Fe-Al Intermetallic Phases Present in Fe Aluminide Coatings

A. Agüero[a], V. González, M[b]. Gutiérrez[c] and R. Muelas[d]
Instituto Nacional de Técnica Aeroespacial
Ctra. Ajalvir Km 4
Torrejón de Ardoz 28850
Spain

[a]agueroba@inta.es, [b]gonzalezmv@inta.es, [c]gutierrezdom@inta.es, [d]modsurf3@inta.es

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Iron aluminide coatings are known to protect steels at elevated temperatures in diverse industrial environments. Depending on the Al content of the Fe-Al phase, a protective Al_2O_3 scale can be formed and maintained and the coatings are relatively stable up to approximately 900º C. At higher temperatures, Al inwards diffusion causes impoverishment of Al at the surface until it reaches a critical concentration below which the protective oxide will not form. Depending on the coating composition an Al content of 4 to 8 wt. % seems to be sufficient to maintain the protective scale [1-3].

Among the diverse coating deposition techniques, the application of slurries is one of the most economical, practical and versatile. Aluminide coatings have been generated by applying an Al slurry followed by heat treatment which depends on the substrate. For instance, it has been shown that on ferritic steels, deposition of an Al slurry followed by heat treatment at 700º C for 10 h generates a complex aluminide coatings composed of several intermetalllic phases including $FeAl_3$, Fe_2Al_5 and FeAl (see figure 1). Under the coating, AlN acicular precipitates can form within the substrate, if the substrate contains sufficient N (≥ 0.01 wt. %) [4-6]. The coatings exhibit thickness-through cracks probably due to brittleness of the Fe_2Al_5 phase and to thermal expansion mismatch between the different phases.

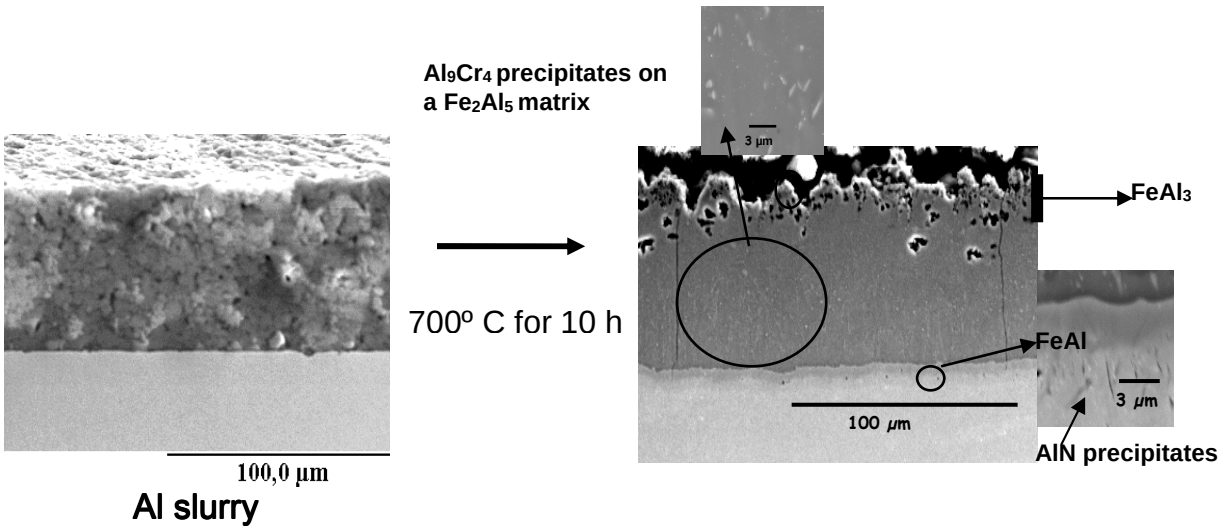
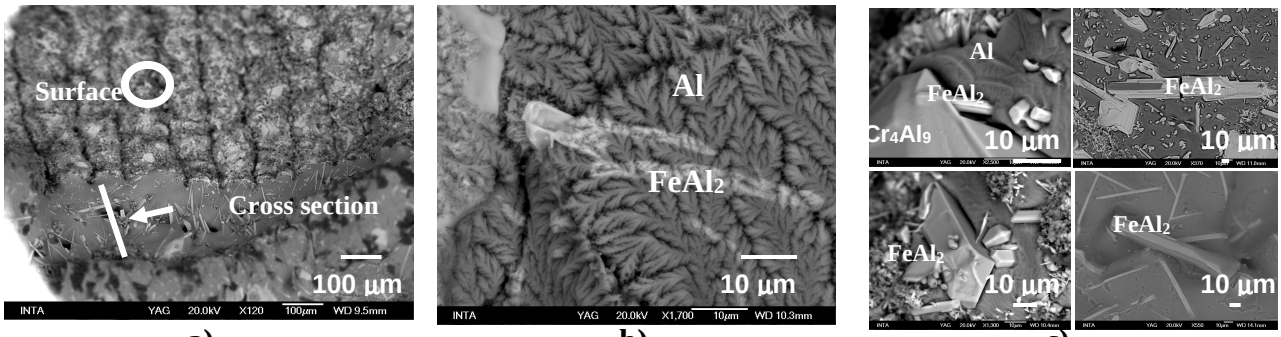


Figure 1: SEM cross sections of an "as deposited" Al slurry coating on P92 followed by heat treatment for 10 h at 700º C

The mechanism of formation of the coating involves melting of Al, followed seemingly by a complex process involving steel dissolution in molten Al, as well as liquid-solid interdiffusion, intermetallic precipitation and solid-solid interdiffusion at the coating-substrate interface. In order to better understand the coating formation process, a SEM investigation was carried out on Al

slurry coated P92 specimens were exposed to 5, 10, 30 and 60 minutes as well as 10 h of interdiffusion at 700º C. If the diffusion treatment is stopped after only 5 minutes, $FeAl_2$ acicular precipitates as well as Cr_4Al_9 are observed within re-solidified aluminium at the top of the substrate as seen in figure 2. Likely, the $FeAl_2$ precipitates continue reacting with molten Al generating the Al richer intermetallic phases $FeAl_3$ and Fe_2Al_5 that constitute the coating.



a) **b)** **c)**

Figure 2: a) SEM 3D view of the top zone of an AL-slurry coated P92 specimen heat treated for 5 min at 650º C, b) surface detail and c) cross section details

Under this layer, a 16 µm coating can be observed, including a thick Al richer layer on top of a very thin Al poorer layer (figure 3a). AlN acicular precipitates (100 nm - 1 µm in length), can be observed within the inner layer as well as in the substrate. EDS analysis indicates a higher Al:Fe ratio near the surface equivalent to $FeAl_3$, as well as several types of very small Cr rich precipitates (white particles) are also present mostly localized within the bottom half of the intermetallic. EDS analysis indicates that the thin layer Al poorer layer is very likely FeAl. In the significantly thicker (36 µm) coating observed in the 10 minute specimen, the Cr rich precipitates seem to tend to align in parallel with the coating surface defining two coating zones, an outer precipitate-free zone with some degree of porosity and an inner precipitate-rich layer. The microhardness of the most external zone is 860 HV whereas that of the zone found beneath the aligned precipitates is 980 HV. The reported values for $FeAl_3$ and Fe_2Al_5 are 892 and 1013 HV respectively [7, 8], and therefore the observed layers could very well be these two phases. TEM electron diffraction confirmed that the top Al richer layer is indeed $FeAl_3$ whereas the thicker zone below the precipitates is Fe_2Al_5. The accumulation of Cr rich precipitates at the inter-phase

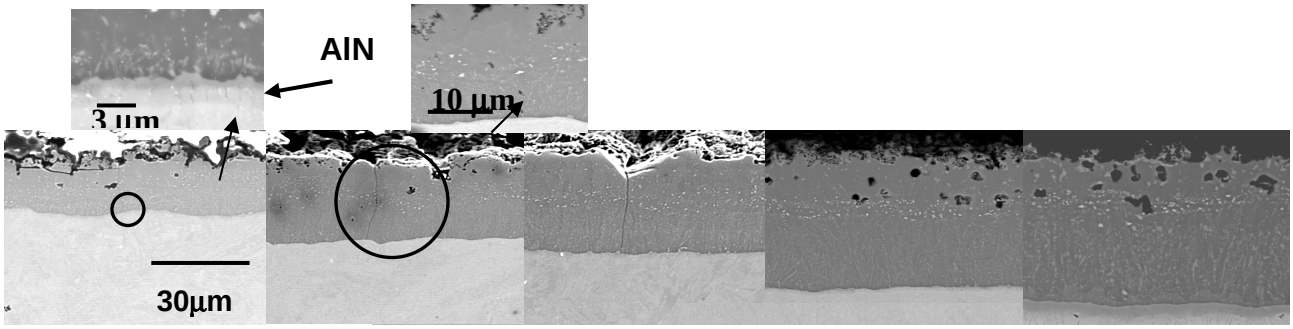


Figure 3: Cross section SEM micrograph of an Al slurry coating on P92 heat treated for 700º C

zone may be caused by a lower solubility in Fe_2Al_5. The 30 and 60 minutes specimens are similar but the Fe_2Al_5 zone below the precipitates has progressively grown in thickness whereas the $FeAl_3$ layer appears to remain constant at about 10-15 µm, but with an increasing degree of porosity.

Finally, the 600 min specimen exhibits a slightly thicker Fe_2Al_5 zone, as well as a thicker FeAl inner layer.

This coating is very protective under a steam atmosphere at 650º C, exceeding 60,000 h in the laboratory and at least 21,000 under supercritical real operating conditions [9]. The initial Fe-Al intermetallic phases evolve as a function of time when exposed to steam at 650º C due to Al inwards as well as Fe outwards diffusion (figure 4). For instance, Fe_2Al_5 transforms into FeAl which starts "precipitation within" the Fe_2Al_5 zone as seen in the specimen taken after 4,600 h of exposure. As Al diffuses deeper within the substrate, AlN continues to precipitate reaching a depth of approximately 200 μm from the coating-substrate interface after 60,000 of exposure. It has also been shown that the cracks present in the as heat treated coating do not propagate into the substrate on exposure to steam at 650º C [10], and that the coating does not affect significantly the creep and the thermo-mechanical fatigue behavior of the substrate [11]. Under steam, the coating initially develops protective χ-Al_2O_3 scale, which slowly transforms into α-Al_2O_3 despite the relatively low temperature. However, after the Al content beneath the scale reaches a critical value (< 7 wt %) Fe and Cr start diffusing into the scale forming a mixed oxide, still protective but not as stable as α-Al_2O_3 [12].

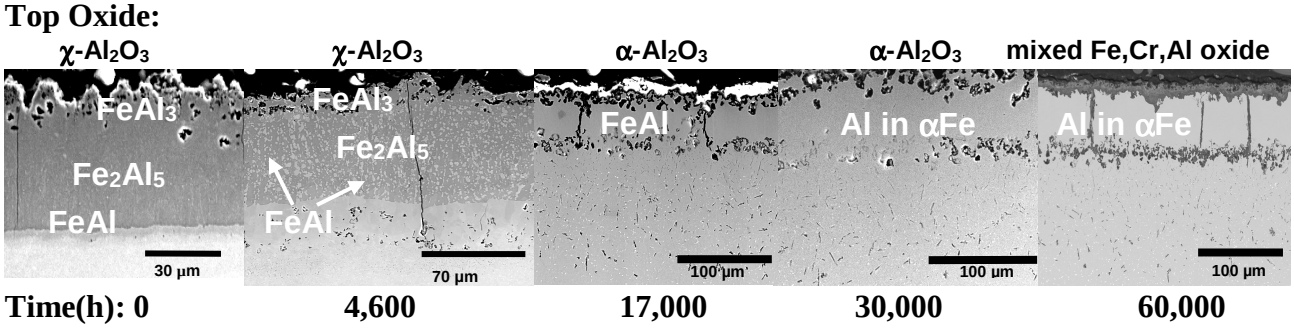


Figure 4: Cross section SEM micrograph of an Al slurry coating on P92 heat treated for 700º C and exposed to steam at 650º C

The Al concentration profile for specimens exposed at different times is shown in figure 5. A clear decrease is observed as a function of time, as well an increase in the diffusion depth within the substrate. However, the initial coating thickness does not vary significantly as a function of time.

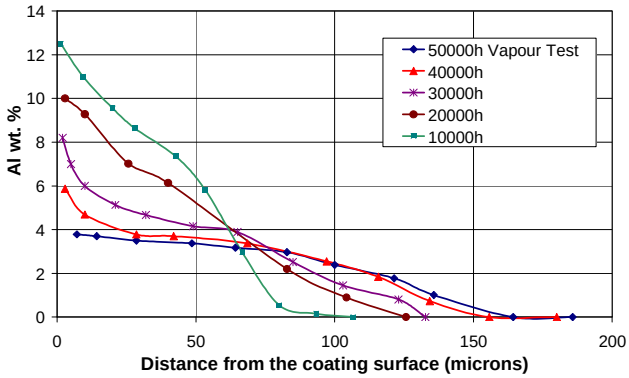


Figure 5: Al content (wt. %) as a function distance from the coating surface for coated specimens exposed to steam for different times at 650º C.

Depending on the heat treatment to which the Al-slurry coated specimen is subjected, different phases will be formed. For instance, a 10 h heat treatment at 1,000 º C will produce only the FeAl

phase over a thick AlN precipitation zone, and a higher degree of Kirkendall porosity is present between these two zones (figure 6). In this case, no through thickness cracks are observed. This may be due to FeAl being less brittle than Fe_2A_5 and/or a lower thermal expansion coefficient mismatch between FeAl and the substrate.

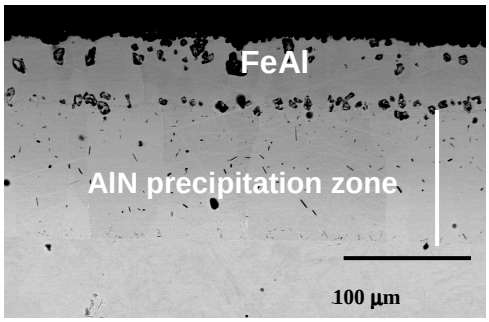


Figure 6: Cross section SEM micrograph of an Al slurry coating on P92 heat treated for 10 h at 1000º C

This study has shown how different phases within the Fe-Al intermetallic phase diagram can be obtained as function of temperature and exposure time when employing Al slurries on P92. The resulting coatings are protective under steam for over 60,000 h of exposure at 650º C as they generate a protective Al_2O_3 scale which transforms into Al, Cr, Fe mixed oxides when the Al content beneath the scale reaches a critical value below 7 wt. %

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