Study of aluminum coating prepared by PVD used as anti-corrosion in liquid lead-bismuth

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Received December 19, 2012; accepted January 8, 2013; posted online June 14, 2013

Liquid metals-such as lead (Pb) or lead-bismuth (PbBi) are used as reactor core coolants for accelerator driven systems (ADS) proposed for high-level radioactive waste transmutation. Compatibility of steels with liquid PbBi is a key problem because steels are attacked by dissolution of the components in PbBi, so it has to form a stable coating on steel surface. There are many methods to prepare anti-corrosion coatings on steel, such as hot dipping, pack cementation, plasma spaying, and physical vapor deposition (PVD). Compared with other methods, the PVD method is easy to control the thickness of the coating and the obtained coatings are dense which is crucial to the anti-corrosion ability of the coatings. In this letter, PVD aluminum coatings are developed on the surface of T91 steel and different heat-treatment atmosphere is used to adjust the microstructure, aluminum content, and the phase of the coatings. It is found that the coatings have good adherence ability with steel. The aluminum content and the phase of the coating can be adjusted by the heat-treatment atmosphere. Corrosion tests are performed in oxygen-saturated liquid PbBi at 550 °C for 1 000 h, the phase and composition of the coating do not change drastically. All the results indicate that the PVD is a useful method to prepare coatings on the surface of steel used in liquid PbBi.

OCIS codes: 310.1515, 310.1860, 310.4925.
doi: 10.3788/COL201311.S10210.

Liquid lead bismuth (PbBi) has been considered as coolants for future accelerator driven systems (ADS)[1,2]. However, one of the concerns with the use of liquid metals is their compatibility with the containment structure[3−6]. At low oxygen content most steels tested show dissolution attack. Therefore most experiments are performed at higher oxygen concentration in the lead-bismuth eutectic (LBE) of about 10^{-6} wt.-% that allows formation of a protective oxide scale on the surface. It is confirmed that unprotected T91 steel is not suitable for the use with liquid PbBi at temperature above 500 °C because it develops thick oxide scales including magnetite and spinel with low thermal conductivity. The magnetite tends to spall off and eventually block cooling channels. Furthermore the thick oxide scale hinders the heat transfer through the cladding wall of fuel pins[7,8]. Therefore, structure parts that are exposed to temperatures above 500 °C have to be protected by a suitable surface modification.

In general, the countermeasure against liquid metal corrosion, which means dissolution of structural components by liquid lead (Pb) alloys, is the formation of a protective oxide scale on the metal surface which is stabilized by oxygen dissolved in the liquid alloy. Al has shown its potential to protect steel surfaces against corrosion and severe oxidation in contact with Pb alloys when its concentration in the surface region amounts to 4–10 wt.-%, because the alumina scale grows only very slowly and prevents migration of oxygen into the steel as well as migration of steel components onto the surface[9]. Various methods have been used in surface engineering techniques, such as hot dipping of the steel into an Al melt with subsequent annealing, pack cementation, and plasma spraying followed by pulsed electrons beam (GESA)[10,11]. Compared with other methods, the physical vapor deposition (PVD) method is easy to control the thickness of the coating and the obtained coatings are dense which is crucial to the anti-corrosion ability of the coatings.

In this letter, PVD aluminum coatings are developed on the surface of T91 steel and different heat-treatment atmospheres are used to adjust the microstructure, aluminum content and the phase of the coatings. It is found that the coatings have good adherence ability with different steel substrates. Furthermore, the behavior of the coatings in stagnant PbBi containing oxygen at temperatures 550 °C up to an exposure time of 1 000 h is studied. During the exposure a thin Al_2O_3 layer is formed at the surface of the specimens. No dissolution attack is observed under this condition which means that the PVD is a useful method to prepare anti-corrosion coatings on the surface of steel used in liquid PbBi.

Coupons were cut from T91 steel, the compositions of this steel were listed in Table 1. Most of the coupons were abraded successively on emery paper from 400 to 1 000 grit.

The aluminizing process is performed by a thermal evaporation process. The experimental procedure is as follows. Before thermal evaporation, all the coupons were degreased with acetone, ethanol and drying in nitrogen gas. The substrates were introduced in the vacuum deposition chamber where a pressure of about 2×10^{-3} Pa

Table 1. Chemical Compositions of T91 Steel (wt.-%)

	Cr	Ni	Mn	C	S	Si	W	V	Mo	N	P	Fe
T91	9.5	0.4	0.6	0.13	0.01	0.5	2	0.25	0.6	0.07	0.02	Bal.

was reached. The substrates were placed in a substrate holder, at 30 cm above the evaporation crucible. The aluminum thread was evaporated from a tungsten crucible by applying a current, which was gradually increased to 200 A, and the evaporation process was maintained for 3 min. After thermal evaporation, the samples were taken out from the vacuum chamber and thermal treated in a furnace at 750 °C under N_2 or air atmosphere.

Corrosion test was performed at 550 °C for 1 000 h under isothermal conditions. It was carried out in an inert atmosphere chamber. The specimens were placed in a monolithic Mo crucible and kept in mantles made of Mo.

After taking the specimens out of the furnace, the PbBi alloy adhering on the steel surfaces was removed by soaking the samples in a mixture of acetic acid, hydrogen peroxide, and ethanol for 24 h. Afterwards, they were cleaned and dried for visual examination and weight measurements. The phase identification of the coating was performed with X-ray diffractometer (XRD, Philips X'pert, Holland) using Cu-Kα radiation. A scanning electron microscope (SEM) (FE-SEM, FEI Sirion-200, USA) with an energy dispersive X-ray (EDX) analysis system were used for the analysis of the topography and compositional uniformity of the coating. The specimens were cut with a diamond disk saw perpendicular to the exposed surface. One part of the specimen was tested to identify crystallographic phases by XRD; the second part of the specimen was embedded, ground and polished for cross-section and concentration profiles by SEM and EDX.

Figures 1 give the FE-SEM images of the aluminum coating on the surface of the untreated T91 steel. It can be seen that the coating is dense without crack and cavity. There are some particles in the surface, and it may be related with the fast evaporation rate.

Figure 2 give the XRD result of the obtained aluminum coating. It can be seen that the coating is pure aluminum without any impurity phase.

After thermal evaporation, the obtained aluminum coating was thermal treated in a furnace in air at 750 °C and the XRD result are shown in Fig. 3. It can be seen that after thermal treated in air, the coating are mainly composed of Fe_2O_3 (ICDD card number 01-1053), Fe_3O_4 (ICDD card number 01-1111), FeAl (ICDD card number 01-1257), and Al_2O_3 (ICDD card number 01-1243) phase. It means that treating the coating in air will cause the oxidation of the Fe element in the steel, so the coatings should not thermal treated in air.

In order to avoid the over oxidation of the steel, the coating are treated under N_2 atmosphere at 750 °C and the XRD result is shown in Fig. 4. It can be seen that the coating treated in N_2 is mainly composed of Fe_2Al_5 (ICDD card number 01-1228), Fe_2O_3 (ICDD card number 01-1053), and Al_2O_3 (ICDD card number 01-1243) phase. The insert of the picture is digital picture of obtained coating, it is gray-black and uniform. Figure 5 give the SEM pictures of the coating with different magnification, and it can be seen that the coating is dense without crack. There are many nicks with the same direction, and it is related with the abraded emery paper.

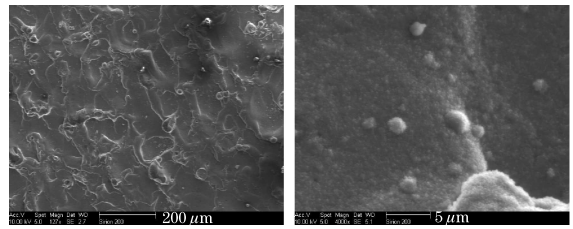

Fig. 1. FE-SEM images of the surface of aluminum coating on T91 steel.

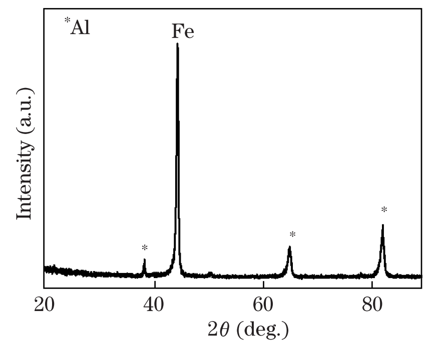

Fig. 2. XRD result of the obtained aluminum coating on T91.

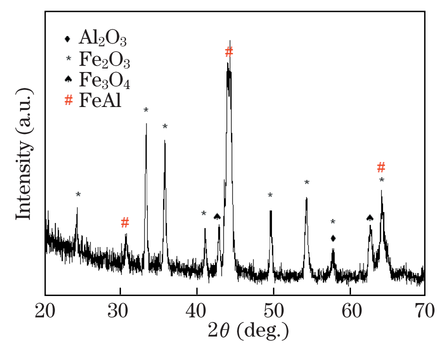

Fig. 3. XRD result of the coating on T91 after thermal treated in air.

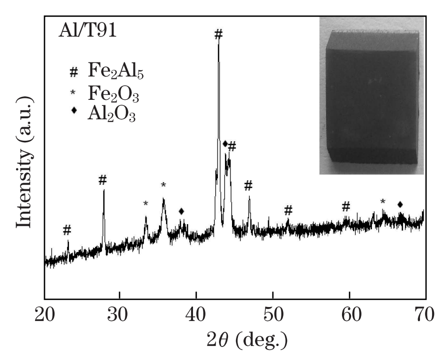

Fig. 4. XRD result of the coating on T91 after thermal treated in N_2.

Furthermore, the aluminum content in the coating is very important to evaluate the anti-corrosion property of the coating. The EDX results of the coating are shown in Fig. 6 and the element composition is shown in the insert. It can be seen that the aluminum content in the coating is about 13 wt.-%. From the previous published articles[8,9], it is suggested that the coatings with 5–15wt.-% aluminum content have superior anti-corrosion property in melt PbBi. So it can be anticipated that the coating treated in N_2 may have good anti-corrosion property in PbBi.

After corrosion in PbBi at 550 °C for 1 000 h, all the specimens were taken out. Visual examination of specimens did not show strong liquid metal corrosion effects. The weight of the specimen before corrosion is 3.1507 g and the weight after corrosion is 3.1503 g, which means that there is no dissolution of steel elements in the presence of PbBi occurred although nickel has a high solubility in Pb alloys[12].

The XRD patterns of the samples before and after corrosion were shown in Fig. 7. It can be seen that the XRD patterns of the two samples are mainly composed of Fe_2Al_5 (ICDD card number 01-1228), Fe_2O_3 (ICDD card number 01-1053), and Al_2O_3 (ICDD card number 01-1243). The enhancement of the Al_2O_3 diffraction peak was correlated with the Al element in the coating are oxidized by the oxygen in melt PbBi, and the thin Al_2O_3 layer can protect the steel free from dissolution attack. There is no other diffraction peaks after corrosion, and it is suggested that the coating are stable and no obvious dissolution and corrosion are occurred under this condition.

Figures 8(a) and (b) give the cross-section and concentration profile of the coating on T91 steel. There is an oxide scale (about 5 μm) on top of the surface, which can protect the steel not only from liquid PbBi attack but also from oxygen diffusion into the coating and bulk material. The diffusion of Fe through the surface to form a magnetite layer on top is also prevented by the thin alumina scale. Follow by this thin alumina layer, an interdiffusion zone of about 7 μm can be recognized in the line scan which is caused by diffusion of iron into the Al layer during annealing[11−14]. Further works should be carried out on higher PbBi temperature and liquid PbBi

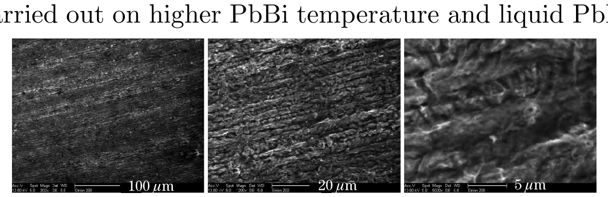

Fig. 5. SEM results of the coating on T91 after thermal treated in N_2.

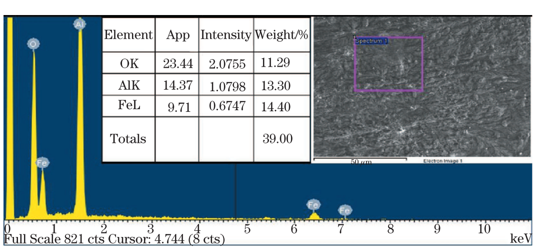

Fig. 6. (Color online) EDS results of the coating on T91 after thermal treated in N_2.

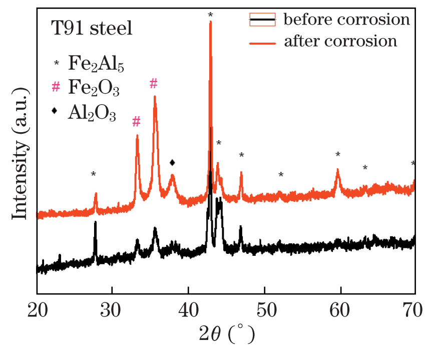

Fig. 7. (Color online) XRD patterns of the coating on T91 before corrosion and after corrosion.

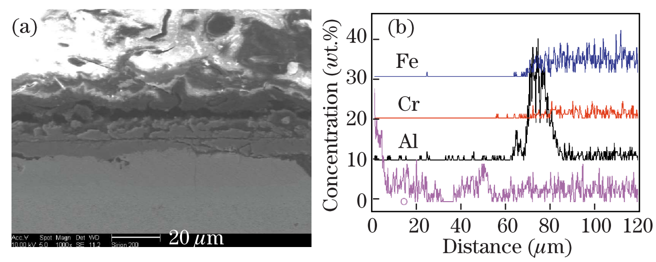

Fig. 8. (Color online) (a) Cross-section and (b) concentration profiles of the coating on T91 steel after exposure to PbBi at 550 °C for 1 000 h.

with different flow velocities to explore the anti-corrosion property of coating obtained by thermal evaporation method.

In conclusion, PVD aluminum coatings are developed on the surface of T91 steel. Thermal treatment of the sample in air causes over oxidation of the Fe element in the steel. When they are thermal treated in N_2, the coatings have acceptable microstructure, aluminum content and phase. After corrosion in PbBi at 550 °C up to 1 000 h, the phase and composition of the coating do not change drastically. There is an alumina layer in the top followed by an interdiffusion zone. No dissolution attack is observed at 550 °C which leads to the conclusion that the coating obtained by thermal evaporation can be used in PbBi conditions at least up to 1 000 h, and the PVD is a useful method to prepare coatings on the surface of steel used in liquid PbBi. The anti-corrosion property of this material will be investigated in higher temperature and flowing PbBi in the future.

The work was supported by the "Strategic Priority Research Program" of the Chinese Academy of Sciences under Grant No. XDA03040000.

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