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Al based coating on martensitic steel

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Abstract

Aluminum based coatings on low activation martensitic (LAM) steels were formed by using CVD method at 973 and 1013 K. After coating, the cleaned specimens were oxidized in 0.133 Pa oxygen atmosphere at 973 and 1013 K to form the Al_2O_3 layer on the surface. The typical coating thickness of the aluminized layer is 20 μm, a 10 μm thick external layer and a 10 μm thick internal layer. The thickness of the Al_2O_3 layer is about 1 μm. The microstructure, micro-hardness profile, composition depth distribution in the cross section of the coating and the electrical resistivity of the layers were measured. The results indicate that the coatings on Chinese low activation martensitic (CLAM) steel have higher micro-hardness and higher density than that on EUROFER-97 steel produced at 1013 K. The Al_2O_3 layer formed at 973 K has higher micro-hardness and higher density than that formed at 1013 K.

1. Introduction

An advanced blanket module design with using a dual coolant concept and using low activation martensitic (LAM) steel as the structural materials has been initiated in China [1]. A kind of LAM steel is also developed in China, named CLAM steel [2]. The chemical composition of CLAM steel is similar to EUROFER97, except for the content of tungsten, magnesium and silicon. Tungsten is increased to 1.5% for increasing strength, but is kept below to 2% to avoid the appearance of Laves phase at 550 °C. Adding a suitable amount of manganese to improve the compatibility with LiPb liquid and a suitable amount of Si to improve the welding behavior.

Thin insulating coatings on LAM steel are proposed as the solution to reduce the MHD pressure drop to acceptable levels in a self-cooled Pb–17Li system; this coating will also be served as the tritium permeation barriers (TPB) to reduce the permeation of tritium from Pb–17Li breeder material into the water coolant (or helium coolant) [3–7]. Only a limited number of materials offer the potential of meeting the most basic requirements for the MHD coatings, viz., electrical resistivity and chemical compatibility with Pb–17Li [8]. The focus and the most attention of the coating development for this application has been on an α-Al_2O_3 layer on LAM steel. The coating on CLAM steel is initiated in our research program by using the chemical vapor deposition (CVD) process [9]. This technique has the advantage of a lower temperature process, typically 650–750 °C, which avoids any modification of the martensitic steel properties. The CVD approach also lends itself to the potential of in situ coating formation, which can provide for self-healing of the alumina scale to acceptable reliability [10].

The CVD process has been applied to the tubes and specimens at 973 and 1013 K [11]. A series of cross section analyses and measurements, such as the thickness of coating layer, the composition distribution and the micro-hardness profile along the depth, the electrical resistivity of the layer, the surface structure of the Al_2O_3 layer and the microstructure of the layer have been conducted to evaluate the technology process. The results show that the Al_2O_3 layer formed at 973 K has higher micro-hardness and higher density than that formed at 1013 K, which indicate that increasing coating

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temperature from 973 to 1013 K during CVD process is not useful to form the coatings on LAM steel. It is important to develop this technology for improving the content of oxygen in the Al_2O_3 layer with various oxygen atmospheres and operating temperature. This paper describes the technology process of the coating, the performance measurements and the analyses of results.

2. Experimental

2.1. The coating process

Two groups specimens were prepared, each group has 10 specimens, five EUROFER-97 steel ($25\times7\times1.5$ mm) and five CLAM steel ($10\times7\times1.5$ mm).

The specimens were coated with a layer system of AlFe and Al_2O_3 by means of CVD. The CVD process involves pack cementation on FeAl with an NH_4Cl activator and an Al_2O_3 inert filler to form a $FeAl/Al_2O_3$ TPB on the LAM steel substrate [9]. The CVD process has been developed for the tubes and the specimens, including EUROFER-97 and CLAM, at 973 and 1013 K for 16 h. After coating, the specimens were cleaned and dipped into a solution of $Ce(NO_3)_3$, were then oxidized in 0.133 Pa oxygen atmosphere at 973 and 1013 K for 16 and 32 h to form the Al_2O_3 layer in the surface.

2.2. Post-coating measurements and analyses

The cross section of the edge of coated specimens were ground carefully and cleaned in water, acetone and ethanol, then electro polished with 10% oxalic acid solution for about 30–60 s. The polishing voltage was 3 V. After that, all of them were used for metallurgical analyses. The metallurgical analyses were performed by using the optical microscope and the scanning electron microscope (SEM). The chemical composition of the coatings, especially the concentrations of Al, O and Fe, were evaluated by the means of SEM/EDS and XPS. The micro-hardness of the coated specimens and the electrical resistivity of the coating layer were also measured.

3. Results and discussion

3.1. Metallurgical analysis

Optical microscopy of cross sections of the specimens showed that two-layer, uniform coatings were formed on the surface of all the specimens. The typical coating thickness of the aluminized layer is about 20 μm, including the external layer (about 10 μm in thickness) and the 10 μm thick internal layer. The internal layer seems to be very homogeneous in thickness and shows good adherence to the base material, shown in Fig. 1(a). Comparison of the specimens coated at 973 K with the specimens coated at 1013 K shows that the coatings produced on specimens at 1013 K were rougher than that produced at 973 K, shown in Fig. 1(c) and (d). The coatings formed on CLAM steel were finer and denser than that formed on EUROFER-97 by using CVD process at the temperature 1013 K, but there were some local cracks on their surfaces, shown in Fig. 1(b).

3.2. Micro-hardness

The results for the measurements of thickness, micro-hardness and electrical resistivity for the coating layer of specimens are shown in Table 1. These data indicate that, at the same coating temperature, the coatings formed on CLAM steel have higher micro-hardness and higher density than that formed on EUROFER-97 steel. The Al_2O_3 layer formed by using CVD process at 973 K has higher micro-hardness and higher density than that formed by using CVD process at 1013 K.

3.3. Cross section analysis of coating layer

SEM/EDS analysis was performed on the cross sections of two types of the specimens. For the specimens coated at 973 K, the composition of the surface is about 23Al, 74Fe and 3Cr, in wt%. The Al profile decreases

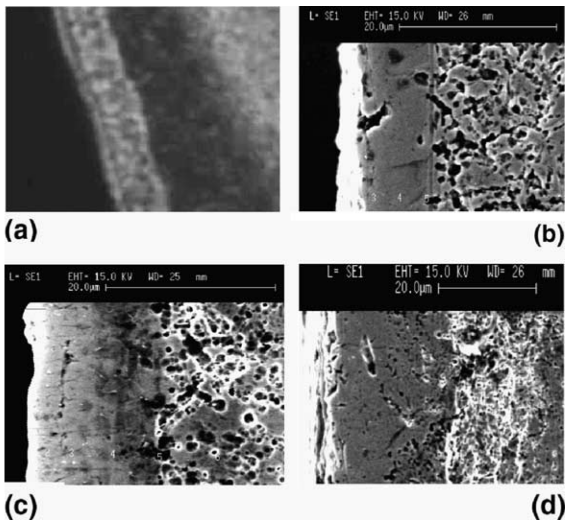

Fig. 1. Metallurgical and SEM images of coatings formed on EUROFER-97 and CLAM steel surfaces at 973 and 1013 K. (a) Metallurgical image of coatings formed on CLAM steel surface at 1013 K. (b) SEM image of coatings formed on CLAM steel surface at 1013 K. (c) SEM image of coating formed on EUROFER-97 steel surface at 937 K. (d) SEM image of coatings formed on EUROFER-97 steel surface at 1013 K.

Table 1
Thickness, micro-hardness and resistivity of CVD coatings formed at 973 and 1013 K

Item	Specimens		
	CLAM (1013 K coating)	EUROFER97 (973 K coating)	EUROFER97 (1013 K coating)
Coating thickness (μm)	25	20	20
Surface micro-hardness (HV)	305	392	286
Interlayer micro-hardness (HV)	230	245	170
Matrix micro-hardness (HV)	182	189	160
Electrical resistivity ($\Omega\,m^2$)	10^3–10^4	10^4–10^5	10^5–10^6

continuously from the surface to the substrate and is detected at a distance of about 22 μm from the surface. The external layer corresponds to the AlFe phase and has a thickness of approximately 6 μm. In the internal layer, the Al content decreases from about 18 wt% to zero which fits well to α-Fe(Al), shown in Fig. 2. But for the specimens coated at 1013 K, Al content of the surface is only about 11 wt% and decreases rapidly to zero, which only corresponds to the α-Fe(Al) phase. But the thickness of this layer is still about 22 μm. These results indicate that increasing the coating temperature is not useful to form the coatings on LAM steel.

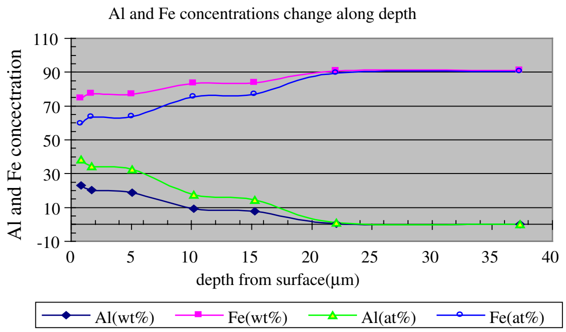

Fig. 2. Al and Fe concentration profile obtained for the specimens at 973 K.

3.4. Surface analysis of the coating layer

The surface analysis on the specimens was carried out by XPS method. For the specimens coated at 1013 K, because the coating layer had a porous structure which adsorbed large amounts of C, N, O and other elements, it is very difficult to survey the concentration of the Al, Fe, O and to determine their valences. But for the specimens coated at 973 K, the analysis results of XPS showed that at the coating surfaces, Al has one peak of

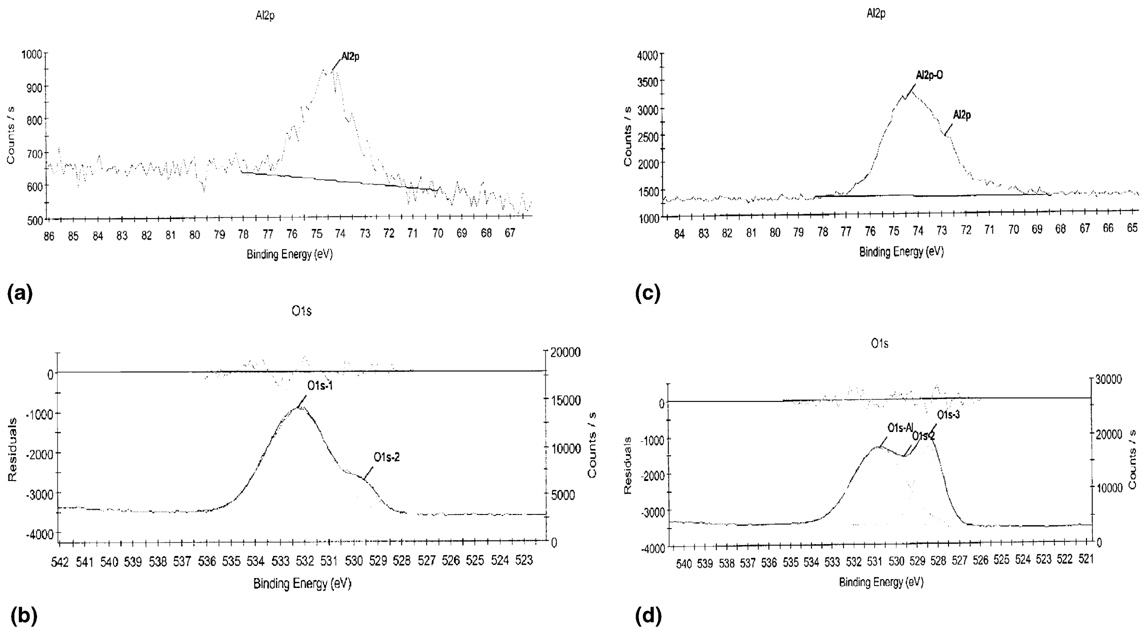

Fig. 3. XPS spectra of Al and O for the coating.

binding energy (BE) 74.5 eV, which corresponds to Al_2O_3, shown in Fig. 3(a). The oxygen O has two BE peaks shown in Fig. 3(b), which corresponds to hydroxides and Al_2O_3 respectively. When ion etched to 5 nm depth, the results for Al and Fe were same. But O has three BE peaks, which indicated that other metal oxide formed in addition to Al_2O_3 and hydroxides. To be ion etched to 10 nm depth, O still has three BE peaks, shown in Fig. 3(d), Fe is not changed, but Al shows two BE peaks, one corresponds to Al_2O_3, we checked the list of metal-oxide's BF found that the other still corresponds to Al_2O_3, but the ratio of mol Al and mol O >2:3, so it corresponds to oxygen deficient Al_2O_3, shown in Fig. 3(d).

3.5. Electrical resistivity measurements

The electrical resistivity of the coating layers was measured by the copper tape method with a Model 2430 1 kW Pulse Source Meter, Keithley Instrument Co. The tape size is 3 mm × 3 mm, has a threadlike copper strip which was used as the probe. When measured the coatings' electrical resistivity, two tapes were clung to each side of the specimens, the copper strips were connected to the instrument Meter.

The results are shown Table 1. Although the resistivity of the coating layers produced by using CVD process at 1013 K is higher than that of the layers produced at 973 K, this is because of the porous structure of the layers coated at 1013 K, which will be less resistant to the Li–Pb corrosion. The coating layer produced at 973 K has a uniform thickness, dense structure, high aluminum composition, high micro-hardness, high electrical resistivity and pure Al_2O_3 on the surface of the layer, which will be useful for the insulator coating.

4. Conclusion

Aluminum based coatings on LAM steel were produced by using CVD processes at 973 and 1013 K. After coating, the cleaned specimens were dipped into the solution of $Ce(NO_3)_3$ and were then oxidized in 0.133 Pa oxygen atmosphere at 973 and 1013 K for 16 h to form an Al_2O_3 layer on the surface.

1. The coating layer is uniform. The typical thickness of aluminized layer is 20 μm, including the external layer (about 10 μm in thickness) and the 10 μm thick internal layer. The thickness of the Al_2O_3 layer is about 1 μm.
2. The coating layer produced at 973 K has uniform thickness, dense structure, high aluminum composition, high micro-hardness, high electrical resistivity and pure Al_2O_3 on the surface of the layer, which will be developed as a useful insulator coating.
3. The coating layer produced at 1013 K has higher electrical resitivity than that of the coating layer produced at 973 K, but the coating layer is less compact, has lower aluminum composition and micro-hardness, and will not resist Li–Pb corrosion. Increasing coating temperature from 973 to 1013 K during CVD process is not useful to form coatings on LAM steel.
4. The coatings on CLAM steel have higher micro-hardness and higher density than that on EUROFER-97 steel produced by using CVD process at 1013 K.
5. The coating surface analysis by XPS method indicated that the coating on the surface is Al_2O_3. At a depth of 10 nm into the coating layer, the constituent phases are pure Al_2O_3 and Al_2O_3 with oxygen deficiency.

Acknowledgements

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