HIGH TEMPERATURE OXIDATION PERFORMANCE OF ALUMINIDE COATINGS

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ABSTRACT

In order to determine the potential benefits and limitations of aluminide coatings, coatings made by chemical vapor deposition (CVD) on Fe- and Ni-base alloy substrates are being evaluated in various high-temperature environments. Testing of coatings on representative ferritic (Fe-9Cr-1Mo) and austenitic (type 304L stainless steel) alloys has found that high frequency thermal cycling (1h cycle time) can significantly degrade the coating. Based on comparison with similar specimens with no thermal cycling or a longer cycle time (100h), this degradation was not due to Al loss from the coating but most likely because of the thermal expansion mismatch between the coating and the substrate. Several coated Ni-base alloys were tested in a high pressure (20atm) steam-CO_2 environment for the ZEST (zero-emission steam turbine) program. Coated specimens showed less mass loss than the uncoated specimens after 1000h at 900°C and preliminary characterization examined the post-test coating structure and extent of attack.

INTRODUCTION

Aluminide coatings are of interest for many high temperature applications because of the possibility of improving the oxidation resistance of structural alloys by forming a protective external alumina scale.[1-5] Steam and exhaust gas environments are of particular interest because alumina is less susceptible to the accelerated attack due to hydroxide formation observed for chromia- and silica-forming alloys and ceramics.[6-13] For water vapor testing, one ferritic (Fe-9Cr-1Mo) and one austenitic alloy (304L) have been selected as substrate materials and CVD coatings have been used in order to have a well-controlled, high purity coating. It is anticipated that similar aluminide coatings could be made by a higher-volume, commercial process such as pack cementation. Previous work on this program has examined as-deposited coatings made by high and low Al activity CVD processes and the short-term performance of these coatings.[5,14,15] The current work is focusing on the long term behavior in both diffusion tests[16] and oxidation tests of the thicker, high Al activity coatings. For long-term coating durability, one area of concern has been the coefficient of thermal expansion (CTE) mismatch between coating and substrate.[5] This difference could cause cracking or deformation that could reduce coating life. Corrosion testing using thermal cycling is of particular interest because of this potential problem and results are presented where a short exposure cycle (1h) severely degraded aluminide coatings on both types of substrates.

To further study the potential role of aluminide coatings in fossil energy applications, several high creep strength Ni-base alloys were coated by CVD for testing in a high pressure (20atm) steam-CO_2 environment for the ZEST (zero-emission steam turbine) program. Such alloys would be needed as structural and turbine materials in this concept. For Ni-base alloys, CVD produces a ≈50µm β-NiAl outer layer with an underlying interdiffusion zone. Specimens of HR160, alloy 601 and alloy 230 were tested with and without coatings at 900°C and preliminary post-test characterization is reported.

EXPERIMENTAL PROCEDURE

The substrates used in this study include Fe-9Cr-1Mo, type 304L stainless steel (Fe-18Cr-9Ni nominally), HR160 (Ni-30Co-28Cr-2.8Si-2Fe), alloy 601 (Ni-22.5Cr-14Fe-1.4Al) and alloy 230 (Ni-23Cr-12W-1.5Fe-1.4Mo). The laboratory-scale CVD reactor and coating process have been described elsewhere.[5,15] For the Fe-base alloys, the higher Al activity was achieved by including Cr-Al alloy pellets in the reactor during deposition for 4h at 1050°C.[15] Characterization of the as-deposited coatings has been provided elsewhere.[14-16] The Ni-base alloys were coated in the same reactor for 6h at 1100°C using a procedure developed for monocrystal Ni-base superalloys.[17,18] Mass gains for the coatings on HR160 averaged 2.4mg/cm^2 which was lower than that observed for alloy 230 (4.2mg/cm^2) or alloy 601 (3.8mg/cm^2).

For the Fe-base alloys, the oxidation testing focuses on 700°C where the substrate alloys are adversely affected by environmental effects but some strength is retained. Cyclic oxidation testing in air with 10±0.5 vol.%H_2O was conducted two ways: (1) in a vertical automated test rig with the specimens suspended from alumina rods using Pt-Rh wire and a cycle consisting of 1h at temperature and 10min cooling at room temperature or (2) in a horizontal tube furnace with the specimens in an alumina boat, the cycle consisting of 100h at temperature with the specimens cooled and weighed after each cycle. In each case, both ends of the high-purity alumina reaction tube were closed and the water vapor was controlled in the carrier gas by a water injection system described elsewhere.[19] For the Ni-base alloys, the high pressure tests were conducted at 2.1 GPa (300 psi) in an alloy 230 reaction tube using a steam-10%CO_2 atmosphere in one of the ORNL Keiser rigs.[20,21] The testing in laboratory air was conducted in box furnaces with the specimens contained in alumina crucibles with lids.[22]

Before and after exposures, specimens were weighed on a Toledo-Mettler model AG245 balance. Selected specimens were examined by light microscopy, field emission gun, scanning electron microscopy (SEM) equipped with energy dispersive x-ray analysis (EDXA) and electron probe microanalysis (EPMA) using wavelength dispersive x-ray. For cross-sections, the surface reaction product was protected by Cu-plating the specimen prior to mounting in epoxy.

RESULTS AND DISCUSSION

Fe-BASE ALLOYS TESTED AT 700°C

Previous testing of CVD coatings on Fe-base substrates for up to 1000, 1h cycles at 700°C in air with 10vol% H_2O had shown excellent coating performance.[14] Without a coating, 304L and Fe-9Cr-1Mo were severely attacked after short exposures in this environment, Figure 1. However, small cracks were noted by SEM in the surface of the thicker coatings after 1000h, Figures 2a and 2b. Limited spallation of the external scale was noted on 304L but not on Fe-9Cr-1Mo where deeper cracks in the coating were observed. Therefore, the test was continued to 2000h. After 2000h, the coated 304L specimen showed a significantly higher mass gain while the coated Fe-9Cr-1Mo specimen began to show an increase towards the end of the second 1000 cycles, Figure 1. Examination of the specimens after 2000 cycles revealed even more extensive macroscopic damage to the coating, Figures 2c and 2d, so the test was stopped and

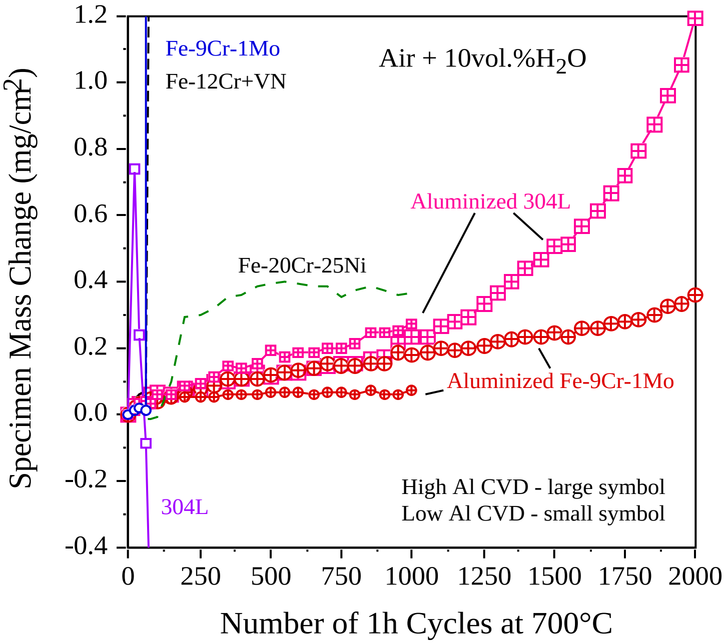

Figure 1. Specimen mass changes during 1h cycles at 700°C in air+10%H_2O. Results are shown for specimens coated with both the high (larger symbol) and low (smaller symbol) Al activity processes.

the coatings were sectioned.

Figure 3a shows the entire thickness of the Fe-9Cr-1Mo coated specimen revealing large cracks through the coating and, in one location, the coating had been penetrated and oxidation of the substrate had begun. At higher magnification, Figure 4a, a crack appears to extend from the outer layer deep into the inner coating layer. For the coated 304L specimen, Figure 3b shows similar cracking and degradation where the coating had been breached at the specimen edge. At higher magnification, Figure 4b, the cracks generally

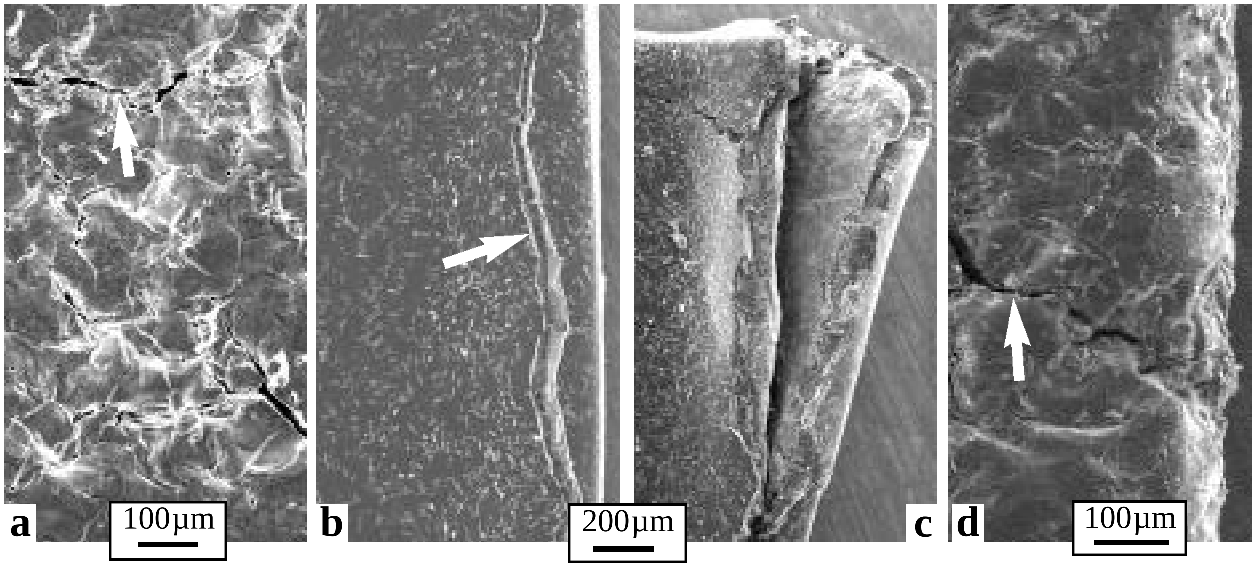

Figure 2. SEM secondary electron plan-view images of coated specimens exposed in 1h cycles at 700°C in humid air; (a) Fe-9Cr-1Mo after 1000 cycles, (b) 304L after 1000 cycles, (c) 304L after 2000 cycles and (d) Fe-9Cr-1Mo after 2000 cycles. Arrows point to cracks in the coating.

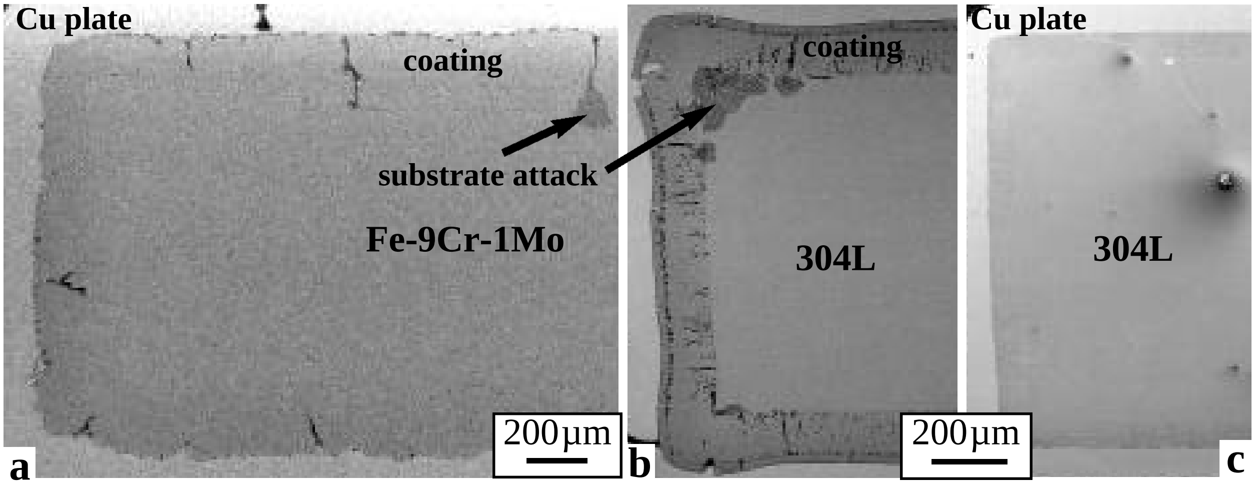

Figure 3. SEM secondary electron cross-sectional images of the coated specimens (a) Fe-9Cr-1Mo and (b) 304L after 2000, 1h cycles at 700°C in humid air, and (c) 304L after an isothermal 2000h exposure at 700°C in laboratory air.

appeared to remain in the outer, Al-rich layer. More pores were observed in this coating than in the ferritic specimen.

The cracks in the coatings are attributed to the CTE mismatch between the coating and substrates. Two pieces of evidence support this hypothesis. First, similar coated specimens were isothermally exposed for 2000h at 700°C in air. After exposure, no deformation or cracking was observed, e.g., Figure 3c, and examination of the Al content of coatings exposed in dry air and humid air showed little depletion compared to the as-deposited coating, Figure 5a. (Some variation in the starting Al content and thickness

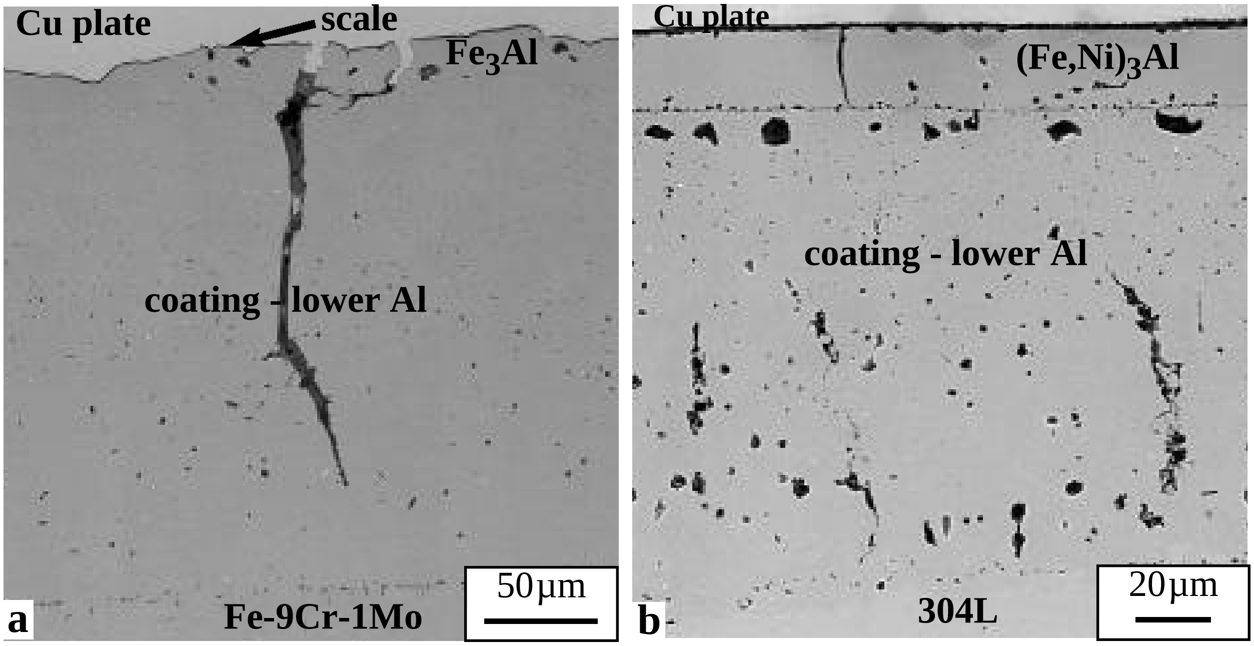

Figure 4. SEM secondary electron cross-sectional images of the coated specimens after 2000, 1h cycles at 700°C in humid air, (a) Fe-9Cr-1Mo and (b) 304L. The coatings consist of an outer Al-rich layer and an inner, thicker layer with a gradually declining Al content.

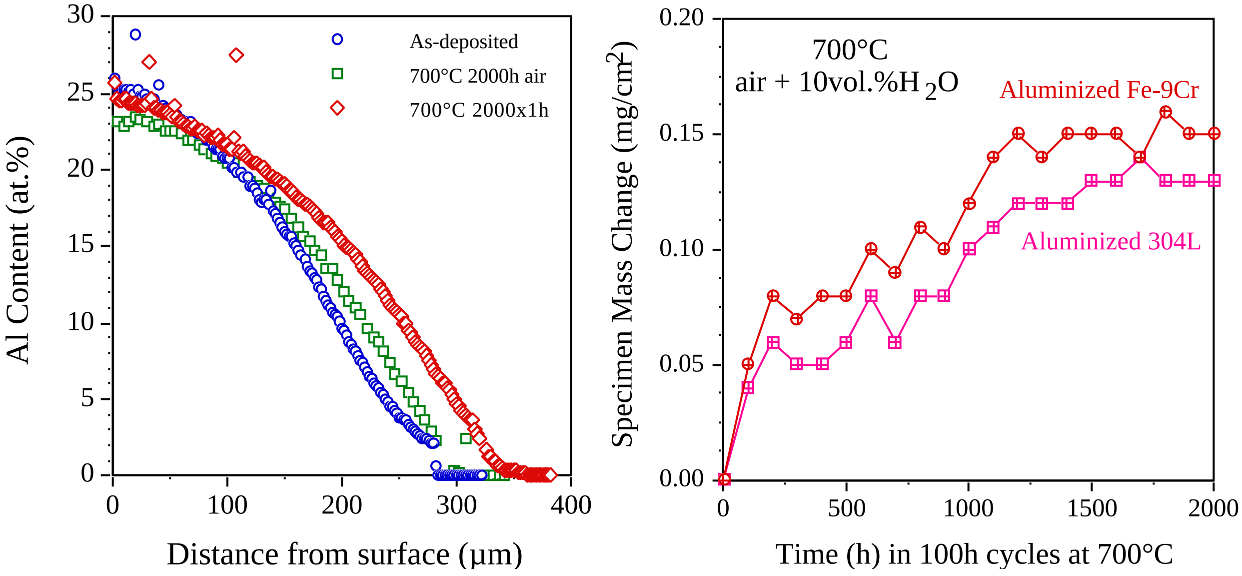

Figure 5. (a) EPMA Al profiles from an as-deposited coating, a coating exposed for 2000h in air and the coating exposed for 2000 1h cycles in humid air. (b) specimen mass gains for coatings exposed in 100h cycles at 700°C in humid air.

may explain the slightly higher Al content in the coating exposed in humid air.) Second, coated specimens are currently being tested in 100h (rather than 1h) cycles at 700°C in air + 10%H_2O and no accelerated attack has been observed after 2000h of testing, Figure 5b. Both of these results suggest that the thermal cycling causes the cracking in the coating and an accumulation of cyclic damage is needed to compromise the oxidation resistance of the coatings. Because of the limited Al diffusion after 2000h, it is anticipated that the coatings in the 100h cycle test may have a significantly longer lifetime than those in the 1h cycle test. The thermal cycling damage to the coating was more severe on the 304L specimen than the Fe-9Cr-1Mo. One explanation for this is that 304L retains more strength at this temperature than the ferritic alloy. A weaker substrate may allow more stress relaxation in the coating layer compared to a stronger substrate. Another possible reason is that the diffusion of Al into the 304L substrate may have caused the inner coating layer to become ferritic. This would result in three different CTE's in the three layers resulting in more strain during each cycle. In the case of the coating on the ferritic substrate, both the substrate and the inner coating layer would remain ferritic.

Ni-BASE ALLOYS AT 900°C

In order to evaluate the potential environmental problems for hot section materials in ZEST, three Ni-base alloys were tested with and without aluminide coatings at 900°C and 1135°C in the anticipated high-temperature, high-pressure ZEST environment (steam-10%CO_2). The full range of results will be reported elsewhere.[21] A summary of the mass change data at 900°C is given in Figure 6. Figure 6a shows that specimen mass gain of the coated and uncoated Ni-base alloys, 601, HR160 and 230, after 2, 500h cycles in the high pressure ZEST test. In each case, the aluminized specimens (arrows) showed less mass change than the uncoated alloys. For comparison, the performance of two alumina-forming alloys, MA956 (FeCrAl) and alloy 214 (NiCrAl), and type 310 stainless steel (Fe-25Cr-20Ni) also are included. In general, the aluminized specimens and alumina-forming alloys showed low mass gains for the test whereas the chromia-forming alloys tended to show higher mass gains due to the formation of faster growing chromia scales or mass losses due to scale spallation and/or volatilization. Figure 6b compares the

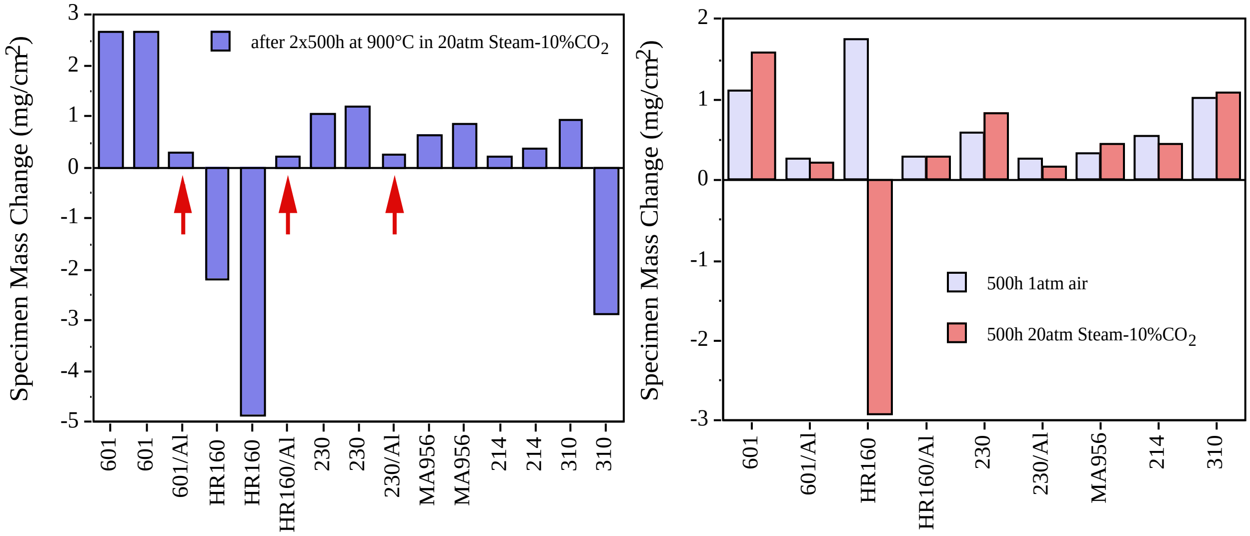

Figure 6. Specimen mass changes (a) after 2, 500h cycles at 900°C in the ZEST test (steam-10%CO_2 at 20atm) and (b) after 500h at 900°C in air and ZEST test.

performance of the same alloys after 500h (1 cycle) at 900°C in the ZEST test conditions and in laboratory air. The aluminized alloys showed similar behavior in air and in the high pressure steam-CO_2 environment. In contrast, the uncoated Ni-base alloys showed higher mass gains or losses in the ZEST test conditions, suggesting a susceptibility to the steam-CO_2 environment. In order to obtain long-term performance data on the aluminized Ni-base alloys, one specimen of each composition is being oxidized in air at 900°C in 500h cycles, Figure 7. After up to 3000h of exposure, the coated specimens are all showing low mass gains and no spallation. The mass gains for the coated specimens after 3000h in air are lower than the uncoated alloys after 500h.

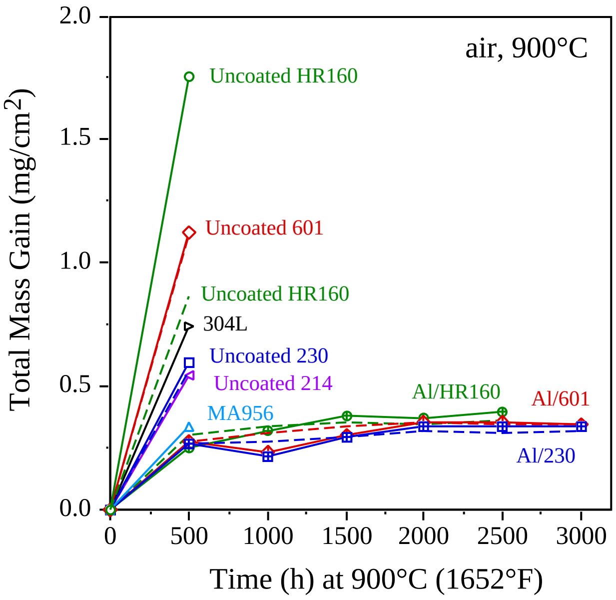

Figure 7. Specimen mass changes during 500h cycles at 900°C in air with and without aluminide coatings. The solid lines show the total mass gain and the dashed lines show the specimen mass gains.

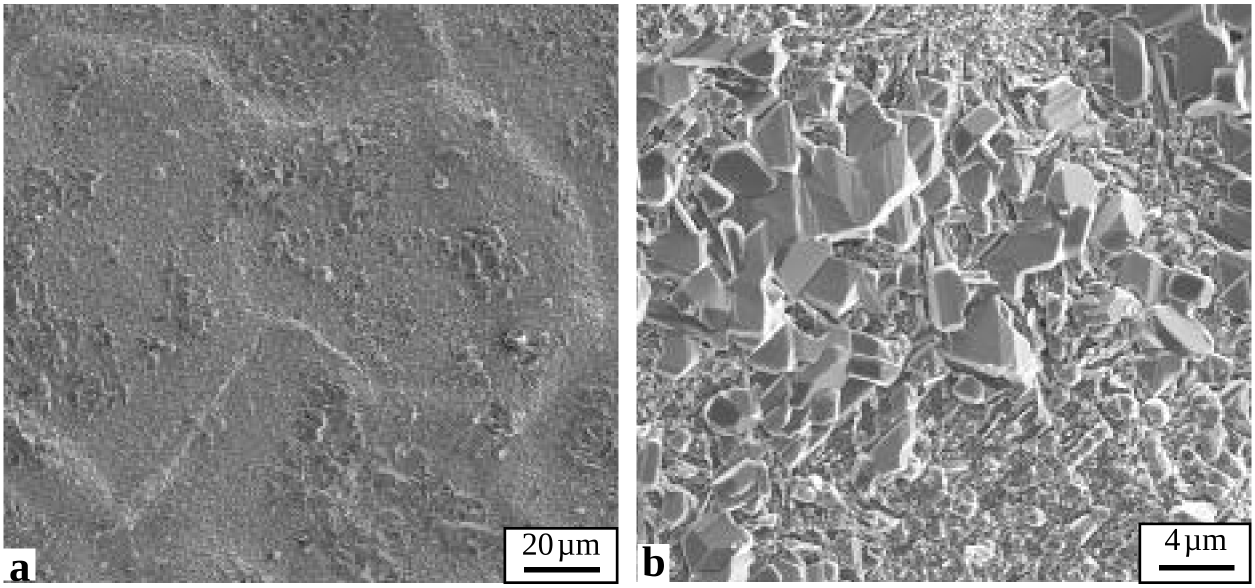

Figure 8. SEM secondary electron plan view images of the scale formed on aluminized alloy 601 after 2, 500h cycles at 900°C in steam-10%CO_2 at 20atm.

The surface scale was examined on the aluminized specimens after 2, 500h cycles at 900°C in the ZEST test conditions. Figure 8 shows plan-view SEM images of the scale formed on aluminized alloy 601 that were typical of all three coated specimens. The slight ridges in Figure 8a mark coating grain boundaries and are typical of the surface morphology of CVD aluminide coatings. At higher magnification, Figure 8b, some larger oxide grains were observed that were rich in Ni. The formation of transient Ni-rich oxide has not been observed in previous work on aluminized Ni-base superalloys in air at 1100°-1200°C.[17-18] The formation may be due to the lower oxidation temperature or the environment. In cross-section, Figure 9, the coatings showed several common features typical of aluminide coatings: a thin, adherent surface oxide, a uniform β-(Ni,Al) coating with some lighter phases (likely lower Al content γ'-Ni_3Al) and an underlying interdiffusion layer. One unusual feature was noted on alloy 230, where voids were observed in the interdiffusion zone, Figure 9c. These may have occurred as a result of diffusion during the aluminization process or may reflect some type of coating penetration during the test. One troubling aspect of these cross-sections is the nearly single-phase, Cr-rich interdiffusion zone. The interdiffusion

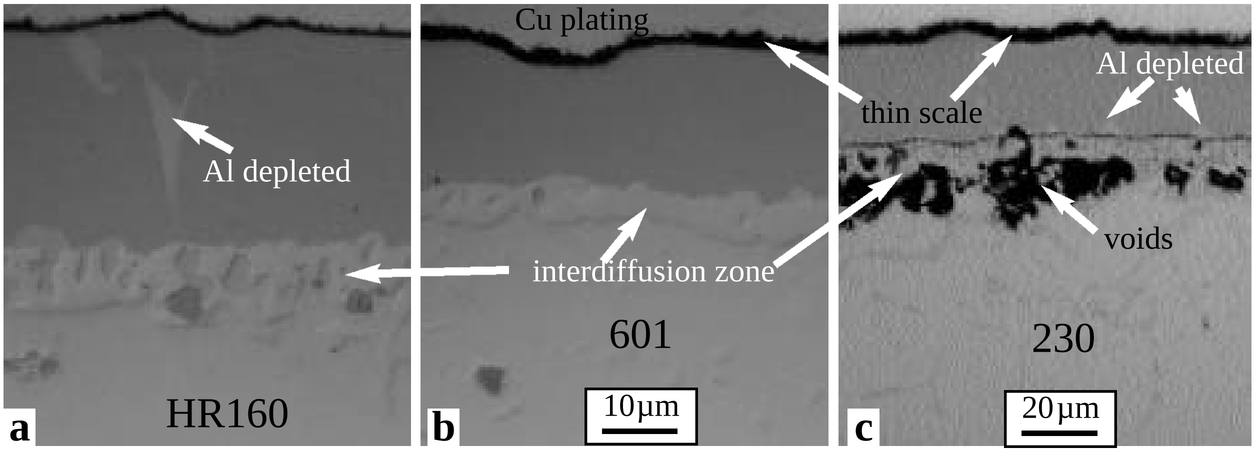

Figure 9. Light microscopy of polished cross-sections of aluminide coatings after 2, 500h cycles at 900°C in the ZEST test: (a) HR160 (b) alloy 601 and (c) alloy 230.

zone becomes enriched in refractory elements when Ni diffuses out to form the NiAl coating. However, monocrystal superalloys with lower Cr contents (6-8wt.%) form an interdiffusion zone which is a mixture of refractory-rich topologically close-packed (TCP) phases and a Ni-base γ matrix.[18] The Cr-rich layer, which is likely a TCP phase, may have poor high temperature fatigue resistance or be susceptible to environmental embrittlement. More work is needed to clarify these issues. However, a MCrAlY-type overlay coating may be more appropriate to protect these alloys for ZEST-type environments.

SUMMARY

Long-term testing of CVD aluminide coatings on one ferritic (Fe-9Cr-1Mo) and one austenitic (304L) Fe-base substrate showed that high frequency cycling caused failure after less than 2000h at 700°C in air+10%H_2O. The deformation and cracking could not be attributed to the environment or the loss of Al due to corrosion or back diffusion. The most likely cause is the thermal expansion mismatch between the Fe_3Al outer coating and the substrate. Initial testing of aluminized Ni-base alloys in a high pressure, high temperature ZEST-type environment showed good performance of the coatings under these conditions.

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