ELSEVIER

Journal of Nuclear Materials 273 (1999) 233–238

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Investigation on the suitability of plasma sprayed Fe–Cr–Al coatings as tritium permeation barrier

C. Fazio [a,*], K. Stein-Fechner [b], E. Serra [a], H. Glasbrenner [b], G. Benamati [a]

[a] *Association ENEA-EURATOM, Fusion Division, CR Brasimone, 40032 Camugnano, Bologna, Italy*
[b] *Forschungszentrum Karlsruhe GmbH, Institut für Materialforschung III, Postfach 3640, D-76021 Karlsruhe, Germany*

Received 7 January 1999; accepted 22 February 1999

Abstract

Results on the fabrication of a tritium permeation barrier by spraying Fe–Cr–Al powders are described. The sprayed coatings were deposited at temperatures below the A_{c1} temperature of the ferritic–martensitic steel substrate and no post-deposition heat treatment was applied. The aim of the investigation was the determination of the efficiency of the coatings to act as tritium permeation barrier. Metallurgical investigations as well as hydrogen isotope permeation measurements were carried out onto the produced coatings. The depositions were performed on ferritic–martensitic steels by means of three types of spray techniques: high velocity oxy fuel, air plasma spray and vacuum plasma spray. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

For the water cooled lithium–lead blanket (WCLLB) concept the control of tritium loss due to permeation through the structural material is an important issue, because of its safety and operational implications. The use of coatings as tritium permeation barrier (TPB) is one of the possible solutions to reduce the tritium loss. As structural materials 8–10% Cr containing ferritic–martensitic steels are considered, the tritium permeability of ferritic–martensitic steels is higher than that of austenitic steels. The required tritium permeation reduction factor (PRF) of 100 under reactor conditions (irradiation, corrosion and fatigue) can only be achieved by applying appropriate coatings [1]. With regard to the permeation barriers, several studies have evidenced the inherent properties of various materials (mainly oxides and intermetallic compounds) in terms of low H-permeability [2]. Moreover, the coatings envisaged as TPB in the WCLLB are required to have a good compatibility with Pb–17Li, an excellent resistance to thermal and mechanical loads, a satisfactory behaviour under irradiation and the possibility of self-healing. At present, the most promising solutions are Al based coatings which generally consist of an interlayer of Fe(Cr,Al) supporting a thin layer of aluminium oxide. A large number of methods is available to deposit Al or Fe(Cr)–Al layers, such as chemical vapour deposition (CVD), hot-dipping and several spray techniques. The deposition of Al by these techniques were intensively studied [3–6]. In all cases a post-deposition heat treatment was necessary in order to ensure the formation of a ductile Fe(Cr,Al) solid solution layer and a dense alumina layer on top. Moreover, the heat treatment was necessary to restore the mechanical properties of the martenisitic structure. The aim of the currently presented work was the investigation of the possibility to coat the steel directly with an Fe(Cr,Al) solid solution layer by several spray techniques. The employed techniques were: high velocity oxy fuel (HVOF), air plasma spray (APS) and vacuum plasma spray (VPS). One of the major advantages of sprayed coatings is that they can be applied without significant substrate heating above room temperature, i.e. a fabricated structure can be coated without changing the substrate microstructure or strength. Other advantages of the spray techniques in view of the blanket structures may be the possibility of coating large areas, easy repairing and low cost production.

---

[*] Corresponding author. Tel.: +39 0534 801 380; fax: +39 0534 801 225; e-mail: concetta@netbra.brasimone.enea.it

0022-3115/99/$ – see front matter
PII: S 0 0 2 2 - 3 1 1 5 (9 9) 0 0 0 5 9 - 8

2. Experimental

2.1. Materials and deposition procedure

The VPS and HVOF coatings were produced and characterised in the frame of the FZK activities, whereas the APS coatings were produced and characterised in the frame of the ENEA activities. The permeation measurements were conducted with a gas – phase measurement device installed at the ENEA – Brasimone laboratory.

The substrates to be coated were the ferritic–martensitic steels MANET II and F82H-mod. The compositions of the MANET II and F82H-mod. steels are given in Table 1. The MANET II discs of 35 mm diameter and 4 mm thickness were coated by RWTH Aachen, Germany, with two different plasma spray techniques (VPS and HVOF) using the powder mixture 3443.3 (Fe–24Cr–8Al–0.5Y [wt%]) delivered by Abler GmbH, Wiggensbach, Germany. The F82H-mod. steel discs of 1 mm diameter and 48 mm thickness were coated with the APS technique by the PMC company of Pieve di Cento, Italy. The used powder 465 was an Fe–Cr–Al mixture (Fe–27.5Cr–6Al–2Mo [wt%]), delivered by Sulzer Metco, Switzerland.

2.2. Coating procedures

The spray techniques used for the deposition of the coatings on the steel surface were VPS, HVOF and APS. In these processes the metal powders are heated to near or above their melting point. The molten or nearly molten droplets are directed against the surface to be coated. On impact the droplets flow into thin lamella platelets that overlay and interlock with each other forming the coating. The main differences among the three spray processes HVOF, APS and VPS are: (1) *The heating source*: In the APS and VPS processes the powder is heated by a plasma jet that is ejected from a nozzle at high velocities; the plasma is formed by passing gases through an arc that is generated between two electrodes where the anode serves as nozzle. In the HVOF process a compressed flame generated by burning an oxygen-fuel gas mixtures undergoes free expansion. (2) *The atmosphere*: In the APS process the heating source is not protected from air infiltration, in the HVOF process the gas shroud technology is employed and in the VPS process the deposition procedure is conducted in an evacuated chamber. (3) *The temperature of the heating source and velocity of the powder particles*: In APS and VPS the heating source increases to a temperature above 6000 K and the velocities of the powder particles are much more below supersonic values, whereas in HVOF the temperature is below 6000 K and the particles velocities achieve supersonic values.

The process parameters used for coating the steels by the three deposition techniques are listed in Table 2. Before coating, the steel samples were degreased in an ultrasonic bath with ethanol in order to remove organic substances and afterwards grit blasted in order to remove the oxide scale and to get a rough surface. Grit blasting increases the surface area significantly. Whether bonding is due to mechanical interlocking, interdiffusion, surface reaction or a combination of these, it is advantageous to increase the bond strength. In any case the coating was applied after grit blasting as soon as possible to insure an active, clean surface.

2.3. Characterisation methods

The surfaces of the specimens were investigated by scanning electron microscopy (SEM) equipped with an

Table 1
Compositions of MANET II and F82H-mod. steels (wt%)

	C	Cr	Fe	Mn	Ni	Mo	W	V	Nb
MANET II	0.11	10.3	bal.	0.78	0.68	0.61	–	0.20	0.14
F82H-mod.	0.09	7.8	bal.	0.18	0.04	<0.01	1.96	0.16	<0.01

Table 2
Vacuum plasma spray (VPS), high velocity oxy fuel (HVOF) and air plasma spray (APS) process parameters

	VPS	HVOF	APS
Max. substrate temperature (°C)	380	150	~300
Spraying distance (mm)	380	280	140
Carrier gas in l_{standart}/min	2.5	80	45
Chamber pressure (mbar)	250	–	–
Plasma gases	Ar, H_2	–	N_2
Power supply	500 A, 30 kW	–	500 A, 60 V
Burn gases	–	O_2, H_2	–
Shroud gas	–	N_2	–

energy dispersive spectrometer (EDS) and low angle X-ray diffraction (XRD). Cross-sectional examinations were carried out by optical and scanning electron microscopy and electron probe microanalysis (EPMA). Line scan and point analyses were done in order to obtain quantitative information of the scale composition. The permeation measurements were performed by a gas-phase method.

3. Results

3.1. Specimen coated by APS

The coated samples were slightly deformed, probably due to the grit blasting or the spraying procedure. The surface of the APS coating appeared in grey colour and the non-coated side of the specimen was brown–grey coloured indicating for both sides the formation of an oxygen rich layer during coating fabrication.

The etched sample cross-section showed the typical plasma spray lamellar structure. The coating thickness ranged between 1 and 150 μm. The coating/substrate interface was undulating and the presence of cavities was detected there. The adhesion between the coating and the substrate can mainly be explained due to mechanical interlocking. Chemical bonding can reasonably be excluded because diffusion zones were not detected. The cross-section of the coating was analysed by SEM/EDS. At the coating/substrate interface and a few μm apart from the interface, the presence of particles was detected inside the substrate. Those particles were composed of alumina. As shown in the micrograph of Fig. 1, the cohesion within the bulk of the coating was very poor. Several defects like cavities and microvoids and areas of different colours were observed. SEM/EDS point analyses have shown that the grey coloured zones are composed of Fe, Al and O whereas the white coloured zones were mainly poor in Al and rich in Cr and Fe.

3.2. Specimens coated by VPS

SEM investigations on the coated specimen revealed a homogeneous scale surface. Powder agglomerations between 20 and 70 μm in size were observed on top of a smooth scale. Low angle XRD has been carried out and the detected peaks correspond to an Fe(Cr,Al) solid solution phase. A cross-sectional cut of the as-sprayed specimen is shown in Fig. 2. The thickness of the coating varies between 46 and 96 μm with an average value of 72 μm. The structure of the coating is characterised by several laminar layers. A few not deformed individual powder particles could be observed within the coating. In general, the coating seems to be rather dense although a few pores and grooves exist. At the substrate/coating interface a narrow gap can be recognised in Fig. 2. EPMA line scans have shown that the chemical composition of the coating is very homogeneous over the whole cross-section, see Fig. 3. The irregularities of the individual element lines in the figure result from structural inhomogeneities of the coating as grooves, pores and small gaps.

3.3. Specimens coated by HVOF

Surface investigations of the HVOF coating revealed that the scale looked somewhat more fissured than the morphology of the VPS coating. Individual powder particles, which have a size of 10–50 μm, are still recognised on the surface. Low angle XRD identified an Fe(Cr,Al) solid solution phase. Fig. 4 shows a cross-sectional cut of the as-sprayed specimen. The thickness of the coating varies between 35 and 135 μm with an average value of 93 μm. Individual powder particles of

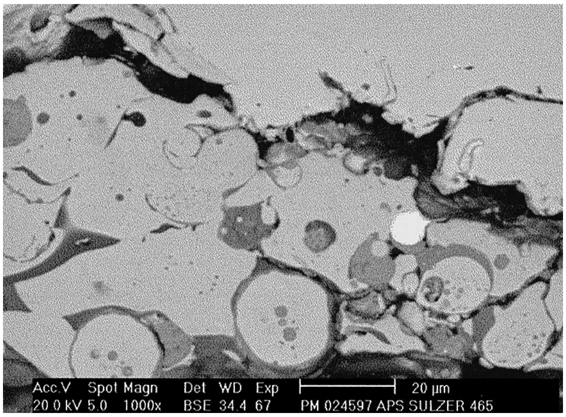

Fig. 1. Scanning electron microscopy image of the as-sprayed air plasma spray (APS) coating on F82H-mod.

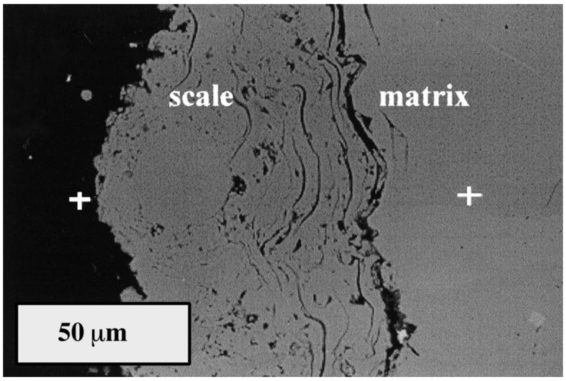

Fig. 2. Scanning electron microscopy image of the as-sprayed vacuum plasma spray (VPS) coating on MANET II. The indicated crosses show the position of the line scan analysis presented in Fig. 3.

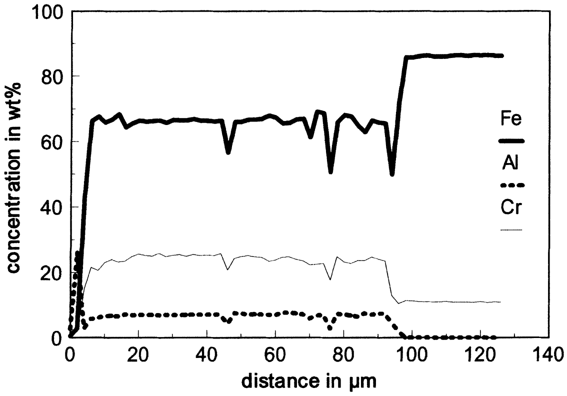

Fig. 3. EPMA line scan analysis of the as-sprayed vacuum plasma spray (VPS) coating on MANET II. The position of the line scan is marked in Fig. 2.

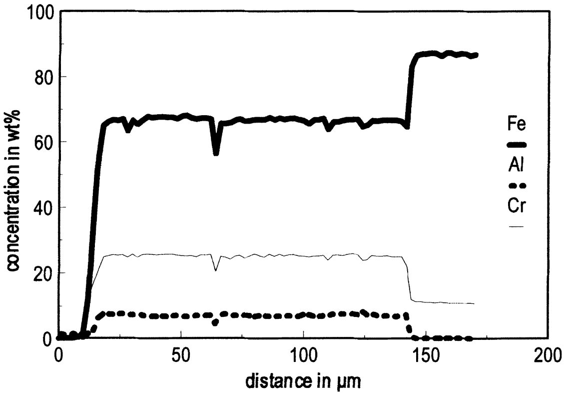

Fig. 5. EPMA line scan analysis of the as-sprayed high velocity oxy fuel (HVOF) coating on MANET II, the position of the line scan is marked in Fig. 4.

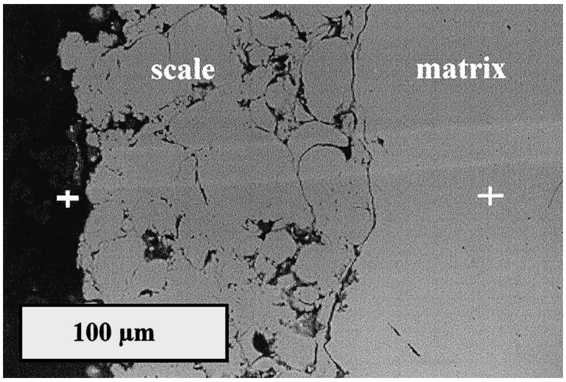

Fig. 4. Scanning electron microscopy image of the as-sprayed high velocity oxy fuel (HVOF) coating on MANET II. The indicated crosses show the position of the line scan analysis presented Fig. 5.

different sizes are still recognised. Due to the low deformation grade of the sprayed powder particles the coating shows a rather high porosity compared to the VPS coating. No gap exists between coating and substrate indicating good scale adherence. EPMA line scan investigations have shown that the chemical composition of the coating is very homogeneous over the whole cross-section, see Fig. 5. The irregularities of the individual element lines in the figure result very probably from structural inhomogeneities of the coating as grooves and pores.

3.4. Permeation measurements

The chosen method for the permeation measurements was a gas-phase technique. A detailed description of it is given in Ref. [7]. Before a specimen disc was inserted into the permeation measuring equipment the uncoated side was mechanically polished. Thus, only an oxide layer resulting from exposure to air at room temperature may exist on the uncoated specimen side. The sample disc has been sealed between two stainless steel flanges by compression sealing using two gold O-rings. Measurements were conducted over the temperature range 373–773 K with deuterium driving pressures of about 7.5×10^4 Pa.

The permeation test was performed only on samples coated by the VPS technique. This choice has been made in view of the metallurgical features of the VPS coating which seems to be the most promising regarding a permeation barrier. The result of the permeation test is demonstrated in Fig. 6. In the same figure the per-

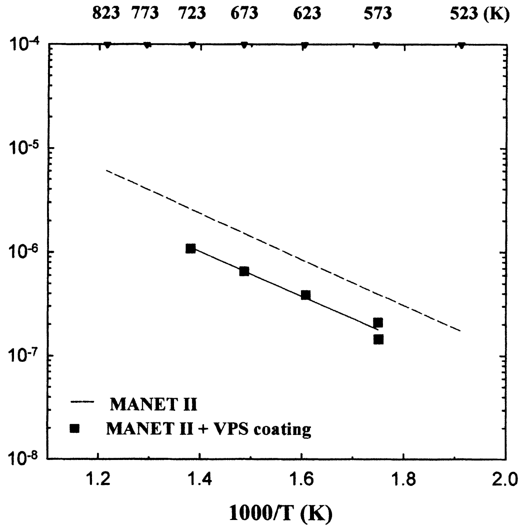

Fig. 6. Arrhenius plot of the deuterium permeation rate through uncoated and vacuum plasma spray coated MANET II. The upstream deuterium pressure was 75 kPa.

meation flux of bare and coated steel is reported. As shown in this Arrhenius plot, the permeation reduction due to the presence of the coating does not occur significantly. The obtained tritium PRF was about 2.5 only.

4. Discussion

The microstructure of all three types of coatings (APS, VPS and HVOF) is characterised by lamellar layers which are formed due to the impact of molten or semimolten powder particles. Furthermore, impacting particles have split and some small droplets branched out resulting in spherical inclusions in the coating. The cooling rate of the impacted particles was very high. For metals, the cooling rate has been estimated to be 10^6–10^8 K/s [8]. As a result of rapid particle cooling residual stresses may occur within the coating which have a significant effect on bond strength and must be considered when the coating is placed in service. In fact, a detachment of the VPS coating observed after the permeation test, could be due to a synergetic effect of residual stresses within the coating and brittleness of the coating. An analogous detachment was observed after the permeation test of an APS coated specimen [9]. Not only the composition but also the density and the structure influence to a large extent the diffusion and permeation properties of a coating. It is known that sprayed coatings have densities varying from 80% to 95% of the theoretical density [10]. The density is a function of the deposition parameters and the powder quality in terms of size and impurities. The bulk of the APS and HVOF coatings showed a high degree of defects like microvoids and cavities. One explanation is that components of the metal powder mixture which have a high affinity to oxygen (Al,Cr) have reacted during the deposition with the oxygen which existed in the vicinity or as impurity in the plasma. The formed thin oxide layer around the particles prevents a complete particle deformation when it impacts on the scale and causes microvoid formation. Some changes in the APS coating composition has been observed which results probably from the selective evaporation of one component of the powder mixture and/or from the oxidation.

With regard to the bonding mechanism of the three types of coatings, mechanical interlocking has been considered to be the most important mechanism. The bonding quality seems to be higher for the HVOF coating compared to the VPS and APS coatings.

The performed permation test indicated that the VPS coated sample showed a tritium PRF of about 2.5 only. The limited barrier efficiency of the coating results from the poor scale adherence which is probably caused by residual stresses in the coating. From the scale structure it can be concluded that the HVOF and APS coatings would not show a better permeation behaviour than the VPS coating.

5. Conclusions

An investigation was performed to evaluate the possibility to produce tritium permeation barriers on martensitic 8–10 wt% Cr-steels by spraying an Fe–Cr–Al powder. The advantage of spraying an Fe(Cr,Al) scale is to avoid post-deposition heat treatments. From the obtained results the following conclusions can be drawn:

- The tritium PRF of the VPS coating was about 2.5. This value is not satisfying in regard of the required tritium PRF of about 100. The low value results very probably from a detachment of the scale before or during the specimen installation in the test section of the permeation device. The detachment of the coating could be due to residual stresses in the scale.
- The APS technique seems to be the less appropriate technique for the TPB development since the oxidation, occurred during the spraying process, lowers the coating quality in terms of defects within the bulk of the coating. The coating obtained with the HVOF technique exhibited similar defects, like those observed in the APS coating. Even if permeation tests were not performed on the HVOF and APS coated samples, it is reasonable to suppose that these coatings would not act effectively as tritium permeation barrier.

In summary, further work has to be accomplished in order to get coatings that could reach the foreseen PRF target. The coatings features that need further improvement, in view of the TPB development, are the mechanical properties and the bulk density. The aim of such work could be the investigation of the deposition parameters such as powder grain size and purity, plasma power, spraying distance, gas purity on the coating quality. Moreover, it seems to be necessary to perform a post deposition heat treatment in order to reduce the residual stresses within the coating.

Acknowledgements

The authors wish to thank Professor E. Lugscheider and C. Herbst from RWTH Aachen, Werkstoffwissenschaften II (Germany) and PMC (Pieve di Cento, Italy) for producing the coatings. The assistance of Mr H. Zimmermann (FZK) and Mr M. Agostini (ENEA) performing the metallographic work is gratefully acknowledged. This study has been performed in the frame of the Nuclear Fusion Project of Forschungszentrum Karlsruhe and Ente per le Nuove Tecnologie l'Energia e l'Ambiente and is supported by the European Communities within the European Fusion Technology program.

References

[1] M.A. Fütterer, L.A. Sedano, L. Giancarli, E. Proust, Proceedings of the fifth Topical Meeting on Tritium Technology in Fission, Fusion and Isotopic Applications, Belgirate, Italy, 28 May–3 June, 1995, p. 614.

[2] K.S. Forcey, D.K. Ross, C.H. Wu, J. Nucl. Mater. 182 (1991) 36.

[3] A. Perujo, E. Serra, H. Kolbe, T. Sample, J. Nucl. Mater. 233–237 (1996) 1102.

[4] G. Benamati, A. Perujo, M. Agostini, E. Serra, N. Antolotti, Proceedings of the 18th Symposium on Fusion Technology, Karlsruhe, Germany, 1994, p. 1341.

[5] A. Terlain, E. De Vito, Proceedings of the 18th Symposium on Fusion Technology, Karlsruhe, Germany, 1994, p. 1337.

[6] H. Glasbrenner, H.U. Borgstedt, J. Nucl. Mater. 212–215 (1994) 1561.

[7] E. Serra, G. Benamati, Mater. Sci. Technol. 14 (1998) 573.

[8] V. Wilms, H. Herman, Thin Solid Films 39 (1976) 251.

[9] C. Fazio, Tritium Permeation Barrier Development for Fusion Application, ENEA Report, MA-A-R-005, 1998.

[10] R.C. Tucker Jr., in: R.F. Bunshah (Ed.), Deposition Technologies for Films and Coatings, NP publications, New Jersey, 1992.