

Some Water Vapor Effects during the Oxidation of Alloys that are α -Al₂O₃ Formers

M.C. MARIS-SIDA, G.H. MEIER, and F.S. PETTIT

Oxidation studies were performed at 1100 °C in dry air and air containing fixed partial pressures of water vapor on a number of alloys and coatings that form α -Al₂O₃ scales under oxidizing conditions. The alloys investigated included RENÉ N5, PWA 1484, diffusion aluminide coatings (with and without Pt modification) on RENÉ N5, and a Ni-8 wt pct Cr-6 wt pct Al model alloy. The water vapor affected the oxidation of the alloys in three important ways: (1) The scales spalled more profusely during cyclic oxidation in wet air than in dry air, particularly for those alloys with alumina scales, which are only moderately adherent under dry conditions. The results were consistent with the mechanism previously proposed (Reference 1), whereby the water molecules decrease the fracture toughness of the alumina/alloy interface. (2) Thicker oxides are formed during oxidation in wet air than dry air. This effect comes primarily from accelerated transient oxidation during exposure in wet air. (3) Spinel was found to form on top of the alumina scales during long-term exposure. This phenomenon occurred in all atmospheres but was much more pronounced for exposures in wet atmospheres. Mechanisms for the preceding observations are proposed.

I. INTRODUCTION

WATER vapor has been found to affect the oxidation of metals and alloys in a variety of ways.^[1-15] Most of these effects are detrimental in that the oxidation rates are increased. The effect of water vapor on the oxidation of alloys that develop oxidation resistance *via* the formation of continuous α -Al₂O₃ scales is important because numerous high-temperature alloys and coatings rely on such a selective oxidation process for oxidation resistance. For these types of alloys, water vapor has been shown to cause the α -Al₂O₃ scales to crack and spall.^[1,15-17] It has been proposed that water vapor lowers the toughness of the α -Al₂O₃/alloy interface. For alloy systems with extremely adherent α -Al₂O₃ scales, water vapor did not cause substantial cracking and spalling of the oxide. It appears that when the interfacial toughness is very high, even with water vapor interaction, the interfacial toughness is still sufficient to inhibit spalling.

The major effect of water vapor on the oxidation resistance of the alumina formers appears to be increased cracking and spalling of the oxide scales. However, Buscail *et al.*^[14] have reported that water vapor causes the transient stage, during which the continuity of the α -Al₂O₃ is being established, to be extended. There are also some results available that show other phases (*i.e.*, Ni (Al,Cr)₂O₄, Cr₂O₃) may form on α -Al₂O₃ scales as the substrate alloys become depleted of aluminum. In some cases, this phase is spinel (*i.e.*, Ni (Al,Cr)₂O₄) and is observed at the α -Al₂O₃/gas interface,^[18,19] whereas in the other cases, this phase is Cr₂O₃ and is located at the α -Al₂O₃/alloy interface.^[20] This article is concerned with examining in more detail the cracking and spalling of α -Al₂O₃ scales in

water vapor, as well as investigating the effects of water vapor on the selective oxidation of aluminum and spinel development on α -Al₂O₃ scales.

II. EXPERIMENTAL

Both isothermal and cyclic oxidation experiments were performed. Cyclic oxidation conditions were achieved by moving the specimens in and out of a furnace once every hour, 45 minutes in the hot zone at 1100 °C and 15 minutes in the cool zone at 100 °C. The experiments were performed in dry air with a dew point of -46 °C ($P_{\text{H}_2\text{O}} = 6 \times 10^{-5}$ atm) and in air saturated with water at 46 °C ($P_{\text{H}_2\text{O}} = 0.1$ atm) and at 88 °C ($P_{\text{H}_2\text{O}} = 0.5$ atm). The air was saturated with water vapor by passing air through two consecutive water baths at the required temperature. The gas flowed through the reaction tube at 0.1 cm/s. The specimens were coupons about 1-cm square and 2-mm thick and were moved from the hot zone to the cool zone or *vice versa* in 250 seconds. The specimens were removed periodically from the apparatus and weight change measurements were performed along with visual examination of the specimens. Upon conclusion of the tests, the specimens were examined in detail using optical metallography, scanning electron microscopy, and X-ray diffraction techniques.

The experiments were performed on Ni-base superalloys RENÉ* N5 and PWA1484, as well as RENÉ N5 with

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aluminide and platinum-modified aluminide coatings. The compositions of the superalloys are presented in Table I. In some experiments, superalloys with low sulfur concentrations were used. These alloys had the same concentration of elements as indicated in Table I, but less than 1 ppm sulfur compared to 5 to 8 ppm sulfur in the normally processed superalloys. The aluminide coatings were prepared using CVD with conditions of high temperature and low aluminum activity. The platinum was electrolytically deposited (5 to

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Manuscript submitted August 20, 2002.

Table I. Nominal Compositions of Alloys in Weight Percent

Alloy	Ni	Al	Cr	Ta	Co	Mo	W	Re	Y	Hf
RENÉ N5	base	6.2	7.0	6.5	7.5	1.5	6.0	3.0	0.01	0.15
PWA1484	base	5.6	5.0	8.7	10.0	2.0	6.0	3.0	—	0.1
Ni-Cr-Al	base	6.0	8.0	—	—	—	—	—	—	—

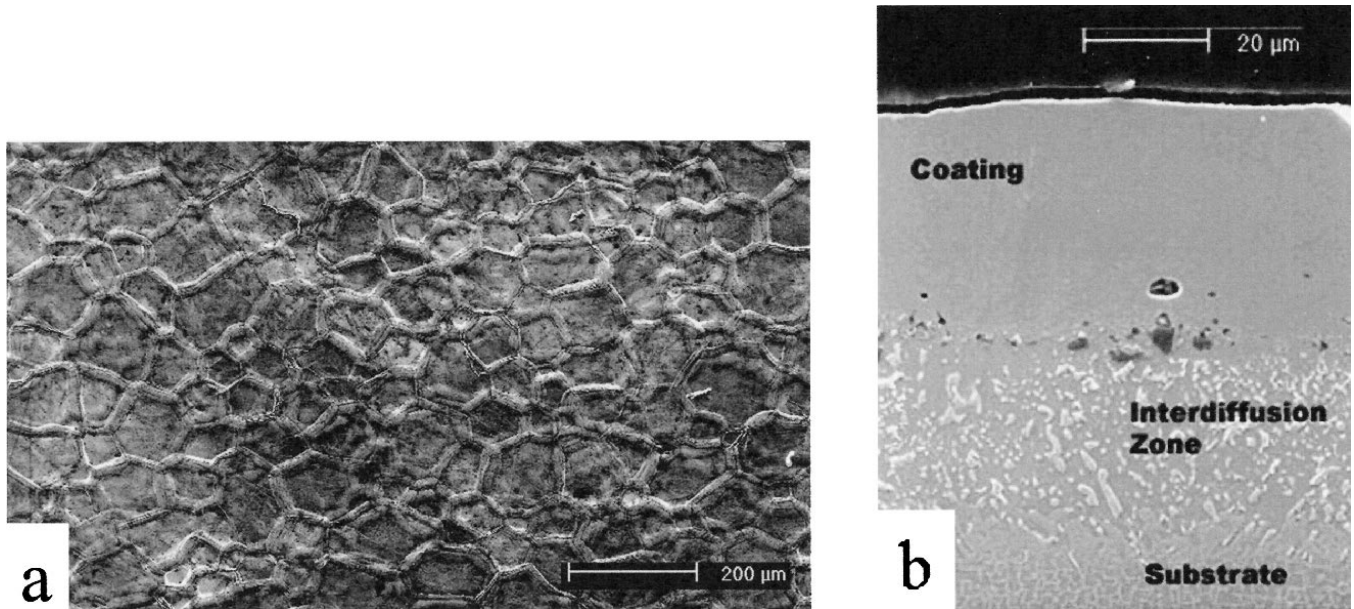


Fig. 1—SEM micrographs showing ridges on the surface of platinum-modified nickel-aluminide coatings, as processed: (a) surface image and (b) cross section.

7 μm) on the surface of the superalloy prior to the aluminizing process. A typical as-processed platinum aluminide coating is shown in Figure 1. In some of the experiments, to investigate the selective oxidation of aluminum, a Ni-8Cr-6Al alloy was used because this alloy had aluminum and chromium concentrations similar to the superalloys without the complications of additional elements.

III. RESULTS AND DISCUSSION

A. Effects of Water Vapor on Cracking and Spalling of $\alpha\text{-Al}_2\text{O}_3$ Scales

In Figure 2, weight change vs time measurements are presented for N5 and low sulfur content N5 specimens exposed at 1100 °C in gases with different amounts of water vapor. It can be seen that the weight losses are less for the low sulfur content N5 compared to N5 specimens. It is also apparent that the amount of degradation of N5 increases as the pressure of H_2O in the gas increases. Surface micrographs of specimens exposed in this test are presented in Figure 3. It can be seen that more spalling of oxide is evident for N5 compared to low sulfur content N5 and the amount of spalled oxide increases as the water vapor pressure in the gas phase is increased, whereas the water vapor pressure had no significant effect on degradation of low sulfur N5. Scanning electron micrographs showing cross-sectional views of the exposed specimens

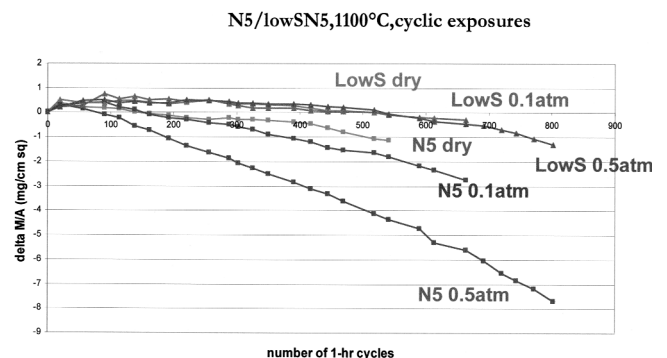


Fig. 2—Weight change vs time measurements for N5 specimens (low S and regular S) cyclically oxidized in dry and wet air at two water vapor pressures (0.1 atm and 0.5 atm).

are consistent with the previous results. An external scale containing NiO with virtually no continuous $\alpha\text{-Al}_2\text{O}_3$ is evident on the N5 specimen exposed for 802 cycles at 1100 °C in a gas mixture with 0.5 atm of water vapor, (Figure 4(a)), whereas the low sulfur N5 exposed to similar conditions (Figure 4(b)) exhibits a scale of continuous $\alpha\text{-Al}_2\text{O}_3$ with an overlayer of transient oxides. The transient oxides in the case of nickel-base superalloys such as N5 are generally NiO, Cr_2O_3 , and Ta_2O_5 , but the oxides of other elements in the alloy can also be present. With the

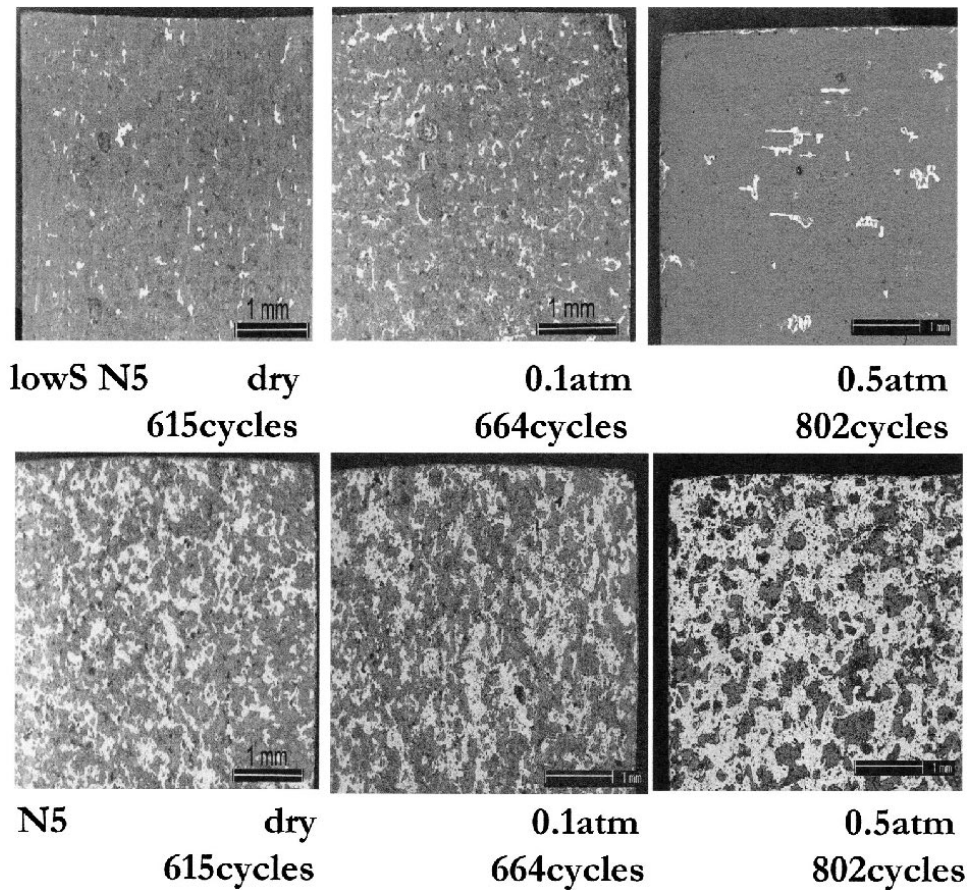
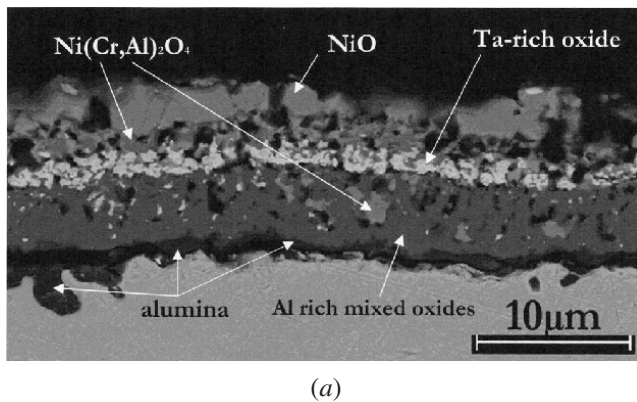
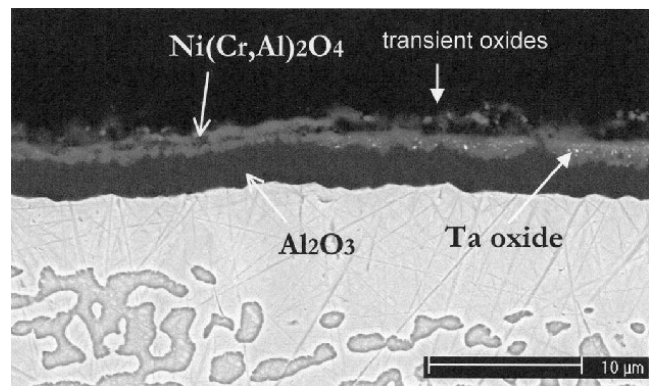


Fig. 3—Cyclic exposures at 1100 °C of RENÉ N5 and low sulfur content RENÉ N5; all surfaces: light coloration-spalled regions, darker coloration-mixed oxides, and α -Al₂O₃.



(a)



(b)

Fig. 4—(a) RENÉ N5 oxidized for 802 cycles at 1100 °C in air with 0.5 atm water vapor. The original α -Al₂O₃ has spalled. (b) RENÉ N5 (low sulfur content) exposed for 802 cycles at 1100 °C in wet air (0.5 atm water vapor). The original α -Al₂O₃ has not spalled.

exception of the reactive elements (*i.e.*, Y, Hf), α -Al₂O₃ is the most thermodynamically stable oxide. Aluminum is selectively oxidized and the transient oxides develop before the α -Al₂O₃ is formed as a continuous layer over the alloy.

In a cyclic test, if the scale does not spall, the α -Al₂O₃ layer becomes continuous for sufficiently long exposure times and the oxidation rate is controlled by diffusion through the α -Al₂O₃ scale. The transient oxides can react with the α -Al₂O₃

to form spinels (*e.g.*, NiAl₂O₄, NiCr₂O₄). A schematic description of such scales is shown in Figure 5. When the scales spall during cyclic oxidation, the oxide scales that develop subsequently exhibit much more transient oxides because the alloy has been depleted of aluminum (Figure 4(a)) and the α -Al₂O₃ layer requires long exposure times to develop continuity (Figure 5). For short cycles, the α -Al₂O₃ layer may not develop continuity and the weight losses are large (Figure 2).

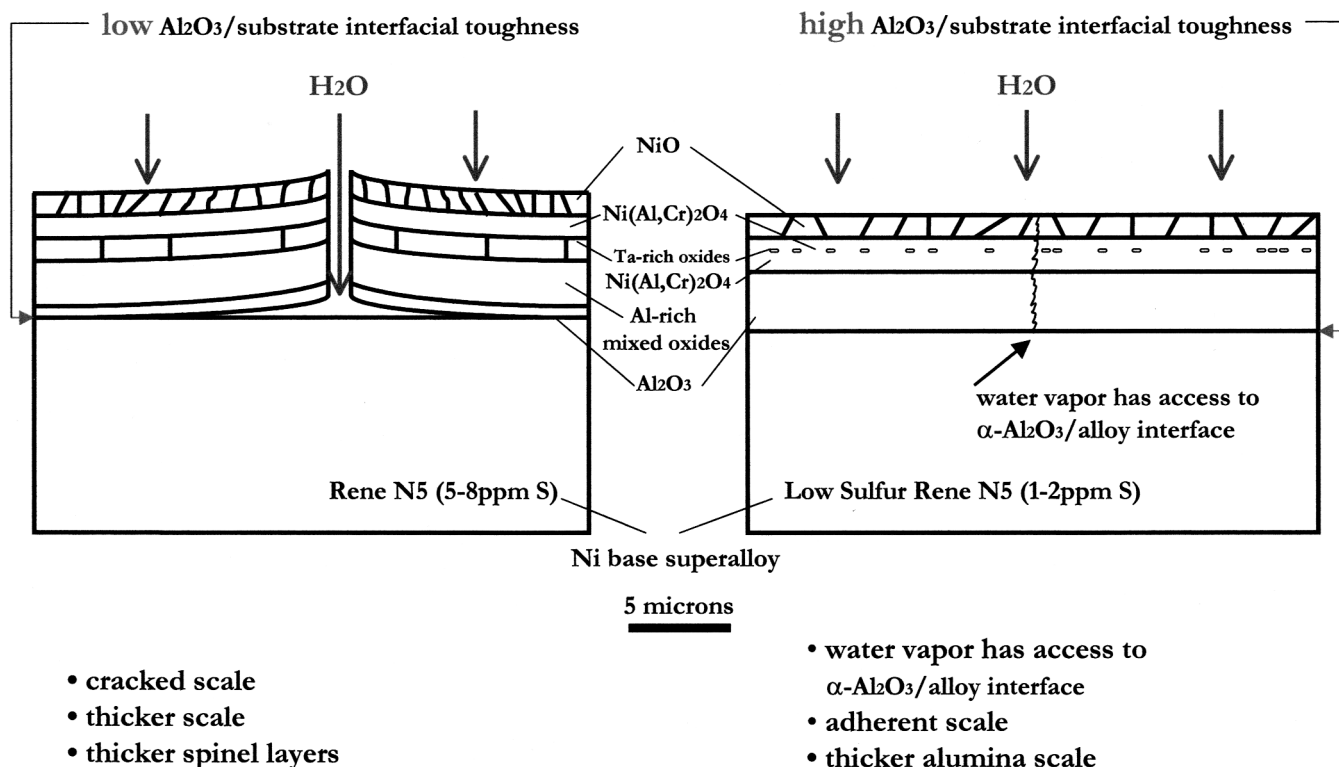


Fig. 5—Schematic showing scales formed on cyclic exposures (hundreds of cycles) at 1100 °C in wet air. When sulfur is present (5 to 8 ppm), the ingress of water vapor along the α -Al₂O₃/alloy interface is rapid.

The results that have been obtained with low sulfur N5 and N5 are consistent with results obtained previously^[1] on other alloy systems (PWA1480, PWA1484, CMSX4). The cracking and spalling of the α -Al₂O₃ scales is more severe in water vapor and this effect becomes less evident as the interfacial toughness becomes greater. Such results are also observed with aluminide coatings (Figure 6), where the α -Al₂O₃ scales are substantially more adherent on a platinum aluminide coating compared to a straight aluminide coating.

As indicated schematically in Figure 5, when the α -Al₂O₃/alloy interface is weak, water vapor causes spalling, whereas when it is strong, spalling of the α -Al₂O₃ is greatly reduced. Kronenberg *et al.*^[21] have determined that annealing α -Al₂O₃ in supercritical water between 650 °C and 1025 °C under pressures in the range 1500 to 2000 MPa introduces interstitial hydrogen defects (H_i^*) and molecular water clusters. These clusters were found to segregate to surfaces, grain boundaries, and cracks. The strength of both α -Al₂O₃ single crystals and polycrystals were reduced by this hydrothermal treatment.^[22] Smialek and Morscher^[23] propose that sulfur and water vapor may interact to promote spalling of α -Al₂O₃ scales. In particular, sulfur at the α -Al₂O₃/alloy interface causes bond stretching and weakening, whereby ingress of H₂O proceeds more rapidly with the final result of oxide scale spalling due to formation of weak Al–OH bonds. It is proposed that water vapor must cause the α -Al₂O₃/alloy interfacial toughness to be decreased, but when this toughness is high, as occurs for α -Al₂O₃ on low sulfur content N5 and on platinum aluminide coatings, the magnitude of the toughness decrease is not sufficient to

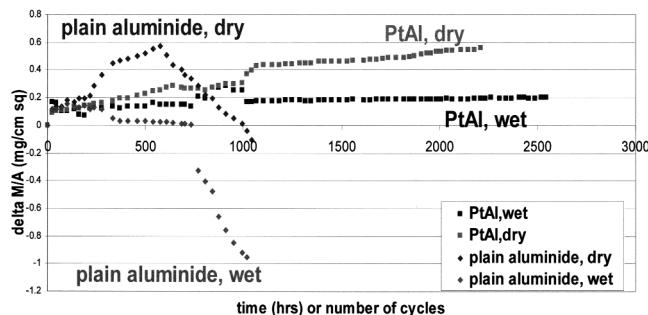


Fig. 6—Change in mass vs time; aluminide coatings cyclically exposed at 1100 °C, dry and wet (0.1 atm) air.

cause significant amounts of oxide scales to spall. The mechanism by which water vapor has access to the α -Al₂O₃/alloy interface may be *via* small cracks that develop in the α -Al₂O₃ during thermal cycling.^[1] In view of Kronenberg *et al.*^[21] results, water vapor may diffuse through α -Al₂O₃ *via* grain boundaries.

B. The Effects of Water Vapor on the Selective Oxidation of Aluminum in Alloys

In order to examine the effect of water vapor on the selective oxidation of aluminum in alloys, specimens of PWA1484 were polished through 600 SiC paper and exposed in water vapor and dry air for 10 minutes at 1100 °C. As can be seen in Figure 7, under water vapor conditions, the growth of the transient oxides is accelerated and the amount of NiO in the scale is quite large. Generally, a thicker, multilayered scale

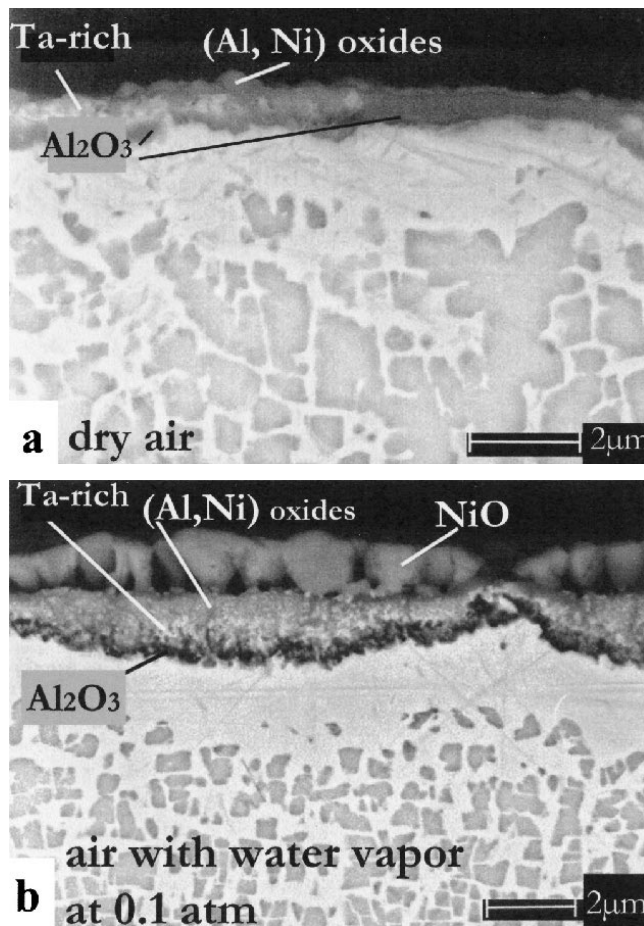


Fig. 7—PWA 1484 isothermally oxidized for 10 min at 1100 °C (initial surface condition 600 grit SiC paper): (a) dry air and (b) air with water vapor at 0.1 atm.

forms on specimens exposed in wet air. When specimens were exposed at 1100 °C to two different water vapor pressures, it appeared that more transient oxidation was evident on the specimen that was exposed to the higher pressure (Figure 8). Specimens of Ni-8 wt pct Cr-6 wt pct Al were exposed for 1 hour at 1100 °C to dry air and air containing 0.1 atm water vapor. As can be seen in the surface micrographs of the exposed specimens, the specimen exposed in dry air formed a continuous scale of α -Al₂O₃ (Figure 9(a)), whereas the specimen exposed to the gas containing water vapor (Figure 9(b)) exhibited stringers of NiO and α -Al₂O₃. The stringers of NiO appeared to be associated with polishing marks on the specimen's surface. Previous work has shown that selective oxidation of elements can be affected by the surface preparation conditions of specimens.^[24] Since the previous specimens had been polished through 600 SiC abrasive paper, additional specimens of Ni-8Cr-6Al were exposed after polishing the specimens through 0.05- μ m α -Al₂O₃. As shown in Figure 10(a), a continuous alumina layer was formed on this specimen upon exposure for 1 hour in dry air. The specimen exposed for 1 hour at 1100 °C in air with 0.1 atm water vapor formed an oxide scale that was rich in NiO, but α -Al₂O₃ appeared to develop at what may have been grain boundaries in the alloy (Figure 10(b)). The surface of this specimen is shown at higher magnification in Figure 11(a), where different oxides are evi-

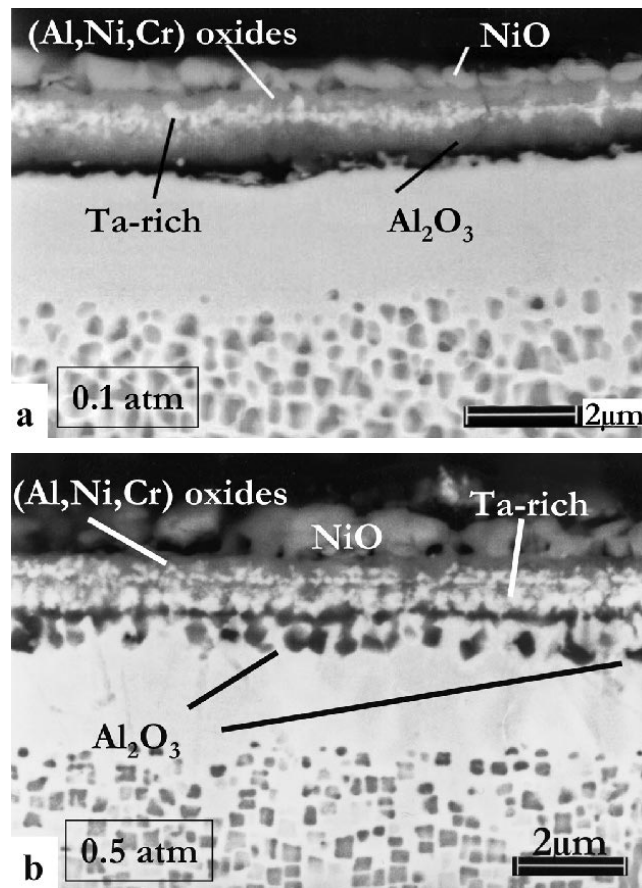


Fig. 8—PWA1484 (low S) oxidized isothermally at 1100 °C for 10 min in air with water vapor (600 grit): (a) 0.1 atm and (b) 0.5 atm.

dent. Figure 11(b) shows a portion of this specimen at a location where the external scale had spalled. The exposed alloy has different features depending upon the oxide scale that had developed. Scanning electron micrographs showing cross sections of the specimens shown in Figures 10(a) and (b) are presented in Figures 12(a) and Figure 12(b)), respectively. In dry air, the scale is α -Al₂O₃ (Figure 12(a)). The specimen of Ni8Cr6Al that was exposed in water vapor has formed NiO in numerous areas (Figure 12(b)), and the continuous layer of α -Al₂O₃ is just beginning to form in a few areas (arrows in Figure 12(b)). In fact, the oxide over grain boundaries in the alloy contains some transient oxides; nevertheless, a continuous layer of α -Al₂O₃ has developed.

Galerie and co-workers have performed extensive studies comparing the oxidation rates of a number of pure metals in oxygen and pure, deoxygenated water vapor.^[25,26,27] They observed that Ti and Cr oxidized faster in water vapor than oxygen even though the effective oxygen partial pressure was substantially lower in the water vapor. The results for Ti were explained as the result of smaller hydroxyl ions ($r = 0.10$ nm) moving over oxide ion vacancies in rutile with a greater mobility than larger oxide ions ($r = 0.14$ nm), thus increasing the inward growth component of the scale. The results for Cr were also explained as resulting from an increased inward growth component in water vapor, except, in this case, it was postulated that the diffusion path for the hydroxyl ions was along chromia grain boundaries. Galerie *et al.*^[25] observed that Ni oxidized slower in water vapor

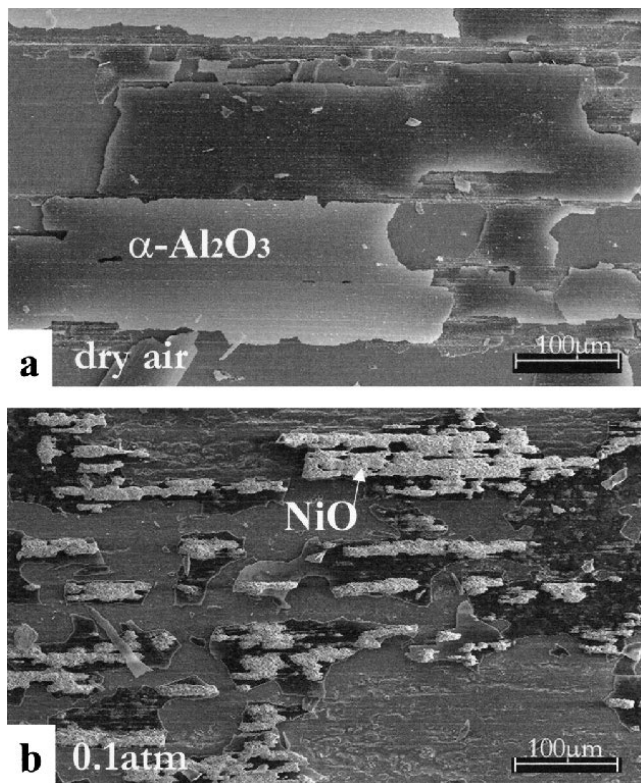


Fig. 9—Ni-8Cr-6Al exposed for 1 h at 1100 °C (surface condition 600 grit): (a) dry air and (b) air with water vapor at 0.1 atm

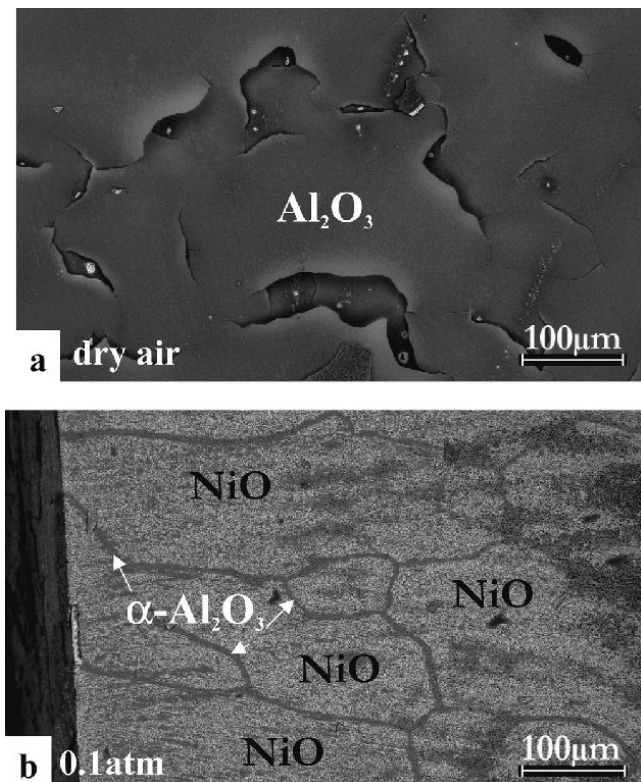


Fig. 10—Ni-8Cr-6Al exposed for 1 h at 1100 °C (initial surface preparation 0.05 μm in alumina): (a) in dry air and (b) in air with 0.1 atm water vapor.

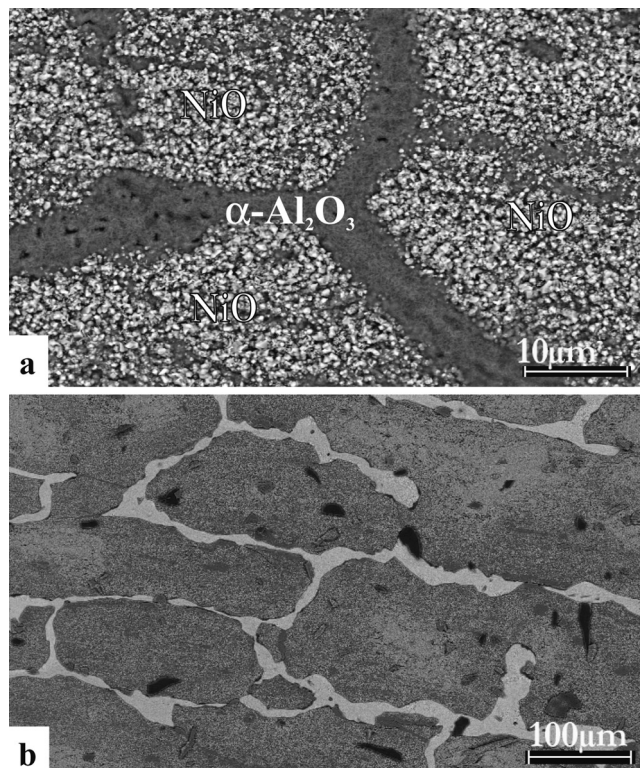
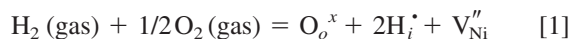


Fig. 11—Ni-8Cr-6Al oxidized for 1 h at 1100 °C in 0.1 atm water vapor atmosphere (initial surface preparation 0.05 μm in alumina): (a) surface of oxide adjacent to the gas surface and (b) alloy surface after spalling of the oxide scale.

than oxygen and the rate changed from parabolic to linear. This was explained as resulting from the difficulty in forming adsorbed oxygen atoms on the surface of NiO, which was considered a “nonacidic oxide” surface, so that the adsorbed species were mainly OH^- . They argue that the hydroxyl ions cannot enter the scale of p-type oxides. Therefore, the rate-controlling step becomes the surface reaction to provide oxygen atoms from the adsorbed OH^- to react with the Ni cations arriving at the scale/gas interface. However, the growth of NiO in air/ H_2O mixtures of the present study could be significantly different than oxidation in pure H_2O . The oxygen from the air can provide the oxidant to react with the Ni cations at the scale/gas interface. Specimens of pure nickel (99.999 wt pct) were oxidized for 1 hour at 1100 °C in dry air and air with 0.1 atm water vapor. It was determined that the NiO scale thickness formed in air with water vapor was twice that formed in dry air (Figure 13). It is possible that hydrogen from the water vapor can enter the NiO and cause the cation vacancy concentration to be increased *via* the following reaction:



whereby the transport of nickel through the NiO is increased due to the higher cation vacancy concentration.

Other investigations have also proposed that hydrogen can affect the defect structure of oxides.^[28] The increased transient oxidation that has been observed for PWA1484 and NiCrAl specimens exposed in gas mixtures containing water vapor must be caused by the increased growth rate of NiO and

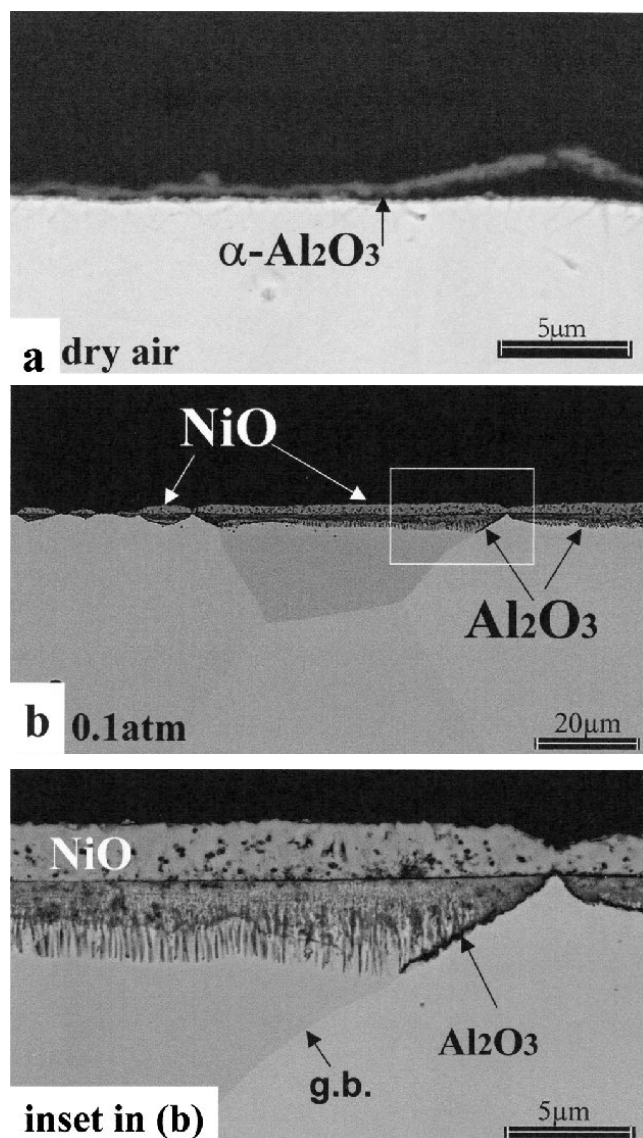


Fig. 12—Cross sections of Ni-8Cr-6Al oxidized at 1100 °C for (a) 1 h in dry air and (b) 1 min in air with water vapor (0.1 atm).

possibly chromium oxides. The observed increased internal oxidation of Al in these alloys could also be associated with accelerated growth of transient Ni and Cr oxides, which would increase the critical Al content required for continuous alumina scale formation.^[29]

C. The effect of Water Vapor on Spinel Formation in Growing α -Al₂O₃ Scales on Platinum-Modified Aluminide Coatings

Results have been obtained that show that during the growth of α -Al₂O₃ scales on platinum aluminide coatings, spinel (NiAl₂O₄) is formed at the α -Al₂O₃/gas interface. The spinel phase was identified by using energy dispersive analysis in a scanning electron microscope. The amount of spinel that was formed for a given set of exposure conditions increased when water vapor was present in the gas phase. Some results obtained in dry air are presented in Figure 14 and show a spinel phase on the ridges of α -Al₂O₃ after

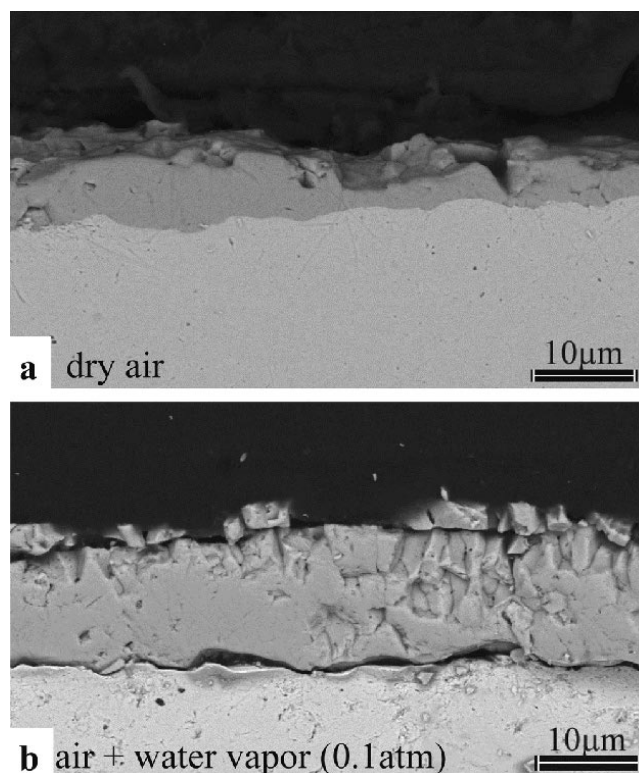


Fig. 13—Ni 99.999 pct pure, exposed for 1 h at 1100 °C, in two different atmospheres (SEM cross-sectional images, showing morphology and thickness of NiO scales).

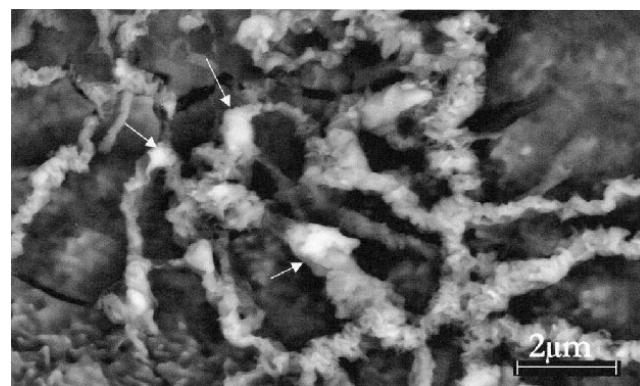


Fig. 14—SEM micrograph showing the surface of a PtAl coating oxidized for 525 cycles at 1100 °C in dry air (spinel at arrows).

525 cycles at 1100 °C. Spinel was not observed at such locations during observations performed after earlier exposures. Consequently, this phase is not a result of transient oxidation processes during the formation of a continuous α -Al₂O₃ layer. The surfaces of platinum aluminide coatings on N5 were examined with the SEM after different exposure times at 1100 °C in air with water vapor at 0.1 atm. Cracks that developed in the α -Al₂O₃ scale after 41 cycles were used to examine the same location on the oxide surface (Figure 15). Inspection of these cracks did not show any oxide formation in them, and it is believed that an alumina layer developed on the alloy at the base of these cracks. Spinel was observed over a period of 1194 cycles showing growth at cracks in α -Al₂O₃ and on top of α -Al₂O₃ in the

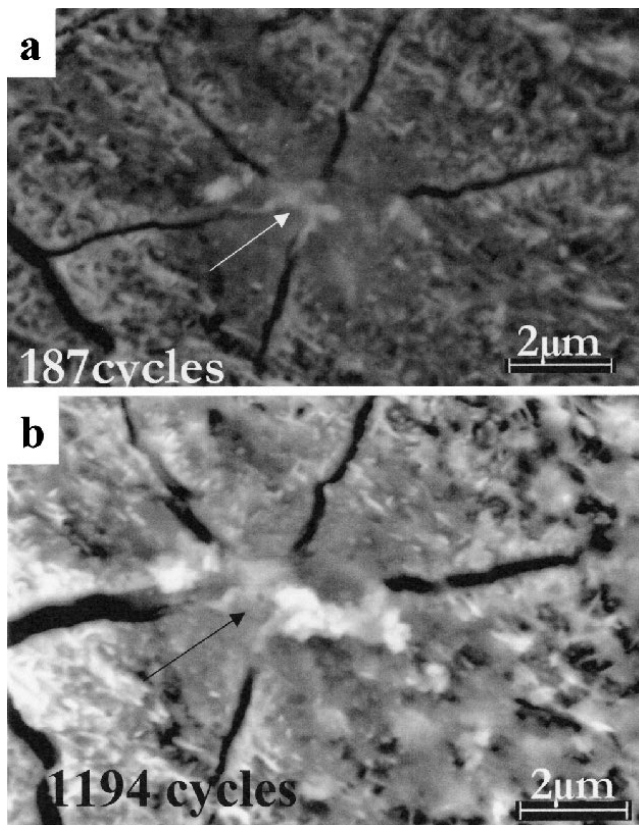


Fig. 15—Scanning electron micrographs of the surface of alumina on a platinum aluminide coating after exposure in air with water vapor (0.1 atm) at 1100 °C (a) for 187 cycles and (b) for 1194 cycles (arrows point to islands of spinel).

proximity of cracks (Figure 15). Lateral spinel growth along cracks was less in comparison to thickening of the spinel layers. Spinel islands were also evident on specimens where no cracking of the alumina scales was evident and the amount of spinel increased with exposure time (Figure 16). Cross sections of platinum-modified aluminide coatings on RENÉ N5 exposed in dry air and in air with water vapor at 1100 °C are compared in Figure 17. Some spinel is evident on the specimen exposed in dry air (Figure 17(a)), but more is apparent in air with water vapor (Figure 17(b)), and the amount of spinel increases with exposure time (Figure 17(c)).

The results strongly suggest that the spinel that is formed at the α -Al₂O₃/gas interface results from the outward diffusion of nickel. Inspection of Figure 17(c) indicates that the spinel layer is relatively uniform in thickness and distribution. Pint *et al.*^[30] have found that NiAl₂O₄ was formed on an α -Al₂O₃ scale at the gas interface during the oxidation of Ni₃Al. It was proposed that cracks developed in the α -Al₂O₃ during thermal cycling and that upon subsequent oxidation NiO was formed in these cracks. Due to the rapid growth of the NiO compared to α -Al₂O₃, it was proposed that the cracks became filled with NiO and permitted NiO to be formed upon the α -Al₂O₃ at the gas interface. Reaction between the NiO and α -Al₂O₃ resulted in NiAl₂O₄ formation. It is possible that a similar mechanism caused spinel to be formed on the platinum aluminide coatings in the present studies. However, cracks filled with NiO were not detected in the α -Al₂O₃ scales shown in Figure 17(c). Furthermore,

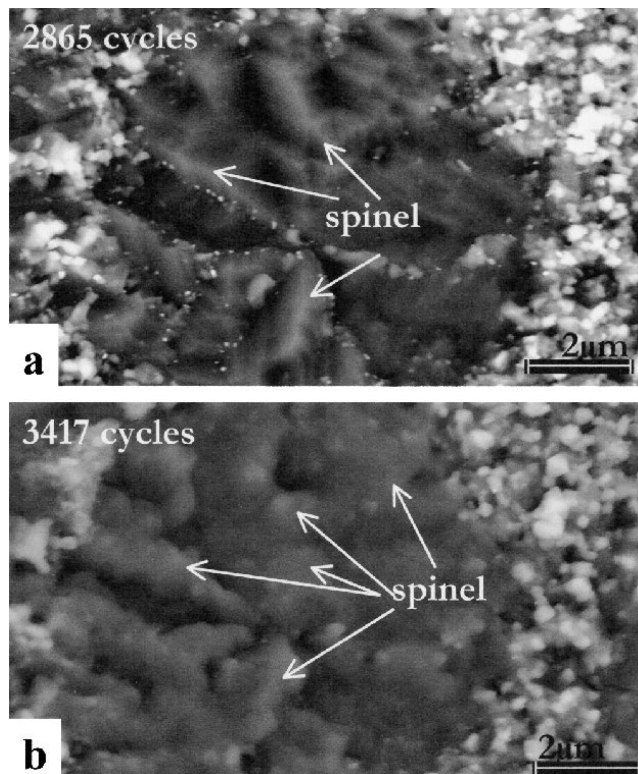
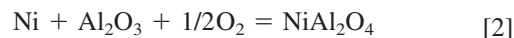


Fig. 16—SEM micrographs of the surface of an alumina scale formed on a platinum aluminide coating after (a) 2865 cycles and (b) 3417 cycles of oxidation at 1100 °C in air with 0.1 atm of water vapor (arrows point to islands of spinel).

the aluminide coating beneath the α -Al₂O₃ was predominantly β -NiAl (Figure 17(d)), and it would not be expected that NiO would be stable at the bottom of cracks in the α -Al₂O₃. In view of these results, another mechanism is proposed for spinel formation that consists of diffusion of nickel through the α -Al₂O₃ layer to the gas interface.

The Ni-Al-O stability diagram is presented in Figure 18. This diagram has been constructed for a temperature of 1000 °C due to the availability of thermodynamic data. At 1100 °C, a similar diagram can be expected. In this diagram, the various phases that can be in equilibrium with one another as a function of oxygen pressure and aluminum activity are indicated. In the Ni-Al alloy region, arrows indicate two-phase equilibria and the nickel activities for these equilibria are presented. As one proceeds through the β and γ' phases to the γ phase, the nickel activity increases. In considering the case of spinel formation on an α -Al₂O₃ scale that in turn is on a Ni-Al alloy, spinel may form *via* the following reaction:



which could occur at the α -Al₂O₃/gas interface or the α -Al₂O₃/alloy interface. In the latter case, the nickel activity at the α -Al₂O₃/alloy interface must be extremely high because the oxygen pressure is so low. For example, if the oxygen activity in the α -Al₂O₃ is 2.5×10^{-6} , a nickel activity of 0.78 is required to form spinel, and nickel activities close to unity are necessary as the oxygen pressure is reduced to the three-phase Al₂O₃-NiAl₂O₄-alloy equilibrium. On the

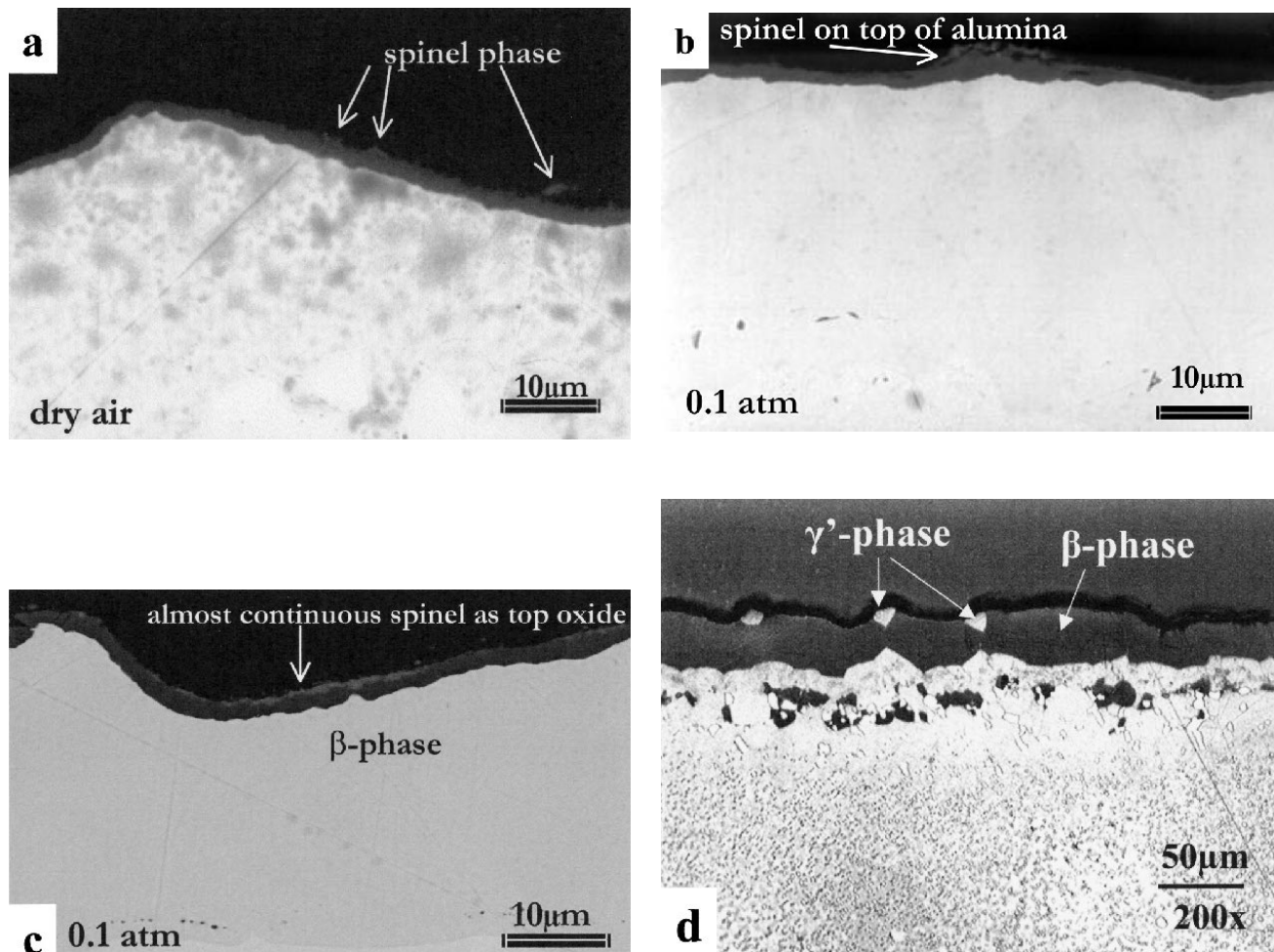


Fig. 17—Cross sections of Pt-modified aluminide coatings on RENÉ N5, exposed in (a) dry air for 1004 cycles, (b) 0.1 atm water vapor pressure for 1194 cycles, (c) 0.1 atm water vapor pressure for 3417 cycles at 1100 °C, and (d) the etched coating from (c); the coating is predominantly β -phase NiAl with some γ' at grain boundaries in the coating.

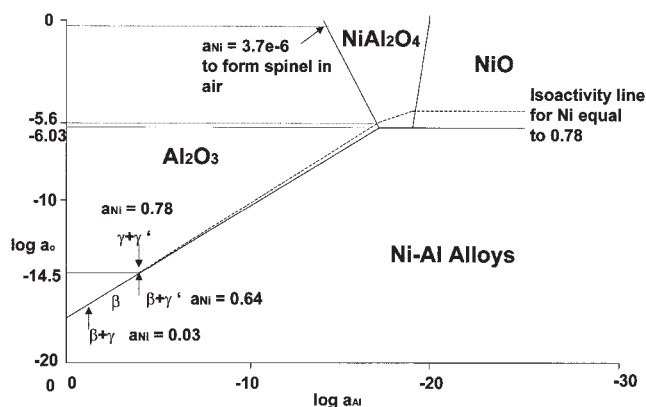


Fig. 18—Schematic of Ni-Al-O stability diagram at 1000 °C with the activities of nickel indicated for various equilibria.

other hand, much lower nickel activities are required to form spinel at the α -Al₂O₃/gas interface where the oxygen pressure is high. For example, considering an oxygen activity of that in air, a nickel activity of 3.7×10^{-6} is required to form spinel. It is proposed that nickel diffuses through the

α -Al₂O₃ to form spinel at the α -Al₂O₃/gas interface. Sahin *et al.*^[31] have proposed that nickel diffuses through α -Al₂O₃.

In considering the defect mechanism by which nickel can diffuse through α -Al₂O₃, it is well established that the growth of α -Al₂O₃ scales is controlled by the inward diffusion of oxygen along grain boundaries^[32] in the oxide. The equilibrium point defect concentrations in α -Al₂O₃ are extremely small and the defect structure is not definitely known. Schottky defects involving aluminum vacancies, V_{Al}''' , and oxygen vacancies, $V_O^{\bullet\bullet}$, have been proposed.^[33] It is possible that nickel may diffuse through α -Al₂O₃ via aluminum vacancies. Two possible reaction schemes for formation of spinel are presented in Figure 19, where the Ni²⁺ and Al³⁺ ions diffuse through the α -Al₂O₃ via aluminum vacancies. In one scheme, the spinel would be formed at the interface between the NiAl₂O₄ and Al₂O₃. In the other, the spinel would be formed at the NiAl₂O₄-gas interface. In both schemes, the oxygen would diffuse inward via grain boundaries in α -Al₂O₃ and NiAl₂O₄. The Ni²⁺ is slightly larger than the Al³⁺ ion. For example, the ionic radius for Ni²⁺ is 0.07 nm compared to 0.05 nm for Al³⁺ and the largest interstice in α -Al₂O₃ is 0.06 nm. If the size difference between Ni²⁺ and Al³⁺ prevents Ni²⁺

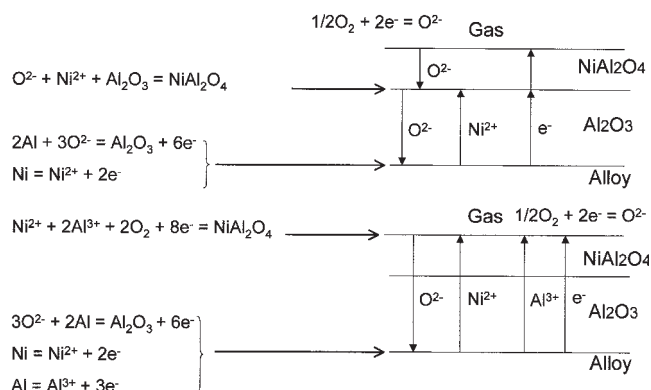
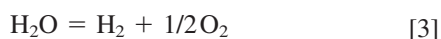


Fig. 19—Two possible reaction schemes for formation of NiAl_2O_4 (spinel) on $\alpha\text{-Al}_2\text{O}_3$. The Ni^{2+} and Al^{3+} ions would diffuse *via* aluminum vacancies. The oxygen would diffuse inward *via* oxide grain boundaries.

diffusing in the bulk crystal, it is possible that the nickel may diffuse along grain boundaries in the $\alpha\text{-Al}_2\text{O}_3$ rather than *via* the bulk lattice. It has been proposed by some investigators that aluminum may diffuse along grain boundaries in $\alpha\text{-Al}_2\text{O}_3$.^[34]

It is important to note that the activity of NiO in $\alpha\text{-Al}_2\text{O}_3$ increases as one proceeds along the $\alpha\text{-Al}_2\text{O}_3$ –alloy boundary towards the three phase equilibrium $\alpha\text{-Al}_2\text{O}_3$ – NiAl_2O_4 –alloy shown in Figure 18. For example, at 1000 °C, the activity of NiO in $\alpha\text{-Al}_2\text{O}_3$ at the $\alpha\text{-Al}_2\text{O}_3$ – γ – γ' equilibrium is 4.3×10^{-10} , whereas this activity is 0.16 at the $\alpha\text{-Al}_2\text{O}_3$ – γ – NiAl_2O_4 equilibrium. This suggests that the solubility of NiO in $\alpha\text{-Al}_2\text{O}_3$ and transport of nickel through $\alpha\text{-Al}_2\text{O}_3$ become more favorable as the metallic substrate becomes depleted of aluminum or, in other words, as the oxygen activity reaches levels sufficient to ionize nickel.

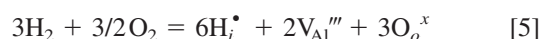
Finally, the experimental results also show that spinel formation at the $\alpha\text{-Al}_2\text{O}_3$ /gas interface becomes enhanced when water vapor is present in the gas. Water vapor does cause $\alpha\text{-Al}_2\text{O}_3$ scales to crack and spall more compared to that in dry air and cracks could be responsible for transport of nickel to the $\alpha\text{-Al}_2\text{O}_3$ /gas interface. If spinel formation occurs *via* the outward diffusion of nickel through the $\alpha\text{-Al}_2\text{O}_3$ *via* aluminum vacancies, water vapor would be expected to accelerate this diffusion process. When water vapor is present in a gas mixture with air, hydrogen is provided to the gas mixture by the dissociation of H_2O ,



The ratio of the hydrogen pressures in wet ($P_{\text{H}_2\text{O}} = 0.1$ atm) and dry air (dew point -46 °C) is given by

$$\begin{aligned} &P_{\text{H}_2}(\text{wet})/P_{\text{H}_2}(\text{dry}) \\ &= (P_{\text{H}_2\text{O}}(\text{wet})P_{\text{O}_2}^{1/2}(\text{dry}))/((P_{\text{H}_2\text{O}}(\text{dry})P_{\text{O}_2}^{1/2}(\text{wet})) \quad [4] \end{aligned}$$

At 1100 °C, this ratio is equal to 1×10^3 . The higher pressure of hydrogen in wet *vs* dry air could affect the atomic defects in $\alpha\text{-Al}_2\text{O}_3$. For example, if hydrogen enters $\alpha\text{-Al}_2\text{O}_3$ as an interstitial, then



the metal vacancy concentration in $\alpha\text{-Al}_2\text{O}_3$ would be increased. The hydrogen may be associated with oxide ions as $\text{OH}_o^\bullet$. The outward diffusion of both nickel and aluminum $\alpha\text{-Al}_2\text{O}_3$ would be increased, but this would not have a significant effect on the growth of the $\alpha\text{-Al}_2\text{O}_3$ because the inward diffusion of oxygen is also large. In the case of nickel diffusion along grain boundaries in the $\alpha\text{-Al}_2\text{O}_3$, the water vapor would have to, in some way, permit more transport of nickel.

IV. SUMMARY AND CONCLUSIONS

The high-temperature oxidation of alumina forming alloys and coatings has been found to be affected by water vapor environments in certain ways, namely, the development of continuous and adherent alumina scales is inhibited in water vapor conditions, more extensive transient oxidation prior to continuous $\alpha\text{-Al}_2\text{O}_3$ formation takes place compared to dry air, the oxide adherence is affected by the presence of water vapor, and substantially more spinel phase forms under water vapor conditions.

It has been proposed that more transient oxidation and inhibition of the development of continuous $\alpha\text{-Al}_2\text{O}_3$ scales is caused by the rapid growth of NiO due to hydrogen from the H_2O causing the cation vacancy concentration to be increased. The water molecule also adversely affects the adherence of $\alpha\text{-Al}_2\text{O}_3$ scales to alloy substrates, causing the $\alpha\text{-Al}_2\text{O}_3$ /alloy interfacial toughness to be decreased. Finally, it is proposed that the observed spinel formation at the $\alpha\text{-Al}_2\text{O}_3$ –gas interface results from diffusion of nickel through $\alpha\text{-Al}_2\text{O}_3$ and this diffusion process becomes more favorable in the presence of water vapor due to hydrogen affecting the aluminum vacancy concentration in $\alpha\text{-Al}_2\text{O}_3$. While progress is being made in understanding the effects of water vapor, much still remains to be understood about this simple and highly prevalent molecule.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of this work by the Office of Naval Research (Contract No. N00014-94-0085).

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