

Characterisation of coatings methods for HLM applications

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ABSTRACT

The use of heavy liquid metals (HLM), such as Lead, Pb, is foreseen as a coolant in Generation IV fast Reactors. However, structural materials suffer significant damage when in contact with the HLM, in certain environmental conditions. In the austenitic steels the prevailing corrosion mechanism is dissolution of the alloying elements in the liquid metal. The ferritic-martensitic steels are instead more sensitive to phenomena such as liquid metal embrittlement and the formation of Fe₃O₄ scales that, being very rough and porous, hinder the thermal exchange and show very low stability under mechanical and thermal loads. Then, the recently developing strategy is to interpose a layer of a different chemical composition between the base material and the liquid metal coolant in order to prevent the core metal from corrosive effects. Coatings are proposed as a valid protection against high temperature damage in this environment. Their capability to grow more stable and protective oxides, by introducing the oxide forming elements in higher amount, is proven to be an effective alternative to material engineering. There are different approaches being investigated; surface

coatings are in fact meant to assure the maximum protection but they should also fit the requirements in terms of stability during exercise, that is to say limited diffusion towards the lattice below, low composition variation with lack of brittle phases, good adhesion to the bulk and compliance with the underneath material under the different kinds of load (creep, fatigue, shock).

Several deposition techniques and compositions have been proposed and tested, some of them reported in this work. High Velocity Oxygen Fuel, HVOF, combined with laser remelting was selected for deposition of FeCrAlY coatings. The combination of the two technologies lead to a compact and adherent coating with an enriched content of Al, enabling the formation of a protective Al_2O_3 oxide scale. The method was evaluated in terms of the corrosion resistance of the coating and also its effect on the microstructure of the substrate alloy.

Another technique is the Physical Vapour Deposition (PVD) applied to different coating compositions. The one investigated in this paper is TiN. This is an inert material that is meant not to react with Lead. The results concerning the TiN coatings are presented in terms of microstructure examinations.

1 INTRODUCTION

In the past few years, there has been a wide interest in the interaction between materials and HLM for the development of the next generation of fast reactors. In fact, there has been a large progress in the understanding on the oxidation processes characteristics of several materials in a wide range of temperatures and experimental conditions [1].

In general, the presence of stable and protective oxide scales is the necessary condition for protection of structural materials against damages induced by HLM, up to about 500°C [1], [2]. Above this temperature, the Fe-Cr-rich oxides might not be stable and their localised failure, with subsequent, rapid penetration of LM, might occur.

A promising technique for the protection of structural materials, even in harsher conditions, is the use of coatings [3]. In fact, surface modification could provide further protection, in terms of more protective oxides, operating as actual barriers between the steel and the HLM. In particular, the coatings are designed either to contain oxide forming elements that are not present in the base material or with materials inert to the environment, in order to provide resistance to damage in a wider range of temperatures.

In this study, the use of a FeCrAlY coating was considered in order to protect the ferritic martensitic steel T91 from damage during exposure to Pb.

In general, the HVOF is a thermal Spray Process, which has been developed to produce extremely high spray velocity. HVOF coatings are very dense, strong and show low residual tensile stress or in some cases compressive stress, which enable very thick coatings to be applied. In general, these coatings have a low percentage of porosity and internal oxidation, due to the high velocity and low temperature applied. However, in this specific study, where low thicknesses were aimed, new spraying parameters were designed in order to adapt the spraying technique to the requested properties.

Laser remelting was used to eliminate porosity and internal oxides; in addition to the possibility to eliminate the interface between the sprayed coating and the substrate.

Moreover, TiN coatings were considered because of their great technological interest, since they are chemically inert in different environments. In this study TiN coatings were deposited on different substrates: T91, AISI316 and 15-15Ti. The deposition technique was

Physical Vapour Deposition (PVD) which consists in the deposition of a film over a surface through evaporation and subsequent condensation. This coating is proposed as a valid alternative to protection in Pb environments. However, in particular, at this preliminary stage the manufactured TiN coatings were deposited and tested in terms of microstructure examinations and adhesion to the underlying substrate.

2 EXPERIMENTAL

2.1 Materials

Coatings were deposited on selected materials. The chemical composition of the substrate materials is listed in Table 1.

Table 1 - Chemical composition of substrate steels, wt. %

Steel	Fe	C	Cr	Ni	Mo	Mn	Si	V	Ti
T91	Bal.	0.10	8.87	0.12	0.87	0.39	0.22	0.20	
316		0.03	17.5	11.5	2.0	2.0	1.0		
15-15Ti		0.08	18.0	10.5		2.0	0.7		0.4

2.2 Coating methods

2.2.1 HVOF and laser

The FeCrAlY powder sprayed on the T91 was provided by William Rowland Ltd, UK. Compositional analyses carried out by the suppliers are given in Table 2: FeCrAlY left-hand side and TiN right-hand side.

Table 2 - Composition of FeCrAlY powder and TiN used for coating in wt%.

FeCrAlY	Fe	Cr	Al	Y	Ni	Co	TiN	Ti	N
	Bal.	15.5	7.6	0.44	0.037	0.01		77	23

Surfaces of specimens were sand blasted, in order to improve the adhesion of the sprayed coating on the substrate. The FeCrAlY coatings were sprayed by HVOF TAF A JP 5000 spraying equipment. Several sets of spraying parameters were used to evaluate the influence of equivalent ratio (the ratio between the amount of oxygen and fuel, representing the flame temperature) and combustion pressure (representing the flame velocity) on the coatings microstructure.

The optimised sets of spraying parameters were set to reach a coating thickness of about 70-100 μm . This, for thermally sprayed coatings is considered a very low thickness. The low thickness was achieved by applying only two spraying passes. Spraying parameters were selected after several attempts (Table 3).

Table 3 – Optimised spraying parameters.

Equivalent ratio	Oxygen flow rate [scfh]	Kerosene flow rate [lph]	Carrier gas	Carrier gas flow rate [l/min]	Powder wheel speed [RPM]	Length of barrel	Feed rate [mm/s]
0,7	1650	16	N	7	250	4"	550

In order to melt the HVOF sprayed layer and eliminate the interface between coating and substrate, a laser was used (direct CW (continuous wave) diode laser COHERENT ISL4000L with maximal output 4.3 kW and 808 mm wavelength). The optimised parameters of laser treatment are summarized in the Table 4.

Table 4 – Optimised laser remelting parameters for the FeCrAlY coating

Laser power [W]	Feed, v [cm/min]	Focal spot dimensions [mm x mm]	Overlap ping [%]	Gas	Pressure of gas [bar]
1650	400,425	6 x 1	60%	Ar 4.8	1,2

2.2.2 PVD (Physical Vapor Deposition)

The Physical Vapour Deposition processes consist in the deposition of a film over a surface through evaporation and subsequent condensation. The vaporized material is transported by vapour or low pressure gas. The range of deposition through PVD processes can vary from few to thousands nanometers.

The arc-PVD is based on the firing of an arc discharge between the material to be deposited (acting as cathode) and the walls of the chamber (acting as anode). The very high density of power taking place within the zone where the arc has been fired (cathodic spot) causes an intense vaporization joined to ionization of the material contained. The limited dimensions of the affected area allows to keep the remaining part of the spring material under the melting point. The substrates to be coated are kept in negative tension in order to catch the ionized vapours accelerating them. An intense ionic bombardment is, this way, generated, favouring the adhesion of the coating to the substrate. The PVD plant at CSM is equipped with two different deposition technologies: there are four cathodic arc springs and one radio frequency sputtering spring. The PVD system of CSM allows the coating of objects with maximum length 40-60 cm, granting uniform deposition for a central length of 50 cm. The key aspects of this kind of deposition are the uniformity of the coating and the high speed of deposition.

2.3 Corrosion test of the FeCrAlY coating

Tests were carried out in the natural convection loop COLONRI II, in lead, at 600°C, for 1000h, with an oxygen content between 10^{-6} and 10^{-5} wt% and a flow rate about 1-2cm/s. Specimens dimensions 25x11x1mm for the corrosion tests.

2.4 Mechanical testing of the TiN coating

The adhesion of the TiN film to the substrate was assessed with three points bending tests for three different thicknesses deposited on the same substrate AISI316. The bending tests have not been executed up to specimen rupture but just to obtain two values of maximum deformation in the middle, respectively equal to 1.5 and 2 mm.

Table 5 – Testing parameters for the 3-point bending

Test temperature (°C)	RT
Distance between tips (mm)	40
Geometry of the specimen (mm)	100x20x4
Speed of deformation	1 mm/min
Pre-load	20 N
Base material	AISI 316
Max. def. in the middle (mm)	1.5, 2, 3

2.5 Tensile tests

A series of tensile tests at 550°C has been planned in order to find-out which is the stress-strain level leading to the detachment of the coating. A first batch of samples has been tested up to the yield stress of the base material (previously achieved through tensile tests on uncoated specimens of the same base material).

Table 6 – Testing parameters for the tensile

Test temperature (°C)	550
Speed of the upper crossbar	0,2 mm/min
Base material	T91, 15-15Ti
Maximum load reached in tension (yield point)	10,23 kN = 362 MPa(T91), 15,61 kN = 552,4 MPa(15-15Ti)

3 RESULTS

3.1 HVOF+laser FeCrAlY coating

The FeCrAlY powder sprayed on the T91 substrate (Fig.1.a) had a thickness of about 60µm. However, due to the reduced thickness of the sprayed layer, the amount of internal oxides was higher than usual. This fact implied that the laser power necessary to remelt the surface layer was higher. As a consequence, the zone affected by the laser treatment was very deep (Fig.1.b). After laser treatment, the microstructure of the new surface layer was completely changed. The surface layer (about 100µm thick) was characterised by typical columnar grains, while the heat affected zone (about 200µm thick) had very small grains.

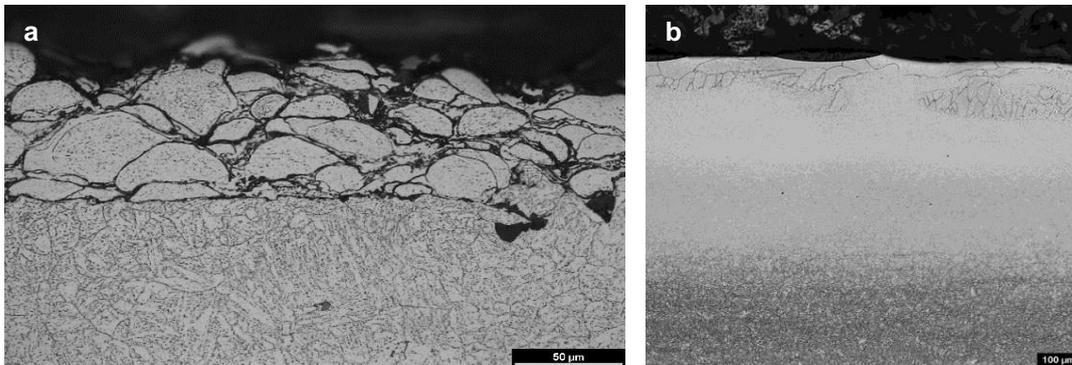


Figure 1 – Cross-section of the FeCrAlY coating on the surface of the steel T91: a) after spraying; b) after laser remelting

In particular, the coated surface had Al₂O₃ highlands produced during the melting of the alloy. The oxide layer was compact and very adherent.

3.2 Corrosion test

After 1000h exposure in the COLONRI II loop at 600°C, a large difference was observed between the coated surface and the bare steel. In fact, the coated side (Fig.2.a) was characterised by the formation of thick oxide highlands in between the Al₂O₃ areas. This oxide had a 3-layers structure: an outer porous layer, which has a composition compatible with the Fe₃O₄ (magnetite); a second intermediate layer, compact and protective, which had a

spinel-like composition and was enriched in Fe-Cr-Al; an inner oxidised layer, depleted of Cr, but with oxygen combined with Fe and Al.

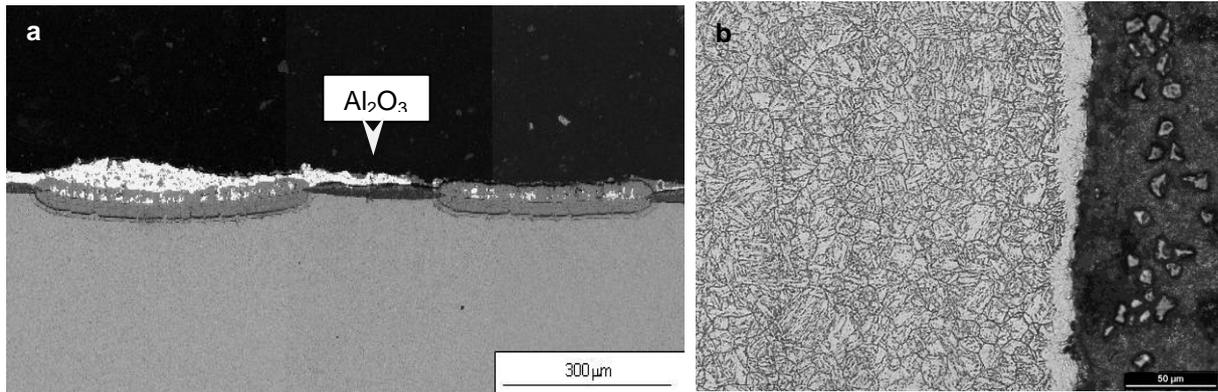


Figure 2 – Specimen exposed for 1000h to flowing Pb at 600°C. a) FeCrAlY coating with oxides; b) damaged steel T91

On the other side, the steel T91 had residual oxides areas, but mostly it was damaged (Fig.2.b). The oxides on the steel were removed and the material was heavily affected by Pb penetration and subsequent removal of material.

3.3 TiN coating

The coated surface were observed in the SEM (Fig.3) and showed that the coating was uniform and without cracks; the surface was very wrinkled due to the underlying layer roughness. It was observed the appearance of TiN droplets on the coating surface, being typical defects of the PVD procedure, characterized by dimensions higher than the coating thickness.

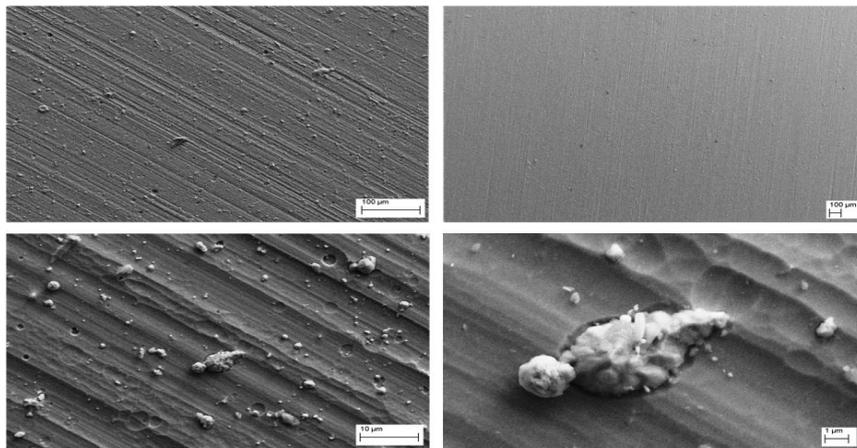


Figure 3: SEM micrographies of the surface of TiN coating on AISI 316 substrate.

The SEM micrographies of the cross-section (Fig.4) revealed a columnar growth of grains separated by different inter-crystal boundaries with highly faceted surfaces, in every examined sample. The thickness of specimens was ranging from about 3 to 5 μm as a function of the deposition times. The coating/substrate interface shows good adhesion, with no occurrence of delamination, cracks and other kinds of defects.

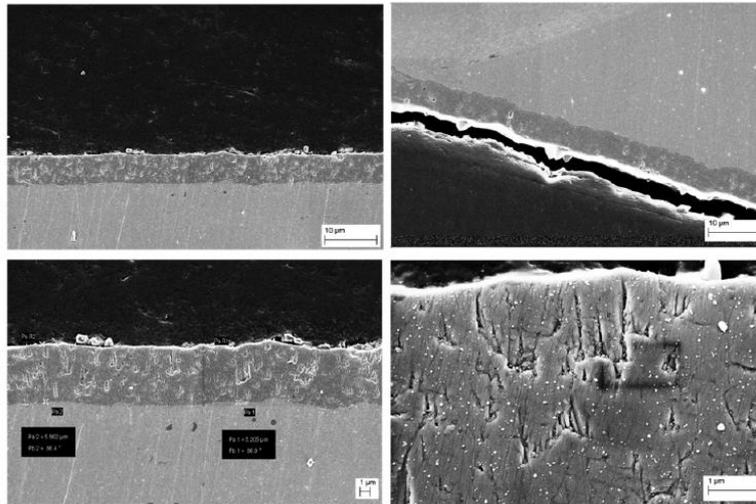


Figure 4: SEM micrographs of the cross-section of the TiN coating on the AISI316

3.4 Mechanical testing of TiN coating

After 3-point bending tests, no detachment was observed for the deformations up to 1.5mm, independently from the thickness of the coating. However, for deformations up to 2mm, an initial detachment of the coating from the substrate was observed.

In addition, also preliminary tensile tests showed the good resistance of the coating. In fact, no detachments were observed (Fig.5) in all the specimens.

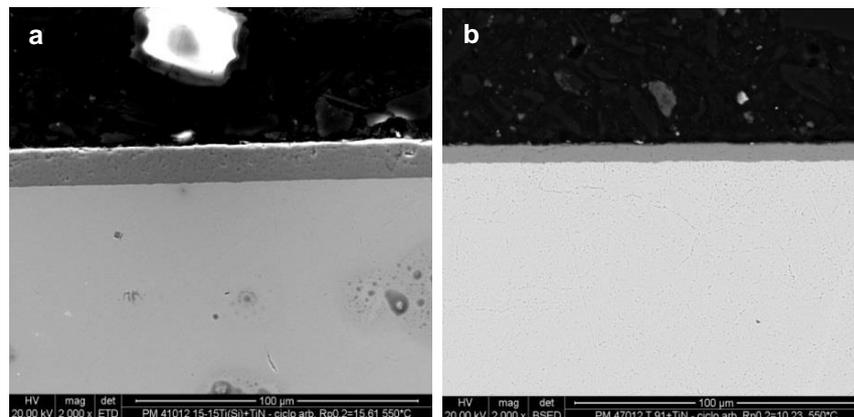


Figure 5: TiN coating on a) 15-15Ti matrix after a load of 15.61 kN in tension (yield point) at 550°C and b) T91 matrix after a load of 10.23 kN in tension (yield point) at 550°C

4 DISCUSSION

In this work two types of coating were proposed for application in liquid Pb. The coating compositions and deposition methods are very different and so the way they react to the environment. In fact, the FeCrAlY coating is based on the establishment of an Al-rich layer, which would produce a protective oxide on the surface of the material. On the other hand, the TiN coating is an inert material in most of the environments and therefore is proposed for use in Pb.

The deposition methods are also based on two completely different approaches. The HVOF method is widely used in the industry and is a thermal spraying technique. Therefore, the powder ejected by the gun is mechanically attached to the surface and this is not sufficient

to guarantee its adherence, especially when spraying thin coatings. Therefore, an additional laser treatment is necessary in order to eliminate the interface between coating and substrate. This further treatment affects to a large extent the material, modifying its microstructure and subsequently properties. Instead, the PVD technique produces thin, homogeneous and adherent coatings, that despite the complexity of the deposition system, do not require further treatment. Therefore, the substrate is not affected by the process.

The preliminary characterisations of these coating were carried out from 2 different point of views and will be further developed.

Concerning the FeCrAlY coating, its superior resistance to damage in liquid Pb was proven up to 1000h at 600°C, compared to the base steel. In fact, the presence of Al and the increase of the Cr content provided an increased capability of developing a protective oxide scale. However, the negative outputs of the coating method was the growth of isolated islands of Al₂O₃ at the surface, which are not reacting with the Pb, but affecting the thermal properties of the material, due to their thickness. Moreover, a large part of the substrate was affected by the laser treatment and this is expected to affect the behaviour of the alloy from the mechanical and irradiation point of views. Nevertheless, in the experimental conditions of this experiment, it was not possible to assess the role of this change in the microstructure in the corrosion resistance of the material.

For TiN coatings, corrosion tests in Pb have been planned in order to demonstrate that this kind of coating remains inert.

5 CONCLUSIONS

A FeCrAlY coating applied by HVOF combined by laser treatment was proposed for applications in Pb.

Preliminary tests in flowing Pb at 650°C showed a superior resistance of the coating compared to the base steel T91.

For the TiN coatings, the requirement of adhesion to the underlying substrate can be considered successfully satisfied, both after bending and tensile uniaxial load.

ACKNOWLEDGMENTS

This work has been supported by the SUSEN Project CZ.1.05/2.1.00/03.0108 realized in the framework of the European Regional Development Fund (ERDF) for CVR; and in the frame of the project MPO FR-TI1/423 "Reliable and safe nuclear power source of new generation for Czech Republic energetic" for UJV.

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