EFFECT OF WATER VAPOR ON THE OXIDATION RESISTANCE OF STAINLESS STEELS

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ABSTRACT

Stainless steel foils are being evaluated for use in exhaust gas environments. In order to examine the effect of water vapor in the exhaust gas on oxidation performance, foil specimens were exposed at 650°-700°C to air containing 4-15% water vapor. In general, stainless steel alloys such as type 310 and 20/25/Nb were only marginally affected by the presence of water. However, alloy type 347 stainless steel was more strongly attacked under these conditions. These results suggest that alloys with Cr contents above 20% are better suited to exhaust gas environments.

INTRODUCTION

In order to increase engine efficiency, there is an incentive to increase combustion temperatures. Typically this has been done incrementally over an extended period of time as engine improvements are introduced. However, at some point, a temperature is reached that has a significant effect on corrosion-limited component lifetimes. Of particular interest are thin-walled stainless steel

components for high-temperature automotive and power generation applications. Such components have a limited reservoir of, for example, chromium required to form a protective, slow-growing external scale. This problem of a limited Cr reservoir is further compounded if the rate of Cr consumption (i.e the scale growth rate) is accelerated by the presence of water vapor[1-4] as a combustion product in exhaust streams. In 1991, Kofstad[5] called the influence of water vapor on alloy oxidation a "forgotten" problem, and, indeed, until recently there had been little work done in the area. More data are available for steam exposures, but missing from the literature are data for 0-10% water contents. The combination of higher temperatures and longer life performance requirements has significantly increased interest in water vapor effects, particularly for material selection studies.

Currently, water vapor effects on oxidation behavior are being explored for both alloys [e.g. Ref.[6-8]] and ceramics [e.g. Ref.[9-10]]. In general, water vapor effects appear stronger for chromia-forming alloys than alumina-forming alloys [5]. However, besides a lack of data, there are also few mechanistic explanations for the influence of water vapor. As a first step in studying water vapor effec several different materials were characterized in order to understand the magnitude of the problem on thin-section stainless steel components and to define critical time and temperature regimes. These results indicate that in the temperature range 650-700°C, the effect of water vapor on oxidation performance is much more severe for an alloy with less than 20wt.%Cr like type 347 stainless steel than for higher Cr content alloys.

EXPERIMENTAL PROCEDURE

The chemical compositions of the alloys studied are listed in Table I. All of the alloys were vacuum cast and rolled to ≈100 μm thickness. The foil designated "standard" 347 was rolled in a commercial mill while the other alloys were rolled in laboratory-scale facilities. Specimens approximately 1.2cm x 2cm were cleaned in acetone and methanol prior to oxidation. Oxidation kinetic data were generated by weighing every ≈168h to totals of 500h and 1000h using a Mettler model AG245 balance.

Oxidation exposures in air (with and without injected water) were conducted by flowing the gas through an alumina tube that was inside a resistively-heated horizontal tube furnace. Distilled water was atomized into the

flowing gas stream above its condensation temperature and heated to the reaction temperature within the alumina tube. Water was collected and measured after flowing through the tube to calibrate the amount of injected water. Up to 10 specimens were held in slots in an alumina boat in the furnace hot zone. After oxidation, selected specimens were Cu-plated and sectioned for metallographic analysis.

RESULTS

650°C Observations

Mass change results after 1000h exposures at 650°C are summarized in Table 2 and Figure 1. In air, all of the alloys exhibited a very low oxidation rate, on the order of 10^{-16} $g^2 cm^{-4}/s$ or <0.5 μm/y. The addition of water vapor had a particularly strong effect on the type 347 foils. In particular, the lab-rolled foils, modified 347 and 347 with Al, were very strongly attacked and would have been fully consumed in a few thousand hours under these conditions. The mill-rolled standard 347 foil showed increased mass gains with water vapor but was not as strongly attacked. These results indicate that a mill-rolled surface finish is preferable to a lab-rolled surface finish for these exposure conditions. The type 310 foils showed relatively little effect. Measured mass losses did not appear to be the result of scale spallation. For the 20/25/Nb foils, mass gains increased with increasing water content. The 20/25/Nb foil with a lower Cr content (18.3%Cr) exhibited a much higher mass gain than the standard 20/25/Nb (19.9%Cr) foil.

From the final mass gain results alone, there does not appear to be much difference between the standard versions of type 347 and 20/25/Nb. However, the entire data set (Figure 2) indicates that most of the total mass gain for 20/25/Nb occurred in the first 168h followed by relatively slow mass gains thereafter. For standard 347, there appears to be an incubation period with no accelerated attack followed by a period of very high mass gain and then a continued higher rate of mass gain that was higher than that observed on 20/25/Nb. Based on the poorer performance of the lab-rolled type 347 foils, the lab-rolled 20/25/Nb may have shown better performance if it also were mill-rolled. The standard 310 foil showed a constant mass loss during the test (Figure 2), which may be the result of increased CrO_3 volatility in the presence of water vapor[11]. Thus, these results indicate that the higher Cr content foils are less strongly affected by water vapor than the lower Cr content 347 foils.

Metallographic examination of foil cross-sections exposed for 1000h at 650°C showed very thin scales formed in air, Figures 3a, 4a and 4c. The addition of water vapor resulted in large nodule formation on standard 347, Figures 3b-d, although other regions showed a thin scale comparable to that formed in air. Based on concurrent work[12], the outer oxide is iron oxide with spinel or another Cr-rich oxide as the inner layer. At the location sectioned, the specimen exposed to 10% water vapor had fewer nodules than observed at 4% or 15% water vapor. The nodules for 4% water vapor were somewhat smaller and fewer in number than that observed for 15% water vapor. Based on the mass gain data at 15% H_2O (Figure 2), the nodules on standard 347 appeared to have formed between 168h and 336h in 15% water vapor. It has not been determined if the subseque mass gain was the result of lateral growth of the nodules or formation of more nodules. One interesting feature of the nodules is that the gas surface appears to have fine whiskers (Figures 3b-d).

Similar nodules were also observed on standard 20/25/Nb after exposure for 1000h to 15% H_2O(Figure 4b). However, based on the mass gain data (Figure 2), these nodules did not appear to grow significantly after the first 168h exposure. This may reflect some surface problem with lab-rolled material which initially results in nodule nucleation but likely due to the higher Cr content in standard 20/25/Nb (compared to 347), the nodules did not continue to grow. No nodule formation was observed on standard 310, Figure 4d. However, due to a problem with the Cu-plating it is difficult to observe the actual scale thickness.

700°C Observations

Mass change results after 500h at 700°C are summarized in Table 2 and Figure 5. As at 650°C, the scales formed in air exposures were very thin a protective as expected for the high Cr levels in the alloys. With the addition of only 4% water vapor, there was already very strong attack of the lab-rolled type 347 foils, and higher water contents resulted in attack of all of the type 347 foils to a similar degree. The data for standard 347 are shown in Figure 6. A 650°C, there appears to be an incubation period where no acceleration was observed. The duration of this period decreased with increasing water vapo content. With 15% water vapor, the drop in rate between 336h and 500h may simply be the result of scale spallation, Figure 7b. Thus, the actual rate of attack probably increased with increasing water vapor content.

The type 310 and 20/25/Nb foils were only moderately affected by the addition of water vapor. Again, the lower Cr 20/25/Nb foil showed the highest mass gain suggesting that Cr content of the alloy is critical. The weight losses for type 310 foils appeared to be real and not the result of scale spallation (there was no visual indication of spallation). As at 650°C, the addition of water vapor appeared to result in scale volatilization. A mass gain of 0.13mg/cm^2 was noted for standard 310 when exposed to 15% water vapor but only 0.01mg/cm^2 for modified 310, indicating some variability in response under these conditions, Table 2.

Metallographic examination of foils after exposure again showed a very thin scale formed in air, e.g. Figure 7a. While most of the surface of standard 347 was heavily attacked in the 15% H_2O environment, there were still regions with a thin surface oxide, Figure 7b. Nodules of similar thickness were observed on 20/25/Nb (Figure 7c) but they were less frequent than on standard 347. Mass gains for 20/25/Nb showed a similar trend as at 650°C (Figure 2) with most of the gains in the first 168h and little gain thereafter. This indicates that the nodules formed initially but did not grow substantially during the remainder of the test. Nodules were also observed on standard 310 (Figure 7d) but the outer iron oxide and inner spinel layers were not as thick as the nodules on standard 347 or 20/25/Nb. For standard 310, the mass gain increased after the first 168h, indicating a different progression than noted on 20/25/Nb. Shorter and longer term tests are required on type 310 and 20/25/Nb foils to clarify their performance at the higher temperature and water contents.

DISCUSSION

The test conditions were selected based on near maximum-use temperature (based on strength) for these types of stainless steels and a wide range of exhaust gas water contents. While not based on actual component exposures, these results suggest that alloys with higher Cr contents are better suited to exhaust gas environments at 650-700°C. The work of Evans et al.[13,14] suggests that, when the near-surface region of a 20/25/Nb steel is depleted in Cr to <14%, faster oxidation can take place. If the addition of water vapor accelerates the chromia formation rate, then localized Cr depletion can occur such that diffusion of Cr in the alloy cannot keep up with the amount of Cr being consumed at the reaction front. This problem may be particularly acute in relatively lower Cr alloys such as type 347 stainless steel.

The work of Quadakkers, et al.[6-7] suggests that the H_2O/O_2 ratio is an important parameter. Thus, it is probably important that further testing be based on actual H_2O/O_2 ratios observed in practice to better simulate exhaust gas environments. It also may be necessary to use a carrier gas other than air t simulate certain environments. In addition, the presence of sulfur in exhaust gas may complicate the evaluation.

This degree of accelerated attack may not be important for thick-section components, but it is significant for thin-sectioned components. As can be seen in Figures 3d and 7b, a significant fraction of the type 347 foil thickness w consumed after only 1000h and 500h, respectively, thereby decreasing the load-bearing cross-section. This type of attack will severely limit component lifetime, and testing in air without water vapor gives no indication of this problem.

These results provide some important indications about the times and temperatures required to observe accelerated attack. Of particular interest is the incubation period (e.g. Figure 6) during which no accelerated attack occurred. However, further work will be required to determine a mechanism for the detrimental role of water vapor. Several authors have suggested that water vapor results in a more defective scale, but characterization at higher resolution prior to the onset of accelerated attack will be required to study that hypothesis. It will be more difficult to confirm point defect models such as that suggested by David and Welsh[15]. They proposed that OH^- replaces O^{2-} in the scale thereby changing the defect charge balance. This may accelerate diffusion of Cr in the scale, particularly at grain boundaries, resulting in Cr depletion in the metal and thus accelerated attack.

The possibility of improving the performance of type 347 stainless steel in this environment appears very limited. The addition of 0.5wt%Al showed a marginal benefit in air exposures but did not reduce the degree of attack in water vapor, Table 2. Previous work[16] showed that for a 1wt%Al addition to type 347 the Al was internally oxidized at 650° and 700°C in air and thus is unlikely to have a beneficial effect. Also, additions of Zr and mischmetal, which may be beneficial to the oxidation behavior of chromia-formers at higher temperatures,[17,18] were not beneficial at these temperatures[16]. Thus, while type 347 stainless steel has excellent inherent oxidation resistance in air, the only apparent alternative when water vapor is present appears to be the selection of

alloys with higher Cr contents.

SUMMARY

The addition of water vapor to the test environment has a major effect on the oxidation performance of stainless steel foils at 650°-700°C. Based on the alloy compositions tested, alloy Cr content appears to be a primary factor in determining susceptibility. Alloys with Cr contents of 20% or more were more resistant to water vapor than alloys with lower Cr contents.

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TABLE 1

CHEMICAL COMPOSITIONS (WEIGHT %) OF THE STAINLESS STEEL FOILS

Material	Cr	Ni	Mn	Mo	Si	C	N	Nb	P	Ti
Std. 347	17.6	9.5	1.6	0.09	0.58	0.04	0.023	0.62	0.016	0.04
Mod. 347	18.57	13.65	1.92	0.26	0.44	0.084	0.036	0.85	0.031	0.037
347 + 0.50%Al	18.57	13.15	2.05	0.22	0.48	0.078	0.024	0.89	0.032	0.08
Std. 20/25/Nb	19.9	25.55	1.02	1.55	0.44	0.102	0.144	0.29	0.027	0.03
Mod. 20/25/Nb	20.0	25.42	0.99	1.54	0.45	0.103	0.143	0.65	0.033	0.077
Low Cr 20/25/Nb	18.27	27.15	0.96	1.42	0.42	0.091	0.135	0.41	0.029	0.06
Std. 310	24.85	20.29	1.28	0.24	0.45	0.077	0.208	0.56	0.03	0.02
Mod. 310	24.78	20.26	1.20	0.01	0.41	0.06	0.232	0.54	0.029	0.002

TABLE 2

SUMMARY OF MASS CHANGEDATA

Material	650°C, 1000h				700°C, 500h			
	air	4%	10%	15%	air	4%	10%	15%
Std. 347	0.044	0.32	0.21	0.92	0.037	0.06	4.89	3.26
Mod. 347	0.027	1.92	2.91	2.64	0.033	4.37	2.78	3.92
347 + Al	0.031	n.t.	3.79	2.94	0.024	3.92	1.31	6.69
Std. 20/25/Nb	0.053	0.07	0.15	0.32	0.055	0.30	0.41	0.21
Mod. 20/25/Nb	0.041	0.04	n.t.	n.t.	0.058	0.15	0.09	0.07
Low Cr 20/25/Nb	0.054	0.36	1.40	1.51	0.087	0.67	0.54	0.67
Std. 310	0.045	-0.05	-0.05	-0.08	0.081	-0.09	-0.19	0.13
Mod. 310	0.034	0.03	n.t.	0.22	0.057	-0.10	0.14	0.01

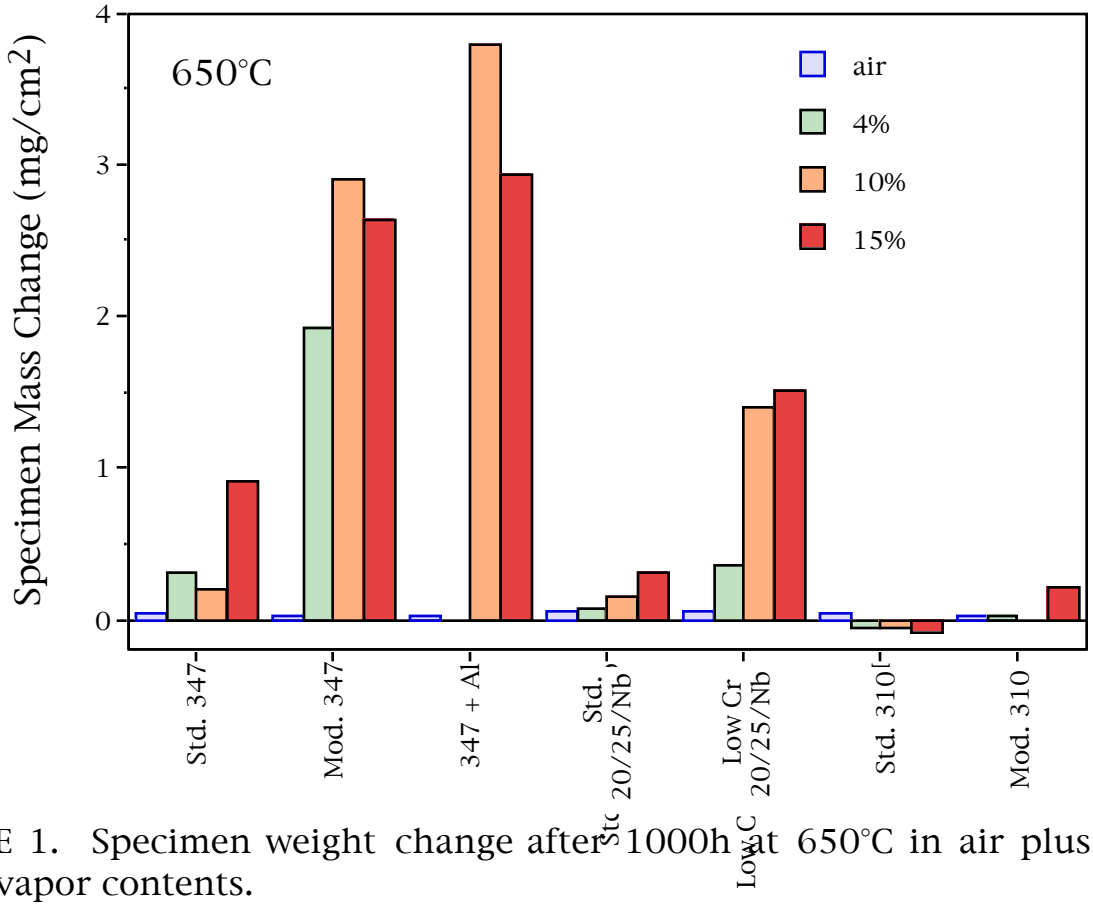

FIGURE 1. Specimen weight change after 1000h at 650°C in air plus various water vapor contents.

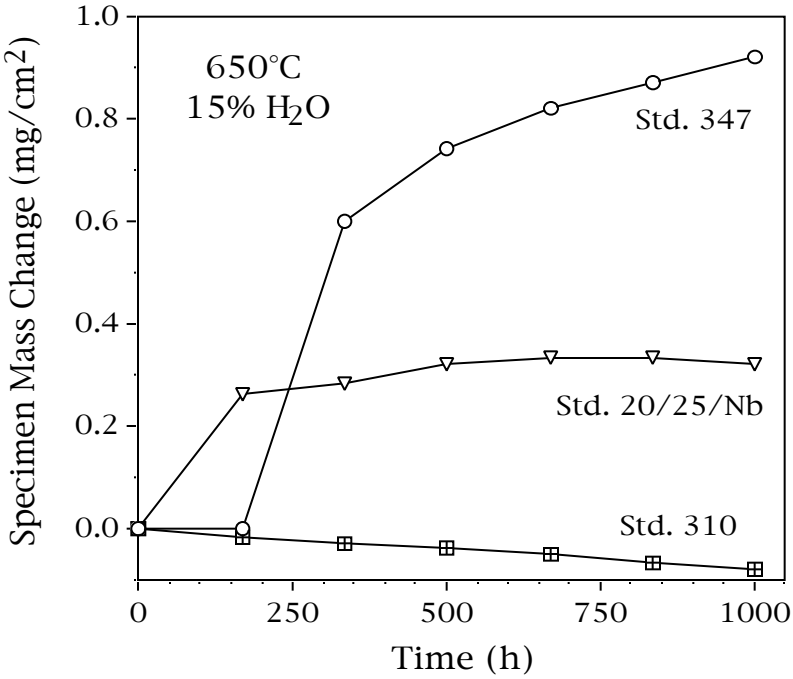

FIGURE 2. Specimen mass gains at 650°C in air plus 15% water vapor for 3 different foils. The 347 specimen showed no acceleration for the first 168h before being strongly attacked. In contrast, 20/25/Nb showed an initial acceleration that did not continue.

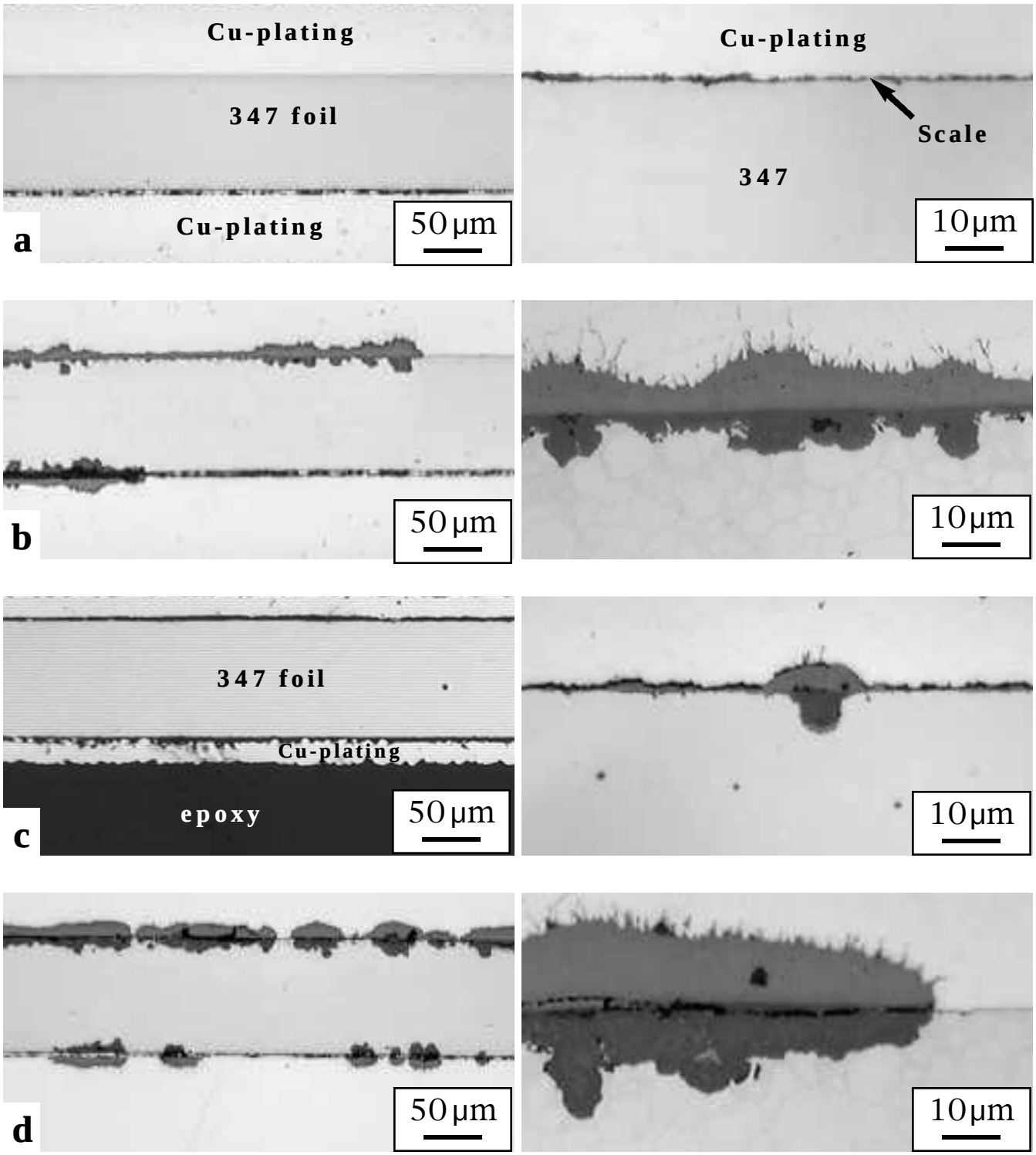

FIGURE 3. Metallographic cross-sections of the standard, mill-rolled 347 foil after 1000h at 650°C in (a) air, (b) 4% H_2O, (c) 10% H_2O and (d) 15% H_2O.

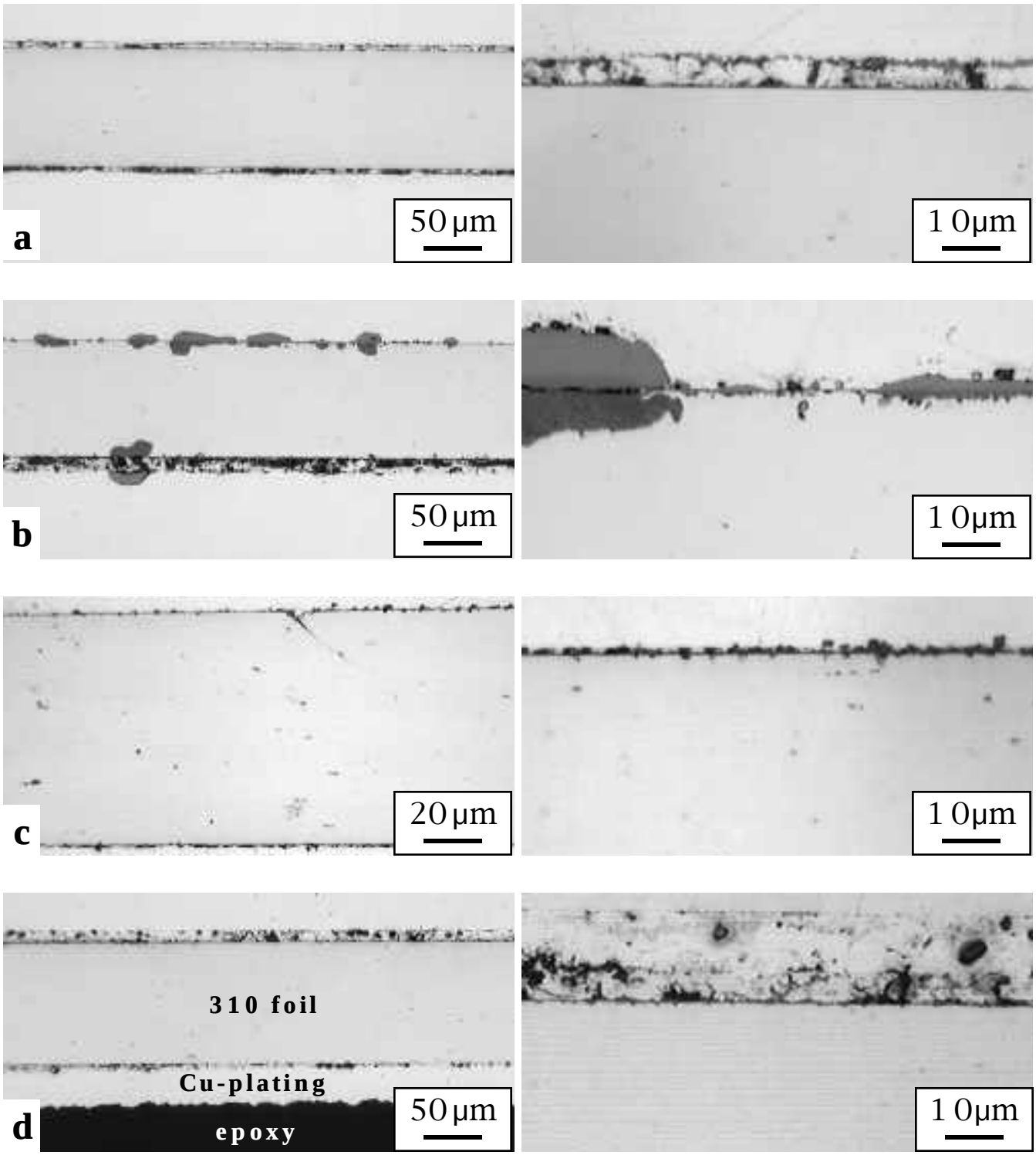

FIGURE 4. Metallographic cross-sections of foils after 1000h at 650°C; Standard 20/25/Nb in (a) air and (b) 15% H_2O; and standard 310 in (c) air and (d) 15% H_2O. A problem with the Cu-plating in (a) and (d) make the scale appear thicker than normal.

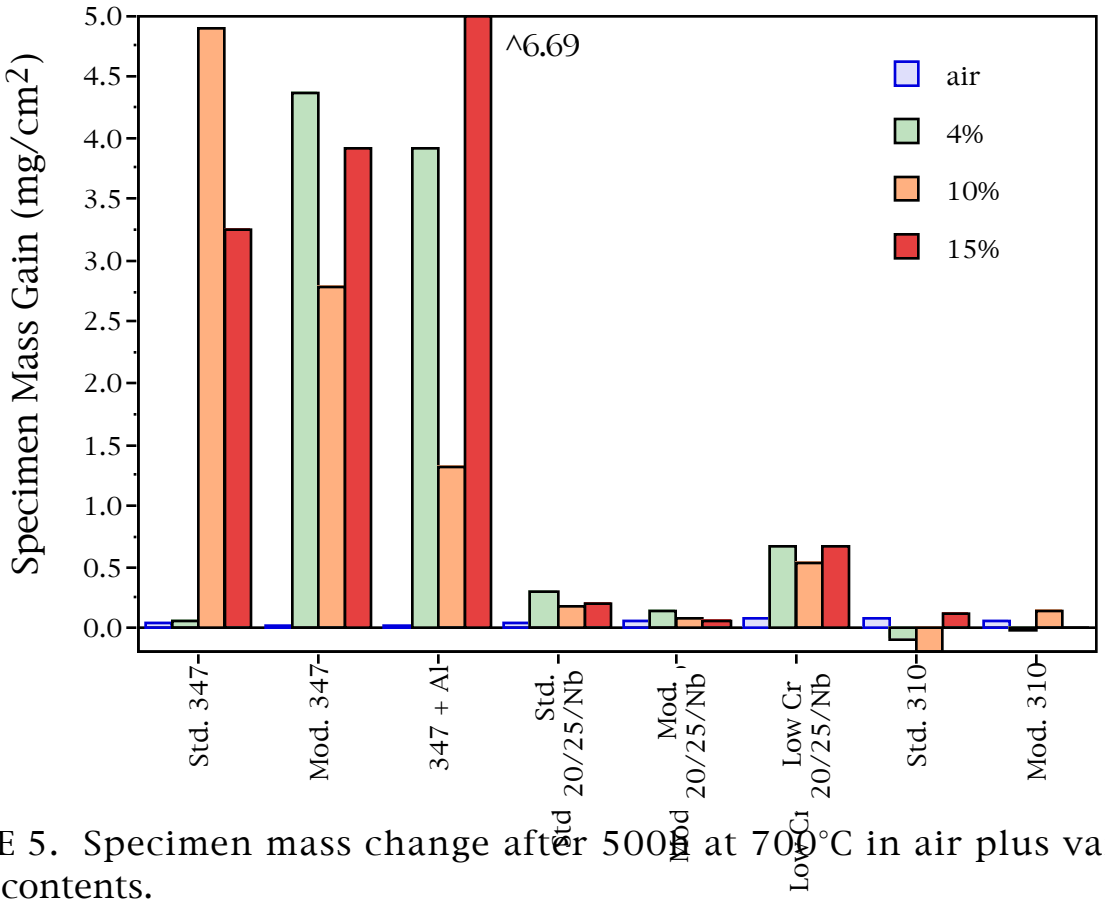

FIGURE 5. Specimen mass change after 500h at 700°C in air plus various water vapor contents.

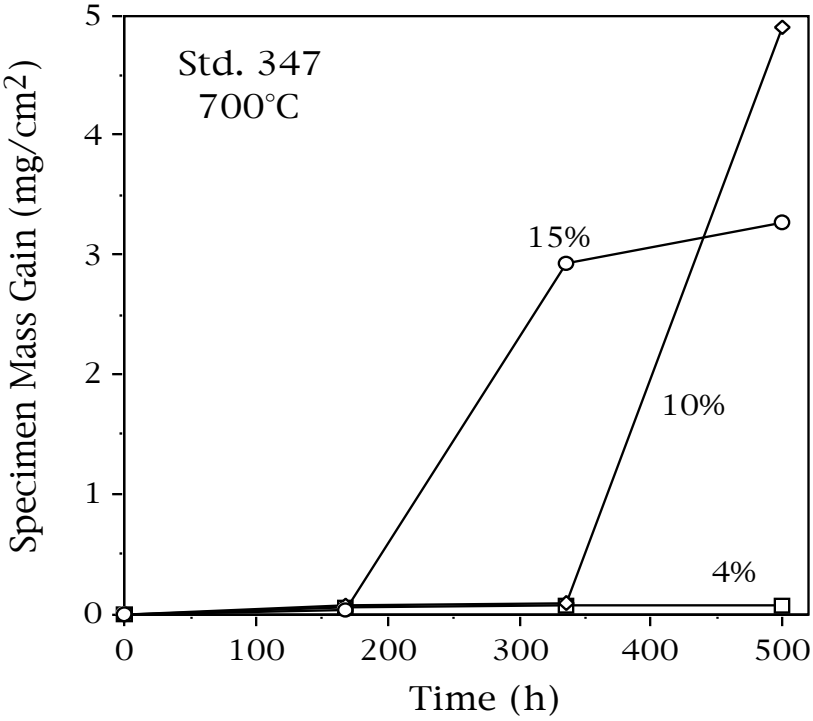

FIGURE 6. Specimen mass changes for standard 347 foils in air plus various water vapor contents at 700°C. The incubation period where no accelerated attack was observed decreased in length with increasing water content.

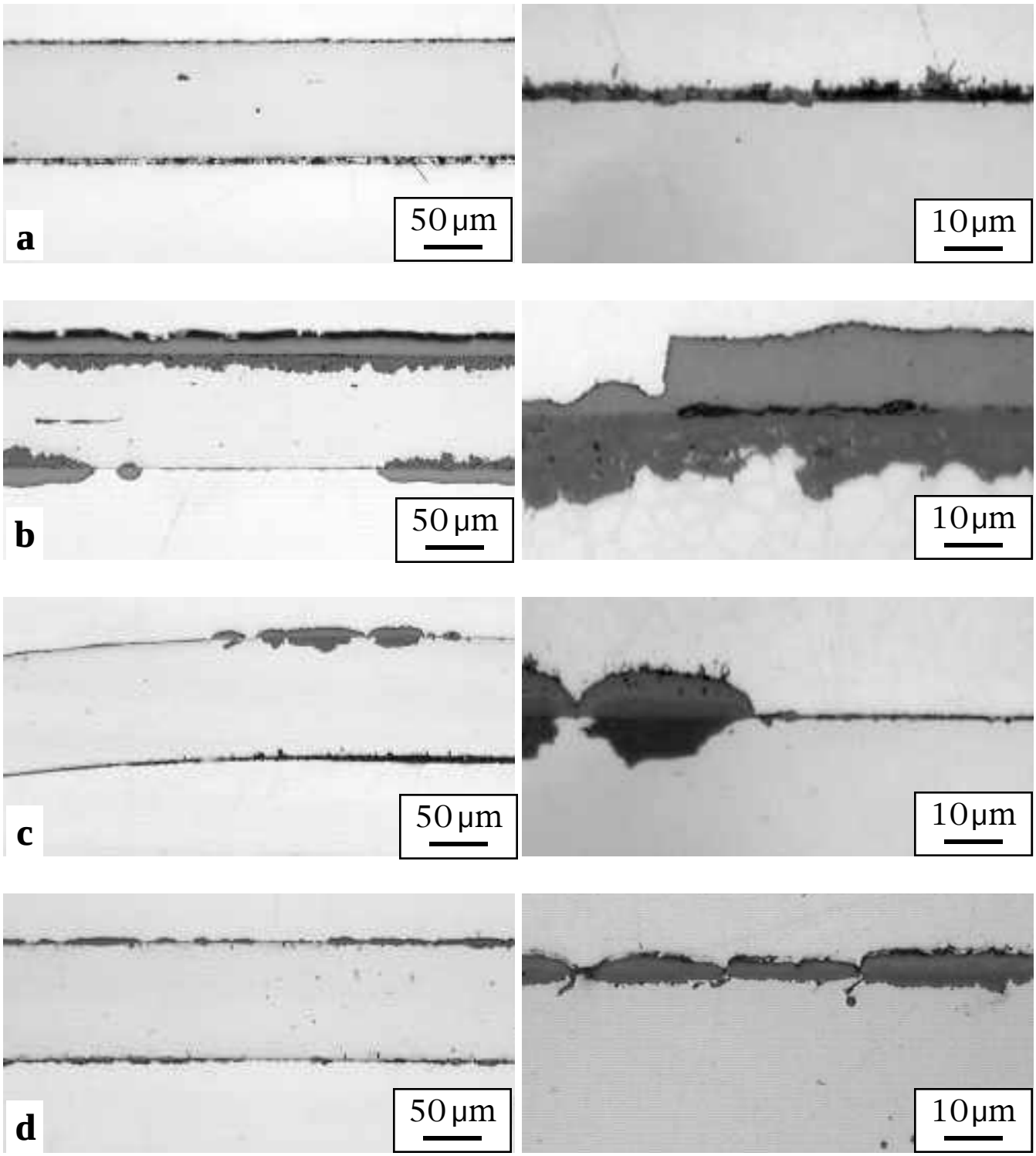

FIGURE 7. Metallographic cross-sections of foils after 500h at 700°C; standard 347 exposed in (a) air and (b) 15% H_2O; (c) standard 20/25/Nb exposed in 15% H_2O and (d) standard 310 exposed in 15% H_2O.