

# OXIDATION OF SUPERALLOYS IN EXTREME ENVIRONMENTS

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## Abstract

With the current interest in increased efficiency and reduced emissions, materials in power generation systems are increasingly exposed to more aggressive environments and higher temperatures. It is important to understand how these environments can increase corrosion rates, possibly reducing performance and likely shortening component lifetimes. Superalloys like 718 and its derivatives primarily rely on the formation of an external Cr-rich oxide layer or scale for environmental protection at typical application temperatures ( $\leq 700^\circ\text{C}$ ). While many laboratory oxidation and creep experiments are conducted in ambient air, the application environment for these alloys often involves combustion products, such as  $\text{H}_2\text{O}$  and  $\text{CO-CO}_2$ . The effect of these environments is not completely understood, especially the impact of long-term exposures, typically required of superalloy components in turbines. Air and fuel impurities, especially S and Na, can result in accelerated degradation such as the well known hot corrosion attack. While the effect of environment on crack growth has been studied, less information is available on the effect of environment on creep and fatigue properties. Initial work is being conducted to better understand the role of environment on creep properties, eventually including in-situ testing. Examples are given from steam and wet air environments and comparisons of different superalloy compositions with cast versus wrought microstructures.

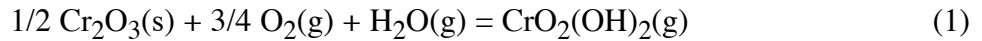
Keywords: oxidation, corrosion, steam, microstructure, turbines

## Introduction

Higher efficiency power generation systems yield benefits in reduced fuel usage, emissions and plant size. However, one of the primary strategies for increasing efficiency is higher temperatures, which can cause decreased component lifetimes or trigger new degradation mechanisms, sometimes requiring new, more expensive material solutions. A good example is the potential transition to Ni-base alloys for advanced ultra-super-critical (A-USC) steam boilers [1,2]. New system requirements for reduced emissions, carbon capture, or use of biofuels or opportunity fuels also can create new operating environments, sometimes referred to as “extreme” environments. In addition to higher temperatures, these extremes can include high levels of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , S or other impurities. For example, burning synthesis gas (derived from coal or biomass) or hydrogen in a turbine can lead to extremely high  $\text{H}_2\text{O}$  contents (30-90 vol.%) compared to the 10-15 vol%  $\text{H}_2\text{O}$  with a natural gas-fired turbine [3-5]. Likewise, natural gas typically has low impurities but new fuel stocks can have significant impurities leading to increased corrosion rates or new types of corrosion attack.

Typically, superalloys like 718 and similar alloys with a base composition of

Ni~20wt.%Cr (Table I) are considered fairly oxidation resistant. This level of Cr typically results in the formation of a dual layer external oxide layer or scale with a base metal outer layer such as NiCr<sub>2</sub>O<sub>4</sub> and a protective Cr-rich inner one, e.g. Cr<sub>2</sub>O<sub>3</sub> [6-10]. Alloy additions that have a higher affinity for O than Cr, such as Ti, Al and Nb, may oxidize internally beneath the scale and increase the rate of degradation, or Si can form a nearly continuous inner layer and reduce the rate of scaling [11]. With higher levels of Al in the alloy, typically found in single-crystal superalloys, an inner alumina layer can be formed, which is more protective at higher temperatures [8,12]. An example of this difference is with oxidation in the presence of H<sub>2</sub>O [13-17]. While most high temperature alloys rely on Cr-rich protective scales, these oxides form volatile Cr oxy-hydroxide in the presence of O<sub>2</sub> and H<sub>2</sub>O resulting in accelerated corrosion rates:



Volatilization follows linear kinetics leading to an accelerated rate of Cr loss and increased Cr depletion in the underlying alloy, which may destabilize the microstructure. Mass losses for Ni-base alloys are routinely observed under these conditions [17,18]. Superalloys with higher Al contents, >3wt.%, can form a protective external alumina scale, which is more stable than chromia such that these alloys do not experience volatilization [19]. However, even alumina-forming alloys and coatings can experience increased scale spallation in the presence of H<sub>2</sub>O [20,21].

Several studies have examined high temperature environmental effects of simple oxidizing environments on crack growth rates and fatigue life, which is extremely important for wrought and cast superalloys [22-24]. Those results have been reviewed elsewhere [25,26], but do not include more aggressive environments, i.e. those containing H<sub>2</sub>O and S. The purpose of this paper is to review some of the extreme environments and how they can impact the degradation rates of

Table I. Alloy chemical compositions (weight% or ppmw for S) determined by inductively coupled plasma analysis and combustion analysis.

Material	Ni	Cr	Mo	Co	Fe	Ti	Al	Mn	Si	C	S	Other
718	54.1	18.0	3.1	0.3	17.6	1.0	0.5	0.1	0.10	0.04	<10	5.0Nb
718Plus	52.5	17.9	2.7	8.9	9.5	0.8	1.3	0.04	0.06	0.02	<1	5.3Nb,1W
939	48.4	22.2	0.01	18.9	0.03	3.8	1.9	<	0.03	0.16	2	2W,1Nb,1.4Ta
740	48.2	23.4	0.5	20.2	1.9	2.0	0.8	0.3	0.45	0.08	<10	2.1Nb
625	63.8	23.1	8.9	0.02	3.3	0.2	0.2	0.04	0.23	0.02	<10	0.2Nb
617	53.5	22.4	9.2	12.5	0.6	0.3	1.1	0.02	0.15	0.06	<3	0.05Nb
282	58.0	19.3	8.3	10.3	0.2	2.2	1.5	0.1	0.06	0.06	<1	
263	50.0	20.3	6.1	19.5	0.6	2.3	0.6	0.3	0.09	0.06	<3	0.1Nb
230	60.5	22.6	1.4	0.1	1.5	0.01	0.3	0.5	0.38	0.10	9	12.3W
105	53.0	15.5	4.7	19.0	0.8	1.4	4.9	0.1	0.13	0.14	20	0.12Zr
31V	56.6	22.4	1.9	0.02	14.5	2.2	1.3	0.05	0.09	0.04	3	0.8Nb,0.06Zr

< indicates below the detectability limit of <0.01%

superalloys like 718. Examples are used from different studies to illustrate the effect of environment, composition and microstructure on oxidation resistance. Furthermore, the early results of a study examining the effect of environment on creep properties are reported. Finally, some concluding thoughts on strategies for improving oxidation resistance of this class of alloys are included.

### Effect of Water Vapor on Oxidation

For convenience, many oxidation studies are conducted in ambient air or otherwise “dry” oxidation conditions. However, most high temperature applications involve combustion of some form resulting in the presence of elevated water vapor in the environment and strongly affecting oxidation behavior. For example, Figure 1 shows mass change data for alloys 718 and 718Plus at 650° and 700°C. While there is little difference in mass change between these two alloys, there is considerable difference between the mass gains in ambient laboratory air and those observed in “wet” air containing 10 vol.% H<sub>2</sub>O. As suggested by equation 1, the presence of O<sub>2</sub> and H<sub>2</sub>O results in the formation of a volatile oxy-hydroxide resulting in a net mass loss at both temperatures. At a longer exposure time, the mass gain increased unexpectedly at 700°C. Further characterization and longer exposures are needed to better understand the performance in this environment. However, initial characterization of 718Plus specimens exposed to the wet air environment for 1 kh confirmed increasing Cr depletion with exposure temperature from 650°-800°C and less Cr depletion in laboratory air. This data is in a companion study [27]. The Cr depletion and mass gain results are consistent with volatilization and the accelerated Cr loss in the

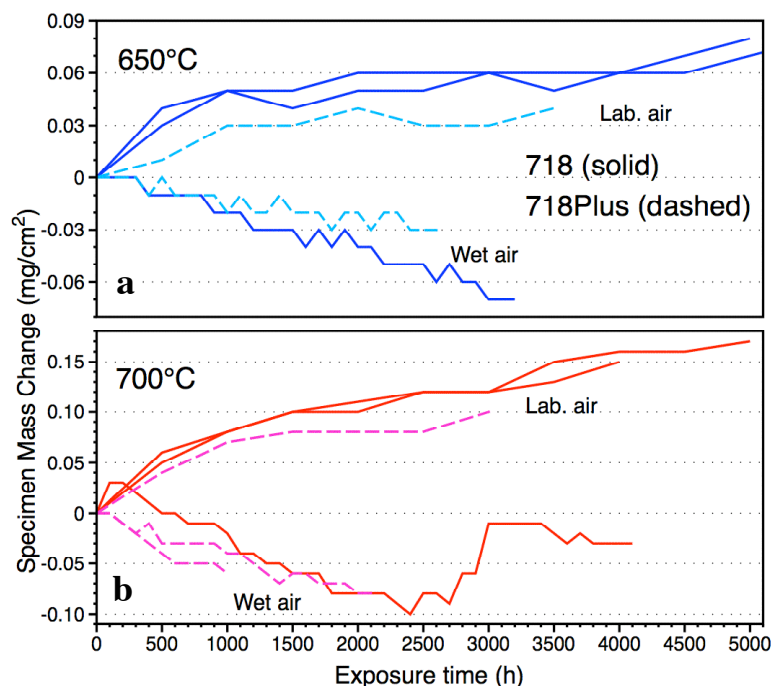


Figure 1. Specimen mass change as a function of exposure time for coupons of alloys 718 (solid lines) and 718Plus (dashed lines) in laboratory air and wet (10 vol.% H<sub>2</sub>O) air at (a) 650°C and (b) 700°C.

presence of  $O_2$  and  $H_2O$ .

While the mass changes in Figure 1 are relatively small, at longer times and higher temperature, the accelerated Cr depletion due to the presence of water vapor can be significant. Alloy 625 foil has been used for high temperature recuperators to improve the efficiency of small turbines [28], including the recuperator for the 24MW WR21 marine turbine and a 4.5MW land-based turbine [29,30]. In addition to creep strength, the presence of water vapor limits the maximum operating temperature of alloy 625 in this application. Figure 2 shows a mass gain followed by a rapid mass loss due to thick scale growth and spallation at 900°C; however, the consistent mass loss at 800°C attributed to volatilization suggests a problem for long-term performance in a foil application with a Cr reservoir limited by the foil thickness. An early stage oxidation study found that water vapor resulted in a thicker Cr-rich oxide scale at 700° and 800°C, Figure 3. However, this had little effect on the long-term behavior compared to the volatilization of the Cr oxy-hydroxide. Figure 4a shows the Cr loss from 100  $\mu\text{m}$ -thick 625 foil specimens exposed in wet air in a laboratory furnace [18]. The data was generated by comparing electron microprobe (EPMA) line profiles across the foil before and after exposure which accounts for Cr depletion gradients, Cr-rich phases and loss of section thickness. Thus, 625 starts with ~23%Cr and has less than 22% after 10kh at 650°C and less than 21% after 10kh at 700°C. The error bars reflect the variation due to selective Cr depletion from alloy grain boundaries and the difficulty in measuring the loss in metal section. Figure 4a shows that after only 6kh at 800°C, the Cr content in 625 foil has dropped to <18% due to oxide formation and Cr volatilization. Obviously, if the recuperator needs to operate for 25-40kh [31], the rate of Cr loss is unacceptably high at 800°C. Almost 25% of the total alloy Cr reservoir in the foil had been consumed in only 6kh. When the Cr content drops below some critical level (~15%Cr), more accelerated oxidation would be

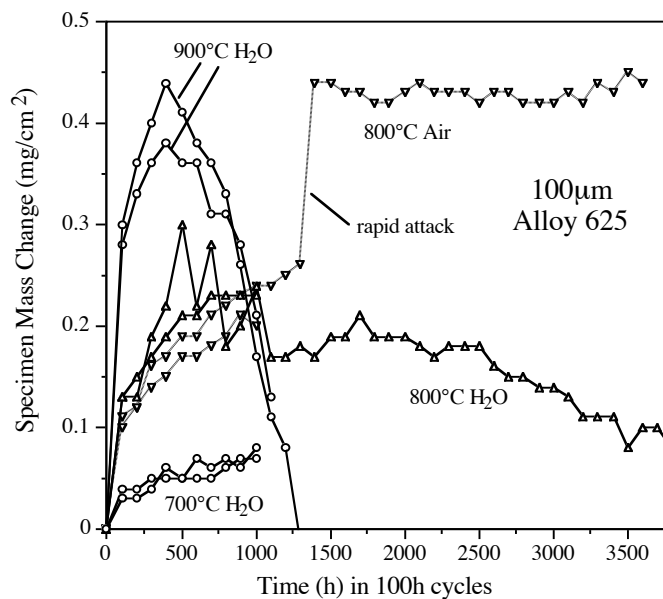


Figure 2. Oxidation data for 100  $\mu\text{m}$  (4mil) thick alloy 625 foil at 700°C-900°C using laboratory air and air+10vol.% $H_2O$  (marked  $H_2O$ ) and 100h cycles. At 700°C, the mass gain was very low, while at 900°C, high mass gains were followed by mass losses. At 800°C, a sharp increase in mass gain was observed in dry air, while in wet air the mass loss was typical of volatilization.

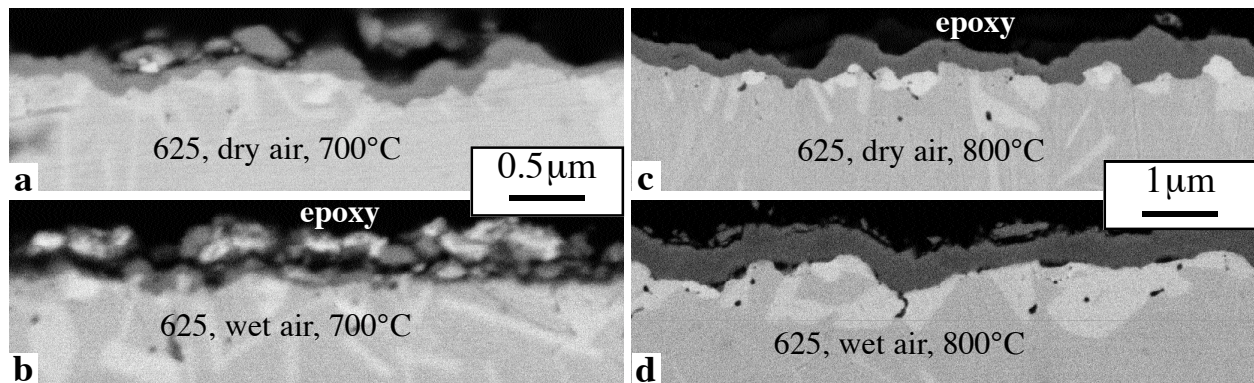


Figure 3. SEM back-scattered electron images of polished cross sections of the scale formed on alloy 625 after 100h at (a,b) 700°C and (c,d) 800°C in (a,c) air and (b,d) air plus 10% water vapor. The round precipitates in the metal are rich in Mo and the acicular precipitates are rich in Nb.

expected as the alloy would no longer be able to form a protective Cr-rich oxide and more Ni-rich oxide would form.

Figure 4b compares the Cr loss from 625 and several Fe-base alloy foils exposed to wet air for 10kh at 650° and 700°C. Compared to bulk specimens, it is much easier to quantify the Cr loss in foils. It can be seen that the Cr loss from the Ni-base alloy was similar to the Fe-base alloys and that Mn content did not affect the Cr loss rate from the metal. It is often assumed that the formation of thick Mn-rich oxides (which strongly affects the mass gain) reduces the loss of Cr by blocking volatilization [32]. These results indicate that Mn additions do not reduce Cr loss under these conditions.

Another application for Ni-base alloys is exhaust valves in reciprocating engines. When

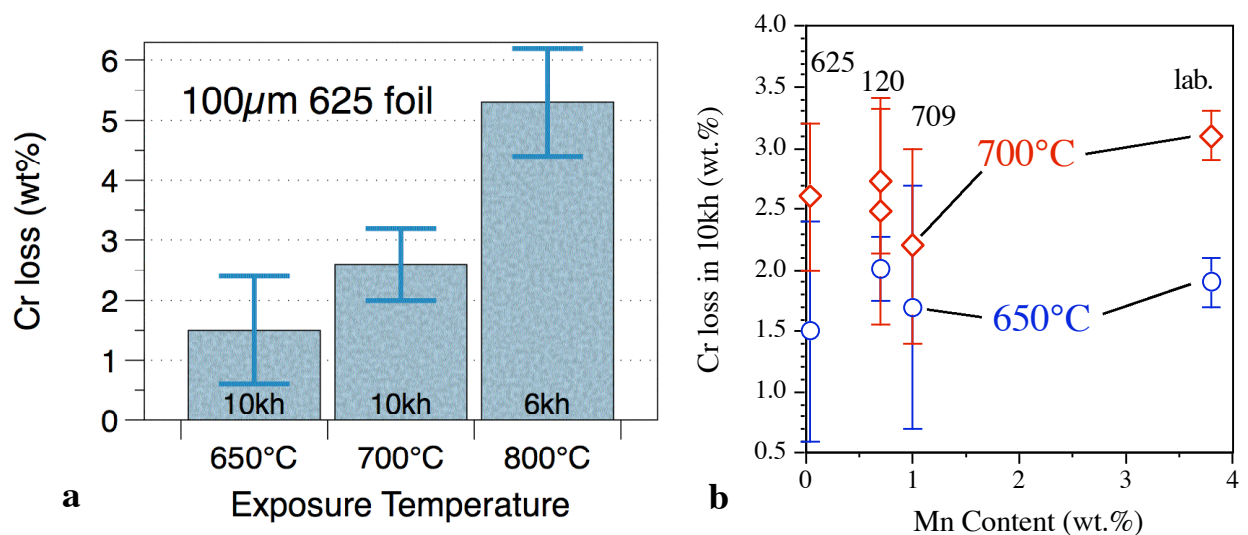


Figure 4. Measured Cr depletion from 100μm foil specimens (a) as a function of exposure temperature in wet air for alloy 625, and (b) as a function of alloy Mn content for 625, 120 (Fe-35Ni-25Cr), 709 (Fe-25Ni-20Cr) and a lab.-made Fe-20Cr-20Ni-4Mn alloy [18].

natural gas is the fuel, the exhaust gas can contain  $\sim 20$  vol.%H<sub>2</sub>O and temperature can exceed 800°C. Valve failure has been attributed to fatigue cracking initiated in the Cr-depleted surface layer [17]. Figure 5 shows mass gain data at 850°C for current valve alloy 31V and two higher strength alloys, 282 and 105. Both 31V and 282 form a Cr-rich oxide and 105 forms an Al-rich oxide with a lower mass gain. The chromia-forming alloys began to lose mass after  $\sim 1500$ h of exposure. Figure 6 shows a cross-section of each material after a 1kh exposure. Both chromia-forming alloys formed an external oxide but more extensive internal oxidation on the alloy grain boundaries was observed on 31V compared to 282. A very thin Al-rich oxide was observed on most of the surface of 105, however, larger oxide nodules also were observed accounting for some of the mass gain. Further characterization is needed to understand how each of these materials will perform in this environment, including the environmental effect on fatigue life.

### Oxidation in Steam and Effect of Microstructure

As mentioned previously, the U.S. A-USC steam program will need to use Ni-base alloys in both the boiler tubing and steam turbine in order to meet the  $\sim 350$  bar (5,000psi) and 760°C operating goals [1,2]. Steam testing has been performed at a variety of temperatures and pressures to better understand the effect of steam on candidate materials [33]. Figure 7 shows data collected for alloy 718 and 718Plus in 17bar steam at 800°C. Unlike the wet air environment, little free O<sub>2</sub> is available to form CrO<sub>2</sub>(OH)<sub>2</sub>. Thus, a mass gain was observed, unlike the mass loss observed in 1 bar wet air [27]. Some scatter was observed in the data, however, as in Figure 1, the two alloys show similar performance. Figure 8 gives examples of the oxide scales formed on 718 and 718Plus in steam at temperatures from 600° up to 800°C. At more typical operating temperatures, 600-650°C, a thin protective oxide formed on 718, Figures 8a and 8b. Exposures at 750°-800°C show increasing amounts of internal oxidation with time and temperature as the Al, Ti and Nb internally oxidizes. (Exposures were conducted at 800°C to simulate longer-term exposures at lower temperatures.) A thinner scale and less internal oxidation was observed on 718Plus

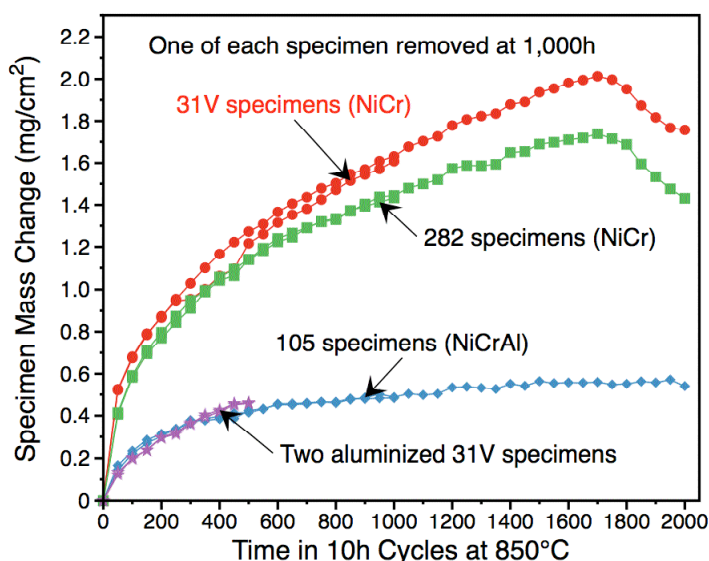


Figure 5. Specimen mass gain as a function of exposure time in 10h cycles at 850°C for specimens of alloys 31V, 105, 282 and aluminized 31V exposed in air with 10 vol.%H<sub>2</sub>O.



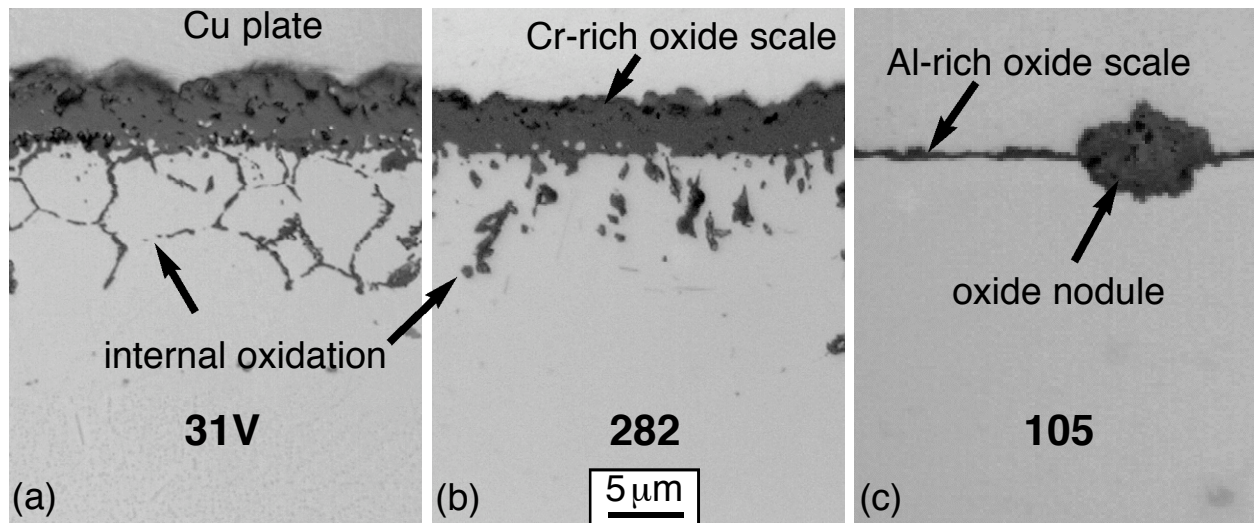


Figure 6. Light microscopy of polished cross-sections of coupons exposed to air+10 vol.%H<sub>2</sub>O for 1,000h at 850°C (a) alloy 31V, (b) alloy 282 and (c) alloy 105.

compared to 718 after 2kh at 800°C in steam, Figures 8d and 8e. The longest exposure, 8kh, did not show significantly deeper internal oxidation or thicker scale, Figure 8f. However, the volume of internal oxide appeared to increase.

In addition to 718, several materials were evaluated at 800°C in steam in both the cast (after heat treatment) and wrought microstructures, Figure 9. Coupons were cut from regions with

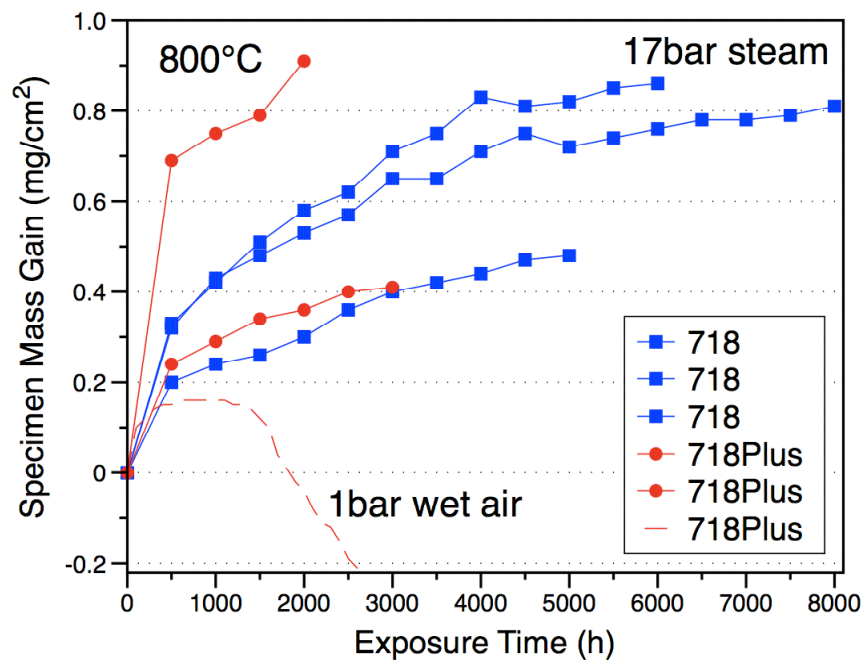


Figure 7. Specimen mass gain as a function of exposure time in 500h cycles at 800°C in 17bar steam.

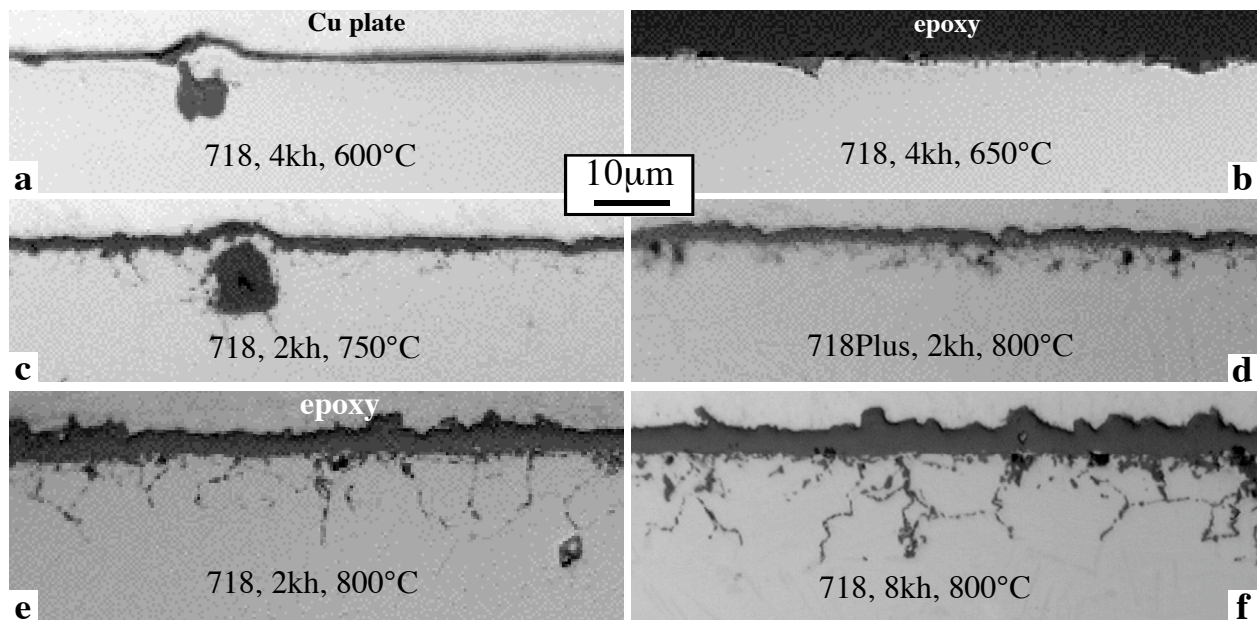


Figure 8. Light microscopy of polished cross-sections of alloy 718 and (d) 718Plus after exposure to 17bar steam (a) 4kh, 600°C, (b) 4kh, 650°C, (c) 2kh, 750°C, (d) 718Plus 2kh, 800°C, (e) 2kh, 800°C and (f) 8kh, 800°C.

columnar and equiaxed grains to compare their behavior. The mass gain for 718 and 939 are shown for comparison. Several materials showed only minor effects of microstructure on mass

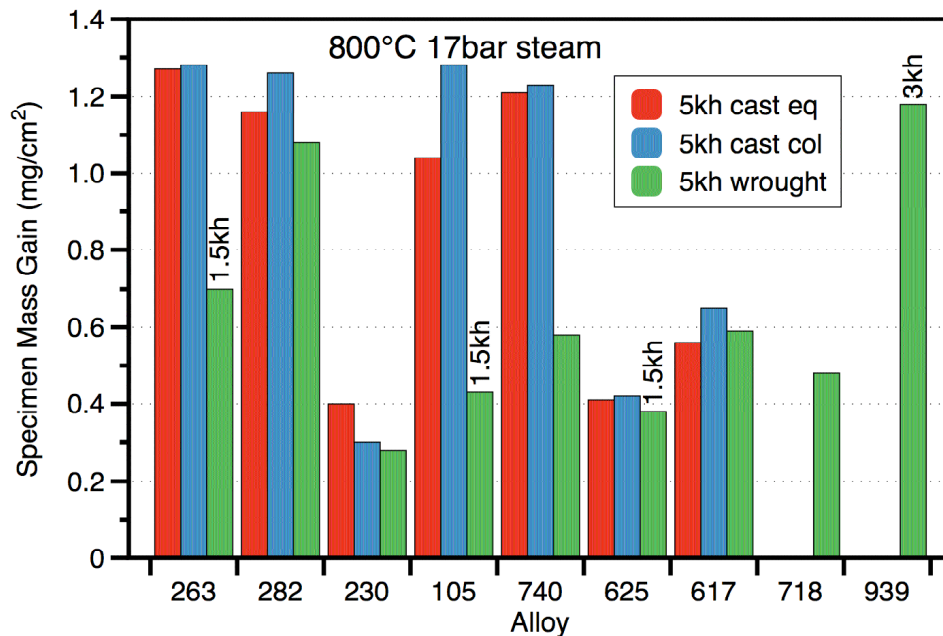


Figure 9. Specimen mass gain of various alloys after 5kh at 800°C in 17bar steam. Wrought and cast microstructures were evaluated with specimens cut from the castings in equiaxed (eq) and columnar (col) grain regions. In some cases where the time is noted, the test is in progress.



change in this environment. Alloy 740 showed higher mass gains for the cast versions. One way to interpret the behavior is based on the Al and Ti contents, which are prone to internal oxidation at this temperature (Figures 8d-f). Figure 10 shows the 5kh mass gains as a function of the (Al+Ti) alloy content from Table I. The mass gains generally increase to a maximum with Al content. Nominally, at higher Al contents, a lower mass gain would be expected as a protective Al-rich oxide scale would be expected to form. However, the presence of H<sub>2</sub>O appears to inhibit the formation of a protective alumina scale, similar to observations in wet air [20]. As noted in Figures 9 and 10, this study is not complete and internal oxidation penetration depth may be more revealing than mass gain when comparing composition effects and cast versus wrought alloys.

### Environmental Effects on Mechanical Properties

As mentioned in the introduction, the effect of environment on fatigue behavior and crack growth rates has been extensively studied in Ni-base alloys [22-26]. A very similar concern has been raised for failure of 31V exhaust valves, which shows extensive internal oxidation along grain boundaries, Figure 6a and reference 17. An additional concern is if this environmental damage will affect creep properties. Furthermore, it is expected that oxidation in the presence of H<sub>2</sub>O causes H injection into the metal as OH<sup>-</sup> ions diffuse through the scale (instead of O ions) liberating H at the metal-scale interface [34,35]. A creep rig for performing in-situ creep testing in steam is currently being constructed. Nominally, it is assumed that creep should accelerate the rate of oxidation due to damage to the brittle surface oxide. However, alloy dislocations due to creep can increase the effective Cr diffusion rate in the metal, thereby reducing the oxidation rate as a Cr-rich oxide is formed more quickly [36]. Previous work examined the effect of reforming gas on creep properties of Ni-base alloys [37] and catalyst environments [38]. Internal oxidation occurred in reforming gas but the 10kh creep properties were not affected.

As a preliminary experiment to the in-situ creep testing, small dog bone tensile specimens

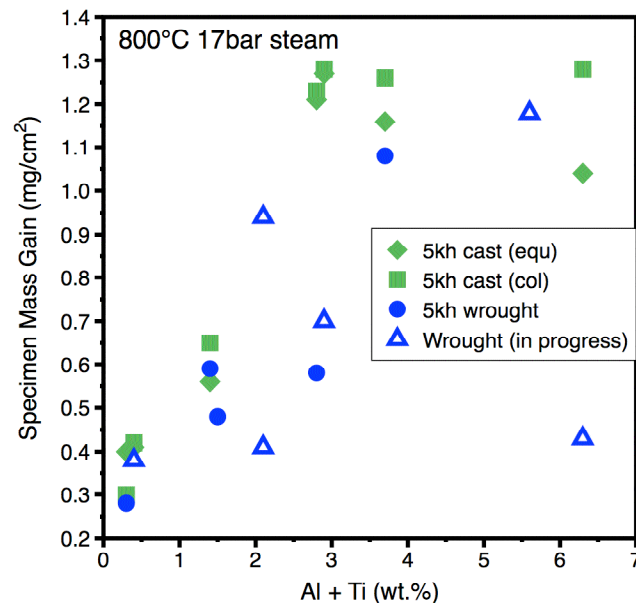


Figure 10. Specimen mass gain from Figure 9 plotted as a function of the alloy Al + Ti content. Some of the wrought experiments are still in progress and have not reached 5kh.

(25mm long, 2mm x 2mm gage) have been exposed for 2kh in 17bar steam at 800°C and then creep tested in air at the same temperature. Initial experiments with alloy 230 showed no detrimental effect of the steam exposure on subsequent creep rates [39]. Figure 11 shows the results for 718 specimens creep tested at 140MPa at 800°C. The exposure in steam significantly increased the subsequent creep rate compared to alloy 230, Figure 11b. However, an additional ageing experiment for 2kh at 800°C in an inert environment is needed to determine how much the thermal ageing affected the alloy 718 creep rate. It is important to fully understand the effect of the environment before demonstrations begin of Ni-base alloys in high temperature steam environments as envisioned by the A-USC initiative. Fatigue experiments in steam and wet air also are planned.

### Other Extreme Environments

In addition to exhaust gas and steam, other environments are seen in applications for superalloys. There is still considerable concern about sulfidizing environments because of the strong acceleration in the rate of attack and the use of impure “opportunity” fuels that can seriously degrade the lifetime of turbine components. Type II hot corrosion occurs at the typical operating temperature of 718 (650°-700°C) while Type I corrosion occurs near 900°C. Hot corrosion and sulfidation have been widely studied for many years [40-43] and little new information is apparent. Alloys with higher Cr contents have superior hot corrosion resistance, however, the melting of the Ni-S reaction product above 700°C severely limits Ni-base alloys in highly sulfidizing environments [44].

Environments of interest for various carbon sequestration strategies may be high in CO<sub>2</sub> and the role of CO<sub>2</sub> in altering corrosion mechanisms, particularly in the presence of other oxidants, is poorly understood [41,45]. However, the role of CO<sub>2</sub> is currently being more thoroughly investigated with the current focus on carbon capture. Nitriding environments may be encountered in some situations including high temperature crevice corrosion [46], and several

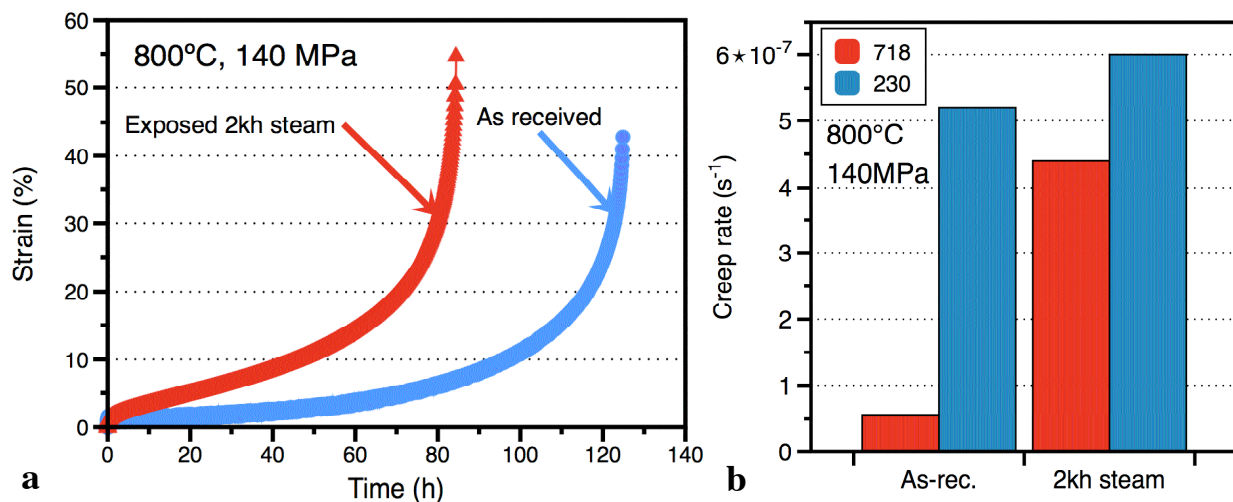


Figure 11. (a) Strain as a function of time at 800°C for 718 specimens with a stress of 140MPa, as-rec. and after the specimen was oxidized for 2kh in 17 bar steam at 800°C. (b) Steady state deformation rate for specimens of alloy 718 (from (a)) and alloy 230.

studies have examined the performance of superalloys under those conditions [47,48]. For gas-cooled nuclear reactors, an improved fundamental understanding of the effect of He impurities on the oxidation behavior of Ni-base alloys has been developed [49]. Finally, environments with high C activity are of interest in the chemical process industry and Ni-base alloys typically perform well in high C, low H<sub>2</sub>O environments [50].

### Thoughts on Improving Oxidation Resistance

While there are many extreme environments to be considered, there are relatively few strategies for improving the environmental resistance of Ni-base alloys. Improvements associated with increasing the Al content have already been mentioned, although higher Al contents result in other issues with mechanical properties, forming and joining. Higher Cr contents lead to phase instabilities and the formation of brittle Cr-rich phases. Minor alloy additions have been well-explored and it is well known that so called “reactive” elements improve the oxidation resistance of Ni-base alloys when added as an alloy addition or oxide dispersion [51-56]. One point to emphasize is that, in chromia-forming alloys, the ion size of the dopant is extremely important, Figure 12. Thus, Zr additions that are commonly added to improve mechanical properties [57] are not particularly effective in improving oxidation resistance compared to larger ions. Larger ions like Y, Ce and La are more effective in blocking anion transport along the chromia grain boundaries [55,56] and changing the chromia scale growth to primarily O transport inward [58], resulting in a better oxidation resistance and a more adherent scale.

Besides changing the alloy chemistry, coatings are a common strategy to improve oxidation resistance of superalloys. Coatings rich in Al have been used for many years to protect superalloys [59], most Al-rich (aluminide and MCrAlY) coatings are primarily used for

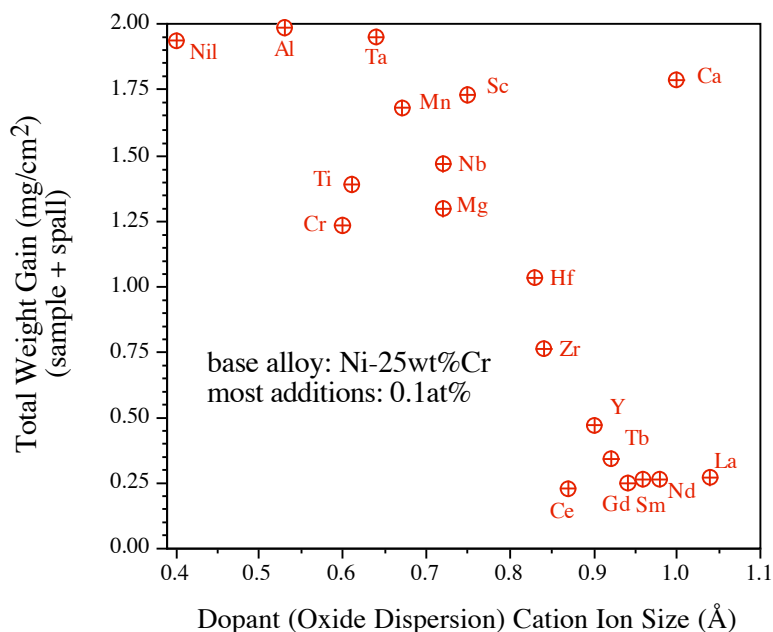


Figure 12. Total mass gain (specimen + spalled oxide) after 100h at 1000°C for various oxide dispersed Ni-25Cr alloys plotted versus the cation size of the dispersed oxide.

applications of 900°C and higher. One reason that aluminide coatings are used at higher temperatures is because they are brittle and less effective below the ductile-to-brittle transition temperature [60,61]. Figure 5 shows an aluminized specimen of 31V with a much lower mass gain, typical of an alumina-forming alloy. Similar slurry aluminide coatings have been previously tested for 5kh at 800°C in wet air and showed excellent oxidation resistance and minimal interdiffusion [17]. The concern for the valve application is the potential drop in fatigue resistance with such a coating. That issue is currently being explored with fatigue testing of coated specimens. Unfortunately, Al-rich coatings are generally not as effective in sulfidizing environments (especially hot corrosion conditions) as in oxidizing or H<sub>2</sub>O environments.

### Summary

New applications for superalloys (and old applications with new requirements) are exposing these materials to higher temperatures and more corrosive environments. Several of those environments have been discussed in order to emphasize the role of water vapor in promoting Cr depletion in the presence of O<sub>2</sub> and understand current results evaluating Ni-base candidate materials for advanced steam conditions. Coatings and minor alloy additions are the standard solutions for improving oxidation resistance. New strategies may be needed to overcome some of the proposed extreme environments in future superalloy applications.

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