

“Latest Results in the Development of Steam Resistant Slurry Coatings for New Generation High Temperature Supercritical Steam Plants”

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Important efforts to develop new steels or to protect high creep strength steels in order to allow operation of steam turbines at 650° C, are being carried out worldwide to increase plant efficiency. Under a steam atmosphere, existing ferritic and austenitic alloys commonly employed in steam plants, form Fe and Cr containing oxides, which become less protective at temperatures higher than 550° C. In the framework of Cost Actions 501, 522 and 536, new alloy development activities have been very successful in improving the creep strength at higher temperatures, but generally by lowering the chromium content [1, 2].

In parallel, a number of commercially available coatings have been explored for steam oxidation protection. These included materials known to have good high temperature oxidation resistance and deposited by techniques that can be employed to coat large steam turbine components either at the plant or at their location of manufacture, and also taking into consideration economical aspects. As part of the above mentioned COST actions and of the EC project “Coatings for Supercritical Steam Cycles” (SUPERCOAT) promising results were obtained both at the laboratory scale as well as at field testing [3-6] Among the tested coatings, diffusion aluminides are very protective. These coatings are deposited by applying commercially available Al slurries followed by a diffusion heat treatment at 700°C, and on exposure to steam the coatings develop thin protective Al₂O₃. Other aluminides have recently been produced on ferritic steels by CVD [7] and pack cementation. [8, 9] In this presentation, the deposition methodology as well as laboratory scale long term steam oxidation as well as thermal cycling testing of slurry aluminide coatings will be described

1.- Coating Application and Microstructure

Slurries are suspensions of particles (metallic or ceramic) on a binder/solvent system that can be applied on a substrate by means of a brush, by spraying or by immersion. After application, the coated specimen is subjected to a curing heat treatment to eliminate liquids and set the coating, resulting in a layer of densely packed particles (figure 1a). If this layer is exposed to steam at 650° C, two processes will occur simultaneously: 1) coating-substrate interdiffusion and b) substrate oxidation by steam reaching the substrate through the initial coating porosity (figure 1b). Slurries need therefore to be heat treated prior to exposure to steam or else protected with an appropriate sealant to prevent steam from reaching the substrate before uniform interdiffusion can take place. Figure 2a shows an Al slurry deposited on P91, similar to that shown in figure 1 subjected to a heat treatment of 700° C for 10 h. A uniform Fe₂Al₅ intermetallic layer with CrAl precipitates forms. The “as heat treated coatings” exhibit thickness through cracks probably due to brittleness of the Fe₂Al₅ phase and to thermal expansion mismatch. If an adequate sealant (silicate or aluminate) is applied to the “as deposited” slurry, no substrate oxidation is observed when the coated specimen is exposed to steam at 650° C.

Most commercially available slurry aluminides are based on acidic phosphate/chromate binders. Chromates are present in order to passivate the Al particles which otherwise react with violently. However, Cr^{+6} is highly carcinogenic and although is present in very low

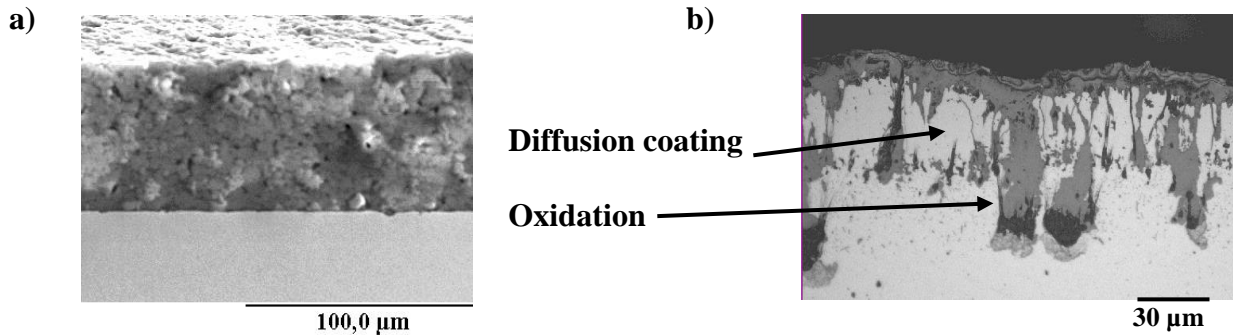


Figure 1: Cross sections of an Al slurry coating: a) “as deposited” (by SEM) and b) after 24 h of exposure to steam at 650° C (by optical microscope)

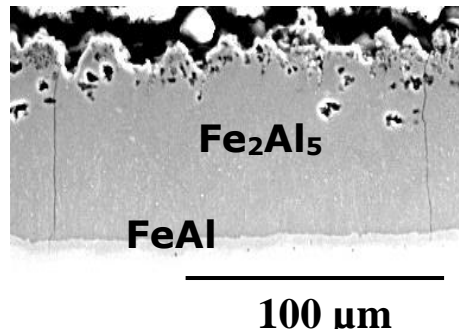


Figure 2: Commercial Al slurry coating after diffusion heat treatment prior to exposure

concentrations, it should be eliminated. Al slurries with neutral silicate binders have been prepared and the resulting coatings are equal to those obtained from the commercially available products. This slurry should be prepared shortly before coating and the residues must be discarded as slow Al oxidation takes place.

Surface preparation is another very important issue related to processing of these slurry aluminide coatings over ferritic steels. For instance, sand blasting results in a non-uniform coating as shown in figure 3a. For obtaining adequate coating uniformity, grinding is required (figure 2). However, for industrial purposes, grinding as surface preparation is not very practical and the same result can be obtained by sand blasting followed by glass beading (figure 3b).

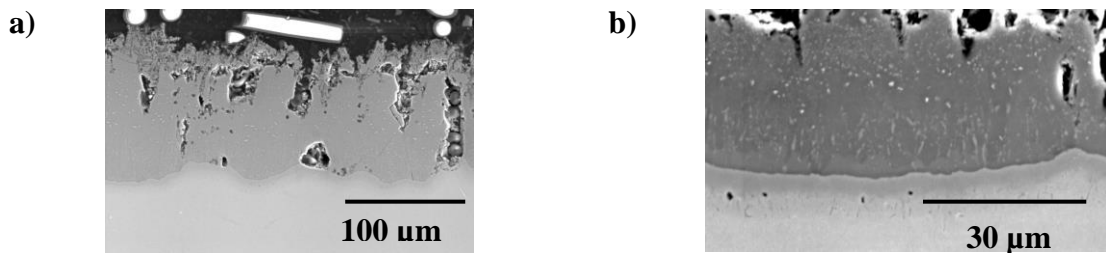


Figure 3: Aluminide slurry coating after a) sand blasting and b) sand blasting followed by glass beading

Slurry aluminides have been deposited on a number of alloys such as P91, P92, T22, T23 as well as CB2 (13 wt.% Cr) and FT4 (11,45 wt.% Cr) both developed within the above-mentioned COST actions. The coating microstructure is very similar for all of these substrates with minor differences related to the amount of CrAl precipitates in Fe_2Al_5 . On the low Cr substrates such as T22 and 23 (≈ 2 wt.%) very few precipitates can be observed whereas in the high Cr substrates such as FT4, these precipitates are quite numerous (figure 4). Moreover, some degree of Kirkendall porosity is present only in the as deposited coating on T22 at the coating-substrate interface.

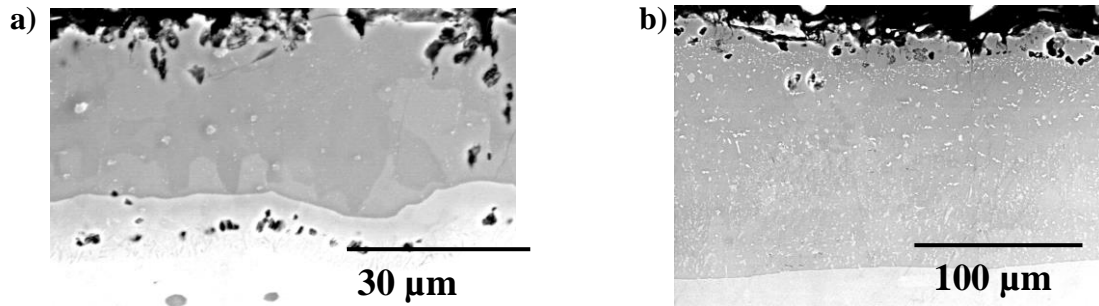


Figure 4: Aluminide slurry coating on a) T22 and b) FT4

2.- Oxidation Testing Results

2.1 Long Term Steam Oxidation.

Slurry deposited aluminide coatings on P92 have been exposed to a flow of pure steam at $650^\circ C$. Up to 40,000h there is very little weight gain as compared to uncoated P92 as seen in figure 5a. No evidence of substrate attack has been found and the thickness through cracks originally present do not propagate into the substrate nor become sites of preferential attack (figure 5b).

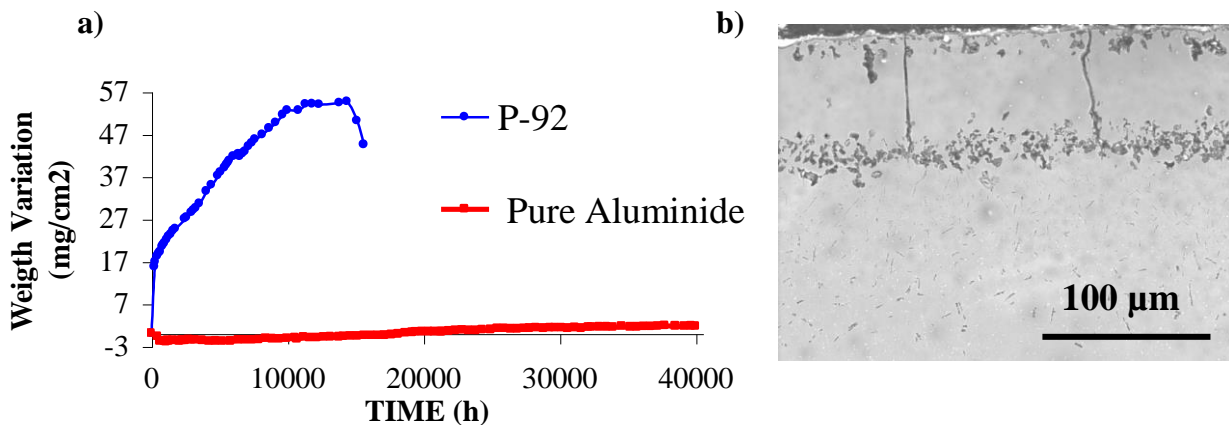


Figure 5: Slurry aluminide coatings on P92 exposed to steam at $650^\circ C$: a) weight variation and b) SEM cross section of a sample taken out after 40,000 h

However, the coating slowly degrades by Al-Fe inter-diffusion resulting in a decreasing Al subscale composition (figure 6a), which will eventually lead to coating failure when the Al subscale concentration reaches a value below the critical lever required to form protective Al_2O_3 . A large degree of Kirkendall porosity develops at the coating-substrate original interface probably due to unbalanced Al-Fe interdiffusion, as with time, Fe outwards diffusion becomes faster the Al inwards diffusion. Interestingly, an empirical fit of the experimental Al concentration below the protective scale as a function of time has resulted in

an equation that allows an estimation of the expected life of the coatings (figure 6b). Most authors agree that the critical concentration of Al required to regenerate a protective Al₂O₃ scale is of approximately 5 w%. However, if Cr is present, this concentration can be lower [9-10]. According to steam turbine manufacturers, the expected life for coatings should be 100,000 h, which is the typical basis for power plant design [11]. Employing the resulting equation (figure 4b), 79,000 h are required to reach an Al w% of 5, whereas the coating may last 124,000 h before it attains 4 Al w%.

Nevertheless, this estimation does not take into account possible failure by spalling due to Kirkendall porosity at the coating-substrate interface. The results of long exposure on-going tests will allow establishing the validity of this equation.

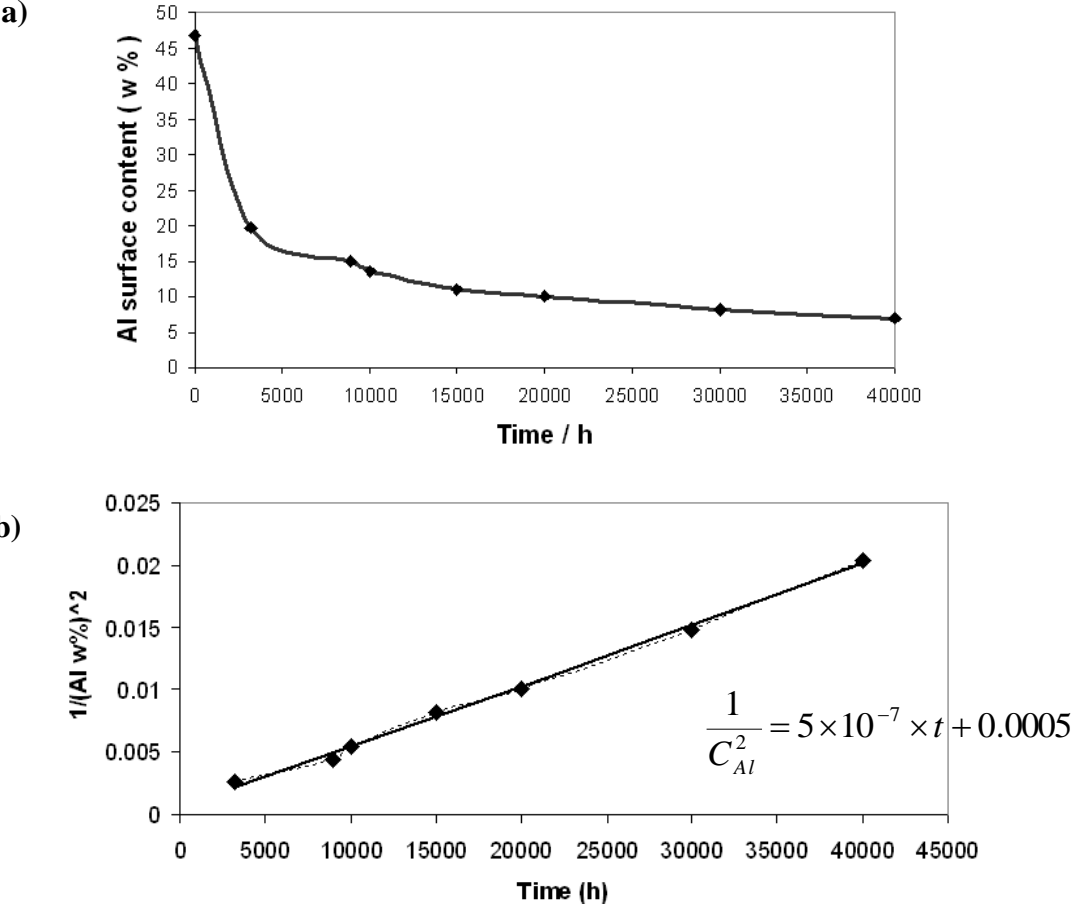


Figure 6: Al w% below the protective scale for a slurry aluminide coating exposed to steam at 650°C: a) as a function of time, b) linear fit

Another consequence of Al inwards diffusion is the precipitation of AlN needle-like particles within the substrate (in N containing substrates) at depths increasing with the exposure time. The loss of soluble N, added to the base material to improve its high temperature strength, may therefore affect its mechanical properties [3, 12].

2.2 Cyclic Oxidation.

The thermal cycling behavior of slurry aluminides has also been studied under air. Each cycle consisted of heating up to 650° C in 5 min, holding 1 h and cooling down to 100° C in 5 min. These cycles are extreme for this application, as a similar situation could only occur in a steam plant, if catastrophic failure would cause flooding of water from the boiler into the

turbine. After 100 cycles no evidence of degradation or crack propagation could be observed as shown in figure 7a. After 1000 cycles the cracks had widened and propagated but deflected at the coating-substrate interface rather than into the substrate (figure 7b). Moreover, oxidation had begun by means of air reaching the substrate through the widened cracks. Although P92 is quite resistant to oxidation at ambient air at 650° C [13], the composition of the substrate near the coating has been modified by interdiffusion with the coating, resulting in an alloy composition less resistant to air oxidation. After 2000 cycles, oxidation has progressed within the substrate but has not affected the coating.

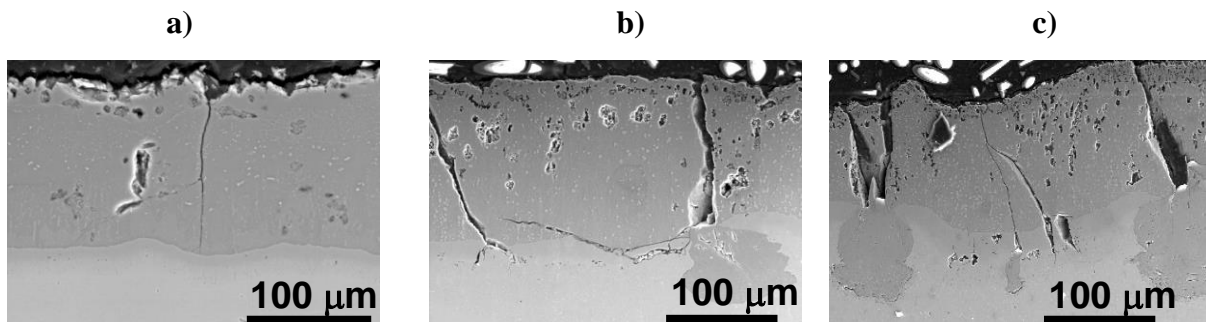


Figure 7: SEM image of the cross section of aluminide coating on P92 specimens after thermal cycling at 650° C after: a) 100, b) 1000 and c) 2000 cycles.

The results of this experiments show that the cracks already present in the coating after the diffusion heat treatment are not detrimental. Cracks in these slurry aluminide coatings form due to thermal expansion coefficient mismatch, in order to relieve stresses, and do not propagate into the substrate even in the worst possible scenario when the coatings are exposed to very fast heating and cooling cycles.

Conclusions

Slurry aluminide diffusion coatings are protective for at least 40,000 h but degrade by coating-substrate interdiffusion leading to a decrease on the Al concentration at the surface, and the deposition of AlN precipitates within the substrate as well as to the development of Kirkendall porosity at the coating-substrate original interface. However, based on long-term steam oxidation experimental data, the life of the coating can be estimated to surpass 79,000 h. Although stress relieving cracks form in these coatings, they do not propagate into the substrate even when the coating is subjected to thermal cycling and moreover, said cracks do not become sites of preferential attack by steam.

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