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Surrogate Studies of the Pu-Be Reaction II

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Introduction

Unusual circumstances could result in contact between molten Pu and solid Be components. Since intimate contact between Pu and Be results in an intense neutron source via the (α, n) reaction it is very difficult to study the kinetics of the Pu-Be interaction. The published Pu-Be phase diagram¹ is characterized by a single intermetallic compound, PuBe_{13} which exists in equilibrium with all of the Pu allotropes, and two eutectics with no measurable solubility range in any of the solid phases. This pattern is known to be followed by all of the rare earths, and some of the actinides². Although most of these phase diagrams are poorly defined in terms of solubility and the location of the eutectics, all have been characterized to the extent of having a single intermetallic compound with a melting point in excess of 1500°C . Consequently it seems reasonable that by studying the reactions of these other metals with Be, it should be possible to predict kinetics and mechanisms of the Pu-Be interaction using known physical and thermodynamic properties.

The most obvious difference between Pu and potential surrogate elements is in their melting points. This is not the most important consideration however due to the presence of the two eutectics in each of the M-Be systems (where M is used to refer to any of the surrogates). In the last meeting of this series we reported the results of studies using Yb as a surrogate for Pu. Here we will discuss the results obtained using Sm and Ce and contrast them with our earlier results as well as with Pu-Be experiments conducted using very similar experimental conditions.

Experimental Procedure

In order to study the reaction kinetics of M-Be (where M indicates either Pu or one of the lanthanides) a series of experiments was conducted in which Be crucibles were filled with solid M and subsequently held at temperatures from 800°C to 1200°C in flowing argon for various times. Three sizes of Be crucibles were used in the reaction experiments in order to vary the surface to volume (S/V) ratio of the M and Be. The crucible was filled approximately 1/2 to 2/3 of its volume with solid metal. The crucible was then placed in a vacuum tube furnace which was evacuated then filled with ultra high purity (UHP) Argon. In the surrogate experiments the furnace was heated at a rate of $16.6^\circ/\text{minute}$, held at temperature for times ranging from 5 minutes to 10 hours and furnace cooled. After the exposure was completed the crucible was sectioned using a low speed diamond saw, mounted, ground and polished using appropriate metallographic techniques. The kinetics and mechanism of the reaction was measured based on the thickness of the reaction layer at the interface between the M and Be, the depth of penetration (if visible) of the reaction layer into the Be, the morphology of the interface, and the amount and distribution of intermetallic inclusions in the solidified metal, all as a function of exposure temperature and time.

Plutonium-Beryllium

Pu-Be experiments were conducted using crucibles with samples yielding a S/V of 2.2. Samples were heated at $30^\circ/\text{minute}$ to 1000°C and held for various times. Below are shown two micrographs at 250x magnification of the interfacial layer grown after exposures of 300 seconds (left) (With short exposures the total time during which the Pu is liquid needs to be considered, in this case approximately 15 minutes on heat up and cool down in addition to the 5 minute hold at 1000°C) and 7 hours (right). Obviously the interfacial PuBe_{13} layer increases in thickness with duration of exposure. We have previously shown that this layer grows with parabolic kinetics, indicating solid state diffusional control, in the Yb-Be system.³ The large faceted particles at the interface are considerably more numerous after the longer exposure, and many more appear in the solidified material. These appear to have broken off from the wall and floated to the top of the melt. Fine particles of PuBe_{13} (not visible here) appear distributed

throughout the solidified Pu. These most likely precipitated during cooling of the Pu as the solubility of Be in the molten or solid Pu decreased.

Pu-Be Interface (Pu right, Be left, PuBe₁₃ between)
After 300 seconds at 1000°C. 250x

Pu-Be Interface (Pu right, Be left, PuBe₁₃ between)
After 7 hours at 1000°C. 250x

Samarium-Beryllium

Samarium was chosen as a potential surrogate for plutonium on the basis of the similarity of the lattice parameter of the intermetallic compounds PuBe₁₃ (1.0282nm)⁴ and SmBe₁₃ (1.0304 nm)⁵. It is worth considering the significance of the close match in lattice parameter as well as the exact match in structure between the lanthanide beryllides and PuBe₁₃. The fact that the compounds have the same structure means, by definition, that in its normal lattice site the electronic structure of Pu in this compound is practically identical to that of all of the similar lanthanide compounds. Furthermore, the effective size of the Pu atom in this site must be very nearly identical to that of Sm in the analogous compound. Since most of the beryllium atoms occupy sites where all of the nearest neighbors are beryllium, the Be radius may be taken to be the normal metallic radius 1.12 Å, which means that the size of the Pu site in PuBe₁₃ is nearly 1.9 Å.

Since Sm melts at 1072°C and Be at 1277° C the range of possible experiments would appear to be quite limited. It turned out however that in experiments conducted for as little as 30 minutes at 1000° C the entire charge of Sm in the crucible melted. This means that the eutectic reaction on the Sm rich side of the phase diagram must be considerably lower than the melting point of the pure metal and the liquidus must decrease quite steeply with minimal additions of Be. Experiments were therefore conducted at 950, 1000, 1050 and 1100° C. As can be seen in the micrographs below, the morphology and growth rate of the intermetallic layer is very similar to that observed in Pu-Be. In contrast to our observations on the Yb-Be system, no significant porosity was observed at the Be-intermetallic interface. This suggests that countercurrent diffusion is taking place (Be diffusion toward the liquid Sm interface, Sm diffusion toward the Be/intermetallic interface) since if the majority of the growth took place by Be sublattice diffusion then there should be significant porosity due to vacancy accumulation behind the intermetallic layer. This mechanism would by analogy also apply to the case of Pu-Be. Therefore we can see that the mechanism of the reaction is affected by temperature, solubility of Be in the liquid, diffusion in the liquid (and therefore liquid metal volume), and diffusion of Pu and Be in the solid.

SEM image of Sm-Be reaction layer (Sm top, Be bottom, SmBe_{13} between) formed after 30 minutes exposure at 1000° C. 500x

SEM image of Sm-Be reaction layer (Sm top, Be bottom, SmBe_{13} between) formed after 2 hours exposure at 1000° C. 500x

Cerium-Beryllium

Cerium was investigated as a surrogate because it is commonly used to chemically simulate plutonium. It also has the lowest melting point of the lanthanides (795° C). Cerium proved to be actually more aggressive than Sm (or Pu). Whereas in the case of Yb-Be, beryllium diffusion predominates in the growth mechanism, and in the case of Pu and Sm diffusion rates appear to be comparable, in the case of Ce, diffusion of Ce and growth of the resulting intermetallic layer into the Be crucible clearly predominates. This is visible in the micrograph below which shows the wetted region at the wall of the crucible near the meniscus in a specimen exposed for 5 hours. The intermetallic layer can be seen to have penetrated into the Be.

Reaction layer formed between Ce and Be after 5 hours exposure at 1000° C. The intermetallic layer has clearly grown into the beryllium crucible wall, demonstrating that the growth mechanism must be primarily via Ce diffusion across the intermetallic. A very similar result is observed in experiments with Praseodymium.

Discussion

The objective of this work has been to understand the physical mechanism of the liquid Pu-solid Be reaction and therefore be able to predict the kinetics of the Pu-Be reaction using data from the reaction between Be and various lanthanides as surrogates for Pu. Our earlier results demonstrated that in the simple Yb-Be system that the intermetallic compound YbBe_{13} is formed at the interface between Be and Yb via Be solid state diffusion. The interface morphologies observed in this system were nearly planar, however, and no intermetallic inclusions or precipitates were found in the solidified liquid unlike the case of Pu-Be. Samarium proved to be a much closer simulant for Pu, based both on similar reaction layer thickness but more importantly on the very similar reaction layer morphology. Careful experiments with

this system have indicated that the interfacial layer must grow via countercurrent diffusion while large inclusions found in the solidified liquid apparently are constitutional dendrites formed at the wall and subsequently broken off. This of course shows that there is a Be concentration gradient present in the liquid. Fine precipitates formed on cooling are also found in the solidified material. By analogy therefore the growth of PuBe_{13} appears to follow the same mechanisms as SmBe_{13} , albeit with different kinetics for the various stages. Since Sm melts at a significantly higher temperature than Pu we conducted a series of experiments with Ce and Pr, which demonstrated that these latter elements are more aggressive than Pu with respect to Be, in the sense that greater penetration into the Be is observed. These might prove useful if large scale simulations of the Pu-Be reaction were planned since the results would be expected to represent a "worst case" condition.

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