COMPATIBILITY OF SILICON CARBIDE WITH LEAD-BISMUTH EUTECTIC - THE EFFECT OF OXYGEN INGRESS

P. Chakraborty, R.K. Fotedar and N. Krishnamurthy
Fusion Reactor Materials Section
and
P. K. Pradhan
Materials Processing Division

This Paper received the Best Poster Award at the National Symposium on Materials and Processing, (MAT 2012), held at Mumbai, from 10th-12th October, 2012

Abstract

In the Indian High Temperature Reactor Program, silicon carbide composites has been proposed as an oxidation and corrosion resistant coating over the graphite fuel tubes inside the Compact High Temperature Reactor (CHTR). The coating will be exposed to molten Lead-bismuth eutectic coolant at temperatures around 1173K to 1273K. The paper discusses the results of 1000 h compatibility study of a SiC pellet exposed to static lead-bismuth eutectic at 1173K and the effect of oxygen ingress into the system pertaining to certain accidental conditions.

Keywords: - Silicon Carbide, Lead-Bismuth Eutectic, CHTR, Oxygen

Introduction

In order to meet the growing energy demand and to mitigate the negative atmospheric effects of using fossil fuels; hydrogen has been proposed to serve as a clean and sustainable energy source. Industrially usable hydrogen can be efficiently and economically produced by the splitting of water, but the process requires comparatively higher temperatures. To achieve this objective, Bhabha Atomic Research Centre (BARC) is developing a prototype Compact High Temperature Reactor (CHTR) which will validate the technologies associated with High Temperature Reactors (HTRs) [1]. The objective of Indian HTRs is to supply the high grade heat required for possible hydrogen production. The CHTR uses U-233 and thorium-based carbide as fuel (TRISO coated particle) compacted in a graphite matrix where beryllium oxide is used both as the moderator and reflector. Cylindrical fuel compacts are packed in fuel bores located at the walls of graphite fuel tubes [1, 2]. The core heat is removed by natural circulation of lead-bismuth eutectic alloy [44.5 wt.% Pb + 55.5 wt.% Bi ], which enters the fuel tube at 1173K, and after taking the reactor heat, leaves the tube at 1273K towards the upper plenum. Lead-bismuth eutectic (LBE) is known to be corrosive towards various structural materials above 623K [3, 4]. Considering this aspect, a protective oxidation and corrosion resistant coating of Silicon carbide (SiC) composite material has been proposed over the graphite fuel tubes. Under some unforeseen accidental situations, this SiC coated graphite fuel tube may get exposed to oxygen. Thus, maintenance of long term integrity of the same in the presence of lead-bismuth eutectic under various reactor conditions will be an important criteria in deciding the feasibility of this process. To assess the compatibility of SiC with Pb-Bi eutectic in the presence of oxygen, an attempt was made to study the corrosion behavior of SiC exposed to static lead-bismuth eutectic at 1123K for 1000 h of exposure.
**Experimental**

The experiment was conducted in an inert gas furnace capable of providing temperatures up to 1673K. Initially, lead-bismuth eutectic chunks weighing 35 g in total, and a cylindrical SiC pellet weighing 1.86 g were placed in an alumina boat. The furnace along with the unloaded alumina boat is shown in Fig. 1. The boat was covered with an alumina lid to avoid spillage of molten mass and was kept inside the vertical furnace. Subsequently, argon-5% oxygen gas was introduced into the furnace at a nominal rate. The setup was maintained at 1173K for 1000 h. Later the furnace was cooled to room temperature and the boat along with the solidified lead-bismuth was taken out of it. Sample analysis was carried out through SEM-EDS and XRD.

On the other hand, the walls of the alumina crucible along with the top surface of the solidified LBE were found covered with a yellowish glassy adherent coating. As shown in Fig. 2, XRD analysis revealed the presence of lead silicate along with lead and bismuth oxides individually, in the glassy coating. To investigate the composition of the exposed lead-bismuth eutectic, SEM-EDS were carried out on the LBE sample. Fig. 3 shows an SEM image of the solidified eutectic and the EDS analysis carried out at two different locations [1 and 2] over the same area could be observed in Table 1 and 2 respectively. Table 1 shows the association of lead with silicon and oxygen whereas Table 2 predicts the formation of bismuth oxide, thus confirming the XRD results.

**Results**

Considerable degradation of the SiC pellet was noted after 1000 h of exposure to lead-bismuth eutectic under oxygen at 1173K. This predicts that under accidental conditions, SiC coating could deteriorate considerably inside high temperature reactors.

---

**Fig. 1: Furnace used for conducting 1000 h static experiment; (Inset) Alumina boat used for holding SiC pellet and LBE chunks.**

**Fig. 2: XRD analysis of the adherent glassy layer present over the exposed LBE sample shows lead silicate and oxides of lead and bismuth.**

**Fig. 3: SEM Image of the LBE sample exposed to SiC pellet at 1173K for 1000 h**
From the results discussed above, the degradation of SiC pellet seems to be possibly associated with a series of events. Due to oxygen exposure, lead-bismuth eutectic started converting into lead and bismuth oxides i.e. PbO₂ and Bi₂O₃ respectively. It is a well known fact that a silicon carbide pellet inherently contains a protective layer of Silica i.e. SiO₂ over its entire surface. In the presence of oxygen and Bi₂O₃, this SiO₂ layer interacted with PbO₂, thus forming lead silicate (Pb₃SiO₅) as obtained in XRD analysis. As a consequence, fresh silicon carbide surface got exposed and in the presence of oxygen, a second layer of SiO₂ was developed. This once again triggered the sequence of events discussed above. The process continued in a cyclic manner each time exposing of new SiC surfaces ready for interaction, thereby forming lead and bismuth silicates leading to formation of the glassy coating. This might be the probable reason for degradation of the silicon carbide pellet.

**Conclusion**

1. Silicon Carbide was considerably degraded by lead-bismuth eutectic at 1273 K in the presence of oxygen.
2. The process was initiated by interaction of inherently present SiO₂ with lead and bismuth oxide formed in the presence of oxygen. This later continued in cyclic manner led to exposure of fresh SiC surface and to the formation of a yellowish glassy layer comprising of lead silicate.

**Acknowledgements**

We would like acknowledge the informative technical discussions with Dr. Abhijit Ghosh, G&ACD, BARC. We would also like to thank Shri A. Nagraj, L&PTD, BARC and Shri Bhaskar Paul, MP.D, BARC for carrying out the XRD and SEM-EDS analysis respectively.

**References**


---

**Table 1:** EDS analysis of the LBE sample exposed to SiC pellet at 1173K for 1000 h showing association of lead with silicon and oxygen

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>16.46</td>
</tr>
<tr>
<td>Si K</td>
<td>11.56</td>
</tr>
<tr>
<td>Pb M</td>
<td>71.96</td>
</tr>
</tbody>
</table>

**Table 2:** EDS analysis of the LBE sample exposed to SiC pellet at 1173K for 1000 h showing association of bismuth and oxygen

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>10.34</td>
</tr>
<tr>
<td>Bi M</td>
<td>89.66</td>
</tr>
</tbody>
</table>

Discussion

From the results discussed above, the degradation of SiC pellet seems to be possibly associated with a series of events. Due to oxygen exposure, lead-bismuth eutectic started converting into lead and bismuth oxides i.e. PbO₂ and Bi₂O₃ respectively. It is a well known fact that a silicon carbide pellet inherently contains a protective layer of Silica i.e. SiO₂ over its entire surface. In the presence of oxygen and Bi₂O₃, this SiO₂ layer interacted with PbO₂, thus forming lead silicate (Pb₃SiO₅) as obtained in XRD analysis. As a consequence, fresh silicon carbide surface got exposed and in the presence of oxygen, a second layer of SiO₂ was developed. This once again triggered the sequence of events discussed above. The process continued in a cyclic manner each time exposing of new SiC surfaces ready for interaction, thereby forming lead and bismuth silicates leading to formation of the glassy coating. This