

THE EFFECTS OF WATER VAPOR ON THE OXIDATION OF NICKEL-BASE SUPERALLOYS AND COATINGS AT TEMPERATURES FROM 700°C TO 1100°C

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Abstract

The oxidation of superalloys that rely upon the development of α -Al₂O₃ or Cr₂O₃ scales for oxidation resistance in air containing water vapor are compared at temperatures from 700°C to 1100°C. It is shown that water vapor affects the oxidation of such alloys in different ways. Water vapor adversely affects the selective oxidation of aluminum in the α -Al₂O₃-formers, and also affects the adherence of these oxide scales. The major effect of water vapor on the chromia-formers is enhanced vaporization of Cr₂O₃. Aluminide coated superalloys are also examined in these cyclic oxidation tests, and it will be shown that water vapor caused spalling of the α -Al₂O₃ scales, but the effect is small for strongly adherent α -Al₂O₃ scales.

Introduction

Water vapor is present in almost all environments unless precautions are taken to exclude it. Furthermore, water vapor has been found to affect the oxidation of alloys and coatings. The effects produced by water vapor depend upon the type of oxide that is formed and the experimental conditions [1-15] (e.g. temperature, water vapor pressure). Most superalloys and coatings for superalloys rely on the formation of α -alumina or chromia scales for oxidation resistance at temperatures above 700°C. This paper is concerned with the effects of water vapor on the oxidation of superalloys and coatings for superalloys that develop oxidation resistance via the formation of α -Al₂O₃ or Cr₂O₃ scales.

Experimental

The compositions of the superalloys that were studied in cyclic oxidation are presented in Table I. Aluminide and platinum modified aluminide coatings on René N5 were also studied in cyclic oxidation. These studies were performed using coupon specimens with areas about 1 cm² and 0.3 cm thick. The experimental procedures have been discussed previously [16]. The specimens were cyclically exposed in the hot zone of a horizontal tube furnace for 45 minutes and 15 minutes in a cool zone (200°C) outside of the furnace. Experiments were performed in dry air and in air with pressures of 0.1 or 0.5 atm water vapor. The test temperatures extended from 700°C to 1100°C, but the chromia-forming superalloys were not tested at 1100°C. The cyclic oxidation resistances of the alloys were evaluated using weight-change versus time measurements and metallographic observations of exposed specimens. In order to account for the observed degradation of these alloys some studies were also performed on more simple binary and ternary alloys containing Ni-Cr and Ni-Cr-Al.

Results and Discussion

The results from these investigations will be presented by first discussing the α -alumina-forming superalloys, which will be followed by results for the chromia-forming alloys, and then finally the results obtained with the aluminide coatings.

Alpha-Alumina-Forming Superalloys:

Weight change versus time data for the cyclic oxidation of PWA 1484, MarM 247, CM 186 and René N5 at 700°C, 900°C and 1000°C in dry and wet air are presented in Figures 1, 2 and 3, respectively. At 700°C the weight gains for PWA 1484, MarM 247 and CM 186 were larger in wet air than in dry air. There was not a large difference between the weight changes for N5 in wet and dry air, Figure 1. Metallographic examination of the specimens that were exposed at 700°C showed that continuous layers of α -Al₂O₃ were not present on any of the alloys but substantial amounts of NiO and internal oxides of aluminum had been formed, Figure 4, especially on the specimens that exhibited the larger weight gains.

At 900°C there was not a large difference between the weight change versus time curves for dry and wet air, Figure 2. For both conditions, it was apparent for all of the alloys that some cracking and spalling of the α -Al₂O₃ scales had occurred followed by transient oxidation with development of the α -Al₂O₃ scales beneath these transient oxides, Figure 5.

At 1000°C the weight gain versus time curves for CM 186 and MarM 247 were significantly larger than those for PWA 1484 and N5. This was the case for both wet and dry air, Figure 3. At this temperature it was found that a substantial amount of HfO₂ was formed as an internal network of oxide, Figure 6, in MarM 247 and CM 186 but not in PWA 1484 and N5, Figure 7. There was some spalling of oxide scales from all of these alloys but oxide scales rich in aluminum were evident on all of the specimens, Figures 6 and 7. The larger weight gains for MarM 247 and CM 186 are due to the larger Hf concentrations for these two alloys compared to PWA 1484 and N5 whereby a large amount of oxygen can enter the former alloys due to rapid diffusion of oxygen in the HfO₂ network.

Only N5 was tested in cyclic oxidation at 1100°C. Two versions of N5 were tested, one with 5-8 ppm sulfur and another with less than 1 ppm sulfur. The results obtained in the cyclic oxidation test are presented in Figure 8. The presence of water vapor caused the oxide scale formed on N5 (5-8 ppm sulfur) to crack and spall but water vapor did not have any effect on the cyclic oxidation

Table I. Composition of Alloys in Weight Percent

Alloy	Ni	Cr	Al	Co	Ta	W	Mo	Ti	B	C	Hf	Zr	Nb	Re
IN 738	Bal.	16.0	3.4	8.5	1.7	2.6	7.1	3.4	0.001	0.11		0.05	0.9	
X-40	10	25.5		Bal.		7.5				0.5				
CM 186	Bal.	6.6	5.7	9.2	3.2	8.5	0.5	0.7	0.01	0.07	1.4			
MarM 247	Bal.	8.2	5.4	9.9	3.0	9.8	0.7	1.05	0.01	0.13	1.3	0.4	0.2	
CMSX-4	Bal.	6.5	5.6	9.0	6.5	6.0	0.6	1.0			0.1			3.0
N5	Bal.	7.0	6.2	7.5	6.5	6.0	0.6	1.0			0.1			3.0
PWA 1484	Bal.	5.0	5.6	10.0	8.7	6.0	2.0				0.1			3.0

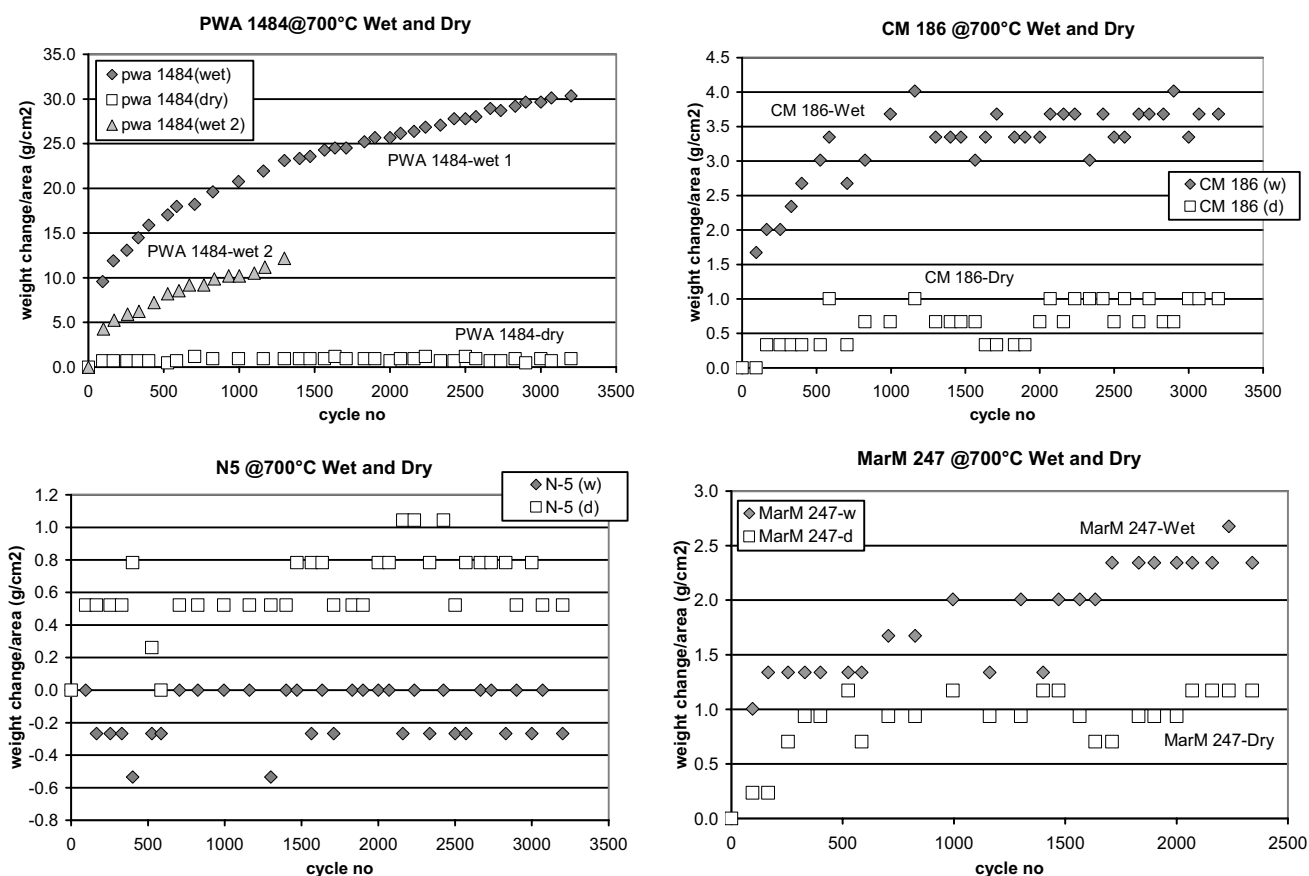


Figure 1. Weight change versus time data for the cyclic oxidation of some nickel base superalloys in dry and in wet air (0.3 atm water vapor) at 700°C.

behavior of low sulfur N5. Metallographic examination of the exposed specimens showed that an adherent layer of α -Al₂O₃ was present on low sulfur N5, but a scale intermixed with NiO, Cr₂O₃ and α -Al₂O₃ was formed on the higher sulfur-containing N5, Figure 9.

The results that have been obtained with the α -alumina forming superalloys show that water vapor has two major effects on the oxidation of these alloys. In particular, the presence of water vapor adversely affects the selective oxidation of aluminum in these alloys and this adverse effect is more pronounced at 700°C compared to 1000°C. Water vapor also causes the α -Al₂O₃ scales to crack and spall. This effect is most severe on alloys for

which the α -Al₂O₃/alloy interfacial toughness is low (e.g. N5 with 5-8 ppm sulfur compared to N5 with less than 1 ppm sulfur). The adverse effect of water vapor on the selective oxidation of aluminum appears to become more severe as the temperature is decreased. For example, in the case of PWA 1484 and CM 186 continuous layers of α -Al₂O₃ were not developed at 700°C in water vapor, Figure 4, but continuous layers of α -Al₂O₃ were evident on these alloys at 900°C, Figure 5. Nevertheless, it does appear that some adverse effects of water vapor on selective oxidation of aluminum do occur even at temperatures as high as 1100°C. Such effects are evident in Figure 10 where a Ni-8Cr-6Al (wt%) alloy was oxidized for 1 hour in dry air and air with 0.1 atm water vapor. In dry air a

continuous layer of α -Al₂O₃ was formed, Figure 10a, whereas much more transient oxidation occurred in a similar exposure time with the wet exposure, Figure 10b. The results that have been obtained show that the selective oxidation of aluminum in all of the alloys is less effective when water vapor is present. In

the cyclic oxidation tests there is some spalling of the α -Al₂O₃ scales and the subsequent oxidation causes the scales to be enriched in elements that are more noble compared to aluminum.

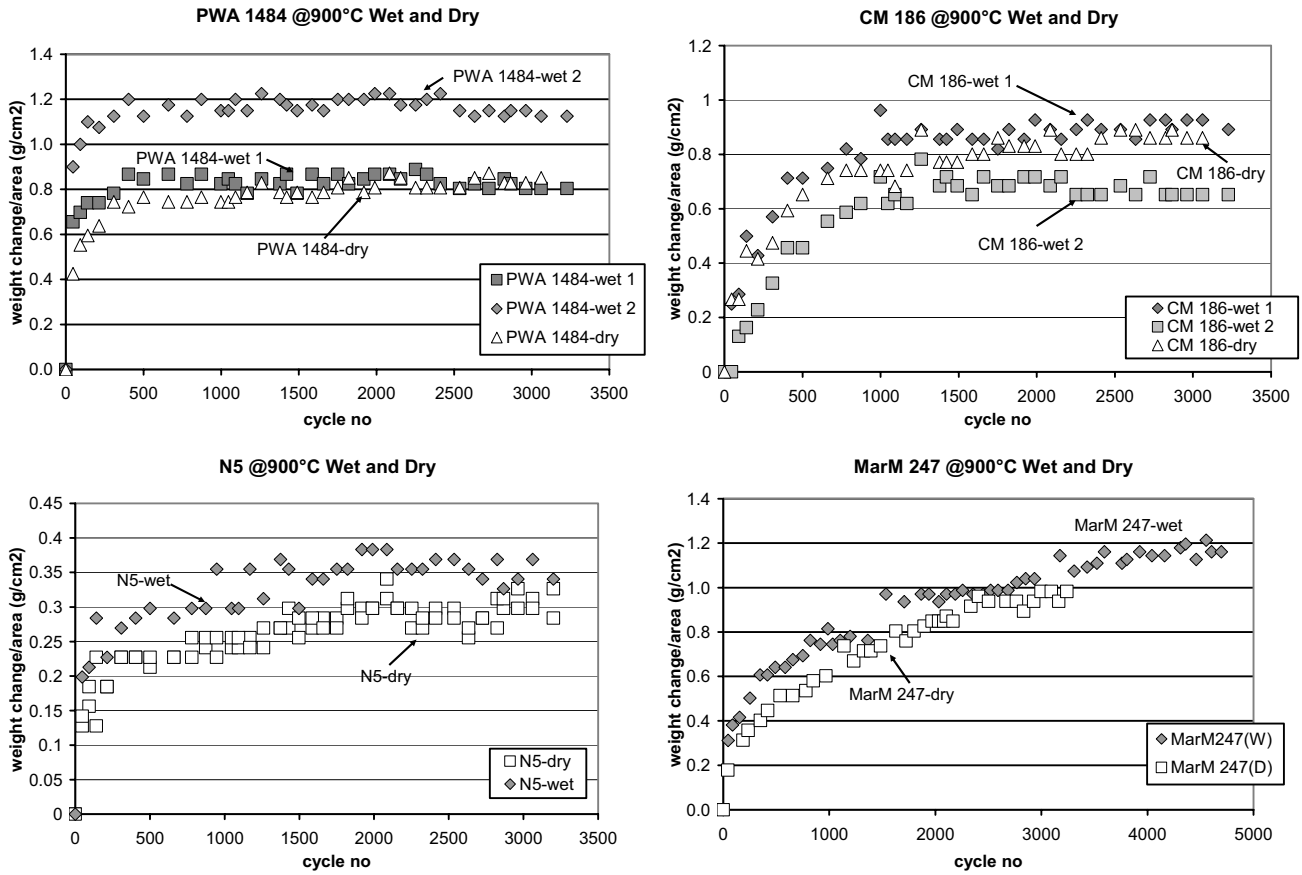


Figure 2. Weight change versus time data for the cyclic oxidation of some nickel base superalloys in dry and in wet air (0.3 atm water vapor) at 900°C.

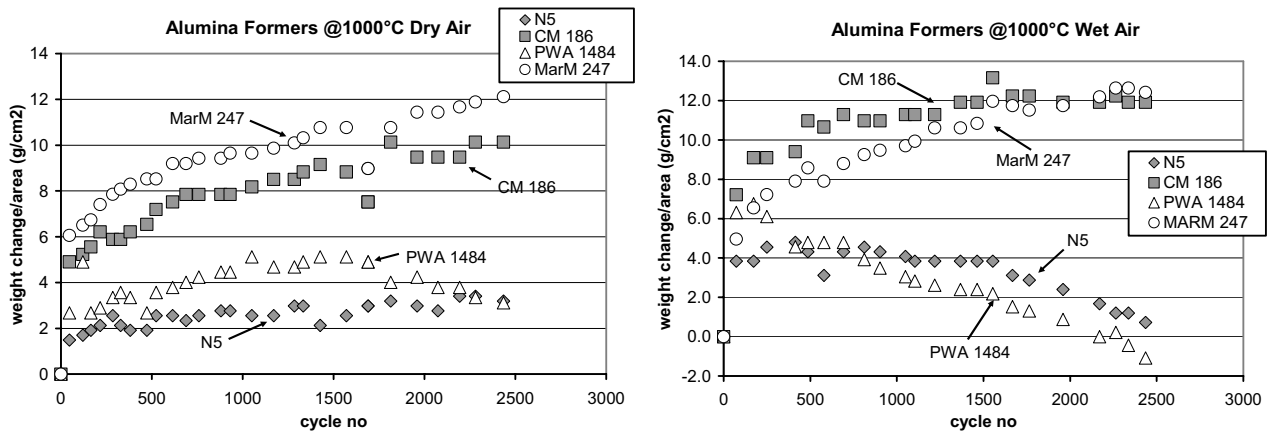


Figure 3. Weight change versus time data for the cyclic oxidation of some nickel base superalloys in dry and in wet air (0.3 atm water vapor) at 1000°C.

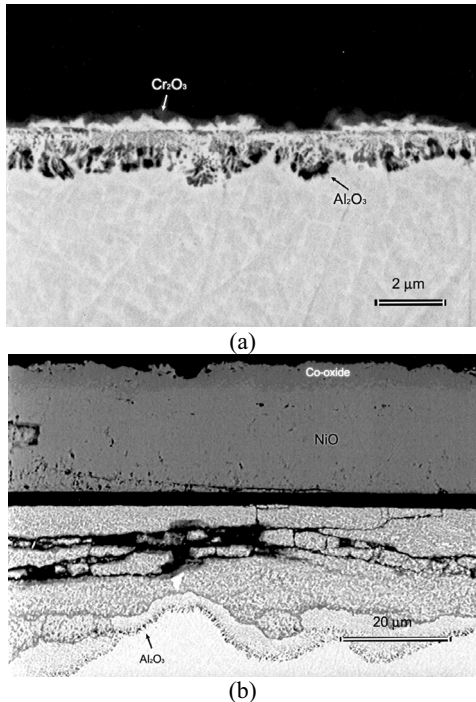


Figure 4. SEM micrographs showing the cross section of PWA 1484 after 3200 hours of cyclic exposure at 700°C (a) in dry, and (b) in wet air. Continuous alumina layers were also not present on the other alumina formers (i.e. MarM 247, CM 186 and René N5). However, the thickness of the transient oxide layer that formed on these alloys was less compared to PWA 1484, René N5 being the thinnest.

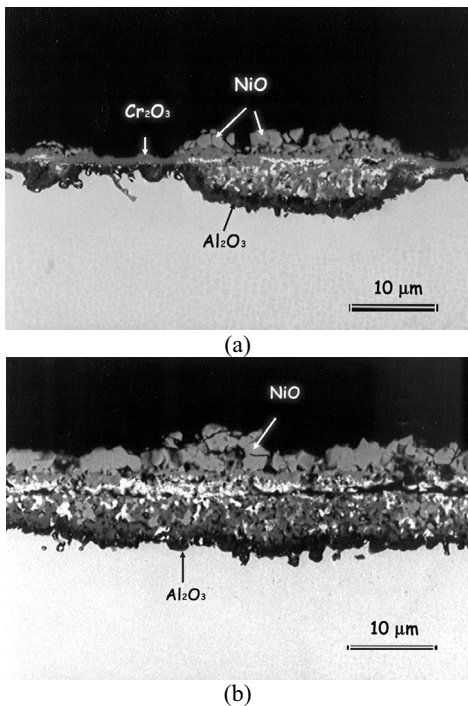


Figure 5. SEM micrograph showing the cross section of CM 186 at 900°C (a) in dry, and (b) in wet air after 3200 cycles. Similar microstructures were observed on MarM 247, PWA 1484 and René N5.

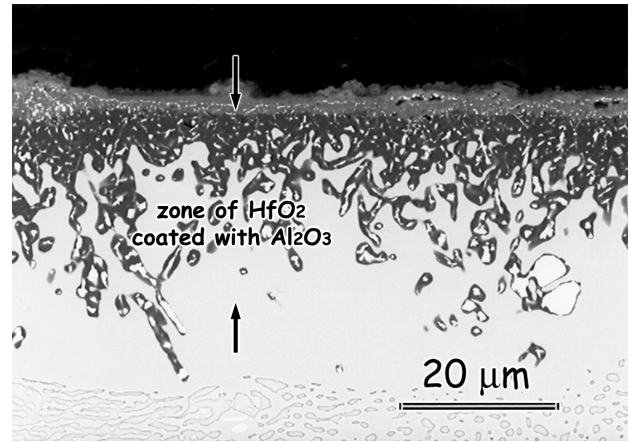


Figure 6. Scanning micrograph of CM 186 after cyclic oxidation for 2500 h in wet air ($P_{H_2O}=0.3$ atm) at 1000°C.

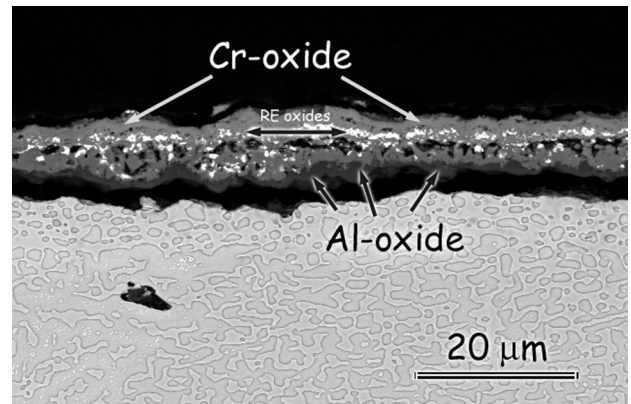


Figure 7. SEM micrograph of N5 after cyclic oxidation at 1000°C in wet air for 2500 cycles.

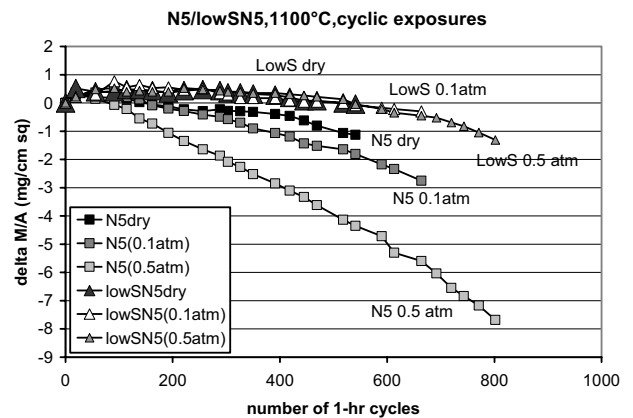


Figure 8. Weight change versus time measurements for N5 specimens (low S and regular S) cyclically oxidized in dry and in wet air at two water vapor pressures (0.1 atm and 0.5 atm) at 1100°C.

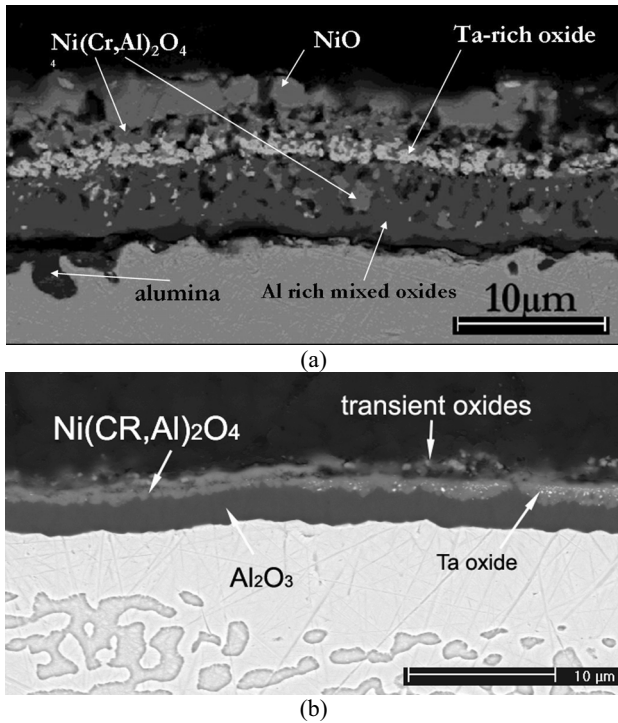


Figure 9. N5 exposed for 802 cycles at 1100°C in wet air (0.5 atm water vapor): (a) alloy with normal sulfur content, (b) alloy with low sulfur content.

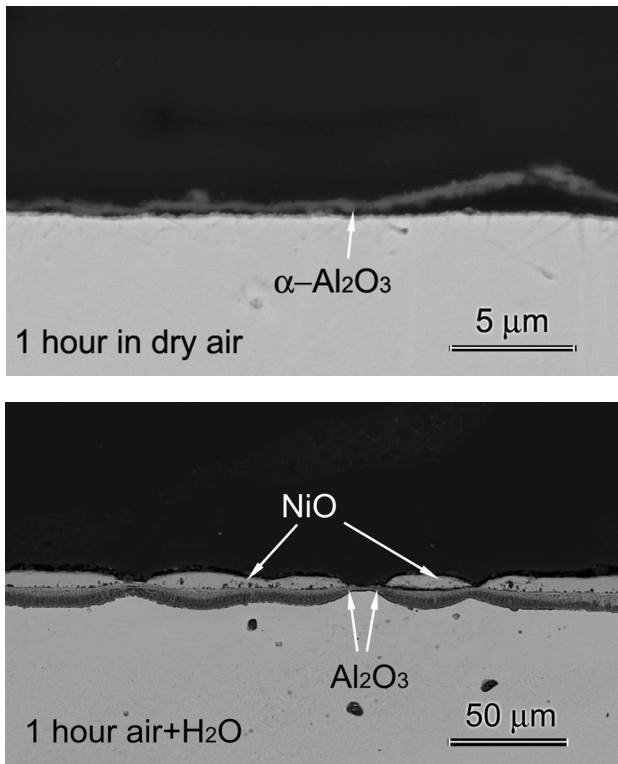


Figure 10. Cross-section of Ni-8Cr-6Al oxidized for 1 h at 1100°C (a) in dry air, and (b) in air with water vapor (0.1 atm).

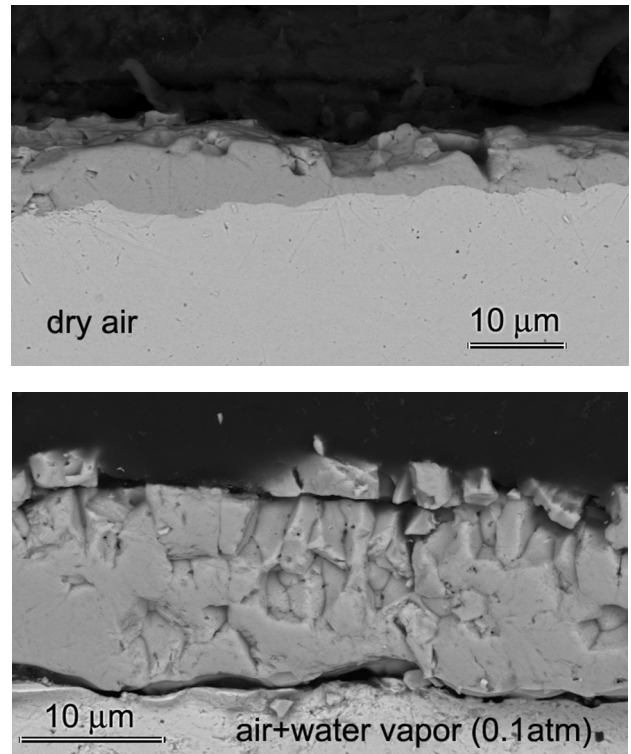


Figure 11. Ni 99.999 pct pure, exposed for 1 h at 1100°C in two different atmospheres (SEM cross-sectional images, showing morphology and thickness of NiO scales).

The detrimental influence of water vapor on the selective oxidation of aluminum may be the result of more rapid growth of the transient oxides in the presence of water vapor. Indeed, specimens of pure nickel (99.999 wt pct) were oxidized for 1 hour at 1100°C in dry air and in 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 11.

Chromia-Forming Superalloys

Weight change versus time data for the cyclic oxidation of IN 738 and X-40 at 700°C, 900°C and 1000°C in dry air and in air with water vapor are presented in Figures 12, 13 and 14. At 700°C it was not clear if there was a difference between the oxidation of IN 738 and X-40 in dry and wet air. Examination of the weight change versus time data indicated that there was some cracking and spalling of oxide but this appeared to be about the same in wet and dry air. Metallographic cross-sections of exposed IN 738 specimens showed external scales of Cr₂O₃ with internal stringers of alumina, Figure 15, for both dry and wet air. The thickness of Cr₂O₃ as well as internal oxide appeared to be thicker in wet compared to dry air. In the case of exposed X-40 specimens, Figure 16, an external layer of Cr₂O₃ was evident for specimens exposed in wet and dry air.

For oxidation at 900°C both IN 738 and X-40 were severely degraded in wet and dry air. The weight change versus time data showed larger weight losses for specimens exposed in wet air, Figure 13, but metallographic sections of exposed specimens

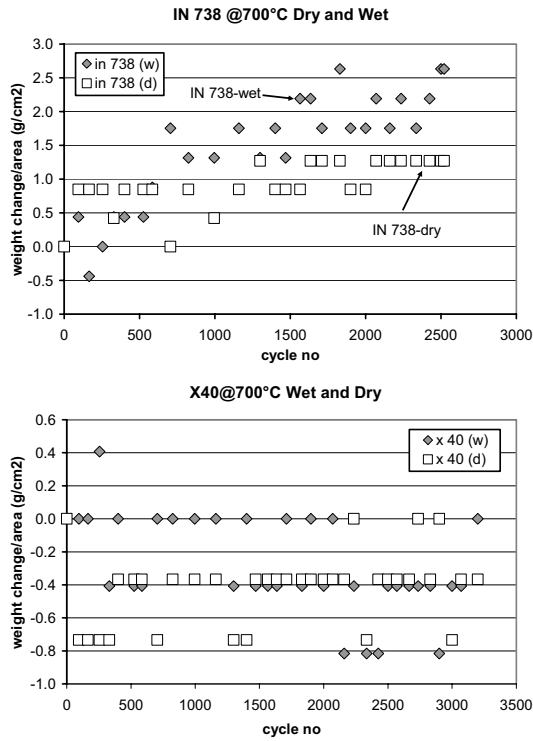


Figure 12. Weight change versus number of cycles plot for the cyclic oxidation of IN 738 and X-40 at 700°C at a total pressure of 1 atm in dry air and in air saturated with water vapor at 0.3 atm.

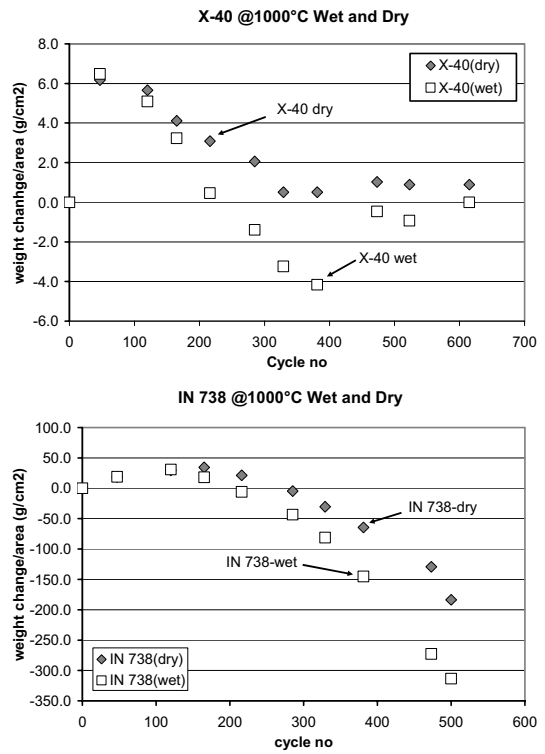


Figure 14. Weight change versus number of cycles plot for the cyclic oxidation of IN 738 and X-40 at 1000°C at a total pressure of 1 atm in dry air and in air saturated with water vapor at 0.3 atm.

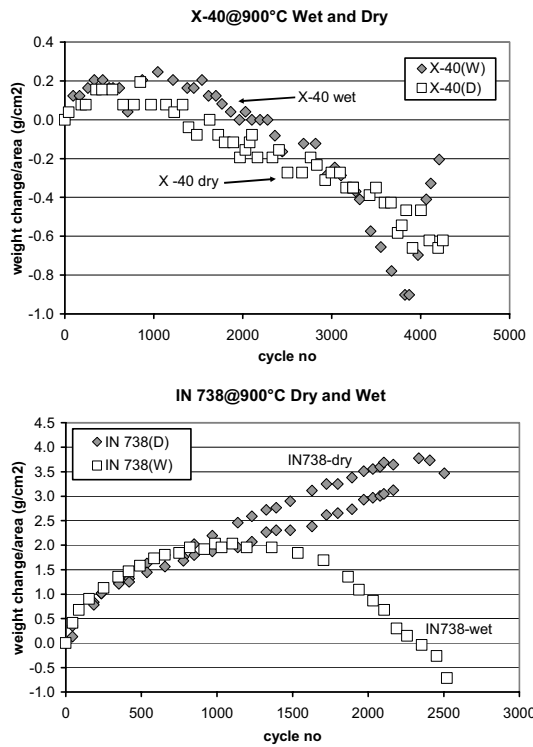


Figure 13. Weight change versus number of cycles plot for IN 738 and X-40 at 900°C at a total pressure of 1 atm in dry air and in air saturated with water vapor at 0.3 atm.

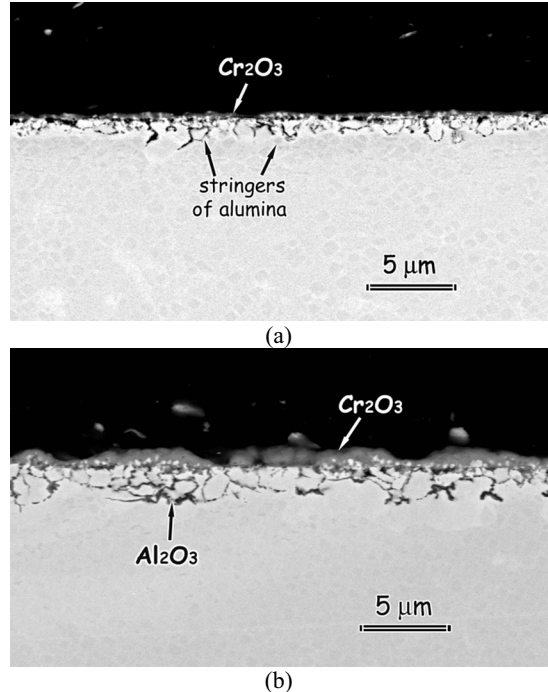
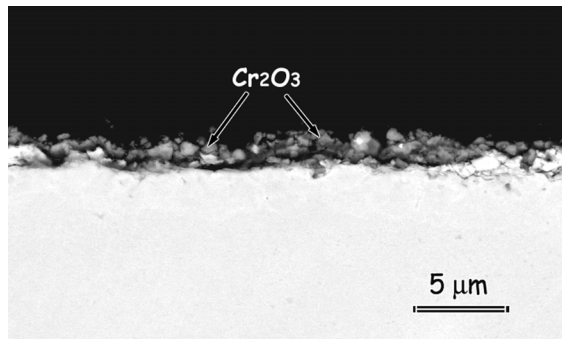
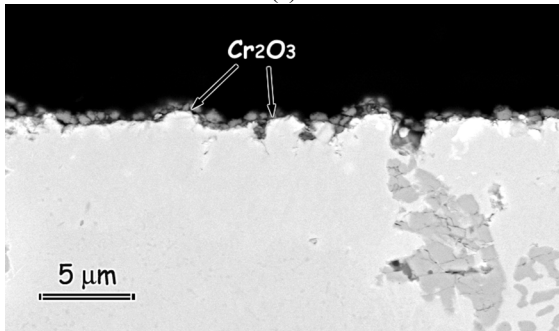


Figure 15. Cross-sectional micrograph of IN 738 after 2520 cycles at 700°C (a) in dry air, and (b) in air with 0.3 atm of water vapor.

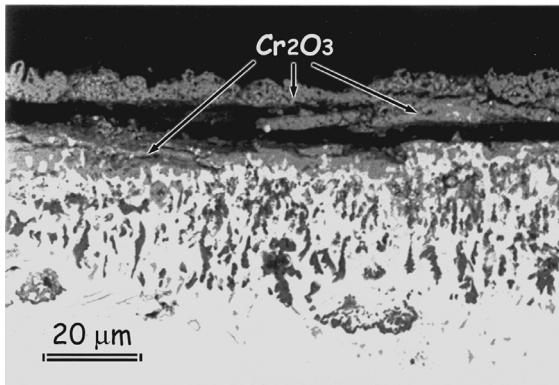


(a)

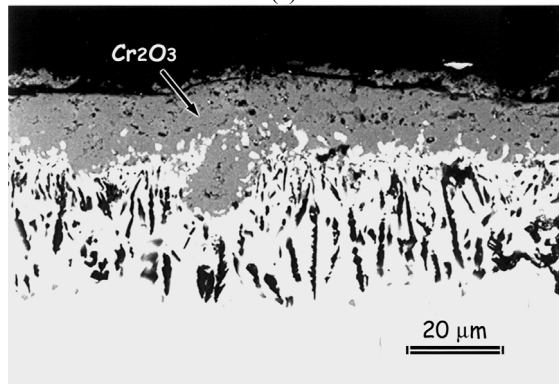


(b)

Figure 16. Cross-sectional micrograph of X-40 after 2520 cycles at 700°C (a) in dry air, and (b) in air with 0.3 atm of water vapor.



(a)

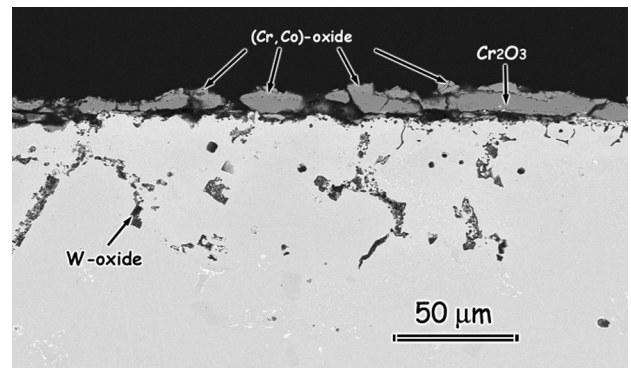


(b)

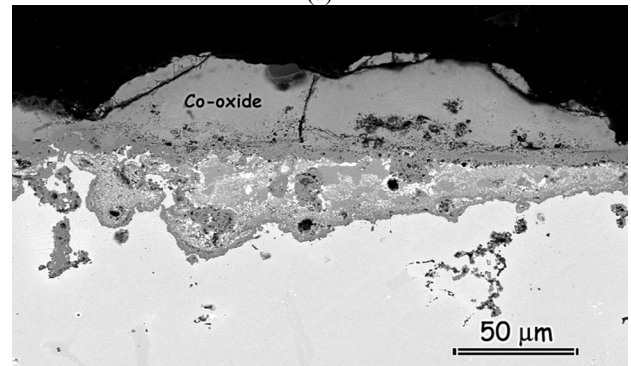
Figure 17. Cross-sectional micrographs of IN 738 after 2520 cycles at 900°C (a) in dry air, and (b) in air with a water vapor pressure of 0.3 atm.

showed significant amounts of degradation in dry air, Figure 17 and 18, had also occurred. In order to examine the degradation of these alloys at 900°C in more detail a Ni-30Cr alloy was cyclically and isothermally oxidized in wet and dry air at 900°C. As can be seen in Figure 19 the weight losses observed for the cyclic oxidation of this alloy are greater for wet air than dry air. However, the weight changes for cyclic oxidation in dry air are less than those for isothermal oxidation. Such results show that there is some cracking and spalling of the Cr_2O_3 from this alloy in the dry cyclic test. The isothermal oxidation kinetics for Ni-30Cr in wet air are presented in Figure 20. It can be seen that after an initial period of weight gain, there is a linear weight loss, which must be due to volatilization of Cr_2O_3 in the wet gas. The vaporization of Cr_2O_3 in dry air appears to be negligibly small. The weight loss observed in the wet isothermal test match quite well the weight losses observed for cyclic oxidation of Ni-30Cr in wet air at 900°C, Figure 20. These results obtained with Ni-30Cr at 900°C show there is some weight loss in dry air due to spalling of oxide. There are also probably weight losses for this alloy due to spalling of oxide during cyclic oxidation at 900°C in wet air, but these weight losses are predominantly due to vaporization of Cr_2O_3 in the wet environment. It is believed that similar processes are dominant during cyclic oxidation of both IN 738 and X-40 at 900°C in wet and dry air.

At 1000°C during cyclic oxidation of both IN 738 and X-40, the degradation was severe. The weight losses for IN 738 were very large with not a large difference between wet and dry air, Figure



(a)



(b)

Figure 18. Cross-sectional micrographs of X-40 after 4250 cycles at 900°C (a) in dry air, and (b) in air with 0.3 atm of water vapor.

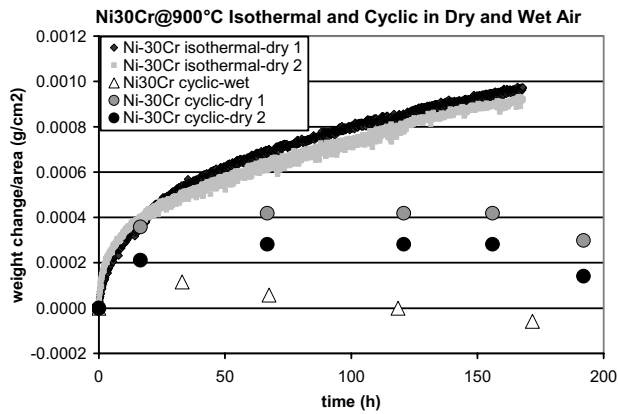


Figure 19. Weight change versus time measurements for the cyclic oxidation of Ni30Cr at 900°C in dry and wet air, and for the isothermal oxidation of Ni30Cr in dry air.

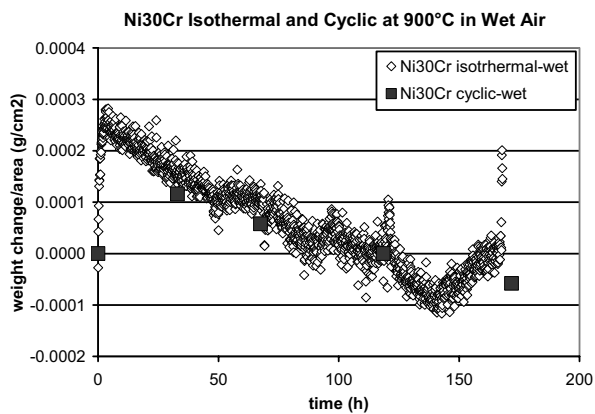


Figure 20. Weight change versus time measurements for the cyclic and isothermal oxidation of Ni-30Cr in wet air at 900°C.

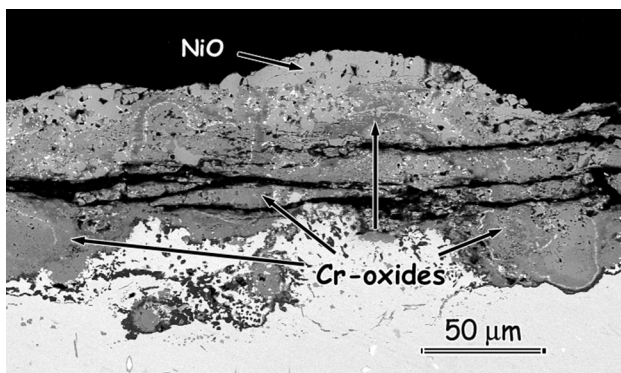
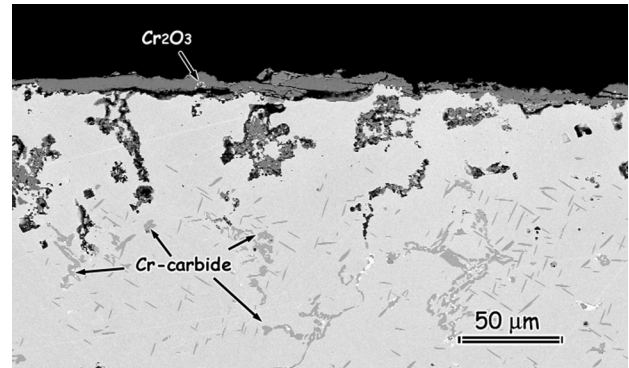
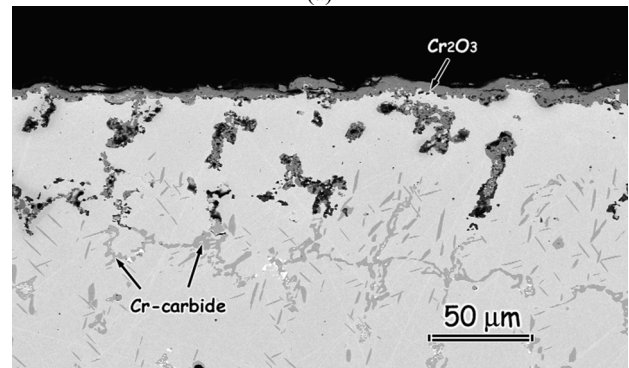


Figure 21. Cross-sectional micrograph of IN 738 after 500 cycles at 1000°C in air with water vapor at a pressure of 0.3 atm.

14, and NiO was present in the oxide scale, Figure 21. The weight losses of X-40 were smaller than those observed for IN 738, Figure 14, but the degradation of this alloy was substantial with substantial amounts of internal oxidation of carbide phases, Figure 22, in both wet and dry air.



(a)



(b)

Figure 22. Comparison of cross-sectional micrographs of X-40 after 615 cycles at 1000°C (a) in dry air, and (b) in air with 0.3 atm water vapor.

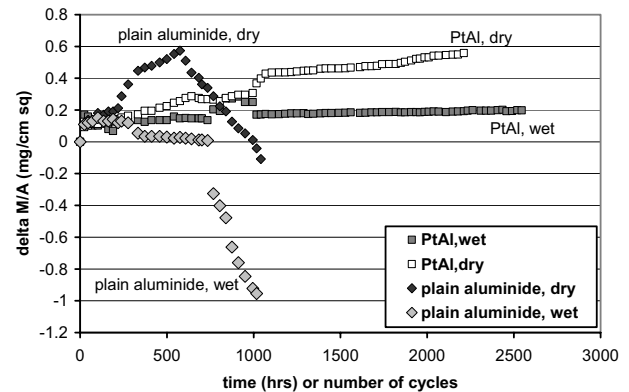


Figure 23. Change in mass vs time for aluminide coatings cyclically exposed at 1100°C in dry and wet (0.1 atm) air.

The results that have been obtained with the chromia-forming alloys show that these alloys are resistant to cyclic oxidation degradation at 700°C with no substantial effects of water vapor. On the other hand, these alloys are degraded rather severely at 900°C. This occurs due to cracking and spalling of the Cr₂O₃ scales which is exacerbated in wet air due to the vaporization of Cr₂O₃ via the formation of hydrated chromium oxides (e.g. CrO₂(OH)₂) [17].

Aluminide Coatings

Both straight and platinum modified aluminide coatings on René N5 were cyclically oxidized at 1100°C in wet and dry air. The weight change versus time curves obtained for these tests are presented in Figure 23. The α -Al₂O₃ scale that formed on the straight aluminide coating began to spall after about 200 cycles and the spalling was more severe in the test with water vapor, Figure 23. The α -Al₂O₃ that formed on the platinum modified aluminide coating was very resistant to cracking and spalling in the cyclic test. Moreover, water vapor did not appear to exert a large effect on the spalling of α -Al₂O₃ from this coating, Figure 23. These results show that cracking and spalling of the α -Al₂O₃ scales is more severe in gases with water vapor and this effect becomes less dominant as the interfacial toughness of the α -Al₂O₃-alloy interface becomes greater. Water vapor must cause the α -Al₂O₃-alloy interfacial toughness to be decreased, but when this toughness is high, as occurs on platinum modified aluminide coatings, the magnitude of the toughness decrease is not sufficient to cause significant amounts of oxide scale to spall [16-18].

Concluding Remarks

Water vapor affects the oxidation characteristics of alloys that develop α -Al₂O₃ or Cr₂O₃ scales for oxidation resistance in different ways. In the case of the α -Al₂O₃ formers, water vapor adversely affects the selective oxidation of aluminum by causing more transient oxides such as NiO to be formed. Water vapor also causes α -Al₂O₃ scales to spall during cyclic oxidation due to decreased toughness of the α -Al₂O₃ interface. In the case of Cr₂O₃-formers, water vapor probably causes more transient oxides to be formed, but this effect is not substantial probably because of the higher chromium concentrations in the chromia-formers compared to the aluminum concentrations in the alumina-formers. Water vapor also causes more spalling of Cr₂O₃ scales from the chromia-formers, but the vaporization of Cr₂O₃ in water vapor causes much more degradation at temperatures of 900°C and above.

Considering applications for superalloys in environments containing water vapor, the chromia-formers should not be used at 900°C or above due to vaporization of Cr₂O₃. In the case of the alumina-forming superalloys, problems related to the development of α -Al₂O₃ scales at low temperatures such as 700°C need to be addressed.

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