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Slurry and Thermal Spray Coatings for Protection of New Generation Steam Engine Components

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Abstract

The principal objective of the European COST Action 522 is to raise the operating temperatures of power generation gas and steam turbines in order to increase their efficiency to reduce fuel consumption and emissions. Concerning steam turbines, the operating temperature is expected to rise from 550 to 650°C and for the first time in Europe, the use of high temperature oxidation and corrosion resistant coatings as well as thermal barrier coatings is being considered for steam engine components.

Deposition techniques were chosen due to the possibility of employing them to coat the inside of large pipes in situ: slurry paints, high velocity oxyfuel spray (HVOF) and atmospheric plasma spray (APS). Other variations of thermal spray could also be appropriate and in some cases more economical, but presently they are not available at INTA. Commercially available materials, known to have good oxidation resistance, were selected for both deposition techniques: one aluminium slurry and two alloyed materials for thermal spray: FeCrAl and NiCr. AlFeCoCr, a quasicrystalline material with very low thermal conductivity is currently being studied at INTA as a coating for a number of applications related to high temperature oxidation and has also been included in this work, applied by HVOF.

The aluminum slurry coating was deposited by means of a brush and a series of post-heat treatments were evaluated in order to generate a uniform and stable diffusion coating. The HVOF coatings were optimized to minimize porosity and maximize adhesion.

The coatings were characterized by metallography, SEM-EDS, and steam oxidation testing was carried out at 650°C. The preliminary findings show that some of the studied coatings are very promising.

1.0 Introduction

Within the European COST Action 522 entitled "Ultra Low Emission Power Plant into the 21st Century", the operating temperature of steam engines is expected to rise from 550 to 650°C in order to increase efficiency and therefore meet the ever increasing stringent environmental regulations[1]. Two approaches are being followed in order to achieve this goal:

1. The development of new materials with both optimum mechanical properties and oxidation resistance at higher temperatures.
2. The use of steam oxidation coatings, thermal barrier coatings, etc. which are being considered for the first time in Europe.

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At temperatures higher than 550°C, steam oxidation of the ferritic steels commonly used in the manufacture of steam engine components causes the formation of very thick oxide scales consisting of a top layer of Fe_2O_3 and Fe_3O_4 and an inner zone mainly composed of Fe_3O_4 with thin films of $(Fe.Cr)_3O_4$ spinels (Figure 1). This scale produces a thermal insulating effect resulting in overheating as well as spalling causing metal cross-section loss, component blockage and erosion of components located down-stream.[2-4]

There is very little published work regarding coatings for this particular application mostly covering the deposition of chromium by pack cementation or chromium oxide by chromate conversion solutions.[5-7] Cr is considered a strategic material which needs conservation[8] and moreover, chromate conversion coatings are slowly being displaced due to the high health and environmental hazards that their deposition process implies.[9] The use of alternative materials seemed advisable. Other coatings have recently been explored in an initial feasibility study carried out by our group within the framework of the COST 522 project.[10] These included commercially available materials known to have good oxidation resistance and deposited by techniques that can be employed to coat large steam engine components either at the plant or during manufacture, taking into consideration economical aspects. P92 (NS616), a 9% Cr steel with h creep rupture strength but poor steam oxidation resistance[11] as coated with an aluminium slurry and AlFe, FeCrAl and NiAl coatings deposited by atmospheric plasma spray (APS). The specimens were exposed to a 50% steam/argon atmosphere at 650°C and the results indicated that all of the tested coatings provided some degree of protection to P92 for at least 500 h (Figure 2). The Al slurry coating had to be heat treated prior to exposure in order to insure uniform diffusion. The NiAl and FeCrAl APS deposited coatings showed promising results although a small degree of oxidation could be observed on the substrate surface probably due to the relatively high level of porosity of these coatings which allowed steam to reach the substrate. The AlFe coating did show signs of degradation.[10]

During the second stage of our work, High Velocity Oxy Fuel (HVOF) was chosen as deposition technique, and to carry out the testing, a new, pure steam oxidation rig was built in order to better simulate the actual engine operating conditions. HVOF is a more recently developed thermal spray technique by which coatings less porous than their equivalent produced by APS are obtained.[12-13] As part of an on-going COST 522 project, this work includes the testing results of the Al slurry coatings with two different diffusion heat treatments and different surface treatments prior to exposure, as ll as NiCr and FeCrAl coatings obtained from commercial powders d deposited by HVOF, and AlFeCoCr, a quasicrystalline alloy that has been currently being studied at INTA as a coating for a number of applications related to high temperature oxidation,[14] also obtained by HVOF.

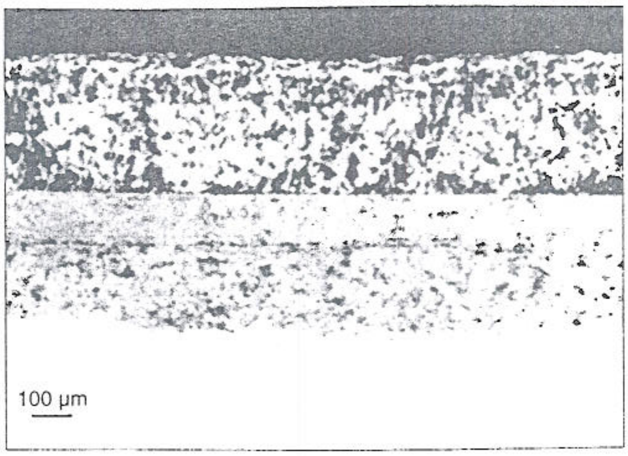

Fig. 1: Cross section optical micrograph of P92 after 2000 h of exposure to pure steam at 650°C.

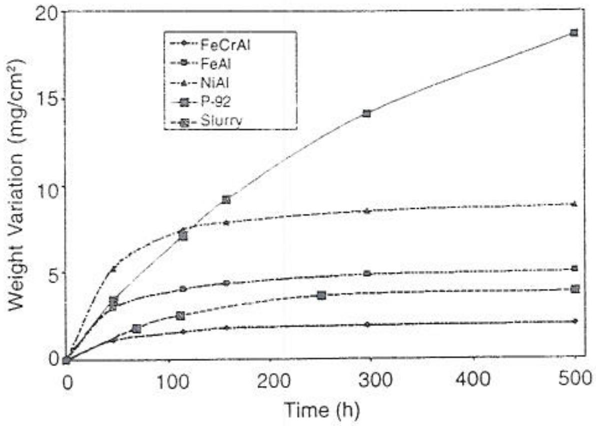

Fig. 2: Weight variation as a function of time for slurry Al and APS deposited AlFe, NiAl and FeCrAl coatings on P92 under steam oxidation conditions (50% steam in argon) at 650°C.

2.0 Experimental Procedures

2.1 Materials

Specimens of P92 (Fe: 87.8, C: 0.115, Mn: 0.46, Si: 0.028, Cr: 8.85, Ni: 0.062, Mo: 0.42, W: 1.85, V: 0.20 wt.%) obtained from Nippon Steel Corporation (15 × 15 × 1 mm) were sand blasted, ground (Struers 1200) and vapor degreased prior to coating. The Al slurry and the powders for HVOF spraying were obtained from commercial sources.

2.2 Slurry Coatings

The Al slurry was applied by brush, and the coated samples were subjected to a "curing heat treatment" at 350°C for 30 minutes in air. Diffusion heat treatment was performed under argon flow at 700°C for 1 or 10 h.

2.3 HVOF Coatings

The coatings were deposited by a Sulzer Metco Diamond Jet Hybrid unit (model A-3120) mounted on a 6 axes robot (ABB) and fed by a twin rotation powder feeder.

2.4 Characterization

The samples were characterized by optical and electron microscopy (JEOL JSM-840 equipped with a KEVEX EDS microanalyser).

2.5 Steam Oxidation Testing

A pure steam oxidation rig was built and its scheme is shown on Figure 3. The oxygen content in the water must be kept to values below the ppb level as it has been shown that O_2 reduces the steam oxidation rate.[11] This is achieved by permanently bubbling N_2 into de-ionized, distilled water. The water is recirculated by means of a condenser connected to the reservoir. Prior to testing, air is displaced from the coating chamber by means of N_2 which is kept flowing while heating to the test temperature (600°C/h). Once the test temperature is achieved, the N_2 flow is cut and the water recirculation pump is turned on. To carry out weight measurements or to remove samples, the samples are cooled to about 300°C under N_2 and removed from the furnace. The reheat cycle (from 300 to the test temperature) is also carried out under N_2.

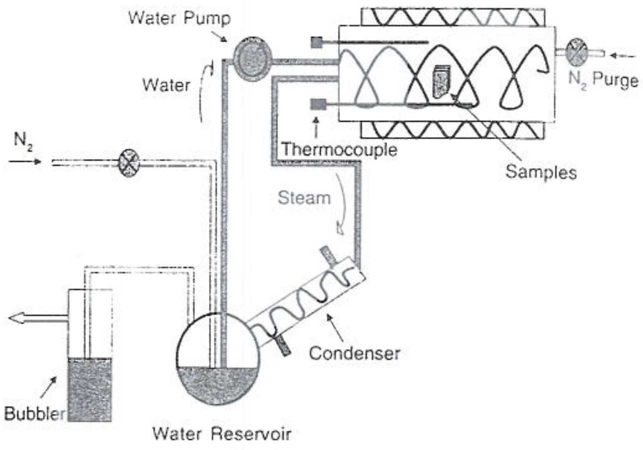

Fig. 3: Schematics of the experimental set-up of the pure steam oxidation rig.

3.0 Results

3.1 Slurry Coatings

Application of a commercial aluminium slurry to P92 was followed by intermediate temperature (400°C) "baking" heat treatments for evaporation of the solvent, and a final diffusion heat treatment at 700°C under Ar flow. Figures 4 and 5 show the resulting coatings after 1 and 10 h of diffusion heat treatment respectively. In both cases a diffusion layer of 50-60 mm was obtained, with some un-diffused "slurry" remaining on top, but with different microstructures. The proposed phase distribution is only tentative since composition was measured by EDS, a semi-quantitative technique. The sample with only 1 h of heat treatment showed only one zone rich in Al, with a composition of Al: 47.4, Fe: 48.5 and Cr: 4.1 wt.% while the sample heat treated for 10 h shows a three layer structure. The most external layer has a thickness of 45 mm consisting of "islands" that could be Fe_2Al_3 and dissolved Cr (Al: 32.7, Fe: 59.8, and Cr: 7.4 wt.%) on a matrix with a higher Al content (Al: 47.5, Fe: 49.4, and Cr: 3.1 wt.%) probably corresponding to $FeAl_2$ with dissolved Cr. The intermediate, 5 mm thick layer of composition Al: 27.5, Fe: 66.3, and Cr: 6.2 wt.% could be attributable to FeAl while the 10 mm most internal layer corresponds to an interdiffusion zone in which carbides of refractory metals precipitate due to insolubility. TEM analysis is presently being carried out in order to establish the precise composition of this coating.

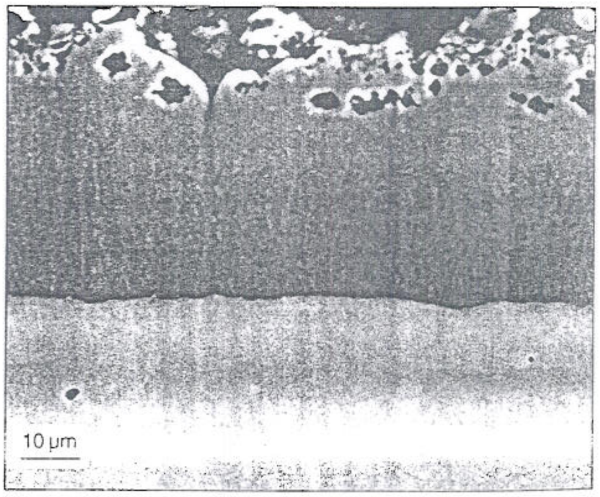

Fig. 4: Cross section scanning electron micrograph of an Al slurry coated sample after a 1 h diffusion heat treatment at 700ºC under Ar.

3.2 HVOF Coatings

The three above mentioned materials NiCr, FeCrAl, and AlFeCoCr, were deposited on P92 by HVOF. An initial round of optimization was carried out in order to minimize porosity and maximize substrate-coating adhesion.

3.2.1 NiCr

The coating obtained after an initial optimization round had a low level of porosity as shown in Figure 6 and a thickness of 150 mm. SEM-EDS analysis of the as deposited coating confirmed a fairly uniform dispersion of both Ni and Cr over the whole coating depth.

3.2.2 FeCrAl

Also known for its good oxidation resistance, this commercially available material was chosen due to its Cr content.[15] Figures 7a and b show the microstructure of the coating obtained by APS and by HVOF respectively. As can be observed, the HVOF deposited coating shows a much lower degree of porosity as was expected. To the best of our knowledge, this is the first example of a FeCrAl coating deposited by HVOF. As with the NiCr coating, a uniform dispersion of the metals is observed in the 140 mm HVOF deposited coating.

3.2.3 AlFeCoCr

AlFeCoCr corresponds to a brittle quasicrystalline alloy with a very low thermal conductivity, close to that of traditional thermal barrier coatings (TBC) based on yttria stabilised zirconia (YSZ). It has been previously deposited by low pressure plasma spray, and the resulting coatings are very resistant to high temperature oxidation and hot corrosion.[14] The material was also deposited by HVOF resulting in a 75 mm layer showing some micro-cracks and porosity as can be seen in Figure 8.

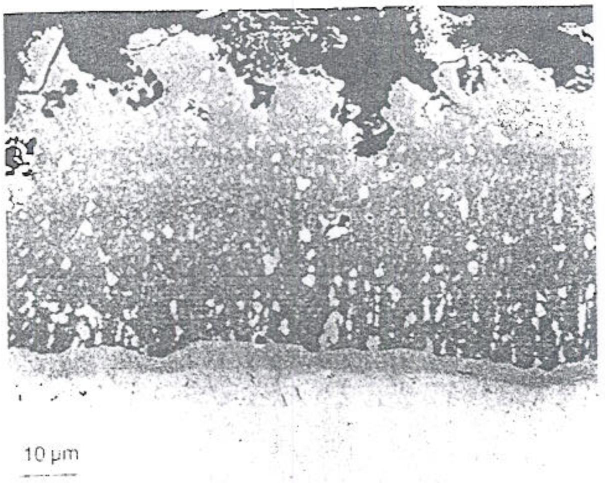

Fig. 5: Cross section scanning electron micrograph of an Al slurry coated sample after a 10 h diffusion heat treatment at 700°C under Ar.

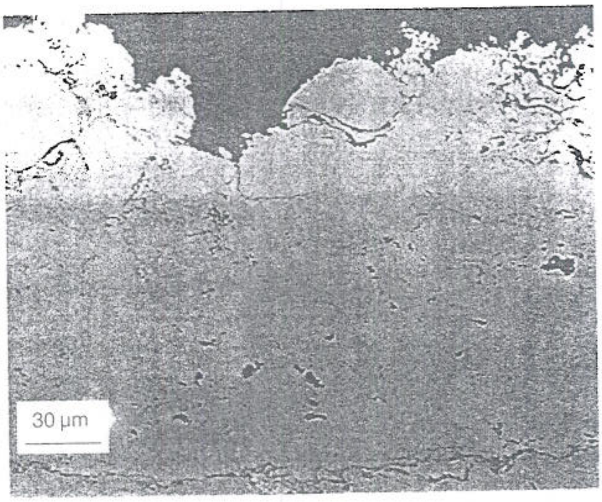

Fig. 6: Cross section scanning electron micrograph of a NiCr coating deposited by HVOF.

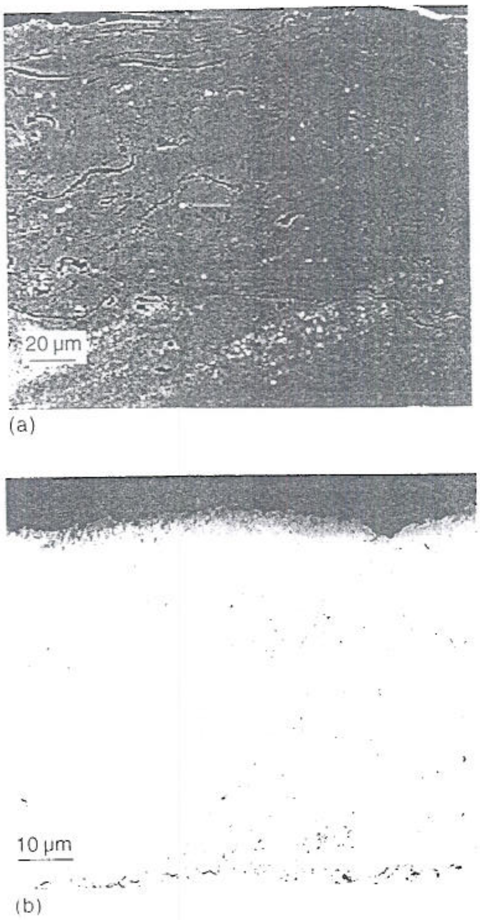

Fig. 7: Cross section scanning electron micrograph of a FeCrAl coating deposited by: (a) APS and (b) HVOF.

3.3 Steam Oxidation Testing

Testing was carried out at 650°C in pure steam (linear velocity: 0.7 cm/s). The weight variation as a function of time is shown in Figure 9 for the slurry coated samples, and in Figure 10 for the HVOF coated specimens. P92 was included in both Figures for comparison purposes. The first important observation is that its oxidation rate is approximately twice that obtained when the test was carried out under a 50:50 steam/argon mixture (compare Figure 2 to Figure 9). Studies of the influence of dilution and of the steam linear velocity are currently being carried out to determine the influence of these parameters on the oxidation rate. In any case, the present results approach field data reported in the literature[16]. As with our prior results, all of the tested coatings showed a higher resistance to steam oxidation than that of the substrate material. Some samples of exposed coatings were taken out at different time intervals in order to carry out metallographic analysis and in some cases SEM-EDS characterization.

3.3.1 Slurries

The slurry-coated samples experienced an initial weight loss that can be attributed to spalling of the un-diffused material (Figure 9). This was confirmed when samples coated and heat treated in the same manner, were slightly ground before testing and a lower weight loss was experienced. After the first 130 h, the weight remains constant during the remaining tested time (1000 h) and both types of heat treated samples seem to behave in the same manner after 1000 h of exposure the microstructures of both the 1 and 10 h heat treated coatings appear similar (Figures 11 and 12 respectively). This observation indicates that although after 1 h of diffusion, a stable microstructure is not reached (Figure 4), it continues to evolve under the test conditions (650°C) until a structure similar to that of the 10 h heat treated sample is achieved. An even shorter diffusion heat treatment may be enough, which may translate into cost reduction.

In both microstructures an external layer has developed on top of the three zone structure observed in the unexposed 10 h heat treated sample (see Figures 5 and 12). Essentially, this layer is composed of a matrix containing Al: 42.5, Fe: 56.7, Cr: 2.8 wt.%,

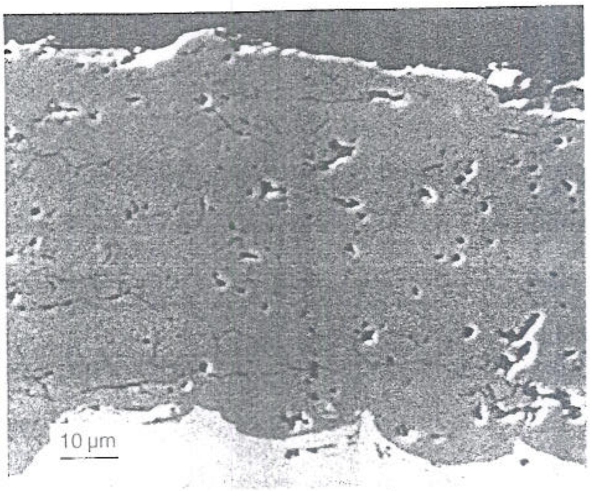

Fig. 8: Cross section scanning electron micrograph of a AlFeCoCr coating deposited by HVOF.

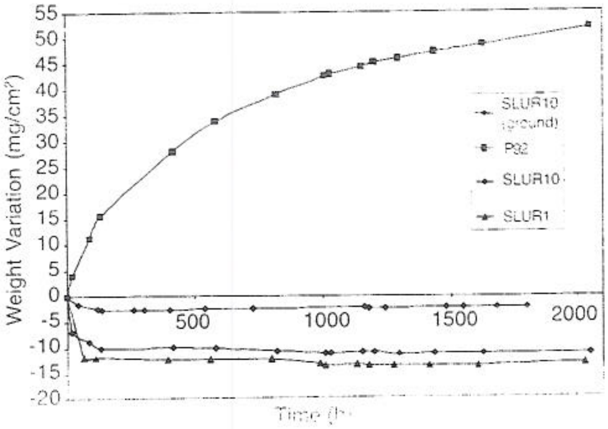

Fig. 9: Weight variation as a function of time for slurry Al deposited coatings on P92 under pure steam oxidation conditions at 650ºC: SLUR1 : heat treated for 1 h; SLUR10: heat treated for 10 h.

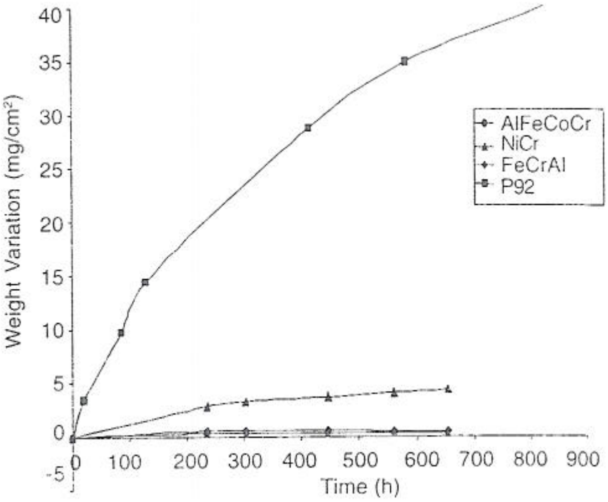

Fig. 10: Weight variation as a function of time for HVOF deposited NiCr, FeCrAl and AlFeCoCr coatings on P92 under pure steam oxidation conditions at 650°C.

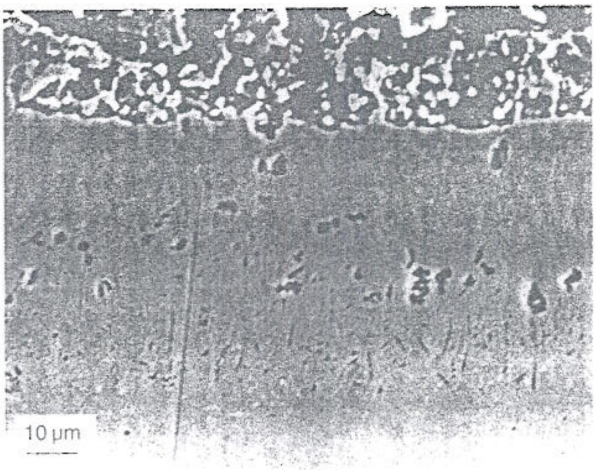

Fig. 11: Cross section scanning electron micrograph of an Al slurry coated sample after a 1 h diffusion heat treatment exposed to pure steam for 1000 h at 650°C.

approaching to the Fe$_2$Al$_5$ phase with "islands" of FeAl with dissolved Cr (Al: 24.5, Fe: 70.5, Cr: 5.0 wt.%). The next zone composition continue the FeAl$_2$ matrix with Fe$_2$Al$_5$ precipitates proposed for the unexposed sample, that has lost thickness (from initially 45 to 20 mm), while the 5 mm FeAl zone remains apparently unchanged. Some Kirkendall porosity has also developed near this FeAl layer.

These coatings possibly work by producing a very thin protective layer of Al$_2$O$_3$, as is known to occur with aluminide coatings exposed to high temperature oxidation by air. The phases that have developed during exposure to steam could result from outward diffusion of Al due to spalling and regeneration of said protective layer: FeAl$_2$ → Fe$_2$Al$_5$ → FeAl. TEM analysis will be carried out in order to confirm the presence of Al$_2$O$_3$ and the proposed phase composition.

3.3.2 NiCr

The NiCr coating experienced an initial slight weight gain after which it seems to stabilize (Figure 10). After 560 h, its microstructure showed no evidence of degradation as shown in Figure 13, and no iron or chromium oxides could be observed.

3.3.3 FeCrAl

In contrast with the FeCrAl plasma sprayed coating, the HVOF equivalent did not experience a significant weight variation during the tested period (Figure 10), nor a variation of its microstructure

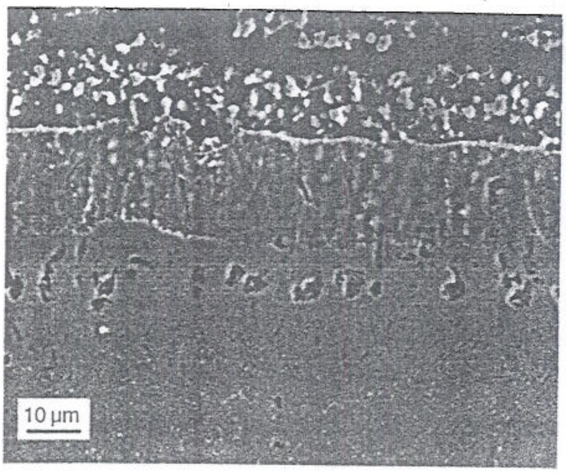

Fig. 12: Cross section scanning electron micrograph of an Al slurry coated sample after a 10 h diffusion heat treatment exposed to pure steam for 1000 h at 650°C.

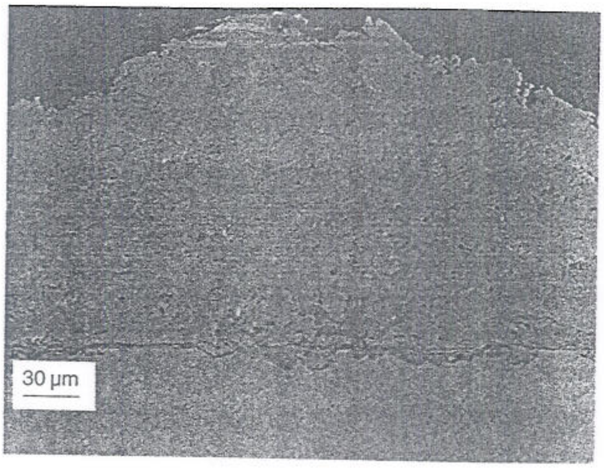

Fig. 14: Cross section scanning electron micrograph of a FeCrAl coating deposited by HVOF exposed to pure steam for 650 h at 650°C.

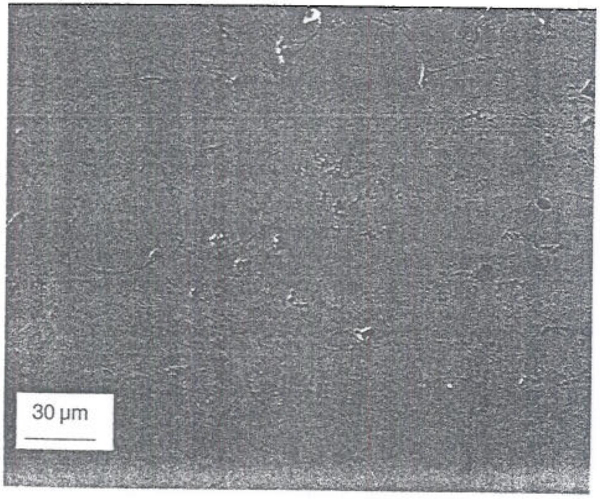

Fig. 13: Cross section scanning electron micrograph of a NiCr coating deposited by HVOF exposed to pure steam for 650 h at 650°C.

which remains unchanged after 560 h of exposure (Figure 14). As expected, the reduced porosity prevented (or retarded) permeation of steam to the substrate surface, which in the APS coated specimen resulted in the growth of a thin oxide layer on its surface.

3.3.4 AlFeCoCr

This quasicrystalline coating behaved in the same manner as FeCrAl, that is, no significant weight variation was observed during the test period (Figure 10). As mentioned earlier, AlFeCoCr has a thermal conductivity similar to that of YSZ and therefore can be employed as a TBC. In contrast to traditional TBCs, where an intermediate oxidation and corrosion bond coating is required, AlFeCoCr is an oxidation and corrosion resistant TBC, and adheres well to the substrate. No evidence of degradation could be observed on the cross section micrograph of the sample exposed to 560 h of steam oxidation (Figure 15). However, an iron oxide layer developed at the coating-substrate interface indicating that steam has permeated through the pores and cracks of the coating. This oxide layer seems to grow very slowly, and its composition will be determined shortly. Longer term tests need to be carried out to measure the growth rate of this layer and also if it will spall or cause spalling of the AlFeCoCr coating. Micro-cracks and pores reduce the thermal conductivity of materials and it may not be necessary to eliminate them if the observed iron oxide layer does not cause coating spallation.

4.0 Conclusions

As part of an ongoing COST 522 project, initial pure steam oxidation testing of a number of slurry and HVOF deposited coatings, indicate that all of the tested coatings provide some degree of protection to P92 for at least 600 h at 650°C.

Heat treatment duration of the Al coated samples does not seem to affect the behavior of the diffused coating as long as an initial diffusion zone is present, and this can be achieved in 1 h or perhaps even less time (to be confirmed). As with the diffusion aluminide coatings employed for high temperature air oxidation protection, a thin alumina scale may form behaving as a steam oxidation barrier but its spallation causes outward diffusion of Al which will eventually end in coating degradation and failure. However, this hypothesis must be demonstrated by TEM analysis of tested samples. SiAl slurries will be explored in an attempt to increase steam oxidation resistance since it has been shown that small Si additions to certain steels significantly reduces the steam oxidation rates[17].

NiCr, FeCrAl and AlFeCoCr coatings deposited by HVOF also showed promising results. HVOF deposited FeCrAl prevented steam diffusion to the substrate surface, as is the case with the APS deposit analogue coating. The AlFeCoCr did allow a very slow oxidation of the substrate, but it could not even be measured by the weight variations of the specimens during the tested period. Substrate oxidation is likely due to steam permeation through the coating

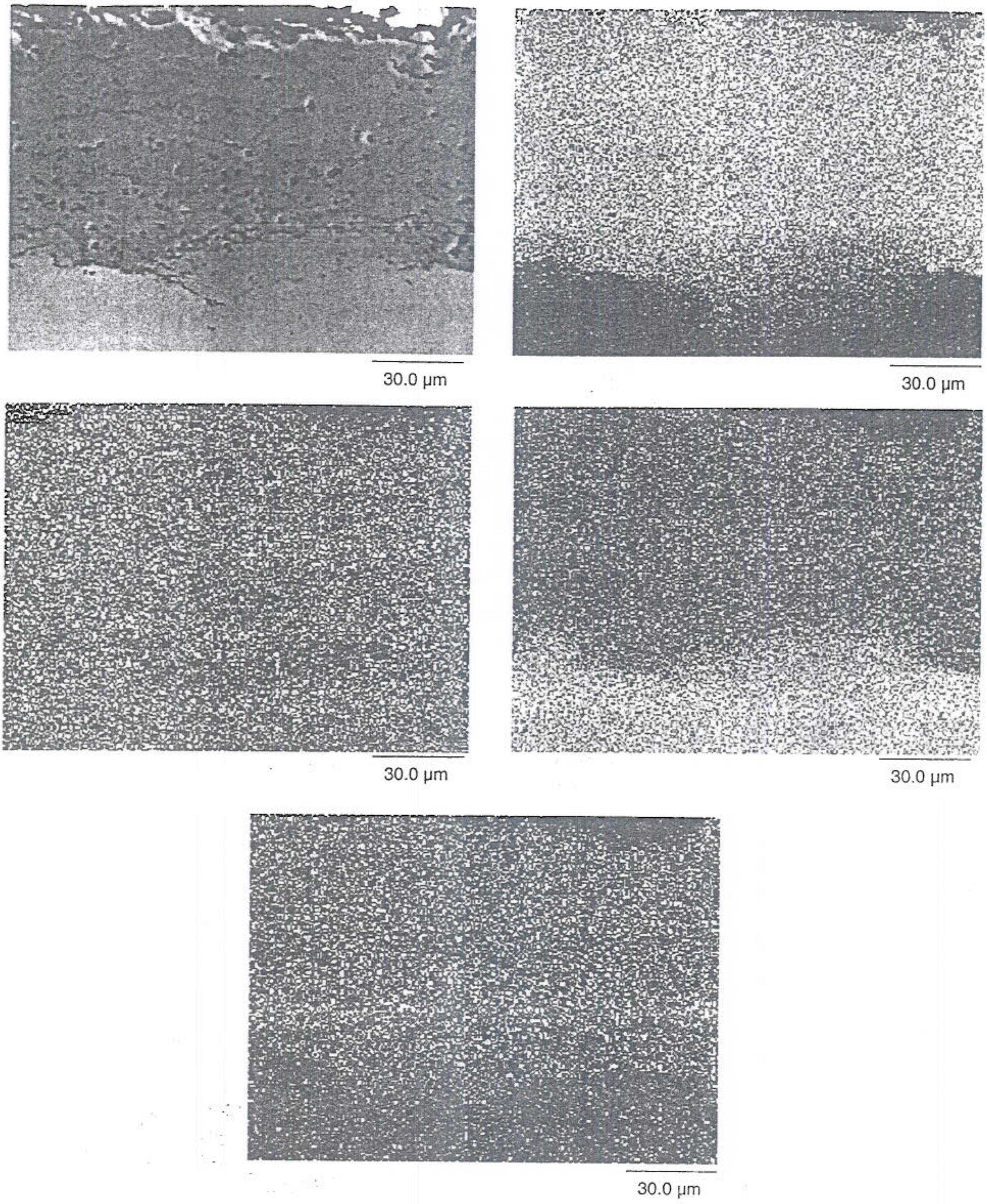

Fig. 15: Cross section scanning electron micrograph and EDS mapping of a AlFeCoCr coating deposited by HVOF exposed to pure steam for 650 h at 650°C.

micro-cracks and pores. Longer exposure experiments are presently being carried out as well as an investigation aimed at determining the mechanism of protection of the studied coatings.

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