Essentially all of the Be has apparently reacted with the BN. Once the reaction starts apparently it proceeds quite rapidly.</p>

### Magnesia (MgO)

The molten beryllium stuck to the side of the crucible. The principle reaction product was BeO. The reactions expected in this system are (similar to Y and Zr oxide systems discussed below)

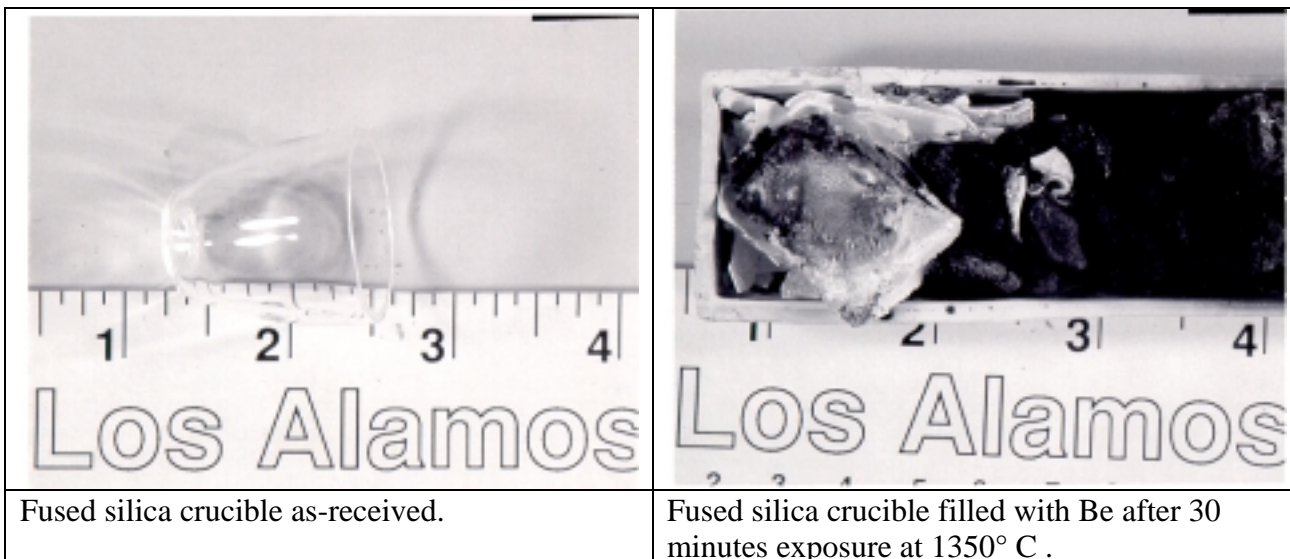


	
<p>MgO crucible exposed for 30 minutes at 1400° C. Cross sectioned. The Be is still visible in the bottom half of the crucible at left.</p>	<p>SEM micrograph of the same crucible, cross section, 25 x magnification. Note the area to the left of the micrograph which has nearly reacted through the bottom of the crucible.</p>



### Silica (fused silica)



Very nearly complete reaction was observed. The products were not identified but are expected to be BeO and Si (see the discussion of silicon carbide results below).



### Silicon Carbide

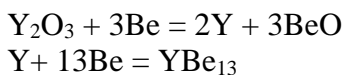
The published Be-C-Si diagram is for a 1000° C isotherm<sup>3</sup>. Equilibria are indicated between Si and Be<sub>2</sub>C and SiC and Be<sub>2</sub>C. Therefore at the interface between molten Be and SiC one would expect that the reaction products would be Be<sub>2</sub>C and elemental Si. This suggests the possibility that SiC could actually be compatible with molten Be, if the beryllium carbide formed acted as a diffusion barrier. The first test of 30 minutes at 1350° C resulted in Be stuck to the crucible. A second test for 2 hours resulted in a nearly complete reaction of the Be with the SiC. The reaction products were identified as Be<sub>2</sub>C and elemental silicon. (This verifies that in the ternary system Si-Be-C there is an equilibrium tie line between Si and Be<sub>2</sub>C at 1350° C.) An attempt was made to cross section the less reacted crucible, (at left below) in order to observe the morphology of the reaction front, however the available saw was not up to the task. We can however conclude that the beryllium carbide layer was not in fact protective.



	
<p>Silicon Carbide crucible exposed to molten beryllium for 30 minutes at 1350° C. The bottom of the crucible has been cut away to show the beryllium stuck inside of it.</p>	<p>New SiC crucible (on left) compared to SiC crucible exposed to molten Be for 2 hours at 1350°C (on right). The reaction products consisted of Be<sub>2</sub>C and elemental silicon. No metallic beryllium was detected.</p>

### Yttrium Oxide (Yttria)

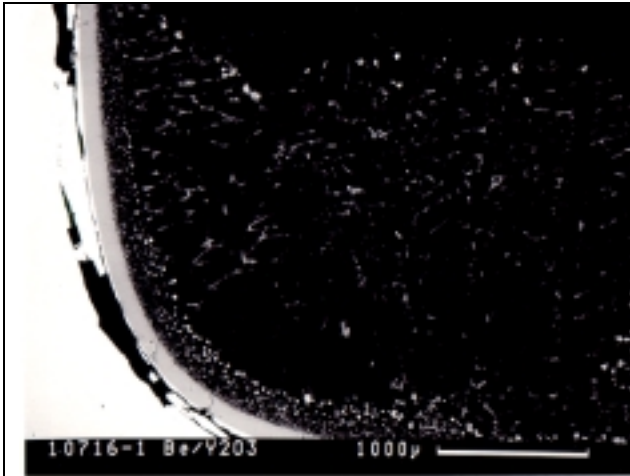
The beryllium clearly reacted with the crucible (i.e. the metal stuck to the side of the crucible). Observing the cross section of this crucible in the figure below, several different reaction products are visible. In the optical micrograph at top left there is clearly a network of some second phase distributed throughout the beryllium (this phase has not yet been identified). A fractured area is visible near the beryllium/yttria interface but no obvious reaction product is visible. At higher magnification a single layer of product is visible. The reaction product was identified as BeO, hence the molten beryllium reduced the yttrium. An intriguing aspect of this study is the intermediate layer visible between the Be and BeO in the backscattered image below on the right (the thicker layer). The contrast suggests that this is a compound whose average Z lies between BeO and Be. Although the stabilities of Y<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> are similar, there are no known stable ternary compounds in the BeO–Y<sub>2</sub>O<sub>3</sub> pseudobinary system (under reducing conditions).<sup>4</sup> Some compounds have been reported under oxidizing conditions but the existence of a phase similar to BeO–Al<sub>2</sub>O<sub>3</sub> has not been confirmed.<sup>4,5,6</sup> The most likely explanation is the formation of the intermetallic compound YBe<sub>13</sub>. This is also consistent with the reaction sequence



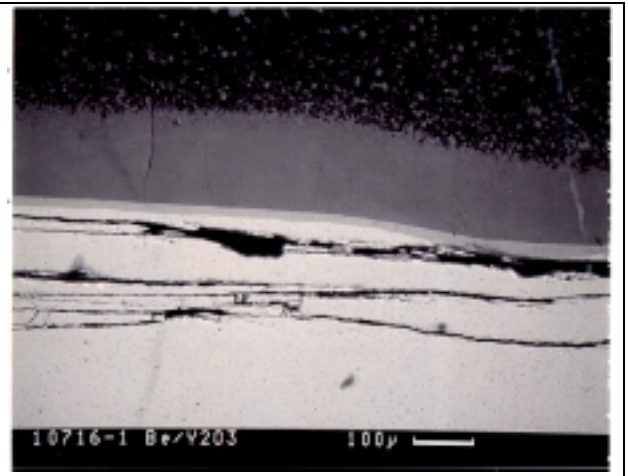
Based on the stoichiometry of the reaction we can calculate the expected relative thickness of the reaction layers (by comparing the relative molar volumes and number of moles of each product from the reaction). The intermetallic layer would be expected to be approximately 11 times the thickness of the BeO layer, based on the relative densities of these phases. This is in fact observed in the micrographs below. Furthermore, the planar

appearance of the reaction layers suggests that the reaction does proceed via the two steps outlined above.

In any case yttria is clearly unsuitable for containment of molten Be.



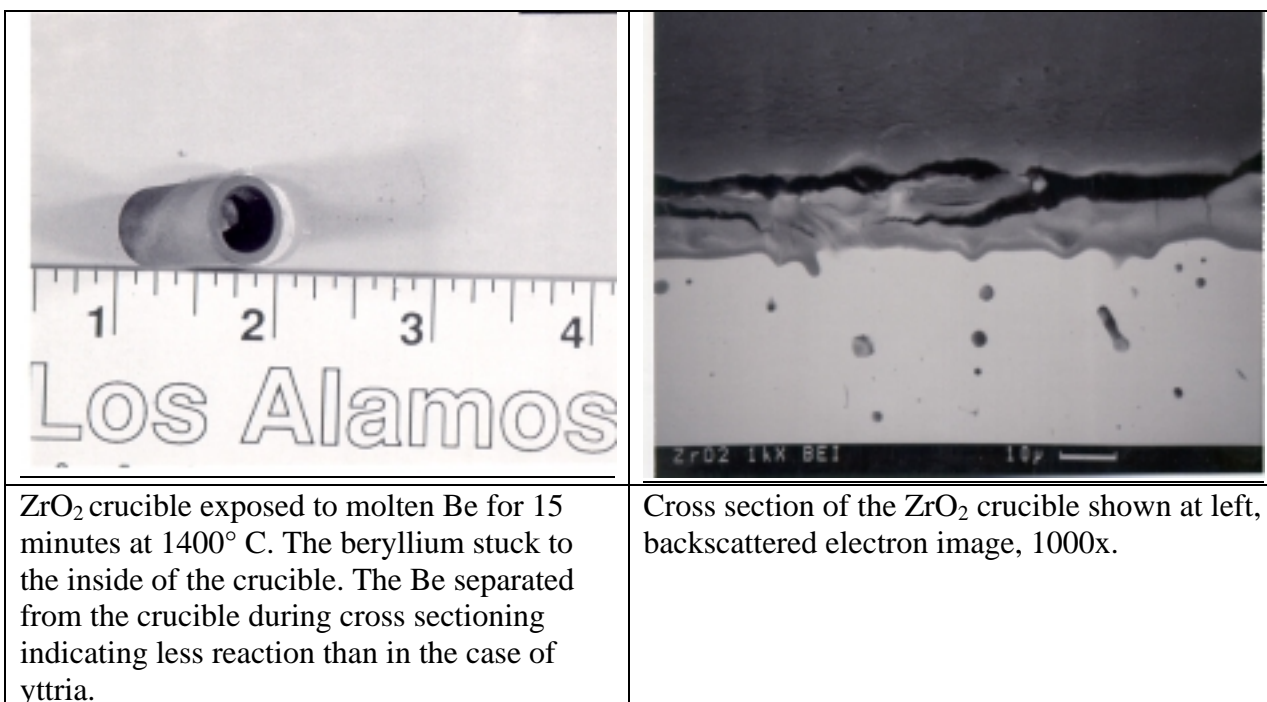
SEM micrograph (backscatter electron image) of the cross section of an yttrium oxide crucible exposed to molten beryllium for 30 minutes at 1400° C. The reaction product is the gray band above the white yttria matrix. A network of another reaction product is visible as white tendrils in the solidified beryllium (black in this image).



Higher magnification micrograph of the interface region in the cross section at right. Notice that two clear reaction product layers are visible above the (fractured) yttria crucible matrix. Based on thermodynamics and a simple mass balance it is concluded that these layers are BeO (thick upper layer) and  $\text{YBe}_{13}$  (thin inner layer).

## Zirconia

The molten beryllium obviously reacted with the  $\text{ZrO}_2$ , as it clearly wet the side of the crucible and stuck to it. The extent of the reaction was not evaluated. However when the sample was cross sectioned the Be separated from the  $\text{ZrO}_2$ . However given that the dimensions of the crucible and the overall appearance of the beryllium were nearly identical to the yttria and  $\text{MgO}$  cases discussed above, the reaction product is expected to be nearly identical. (Except in the case of  $\text{ZrO}_2$  we might expect to see two intermetallics in the intermediate layer.) The extent of the reaction was sufficiently limited however that it is possible that this material could be used as a disposable crucible.



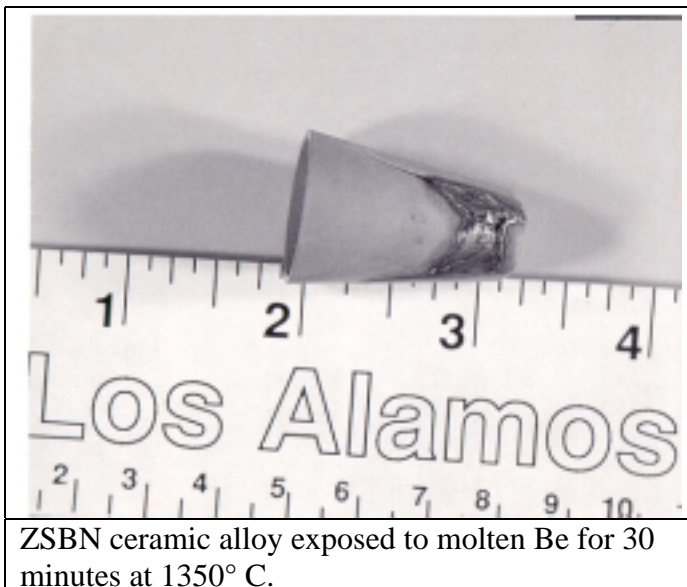
## ZSBN

ZSBN is a ceramic alloy of zirconia, boron nitride, and silicon carbide. This material is used to manufacture nozzles used for plasma spraying of molten metals. Therefore it was considered a potentially compatible material. Results were inconsistent in terms of the failure mode however no tests indicated full compatibility.

Crucibles were purchased from Carborundum corp. The dimensions were identical to the boron nitride discussed above.

According to the manufacturer's website (<http://www.carbobj.com/mainitems/mainframe.html>), "Grade ZSBN is composed of boron nitride, zirconia and small amounts of silicon carbide, offers superior hardness and wear resistance. It is the material of choice for breakrings and other molten metal applications. This composite material combines the thermal performance and machinability of boron nitride with the strength and corrosion resistance of zirconia and silicon carbide."

In retrospect since the pure components were not compatible with the molten Be the failure of the ZSBN crucibles is not surprising.



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