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Journal of Nuclear Materials 271&272 (1999) 391–395

journal of nuclear materials

Section 13. Breeding blanket materials, plasma facing materials and high heat flux materials (II)

Development of tritium permeation barriers on Al base in Europe

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Abstract

The development of the water cooled lithium lead (WCLL) DEMO fusion reactor requires the production of a material capable of acting as a tritium permeation barrier (TPB). In the DEMO blanket reactor permeation barriers on the structural material are required to reduce the tritium permeation from the Pb–17Li or the plasma into the cooling water to acceptable levels (<1 g/d). Because of experimental work previously performed, one of the most promising TPB candidates is A1 base coatings. Within the EU a large R&D programme is in progress to develop a TPB fabrication technique, compatible with the structural materials requirements and capable of producing coatings with acceptable performances. The research is focused on chemical vapour deposition (CVD), hot dipping, hot isostatic pressing (HIP) technology and spray (this one developed also for repair) deposition techniques. The final goal is to select a reference technique to be used in the blanket of the DEMO reactor and in the ITER test module fabrication. The activities performed in four European laboratories are summarised here. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The development of a water cooled lithium lead (WCLL) for DEMO requires, among others R&D activities, the development of a system able to reduce the tritium leakage from the breeder to the coolant at a level less than 1 g/d [1]. The use of tritium permeation barrier (TPB) was identified as the most promising route to achieve this goal. For some years experimental work has been done in Europe in order to select and to develop the most promising materials [2]. Taking into account an acceptable efficiency of the tritium extraction system [1], a TPB factor of about 100 is necessary at the end of the blanket lifetime. On the basis of the results obtained in the frame of the European fusion technology programme 1996–1998, Al base coatings have been selected as the reference material for TPB. A common programme has been established within EU to develop and qualify aluminised coatings produced by different technologies. The final goal of this activity is the selection of a reference fabrication process for TPB compatible with the module manufacture sequence and the production of qualified coatings for irradiation experiments planned beyond 1998. The selection of the reference process is based on the comparison of the coatings performance in several qualification tests. These experimental tests include the measurement of the hydrogen permeation in gas phase, in presence of Pb–17Li, with and without mechanical stresses applied to the specimens, and the compatibility studies in water and in Pb–17Li [3]. Self-healing experiments are also planned. Presently four different techniques are under investigation: chemical vapour deposition (CVD), hot isostatic pressing (HIP), hot dipping and spray.

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PII: S0022-3115(98)00792-2

2. Chemical vapour deposition

A specific pack-cementation method has been developed in order to obtain Fe–Al coatings without brittle Fe_2Al_5 intermetallic phases, which is one of the major problems of conventional aluminising [4]. The originality of this work consists in:

- using an (Al, Fe) donor instead of pure Al in order to decrease the Al activity of the gaseous phase and to allow an Fe co-deposition,
- performing the deposition at low pressure which modifies the nature and the quantity of solid and gaseous species present at the equilibrium according to thermodynamical calculations,
- testing the deposition under 1023 K so as not to modify the substrate properties.

The piece to be treated is put in a box in contact with a cement, which is composed of the donor (47.5 wt%), a pure Al powder and a (30 wt% Al, 70 wt% Fe) powder mixture. NH_4Cl is used as an activator (5 wt%), which decomposes under temperature and reacts with the donor to produce metallic chlorides, and Al_2O_3 as inert filler (47.5 wt%).

The deposition temperature is fixed at 923 K for times varying between 5 and 15 h. Two pressure levels are being tested: atmospheric pressure (Patm) and low pressure (10 mbar). The substrate is a martensitic steel (8.3% Cr) quenched and tempered at 1023 K. If the pure Al donor is used at Patm, the resulting layer (~20 μm) only consisted of Fe_2Al_5 and presented many cracks. When the (Al, Fe) donor is used at 10 mbar, Fe_2Al_5 totally disappears and the coating only consisted of FeAl and Fe_3Al (Fig. 1). The layer is very dense and uniform without cracks or porosities and with a good surface roughness in comparison with the Fe_2Al_5 top layers. The Vickers microhardness is, respectively, 550 and 275 HV_{100} for these coatings whereas the substrate hardness (200 $HV_{0.1}$) is unchanged. Their brittleness is qualitatively evaluated using a scratch test. The scale's appearance at very low loads (20 N) for the Fe_2Al_5 coating indicates a brittle behaviour whereas the FeAl/Fe_3Al coating seems more ductile (neither scale nor crack observed up to 100 N). The coating adhesion is excellent due to an interdiffusion phenomenon between the coating and the substrate. The development of this pack-cementation process provides an Fe–Al CVD feasibility with promising coating characteristics. Two routes are considered for the Al_2O_3 top layer formation: CVD using metalorganic precursors [5] or thermal oxidation of the Fe–Al coating (under investigation). The optimisation of these coatings seems to be achieved from a metallurgical point of view. Their permeation reduction factor (PRF) must be determined in order to qualify their barrier efficiency.

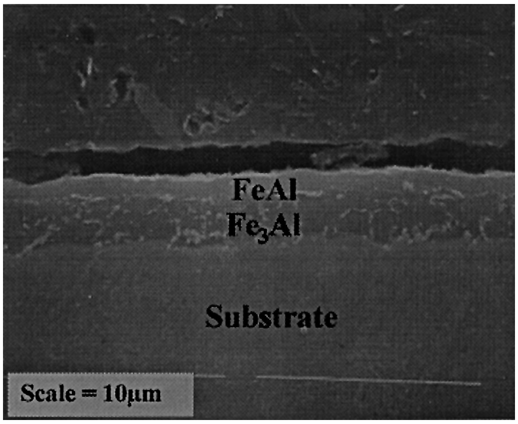

Fig. 1. CVD coating using: (Fe, Al) donor – 10 mbar (SEM).

3. Hot isostatic pressing

Two different alloys have been considered for TPB joining on the inner side of martensitic steel double-wall tubes in CEA/CEREM. Both of them are aluminium-containing alloys susceptible to grow on alumina scale by further oxidation.

3.1. Aluminium alloys

Main problems are (i) the high stability of aluminum oxide associated with the low solubility of oxygen in Al and (ii) the nucleation of fragile Fe_xAl_y intermetallic phases. Point (i) makes difficult to obtain desired metal–metal contact during joining whereas (ii) decreases the strength of the joint. Diffusion welding of different aluminium alloys on F82H steel shows that best results are obtained with Al6061 HIPped at 723 K (see Table 1). No intermetallic phases are observed at the interface while Mg enrichment at the interface is noted. However, on ageing at 623 K for 3 days, nucleation of intermetallic phases is observed. Furthermore, it is foreseen to submit the entire module to a heat treatment at a temperature higher than 923 K, making the Al alloys no longer suitable. These are the reasons why FeCrAl are now under study [6].

3.2. FeCrAl alloys

FeCrAl alloys are heat resistive materials often used under severe oxidation in air. Their resistance to oxidation is due to diffusion of Al from the matrix towards the surface of the alloy where it oxidises and forms Al_2O_3. In this study 22Fe–5Cr–Al has been used. The technique for diffusion welding on 9%Cr–1%Mo steel tubes involves the following steps:

- machining FeCrAl tubes down to 0.2 mm wall thickness and steel tubes to ID/OD 14/17 mm,

Table 1
Pure Al and Al–Mg–Si alloys joining on F82H steel by diffusion welding

HIP parameters / Alloy	Al 99.998%	Al 0.6%Si, 1%Mg (Al6061)
1 h at 773 K, 100 MPa	~10 μm discontinuous intermetallic layer, weak joint	No intermetallic phase, strength 137 MPa; Mg enrichment close to Al alloy
1 h at 823 K, 100 MPa	10–20 μm continuous intermetallic layers, Al73% Fe25% Cr2% (at%) (~Fe_2Al_5); strength 110 MPa	~5 μm intermetallic phase, Al69% Fe22% Cr2% Si7% (at%) (~Fe_3Al), strength 100 MPa; Mg enrichment close to Al alloy

- degreasing and acid cleaning both materials,
- threading tubes, TIG welding both sides and degassing interface,
- HIPping at 1313 K for 1 h, quenching, annealing at 1023 K, cooling.

The microstructure of the interface between both materials is characterised by the presence of a 70 μm wide decarburised ferritic layer on the steel side (see Fig. 2). A Cr_3C_2 precipitates rich layer exists close to the interface in FeCrAl alloy. The FeCrAl alloy shows a ferritic structure with coarse grains. During HIPing the surface of FeCrAl alloys gets oxidised due to the oxygen content of argon. EDX analysis reveals Al enrichment close to the surface. Low angle X-ray diffraction reveals the presence of alumina on the surface. It is concluded that it is possible to provide joining and oxidation during one step. Permeation reduction has to be assessed.

4. Hot-dip aluminising process

A hot-dip aluminising process seems to offer a good chance to produce aluminide coatings on the structural materials by pumping liquid aluminium through the whole blanket to form the required layer on the surface. The material to aluminise is taken from a 5 t heat of a modified (high purity) F82H fully martensitic steel produced by JAERI/NKK Corporation Japan, and the composition is reported in Ref. [7]. The samples were machined from a 7.7 mm thick plate to 50 × 15 × 1.5 mm^3 each having a small hole on one side for fixing during immersion. The aluminising test facility developed in FZK is described elsewhere [8]. The samples, fixed by a hook and stainless steel wire to a crane system, were dipped into the melt. After 30 s of exposure they were pulled out of the melt. Cooling down took place in the glove box by natural cooling. The heat treatment was carried out in a horizontal quartz rig. The time and temperature chosen corresponds to the required heat-treatment of the steel: austenisation at 1313 K for 30 min and tempering at 1023 K for 2 h [9]. After aluminising, the samples were rather homogeneously covered by a 20–30 μm thick layer of solidified Al melt. Beneath the Al layer a 15–30 μm thick intermetallic scale has been formed mainly by Al diffusion into the steel substrate. The interface between the substrate and the intermetallic scale is smooth although the scale grew somewhat tongue-like into the substrate. The interface between the Al overlayer and the intermetallic scale appears very inhomogeneous. Some cracks could be observed across the intermetallic scale. SEM/EDX point analyses have shown that the main part of the scale corresponds to Fe_2Al_5 phase. Just beneath the solidified Al–intermetallic scale interface a higher Al concentration compared to the rest of the scale was measured indicating the existence of the $FeAl_3$ phase. Also, the striation-like precipitates in the Al melt were found to be $FeAl_3$ phase. SEM investigations have shown that the oxidised sample surface was homogeneously covered by a scale of small corrosion products. EDX analyses (using an acceleration voltage of 15 keV) have revealed that the homogeneous surface scale mainly contains Al and smaller concentrations of Fe and Cr. Analysis of XRD spectra from the surface showed the presence of Al_2O_3 and Fe_3Al phases. EPMA results indicated that during high-temperature oxidation of the aluminised steel sheets a complete transformation of the brittle intermetallic Fe_2Al_5 compound into a softer and more ductile phase, α-Fe(Al), has occurred. The metallographic cross-section of aluminised F82H-mod. specimen after heat-treatment at 1313 K for 0.5 h is shown in Fig. 3. Three different areas within the coating can be identified: an internal and external layer which were separated by a porous band. The internal layer in contact

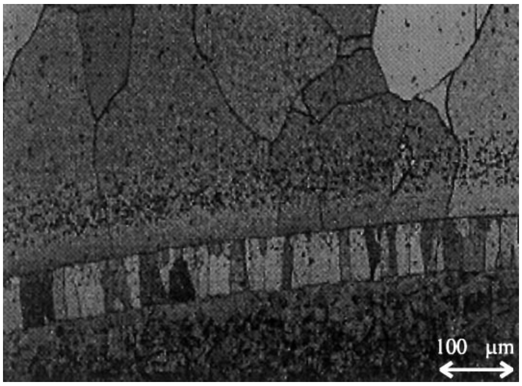

Fig. 2. FeCrAl alloy coating: 9%Cr–1%Mo steel (bottom)/FeCrAl (up) joint.

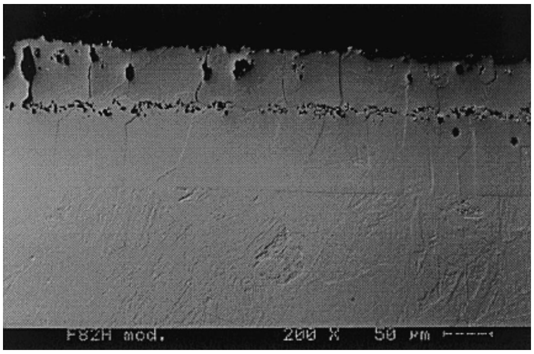

Fig. 3. Cross-section of aluminised F82H-mod. sample heat-treated at 1313 K for 0.5 h.

with the steel is about 70 µm in thickness. The layer is dense and homogeneous and no pores or cracks are present. The thickness of the external layer varies between 20 and 70 µm. In the upper region of this layer, some pores and cracks can be observed. Compared to MANET, the surface on the F82H-mod. specimen seems to be quite smooth [10]. Therefore, better results for the permeation measurements on aluminised F82H-mod. specimens are expected compared to the PRF indicated for MANET [11].

5. Spray techniques

5.1. Al_2O_3 deposited by vacuum plasma spray

Earlier permeation tests on aluminide-coated MANET II developed at JRC Ispra yielded a reduction in the permeation rate by up to three orders of magnitude [12]. The aluminide layer produced by VPS, see Table 2, and subsequent heat-treatment, was incorporated into the standard heat-treatment required by the substrate in order to obtain a δ-ferrite free martensitic steel (1238 K/2 h + 1348 K/30 min, fast cool and tempering 1023 K/2 h). VPS was chosen because the aluminium deposition temperature can be kept fairly low (<500 K), hence ensuring no substrate deformation. However, the hard aluminide coating produced was not homogeneous containing a number of fine cracks that could seriously reduce the effectiveness of the coating as a permeation barrier. After studying the mechanical characteristics (tensile and low cycle fatigue) of aluminide-coated MANET II, which had undergone various heat-treatments to produce aluminide layers containing different aluminium contents [13], it was concluded that the lower aluminium content coatings, exhibiting a lower hardness and greater ductility, had greater crack resistance in comparison with those having a higher aluminium content. In order to improve the effectiveness of low aluminium content aluminides coatings as TPB, post-oxidation in air was carried out in Ref. [14] at 1023 K for 15 h and at 1223 K for 10 and 1 h. A maximum PRF of 500 has been obtained for oxidation at 1223 K for 1 h. This is a moderate value if compared to that of the non-oxidised aluminide case (PRF = 100). This reduction factor was constant in the temperature range studied (573–800 K). A previous study of in situ oxidation of aluminide layers of MANET [15] did obtain a reduction factor of up to 3 orders of magnitude at the higher temperature studied (873 K) in a controlled atmosphere (10^5 Pa H_2 with 10^{-2} to 10^{-3} Pa H_2O). However, the observed reduction factor decreased to 2 orders of magnitude at lower temperature [15]. Following the above development VPS of Al on F82H mod. martensitic steel is being performed. The specimen was subsequently heat-treated at 1313 K for 30 min and 1023 K for 1 h. Preliminary results on the structure of the deposit seem to indicate that a layer of about 150 µm represents the ductile solid solution phase, i.e. (Fe, Cr) Al, with a HV_{50} similar to that of the substrate. This is an encouraging result because the substrate and the developed TPB are similar to that already obtained for MANET. Therefore, PRF of the same order should be easily obtained. The characterisation of the TPB on F82H mod. steel from its hydrogen permeation behaviour is under way.

5.2. Aluminisation by Detonation Jet and VPS

Spray techniques are under also study in ENEA Fusion Division to be applied directly to the module and water cooling tubes or to be used as repair techniques.

Table 2
VPS parameters

Substrate material	DIN 1.4914 (MANET II), F82H mod.
Cleaning	Sand blasted, chemical cleaning, VPS sputter cleaning
Substrate temperature	<500 K
Chamber pressure	15 kPa (150 mbar)
Gas flow rate	Primary gas (Ar): 50 l/min, Secondary gas (H2): 1 l/min, Carrier gas (Ar): 2.2 l/min
Powder	Metco Al 54
Spraying distance	220 mm

After preliminary and encouraging application of the Detonation Jet spray of pure Al on MANET [16] the high temperatures necessary to transform completely the brittle Fe_2Al_5 into more ductile phases [17] suggested the idea of a direct spray of Fe–Al alloys. This solution would have the advantage, in respect to the use of pure Al, to avoid a heat-treatment of the whole module. At present four different commercial powders are under investigation (10Al52Fe38Ni, 6Al64.5Fe27.5Cr, 75Fe25Al, 25Al65Fe10Ni) and the first measurements of the permeation rate are in progress. On the other hand, the possible use of spray techniques has been demonstrated to be potentially attractive for repairing [18]. In fact a process based on Al deposition by Detonation Jet with successive local heating in agreement with the material heat-treatment, and an in situ oxidation seems to be possible [18].

6. Conclusion

A large research programme has been undertaken in the EU in order to develop a suitable Al-based coating capable of acting as TPB. This coating should consist of ductile compounds (FeAl, Fe_3Al and α-Fe(Al)) and should be compatible with the material heat-treatment and the geometry of the pieces that have to be manufactured. The status of the work appears satisfactory and all the proposed techniques seem to be able to provide good quality coatings. An experimental TPB qualification exercise has been defined and is being performed (permeation experiments in gas-phase and in the presence of Pb–17Li as well as mechanical tests). The next step, after the selection of the most promising fabrication technique, would be the design and the realisation of irradiation experiments.

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