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Preparation and investigation of aluminized coating and subsequent heat treatment on 9Cr–1Mo Grade 91 steel

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HIGHLIGHTS

- Hot dip aluminizing and heat treatment was carried out on 9Cr–1Mo Grade 91 steel.
- Sample heat treated at 650 °C showed Fe_2Al_5 phase and at 750 °C showed Fe_2Al_5/FeAl.
- Samples heat treated at 950 °C showed FeAl/α-Fe(Al).
- The scratch test showed the best result with 950 °C/5 h + 750 °C/2 h sample.
- α-Al_2O_3 and γ-Al_2O_3 were present on the surface of the samples treated at 950 °C.

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ABSTRACT

Iron aluminide inner coating with alumina top layer is being considered as a potential solution for tritium permeation barrier and mitigating MHD pressure drop for liquid metal blanket concepts in the fusion reactor systems. Hot-dip aluminizing with subsequent heat treatment seems to offer a good possibility to produce aluminized coating with alumina top layer. 9Cr–1Mo Grade 91 steel samples were hot dipped in Al melt containing 2.25 wt% of Si at 750 °C for 3 min. Heat treatment was performed at 650, 750 and 950 °C for 5 h; samples were either air cooled or furnace cooled. Coatings have been evaluated by SEM, EDX, X-ray diffraction, microhardness, scratch adhesion and Raman spectroscopy. The thickness of the layers and phases formed were influenced by the heat treatment adopted. Fe_2Al_5 was the major phase present in the samples heat treated at 650/750 °C, whereas FeAl and α-Fe(Al) primarily made up the outer and inner layers respectively in the samples heat treated at 950 °C. Cooling method deployed affected the hardness. Air cooled samples had comparatively higher hardness than furnace cooled samples. The scratch test showed the adhesion for the samples heat treated at 950 °C was much better as compared to the samples heat treated at 650/750 °C. Raman spectroscopy analysis showed the presence of both α-Al_2O_3 and γ-Al_2O_3 on the surface of the samples heat treated at 950 °C, while Fe_3O_4 was present in the furnace cooled sample only.

1. Introduction

India has proposed Lead–Lithium Cooled Ceramic Breeder (LLCB) as the blanket concept for the International Thermonuclear Experimental Reactor (ITER) [1,2]. It consists of lithium titanate as ceramic breeder material in the form of packed pebble beds and Pb–Li eutectic as multiplier, breeder and coolant. Reduced activation ferritic martensitic steel (RAFMS) is to be used as the structural material for the Test Blanket Module (TBM). Helium-cooled Ceramic Breeder (HCCB) is an alternative Indian solid breeder blanket concept [3].

There is a need to develop an effective and reliable coating for viability of the fusion blanket systems. Electrically insulating coatings have been proposed to mitigate the magneto hydrodynamic (MHD) pressure drop in the high magnetic field for liquid metal blankets [4–10]. Diffusion barriers coatings have been proposed to reduce the tritium permeation from the breeder blanket to the environment through structural material [11–14]. Coatings have also been proposed to reduce the corrosion in liquid metal blankets, between the coolant and the channel walls [15].

Hot-dip aluminizing (HDA) process seems to offer a good chance to produce aluminized coating by pumping liquid

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aluminum through a complex geometry of TBM to form the required layer [16]. Subsequently, this aluminized layer could be oxidized at high temperature to form an alumina layer on the surface. Aluminide layer formed during HDA has the ability to act as hydrogen diffusion barrier. Previous studies have shown that a thin surface layer of alumina obtained after oxidation of aluminized steel substrate can reduce the hydrogen permeation rate by 2–3 orders of magnitude, provided the layer is free from cracks and pores [17–19]. Minimum requirement for an insulating coating to mitigate the MHD drop is to have the value of $\rho_i\ t_i > 0.01\ \Omega\,m^2$ (where ρ_i = electrical resistivity and t_i = thickness of the coating). The electrical resistivity of alumina varies from $1.0 \times 10^{14}\ \Omega\,m$ at 20 °C to $3.0 \times 10^{10}\ \Omega\,m$ at 400 °C, which is several orders of magnitude higher than the minimum requirement, leaving a large margin for degradation by irradiation [20]. Hence a thin surface layer of alumina is capable of mitigating the MHD drop as well.

Objective of the present study was to prepare hot dip aluminized coating on 9Cr–1Mo Grade 91 steel and to carry out subsequent heat treatment. Coatings have been characterized by various techniques. 9Cr–1Mo Grade 91 steel was selected as it is having close proximity to RAFM steel. RAFM steels have been developed from the now common Grade-91 (modified 9Cr1Mo) steel being used in fast reactors and fossil-fired power plants, by substituting several alloying elements to reduce residual activity induced by neutrons [21,22].

2. Materials and methods

Commercial 9Cr–1Mo Grade 91 steel was used as the substrate material in this study. The material was analyzed for the chemical composition by X-ray florescence (XRF) spectroscopy. Composition of the alloy was Cr-8.64, Mo-0.94, Si-0.24, Mn-0.49, V-0.24, Ni-0.22, C-0.10 in wt%, and balance Fe. Rectangular specimens of dimension 15 mm × 10 mm of 2 mm thickness were used for the study. A 3 mm hole was made near the edge of one side of the specimens to facilitate hanging by stainless steel (SS) wire for dipping in Al melt bath. Samples were polished with different grit of sandpaper followed by diamond polishing to a surface finish of 0.08 μm. Samples were cleaned ultrasonically in an alkaline solution to remove grease and other saponifiable compounds, and then rinsed in water. After alkaline degreasing, specimens were pickled in 15% HCl to eliminate any surface oxide that might develop during cleaning and further processing. To ensure a clean metal surface contacted with molten aluminum, fluxing was carried out on the specimens. Specimens were immersed in an aqueous flux solution containing 50% NaCl, 40% KCl and 10% Na_3AlF_6 and dried. For aluminizing, specimens were dipped manually in an Al-2.25 wt% Si bath at 720 °C in an alumina crucible placed in the furnace. Dipping was performed for 1, 2, 3 and 5 min. It was found that 5 min dipped samples had too thick coating, while 1 min and 2 min dipped samples had non-uniform coating. Samples dipped for 3 min were found to give uniform coating. Therefore, all the samples for subsequent heat treatments were hot dip aluminized for 3 min. Addition of small amounts of Si to the Al melt helps reduce the thickness of the brittle intermetallic layer after dipping process [23]. Yajiang et al. [24] and Han et al. [23] have carried out hot dip aluminizing on steels with the melt containing 3 wt% Si. In the present study, high purity Al-2.25 wt% Si available with us was chosen for the HDA. The aluminized samples were cleaned ultrasonically in ethanol, dried and placed in alumina crucible for subsequent heat treatments. Temperature, time period and cooling method employed during heat treatment are given in Table 1.

The morphology and compositional analysis of aluminized and heat treated samples was performed using scanning electron microscopy (SEM-make AIS 2100 Seron Tech) at 20 kV coupled with energy dispersive X-ray (EDX) analysis (INCA E350). Point scan at different positions was performed across the cross-section of the coated samples. X-ray diffraction (XRD) analysis was carried out to reveal the phases present. XRD (make DIANO) was performed at 20 mA and 35 kV using Cu Kα radiations in routine Bragg–Brentano θ–2θ geometry. Hardness was determined using Vickers micro hardness tester (Future-Tech FM-7 Model). 3–4 readings were performed at each location and the average values were reported. Presence of oxide layer on the surface of the samples was evaluated by Micro-Raman spectrometer. Raman spectra were recorded using micro laser Raman spectrometer with 514.5 nm green line from an argon ion laser as the excitation source with a power of 50 mW. Scratch adhesion tester (CSEM, Revetest) was used to evaluate the adhesion of the coatings. Critical load for failure of the coating on the substrate was observed. The scratch length was kept at 0.5–2 mm. The scratches were performed across and along the coating on the X-section. Constant load of 5/8/10 N was applied across the coating, and a progressive load of 1–30 N was applied along the coating. The scratch indenter used was a 200 μm tip radius Rockwell type diamond indenter. Friction force, depth of penetration and acoustic emission signals were recorded online along with the applied load during scratch tests. The scratch tracks were visualized in the optical microscopy immediately after the tests and pictures were taken at different loads.

Table 1
Heat treatments deployed for aluminized 9Cr–1Mo Grade 91 steel samples.

Sample	Temp and duration	Cooling method
A	650 °C, 5 h	Air cooled
B	750 °C, 5 h	Air cooled
C	750 °C, 5 h	Furnace cooled
D	950 °C, 5 h	Air cooled
E	950 °C, 5 h	Furnace cooled
F	950 °C, 5 h + 750 °C, 2 h	Air cooled

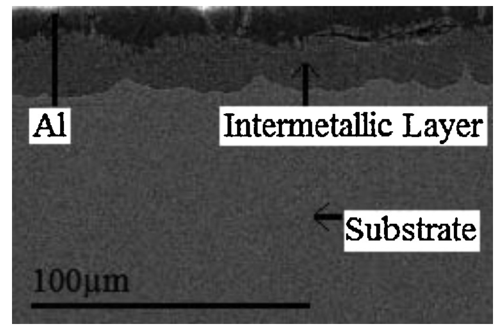

Fig. 1. SEM of cross-section of hot dip aluminized 9Cr–1Mo Grade 91 steel sample (without heat treatment).

3. Results and discussion

3.1. SEM & EDX analysis

Fig. 1 shows the cross-sectional image of the HDA 9Cr–1Mo Grade 91 steel sample without heat treatment. It has an outer layer of Al of about 15–20 μm thickness and an inner intermetallic layer of thickness 20–25 μm.

Scanning electron micrographs of the cross-section of all the six different aluminized and heat treated samples are shown in Fig. 2. Sample A showed a single diffusion layer of about 100 μm thickness (Fig. 2a). This diffusion zone increased to 115 μm for the sample B (Fig. 2b). However, for the sample C, the thickness of the diffusion zone further increased to 140 μm (Fig. 2c). Samples B and C also showed an inner diffusion layer of about 10 and 20 μm thickness