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Compatibility of surface-coated steels, refractory metals and ceramics to high temperature lead–bismuth eutectic

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Abstract

Compatibility of cladding material with lead–bismuth eutectic at temperature higher than 650 °C is one of the most crucial issues for feasibility of lead–bismuth-cooled fast reactors with cycle efficiency as high as 40%. In order to search for corrosion-resistant materials with lead–bismuth eutectic at temperature higher than 650 °C, surface-coated steels, some refractory metals and various ceramics were tested by means of stirred-type corrosion test. Lead–bismuth was heated up to 700 °C electrically in an alumina crucible, and oxygen concentration in the lead–bismuth was adequately controlled by injection of argon, steam and hydrogen gas mixture into the lead–bismuth. Specimens of aluminum–iron-alloy-surface-coated steels, refractory metals and ceramics including SiC/SiC composites were immersed in the stirred lead–bismuth for 1000 h. It was found that the surface-coated steels showed good compatibility with the lead–bismuth due to formation of a thin and stable protection layer on the surfaces. Tungsten and molybdenum exhibited high corrosion resistance. On the other hand, niobium is not a reliable material for the high temperature LBE. SiC and Ti_3SiC_2 also exhibited high corrosion resistance. On the other hand, the physical performance of the SiC/SiC composite must be improved especially by minimizing the porosity.
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1. Introduction

The deployment of the lead alloy-cooled fast reactors (LFRs) and the accelerator driven system (ADS) depends strongly on the development of materials. Compatibility of cladding materials to the coolant at temperature above 650 °C is required for the feasibility of the high efficiency lead alloy-cooled fast reactors that are competitive to sodium-cooled reactors.

It has been expected that surface-treated steels, refractory metals and ceramics can be the candidates of the cladding materials of the high temperature and high efficiency LFRs. Müller et al. (2000) reported that steels with an aluminum-alloyed surface by pulsed electron beam heating exhibited inhibition of oxidation corrosion and no corrosion attack in a stagnant lead at 550 °C. Kurata et al. (2004) reported that

the steels with surface coating layers of Al_2O_3, $FeAl_2$ and $AlCr_2$ produced by the gas diffusion method exhibited corrosion resistance in a stagnant lead–bismuth eutectic (LBE) at 450 °C and 550 °C, while the steels with surface coating layers produced by the melt dipping method suffered a corrosion attack in the stagnant LBE. As for the refractory metals, Fazio et al. (2003) reported that tungsten and molybdenum exhibited two orders of magnitude greater corrosion resistance than AISI316L and T91 in a flowing LBE at 400 °C. Hata and Takahashi (2005) reported that the refractory metal of Mo exhibited higher corrosion resistance than 12Cr steel in a stirred pool of LBE at 450 °C. Takahashi and Kondo (2005) reported that the ceramics of SiC and Si_3N_4 showed good corrosion resistance in a flowing LBE at 550 °C with negligibly small weight losses, although cracks were observed on the surfaces. Hata and Takahashi (2005) also reported that SiC and Si_3N_4 exhibited good corrosion resistance with weight losses in two-order of magnitude lower than those for HCM12A-12% Cr steels in a stirred pool of LBE at 450 °C.

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Lee et al. (2005) investigated the applicability of SiC/SiC composites to the fuel cladding tubes, and found that its mechanical strength was the highest when it was made at the conditions of 1820 °C and 20 MPa and its fracture behavior was stable when it was made at the conditions of 1800 °C and 15 MPa.

It can be seen that the corrosion behavior of surface-treated steels, refractory metals and ceramics has been investigated extensively in lead alloy at temperatures lower than 650 °C in the previous studies. There are few investigations on corrosion behavior of the materials in lead alloys at the temperature higher than 650 °C. It is necessary to further investigate the compatibility of various material candidates to high temperature lead alloys for development of the high temperature and high efficiency lead alloy-cooled fast reactors.

In the present study, the corrosion behavior was investigated for Al–Fe-coated steel, refractory metals, silicon carbide types of ceramics materials and Ti_3SiC_2 in molten LBE at the temperature of 700 °C.

2. Experiment

2.1. Experimental apparatus

The corrosion tests were carried out in a pot-type liquid metal test apparatus with stirred condition where Ar and Ar + 3%H_2 gas were injected continuously. The parameters of the test apparatus and the test conditions are shown in Table 1. A schematic of the corrosion test apparatus is shown in Fig. 1. The apparatus consists of a steam generator, a moisture dew-point sensor, a heater section of injection gas, an oxygen sensor, a test pot and a gas exhaust system. An alumina crucible was used as the test pot for molten LBE. It contains an oxygen sensor, a molybdenum wire to detect the output signal of the sensor, a ceramics nozzle for gas injection and a thermocouple for LBE temperature measurement. The crucibles are 180 mm in length, 60 mm in outer diameter and 5 mm in thickness. The quantities of LBE were 1650 g and 1950 g in two experiments. The injection gas flowed through a stainless steel tube and entered the test pot from the ceramics nozzle. The oxygen concentration was controlled by the sensor made of a sintered yttria-stabilized zirconia electrolyte, i.e. YSZ. As an internal

reference, oxygen-saturated bismuth (Bi/Bi_2O_3) fluid was used. The composition ratio of Bi to Bi_2O_3 was 95:5 wt%. The sensor output signal was detected by two molybdenum (Mo) wires which were inserted into the internal reference fluid in the cell of oxygen sensor and the LBE in the crucible. The electromotive force (EMF) signals were measured using an electrometer.

2.2. Materials

The tested materials were surface-coated steels, i.e. Al–steel-sputtering-coated steels, STBA26 with no surface coating, refractory metals, silicon carbide and Ti_3SiC_2.

The surface-coated steel material was Al–steel-sputtering-coated STBA26 which was coated by physical vapor deposition (PVD) technique using the Unbalanced Magnetron Sputtering (UBMS) method. Ar gas was used in this method to bombard the atoms of target materials. Sputtering targets in this experiment were Al and SUS-304. The temperature of UBMS core was 330–349 °C during operation with 400–500 V in voltage and 10 A in current. The thickness of Al–steel-sputtering film was 21 μm. The STBA26 itself has been used and developed as a material for high temperature service in boilers. This steel contains 9% Cr, 1% Mo and 0.2% Si. The shapes of Al–steel-sputtering-coated STBA26 and STBA26 as received specimens were rectangular with $15 \times 15 \times 2$ mm and $15 \times 10 \times 2$ mm in sizes, respectively.

The tested refractory metals were tungsten (W), molybdenum (Mo) and niobium (Nb). The tungsten is the metallic element with the highest melting point of 3410 °C among any metals and has a density of 19.5 g/cm³. The molybdenum melts at 2610 °C and has a density of 10.2 g/cm³. The niobium melts at 2468 °C and has a density of 8.57 g/cm³. The purities of tungsten, molybdenum and niobium specimens in this experiment were 99.95%, 99.95% and 99.9%, respectively. These materials were supplied by the Nilaco Company. The shapes of tungsten, molybdenum and niobium specimens were rectangular with $10 \times 5 \times 2.3$ mm and $10 \times 10 \times 2.3$ mm, $10 \times 5 \times 2$ mm and $15 \times 5 \times 2$ mm, and $10 \times 5 \times 2$ mm and $10 \times 5 \times 2$ mm in sizes, respectively.

The ceramic materials tested were silicon carbide SiC, titanium silicon carbide Ti_3SiC_2 and SiC/SiC composites. The compositions of the SiC were 98SiC–0.2SiO_2–0.1Si–1.2C. The density of the SiC was 3.1 g/cm³. It was also supplied by the Nilaco Company. The Ti_3SiC_2 is one of the new types of solids. It is relatively light with similar density as Ti, i.e. 4.5 g/cm³, but is roughly three times as stiff with the strength of ~325 GPa and is readily machinable with nothing more sophisticated than a manual hack saw (Barsoum et al., 2003). This specimen was supplied by the 3-ONE-2 LLC. The SiC/SiC composite is quite light with a density of 2.1 g/cm³. This density is lower than SiC and more than half of Ti_3SiC_2. Recently, SiC/SiC composite has been proposed as the candidate material of high temperature reactors. The SiC/SiC composite material was supplied by the Art Kagaku Co. Ltd. The shapes of SiC, Ti_3SiC_2, and SiC/SiC composite specimens were rectangular with $15 \times 15 \times 2.3$ mm and

Table 1
General condition of corrosion test apparatus

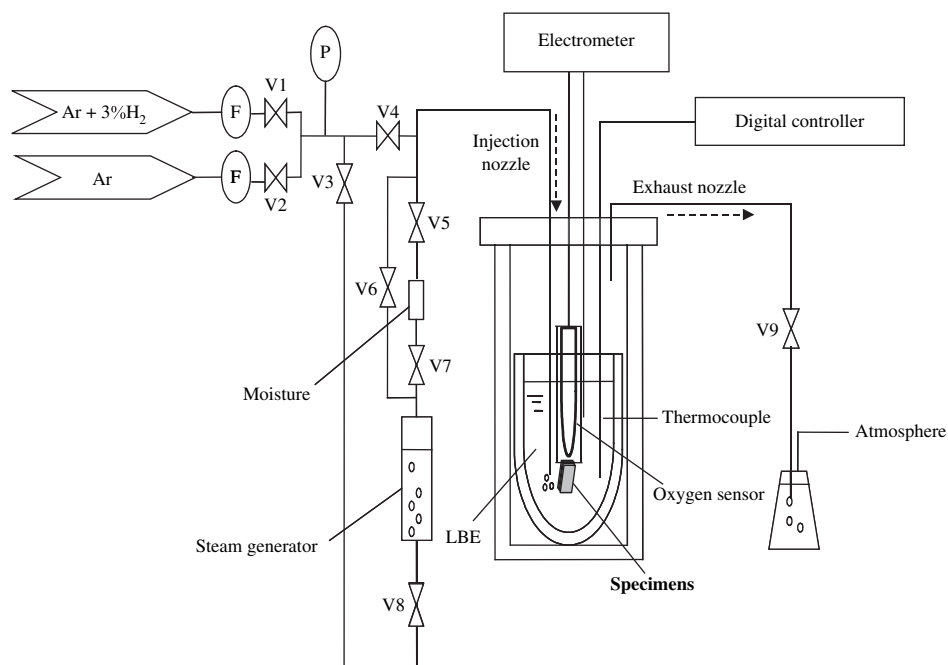| Parameter	I	II
Temperature of LBE	700 °C	700 °C
Oxygen concentration (wt.%)	~6.8×10^{-7}	~5×10^{-6}
EMF (V)	0.477	0.393
Immersion period (h)	1000	1000
Tested materials	Al–Steel-Sputtering-coated STBA26, STBA26 as received and SiC/SiC composite	Tungsten, Molybdenum, Niobium, SiC, Ti_3SiC_2

Fig. 1. Schematic of corrosion test apparatus.

$15 \times 15 \times 2.3$ mm, $10 \times 10 \times 2.3$ mm and $13 \times 10 \times 2.3$ mm, and $15 \times 15 \times 2.3$ mm and $15 \times 15 \times 2.3$ mm in sizes, respectively.

2.3. Experimental procedure

The concentration of oxygen was 6.8×10^{-7} wt% for the corrosion test of Al–steel-sputtering-coated STBA26, STBA26 as received and SiC/SiC composite and 5×10^{-6} wt% for the other materials. The former oxygen concentration was equal to the formation potential of the iron oxide. These concentrations were estimated from the measured EMF and Gromov's oxygen solubility equation (Gromov et al., 1998).

The corrosion behavior of the tested materials was analyzed by the Scanning Electron Microscope (SEM) – Energy Dispersive X-Ray Microanalysis (EDX) and weight loss analysis. The weight loss data were used for the estimation of the corrosion rate of the refractory materials, the silicon carbide and the Ti_3SiC_2. The weight loss of Al–steel-coated STBA26 and STBA26 as received was not considered in this study. For the measurement of the weight change, in the first step, all the specimens were immersed in a hot sodium pool at 260–280 °C, and then washed with ethanol. The weight change was measured using an electronic balance with the accuracy of 0.1 mg.

For the SEM–EDX analysis, after the immersion in molten LBE at 700 °C, the specimens were washed in a hot glycerin pool at 160–180 °C to remove the residual LBE. Afterwards the glycerin was removed using water at 70–80 °C. The specimen's surfaces were coated by gold to protect the formed oxide layer. Afterwards the specimens were cut in the middle, solidified by resin and polished with a mechanical grinder using polycrystalline diamond grains.

3. Results

3.1. Al–steel-sputtering-coated steel

Fig. 2 shows the SEM micrograph of the cross section of the sputtering-coated surface layer. It is found that the coating layer remains intact on the base surface of the STBA26. The thickness of the coating layer of ~ 21 μm is the same as the thickness of this layer before immersion in the LBE. It is also found that the thin-stable layer with 3.77–4.50 μm in thickness was formed during the test operation. The characteristics of the thin-stable layer are shown in Fig. 3. Figs. 3a,b,c show
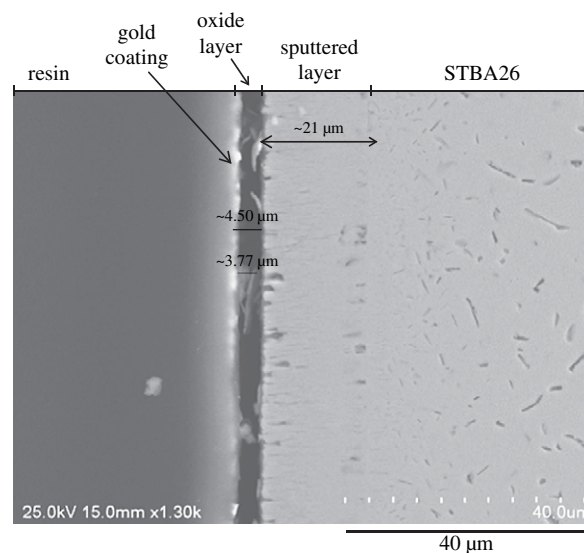

Fig. 2. SEM micrograph of Al–steel-sputtering-coated STBA26 after immersion in 700 °C LBE for 1000 h.
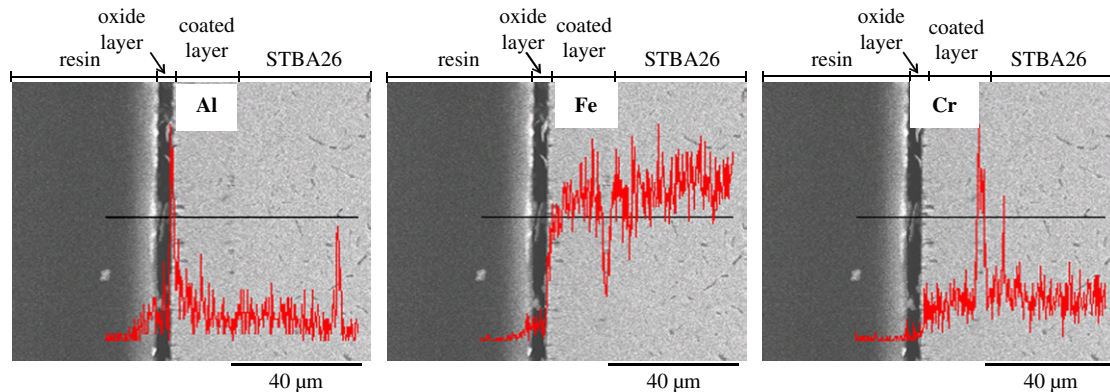
Fig. 3. EDX micrograph of Al–steel-sputtering-coated STBA26 after immersion in 700 °C LBE for 1000 h. (a) Al analysis, (b) Fe analysis and (c) Cr analysis.

the results of the EDX analysis of aluminum, iron, and chromium, respectively. Fig. 3a shows that aluminum content has high peak in the oxide layer area. Fig. 3b,c shows that iron and chromium contents have no significant peaks in the thin-stable layer area. In the thin-stable layer, oxygen content has high peak as shown in Fig. 4. It could be analyzed that the thin-stable layer is an oxide layer mainly containing aluminum oxide. The SUS-304 used for the target in the UBMS technique, mainly contains iron and chromium (18–20%). The oxygen concentration in LBE of this experiment was 6.8×10^{-7} wt% which was much higher than the formation potentials of aluminum oxide and chromium oxide and was nearly equal to the formation potential of iron oxide. The compositions of this sputtering-coated surface layer and oxygen concentration have the possibility of iron and chromium oxide formation. However, the iron and chromium oxides were not formed appreciably after 1000 h immersion in LBE at the 700 °C. The SEM–EDX analysis showed that the oxide layer which contained aluminum oxide was thin and stable and protected the surface from the attack of LBE at 700 °C, that is, there was no penetration of LBE into this layer after 1000 h immersion. The results showed that the Al–steel-sputtering-coated surface using the UBMS

technique effectively protects the steel from the attack of LBE at 700 °C.

For the comparison, the STBA26 as received was also investigated. The specimen was immersed in the same LBE in the crucible together with the STBA26 with sputtering-coated surface treatment. Fig. 5 shows the SEM micrograph of the cross section of the as received STBA26. It is found that no oxide layer was formed and that LBE penetrated deeply into the base material of the specimens. According to the level of oxygen concentration, STBA26 which contains 9% chromium, has the possibility for formation of the chromium oxide layer. Kondo et al. (2006) reported that after 1000 h-test in LBE at 550 °C with the oxygen concentration of 1.7×10^{-8} wt%, the surface of the STBA26 was covered by chromium oxide layer and no LBE penetration was observed. However, our investigation showed that the chromium oxide layer was not formed appreciably in the surface of the STBA26 at the temperature of 700 °C.

The formation of the thin and stable aluminum oxide layer which is effective as a barrier against the dissolution attack of LBE at the surface of aluminum surface-treated specimens has been reported by the other researchers for various techniques of alumina surface-treatments. Heinzel et al. (2006)
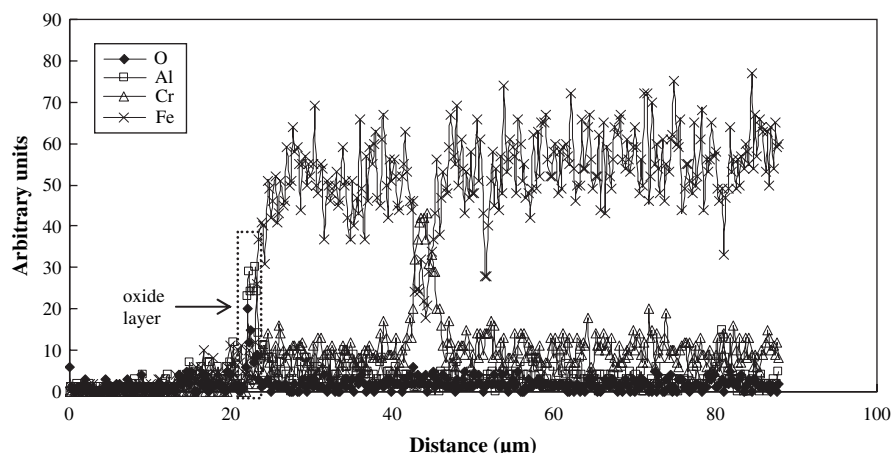

Fig. 4. Atomic analysis of cross section of Al–steel-sputtering-coated STBA26 after immersion in 700 °C LBE for 1000 h.

resin | Pb-Bi penetration | STBA26
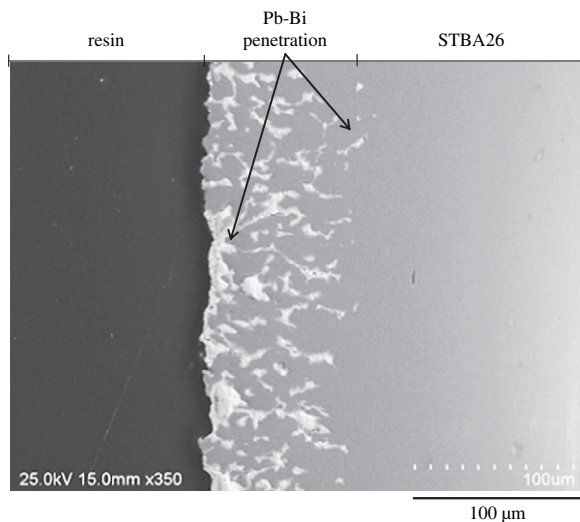
25.0kV 15.0mm x350   100um

100 μm

Fig. 5. SEM micrograph of STBA26 as received after immersion in 700 °C LBE for 1000 h.

reported that a thin alumina oxide layer was developed and no dissolution attack of LBE (550 °C) at that part was observed for the surface-Al-alloyed specimens obtained by the pulsed electron beam heating to Al-foil wrapped surface. However, it is a problem to put an Al-foil manually on the surface of steel for the pulsed electron beam heating process because the surface cannot be uniformly aluminum-alloyed. Aluminum dissolves into LBE easily on the surface with high Al content, and LBE attack occurs on the surface with poor Al. Kurata et al. (2004) reported that surface-coated specimens obtained by the gas diffusion method developed thin alumina oxide layer and no dissolution attack of LBE was observed at 450 °C and 550 °C. However, the compatibility of aluminum surface-treated specimens in LBE depend on the techniques of treatments. For example, surface-treated specimens obtained by aluminum hot-dipping were attacked by LBE and penetration occurred due to high solubility of aluminum (Müller et al., 2002; Kurata et al., 2004). It is necessary not to make a pure aluminum coating layer but an aluminum–iron coating layer. The advantage of the present UBM sputtering technique is the capability of making a uniform and fraction-controlled aluminum–iron-alloy-coating layer.

3.2. Refractory metals

The corrosion behavior of tungsten, molybdenum and niobium was analyzed after the immersion in high temperature LBE for 1000 h. The cross sectional observation and weight change analysis were performed. Fig. 6a shows the SEM micrograph of the cross section of the tungsten. It is found that no penetration of LBE into tungsten and no trace of corrosion were observed. The surface of tungsten was smooth without any damage or cracks. Fig. 8 shows no significant weight change of tungsten specimen after the immersion in high temperature LBE for 1000 h. From these results it can be concluded that there is no penetration of LBE into tungsten.

Fig. 6b shows the SEM micrograph of the cross section of the molybdenum. It can be seen that there was no penetration of LBE into the molybdenum matrix and no trace of corrosion. There was observed neither damage nor cracks in this molybdenum cross section. Fig. 8 shows no significant weight change of the molybdenum specimen. These results show that after the immersion in high temperature LBE for 1000 h there was neither penetration of LBE nor dissolution of molybdenum element into LBE.

From the SEM and weight change analysis it can be seen that tungsten and molybdenum are highly corrosion-resistant, and compatible with LBE at 700 °C up to 1000 h. At lower temperature, high corrosion resistance of tungsten and molybdenum in liquid LBE has been also reported previously. Fazio et al. (2003) reported that in flowing LBE at 400 °C tungsten and molybdenum exhibited smooth surface with no evidence of LBE on the surface and growth of oxide layer. Hata and Takahashi (2005) reported that in the stirred LBE pool at 450 °C molybdenum had good corrosion resistance.

Fig. 6c shows deep penetration of LBE into niobium. This penetration of LBE was spreading over the almost whole surface. Fig. 8 shows that the weight loss of niobium was 190 g/m^2 in this corrosion test. From SEM and weight change analysis it can be seen that niobium is not compatible with LBE at 700 °C. Significant corrosion of niobium in LBE at 750 °C has

gold coating
resin | W   gold coating resin | Mo   Pb-Bi penetration resin | Nb

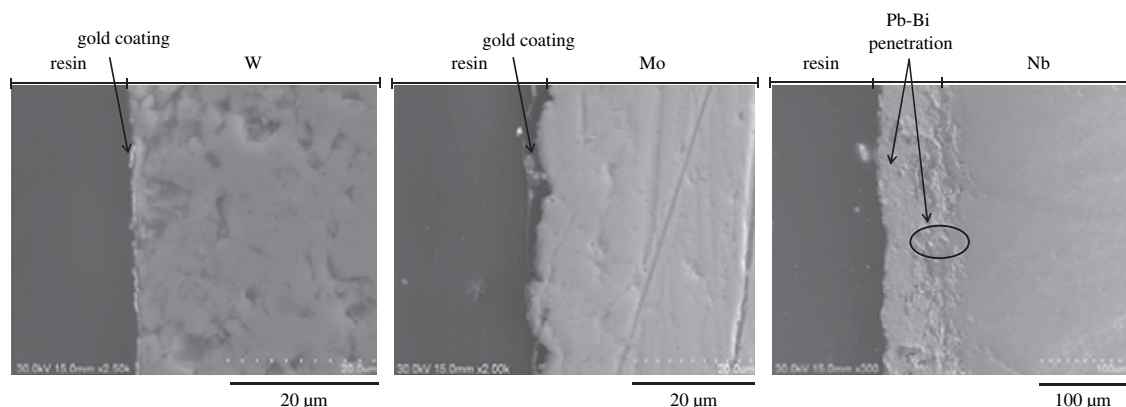20 μm   20 μm   100 μm

Fig. 6. SEM micrograph of refractory metals after immersion in 700 °C LBE for 1000 h. (a) W, (b) Mo and (c) Nb.
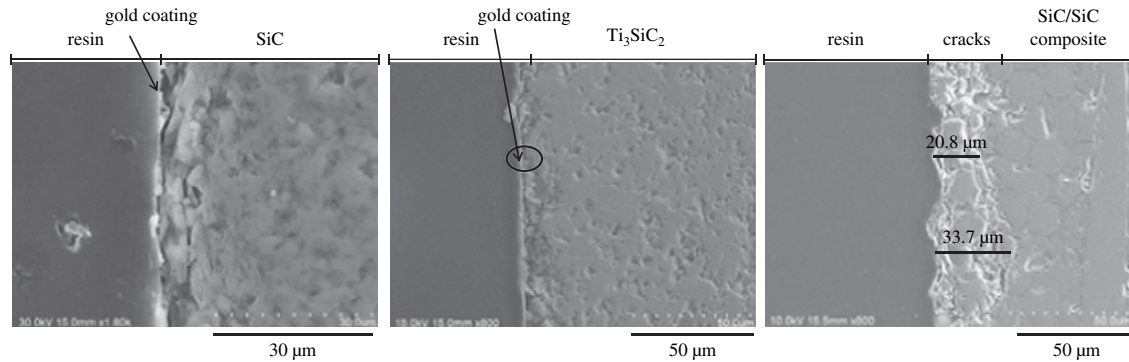
Fig. 7. SEM micrograph of ceramics after immersion in 700 °C LBE for 1000 h. (a) SiC, (b) Ti3SiC$_2$ and (c) SiC/SiC composite.

been also reported by Weeks (1971), although good corrosion resistance of niobium in LBE at 450 °C has been reported by Hata and Takahashi (2005).

3.3. Ceramics

Corrosion behavior of SiC, Ti$_3$SiC$_2$ and SiC/SiC composite specimens after immersion in LBE at 700 °C was evaluated by cross sectional observation and weight change analysis.

Fig. 7a shows the SEM micrograph of the cross section of the SiC. It is found that no penetration of LBE into SiC matrix and no trace of corrosion are observed. No significant weight change is observed after the immersion in high temperature LBE for 1000 h as shown in Fig. 8. These results show that neither penetration of LBE nor dissolution of the constituent elements of SiC into LBE occurred.

Fig. 7b shows the SEM micrograph of the cross section of the Ti$_3$SiC$_2$. It is found that there were observed no penetration of LBE into Ti$_3$SiC$_2$ matrix occurred and no trace of corrosion. There was no significant weight change after immersion in high temperature LBE up to 1000 h as shown in Fig. 8. These results show that neither penetration of LBE nor dissolution of constituent elements of Ti$_3$SiC$_2$ into LBE took place.

From the SEM and the weight change analysis, it can be seen that the SiC and the Ti$_3$SiC$_2$ exhibit high corrosion resistance and are compatible with LBE at 700 °C up to 1000 h. At lower temperature of 550 °C, the SiC showed good corrosion resistance in flowing LBE (Takahashi and Kondo, 2005).
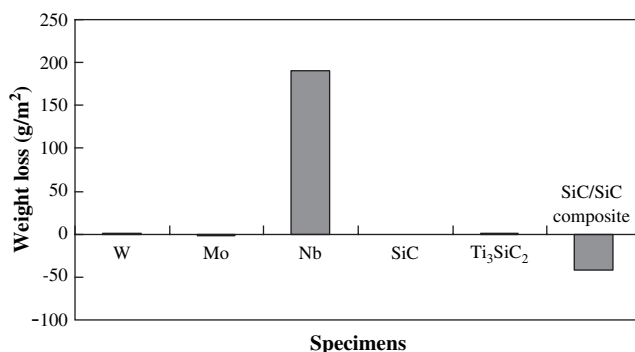
The SEM micrograph of the SiC/SiC composite after the immersion in 700 °C LBE for 1000 h shows that the LBE could penetrate to the pores of the composite, as shown in Fig. 7c. Improvement of this material to prevent LBE from penetration could be done by making the SiC/SiC composites denser. Fig. 7c shows that the thin crack layer appeared in this SiC/SiC composite specimen with 20.8–33.7 μm in thickness. However, there were no detachment and lost of the crack layer from the SiC/SiC composites. The crack layer still remained in the specimen. The crack occurred possibly because of the thermal shock or due to the difference of thermal expansion between materials near the surface. Fig. 8 shows that the weight loss of SiC/SiC composite was negative. After immersed in 700 °C LBE for 1000 h and washed by hot sodium, LBE still remains in the pores of this specimen.

4. Conclusions

The corrosion behavior of surface-coated steels, i.e. Al–steel-sputtering-coated steels, refractory metals and ceramics has been investigated after immersion in LBE at 700 °C for 1000 h. From this investigation it can be concluded that:

1 The unbalanced magnetron sputtering technique could form good protection layer on the surface of steels. Aluminum oxide formed on the surface of the sputtering-coated layer is stable and prevents the penetration of LBE at 700 °C. The result of the corrosion behavior shows that the UBMS technique is a possible option for the coating of cladding and structural materials that contact with high temperature LBE in LBE-cooled fast reactor.

2 Tungsten and molybdenum exhibit high corrosion resistance to LBE at 700 °C. The results of corrosion behavior indicate that the tungsten and molybdenum are the potential materials for cladding and core structure materials for high temperature LBE-cooled fast reactors. On the other hand, niobium is not compatible with the LBE at 700 °C.

3 SiC and Ti$_3$SiC$_2$ also exhibit high corrosion resistance to LBE at 700 °C, which means that they can be potential materials for high temperature LBE-cooled fast reactors. The physical performance of the SiC/SiC composite must be improved especially by minimizing the porosity.

Fig. 8. Weight loss of refractory metals and ceramics after immersion in 700 °C LBE for 1000 h.

Acknowledgement

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