COMPATIBILITY OF SILICON CARBIDE COATED GRAPHITE WITH LEAD-BISMUTH EUTECTIC AT 900°C

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ABSTRACT

A uniform and adherent coating of β-silicon carbide (SiC) was formed over a graphite pellet through slurry based silicon coating technique followed by in-situ reaction at 1600°C. The compatibility of this pellet was studied with molten lead-bismuth eutectic (LBE) at 900°C in static condition for 200 h continuously. Analysis of the exposed pellet through weight loss measurement, X Ray Diffraction (XRD) and Secondary Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) confirmed that the SiC coating could effectively prevent molten LBE from attacking the inner graphite material under the present experimental conditions.

Keywords: Silicon Carbide, Graphite, Lead-Bismuth Eutectic, Compatibility

I. INTRODUCTION

In order to meet the growing energy demand and to solve some of the negative atmospheric effects of using fossil fuels; hydrogen has been proposed to serve as a clean, reliable and sustainable energy source [1]. In this regard, Bhabha Atomic Research Centre (BARC) is developing a prototype Compact High Temperature Reactor (CHTR), which aims at the production of industrially usable hydrogen by splitting of water [1-2]. The CHTR uses U-233 and thorium-based carbide as fuel (TRISO coated particle) compacted in a graphite matrix [3]. Cylindrical fuel compacts are packed in fuel bores located at the walls of each graphite fuel tube. The arrangement of the fuel tube placed along with the BeO moderator has been shown in Figure 1. 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 900°C at the lower plenum, takes the reactor heat and leaves the tube at 1000°C towards the upper plenum. Thus, maintenance of long term integrity of the graphite fuel tube in the presence of lead-bismuth eutectic (LBE) in the temperature range of 900°C -1000°C is an important factor in deciding the feasibility of this process.

Fig. 1: Schematic of CHTR fuel tube
Lead-bismuth eutectic has been found to be substantially corrosive towards various structural materials like austenitic stainless steels [4-5]. Moreover, experiments to study the compatibility of graphite with LBE at 800° C have revealed the formation of a Pb-C reaction layer over the graphite surface which had an estimated growth rate of 61.3 µm/ year [7]. Considering this aspect, a protective oxidation and corrosion resistant coating of silicon carbide material (SiC) has been proposed over the graphite fuel tubes. Nevertheless, obtaining a uniform and adherent SiC coating over graphite material is a major challenge. Although SiC is a relatively hard and inert material, compatibility of the same with LBE at the working temperature remains another important area of investigation. With this view, a layer of SiC was formed on a graphite pellet through slurry based silicon coating followed by in-situ reaction at a high temperature. Later, the corrosion behaviour of the coated pellet with molten LBE was studied in static condition at 900°C for duration of 200 h.

II. EXPERIMENTAL

II. A. Coating of Silicon Carbide over Graphite

Few commercially available graphite pellets of 17 mm diameter were coated with silicon (Si) slurry prepared in-house. The pellets were initially manufactured from nuclear grade graphite material and had a density of 1.8 gm/cc. The coating of silicon over the graphite pellet was carried out by simple brush painting method. Silicon coated samples were subsequently heat treated at 1600 °C to form the SiC coating on graphite surface. Figure 2 show the photograph of the silicon carbide coated graphite pellet.

Afterwards, the surface of one of the samples was investigated through X - Ray Diffraction (XRD). Later, the cross section of the same sample was analysed through Secondary Electron Microscopy (SEM). The rest of the samples were kept intact for use in compatibility studies.

![Fig 2:- Silicon carbide coated graphite pellets](image)

II. B. Compatibility of SiC coated Graphite with Lead- Bismuth eutectic

The compatibility study was performed in a retort fabricated with 50NB Inconel 625 pipe which was closed at the bottom with a 10 mm thick Inconel 625 plate. The length of the retort was 250 mm and was provided with flanged connection at the top. A 5 mm thick graphite crucible having an inside diameter of 40 mm and a length of 90 mm was placed inside the Inconel retort. This graphite crucible was used for containing the LBE. The schematic diagram of the completely assembled test facility equipped with online sample mechanism is shown in figure 3.

On the other hand, the sample holder consisted of a small molybdenum cup having 20 mm inner diameter and 35 mm length. Holes were drilled on its sides and bottom of this cup to allow liquid metal to flow in and wet the sample (pellet) placed inside it. The cup was covered with a graphite cap which was in turn connected to a sample holding rod made out of Inconel 625 material through threaded joint. This rod passed vertically through a 200 mm long SS tube, the bottom end of which was welded to the cover flange of the Inconel retort. The top end of the SS tube was fixed to the sample holding rod with the help of a high temperature dynamic seal which allowed movement of
the sample holder inside the retort without breaking the controlled atmosphere inside it. Provisions were made for purging inert gas in the retort and temperature was measured through K type thermocouples kept in contact with the graphite crucible. Band heaters were wrapped around the Inconel retort up to a height of 100 mm and appropriate insulation was placed over it.

In the present experiment, the SiC coated graphite pellet was placed inside the molybdenum sample holder. The sample holder was then covered with its graphite cap and fixed to the Inconel rod. On the other hand solid LBE chunks having a total weight of 0.5 Kg was placed inside the graphite crucible so as to fill the crucible up to a height of 50 mm with molten LBE later. The crucible was placed in the Inconel retort and the retort was sealed through suitable gaskets. During this time, the sample holder was fixed at its top most position. The assembly was checked for leak tightness and inert atmosphere was maintained by purging high purity argon gas inside. Afterwards the retort was externally heated up to 300°C and held at that temperature for 2 hours to ensure that the entire LBE had melted (Melting point of LBE - 123°C). Later the sample holder was lowered down and immersed into the molten LBE up to the desired level as indicated by markers. Finally the temperature of the retort was raised to 900°C with continuous argon purging and maintained in that condition for 200 hrs continuously.

![Fig. 3: Schematic of Compatibility test set up.](image)

On completion of 200 h of exposure, the temperature of the retort was lowered down to 300°C again and the sample holder was lifted above the level of liquid metal. Later the retort was cooled down to room temperature. The SiC coated graphite pellet was removed from the sample holder and was cleaned off the adhering LBE by repeatedly exposing it to a mixture of acetic acid, acetone and hydrogen peroxide in the ratio 1:1:1. Later, the weight loss due to corrosion was recorded. The surface of the exposed pellet was analyzed before and after cleaning with the help of
XRD. Afterwards, the cross section of the same was investigated with the help of SEM-EDS (Secondary Electron Microscopy-Energy Dispersive Spectroscopy).

RESULTS AND DISCUSSIONS

The SEM micrograph of the cross section of the SiC coated graphite pellet before exposure to LBE is shown in figure 4. A satisfactory adherence could be noted in between the graphite and SiC material. Since the graphite had a low density (< 90%), it is expected that the silicon slurry would have entered into its surface pores and later got converted into SiC during heating at 1600°C. This would give a much better coating adherence than mechanical interlocking. Moreover, the coating appeared sufficiently impervious which would prevent liquid LBE from attacking the inner graphite substrate.

![Fig 4: SEM image of the cross section of SiC coated graphite pellet before exposure to LBE.](image)

![Fig 5: XRD plot of SiC coated graphite pellet before exposure to LBE for 200 h](image)
Figure 5 shows the XRD plot of the SiC coated graphite pellet before exposure to Pb-Bi. The conversion of Si in the slurry to SiC during heat treatment was confirmed by the presence of β-SiC in figure 5 [7]. Other than the prominent peaks of graphite (C) {JCPDF: 026-1080} and β-SiC {JCPDF: 029-1129}, one peak of pure silicon (Si) {JCPDF: 027-12402} was also noted in figure 5. This indicated that some part of the Si present in the slurry might have remained untransformed towards the outer surface of the SiC layer. Nevertheless, this is not expected to have any negative effect on the protective nature of the SiC coating.

The appearance of the SiC coated graphite pellet did not change significantly after exposure to LBE. Weight loss was measured after cleaning of adherent LBE present over the exposed pellet. As shown in Table 1, the pellet suffered a weight loss of 17 mg after exposure which corresponds to 0.78 % of the initial weight. Further studies in XED and SEM were conducted to understand the reason behind this weight loss.

Table 1:- Weight Loss of SiC coated graphite pellet after exposure to molten LBE at 900°C for 200h

<table>
<thead>
<tr>
<th>Initial Weight</th>
<th>Final Weight</th>
<th>Weight Loss</th>
<th>% Weight loss</th>
<th>Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3304</td>
<td>2.3133</td>
<td>0.0171</td>
<td>0.73%</td>
<td>85 µg/hr</td>
</tr>
</tbody>
</table>

XRD analysis was carried out on the exposed pellet both before and after cleaning the solidified LBE layer. Individual peaks of LBE {JCPDF: 044-1246} and Si along with prominent peaks of graphite (C) and β-SiC was noted in the unwashed exposed pellet. The position of the pure Si peak exactly matched with that observed for the unexposed pellet. On the other hand, the XRD analysis of the exposed and cleaned pellet (figure 6) showed the presence of graphite and SiC only. This indicated that cleaning of the exposed pellet might have caused removal of the outer Si layer along with the adherent LBE. It is thus possible that the weight loss observed in the exposed pellet as given in Table 1 might be a result of removal of the residual Si while cleaning.

Fig 6: Cleaned SiC coated graphite pellet after exposure to LBE

Fig 7 shows the SEM micrograph of the the cross section of a SiC coated graphite pellet after exposure to LBE. The SiC layer over the graphite material was found to remain intact even after exposure and the unaffected interface between the graphite - SiC coating was distinctly visible.
To investigate the possibility of LBE penetration across the SiC coating, composition profiles of carbon (C), silicon (Si), lead (Pb) and bismuth (Bi) were recorded with the help of EDS as indicated in figure 8. The horizontal line in the inset image shows the path of EDS line scan in figure 8. The decrease in C and increase in Si near the surface of graphite material indicated the diffusion of Si into graphite matrix which had possibly taken place during heat treatment at 1600°C. This would have caused an increase in the coating adherence. The formation of SiC layer over the graphite matrix is also clearly reflected in figure 8. No significant penetration of Pb or Bi was noted into the SiC layer or the graphite matrix. This confirmed the effectiveness of the β-SiC coating in preventing LBE attack on the graphite material at 900°C up to duration of 200 h. Some corrosion studies reported in literature have similarly confirmed the excellent corrosion resistance of β-SiC in pure lead at 800°C with no interaction occurring between the SiC and the Pb. [8]
CONCLUSIONS

1) An adherent coating of β-silicon carbide (SiC) was formed over a graphite pellet through slurry-based silicon coating technique followed by in-situ reaction at 1600°C.

2) A static corrosion test facility equipped with online sample removal mechanism was designed and fabricated for testing the compatibility of this pellet with molten lead-bismuth eutectic (LBE).

3) The SiC coated graphite pellet was exposed to LBE at 900°C in the above facility for 200 h continuously.

4) A minimal weight loss of 0.78% of the original weight was recorded for the SiC coated graphite pellet after exposure to LBE. This loss was attributed to the removal of residual silicon during cleaning of the adherent LBE layer.

5) The SiC coating was found effective in preventing molten LBE from attacking the inner graphite substrate at 900 °C for 200 h.

ACKNOWLEDGMENTS

We would like to acknowledge the support provided by the technical staff of MPD and GAMD, BARC in carrying out the experiment.

REFERENCES