7th International Symposium on Superalloy 718 and Derivatives
Edited by: E.A. Ott, J.R. Groh, A. Banik, I. Dempster, T.P. Gabb, R. Helmink, X. Liu, A. Mitchell, G.P. Sjöberg, and A. Wusatowska-Sarnek
TMS (The Minerals, Metals & Materials Society), 2010

OXIDATION OF SUPERALLOYS IN EXTREME ENVIRONMENTS

B. A. Pint, S. Dryepondt and K. A. Unocic

Corrosion Science and Technology Group, Materials Science and Technology Division
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6156

Keywords: Oxidation, environment, steam, water vapor, creep, 718Plus

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 (≤700°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 H_2O and 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 CO_2, H_2O, S or other impurities. For example, burning synthesis gas (derived from coal or biomass) or hydrogen in a turbine can lead to extremely high H_2O contents (30-90 vol.%) compared to the 10-15 vol% H_2O 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 $NiCr_2O_4$ and a protective Cr-rich inner one, e.g. Cr_2O_3 [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_2O [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_2 and H_2O resulting in accelerated corrosion rates:

$$1/2\ Cr_2O_3(s) + 3/4\ O_2(g) + H_2O(g) = CrO_2(OH)_2(g) \tag{1}$$

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_2O [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_2O 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_2O. As suggested by equation 1, the presence of O_2 and H_2O 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 1kh 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

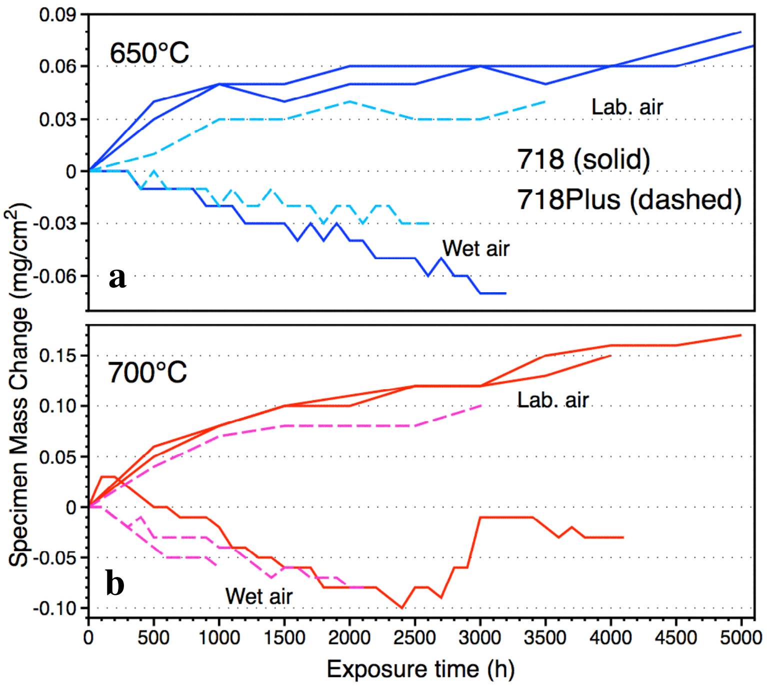

Figure 1. Specimen mass change as a function of exposure time for coupons of alloys 718 (solid lines) and 718Plus (dashed lines) in laboratory air and wet (10 vol.% H_2O) air at (a) 650°C and (b) 700°C.

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 24 MW WR21 marine turbine and a 4.5 MW 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 μm-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

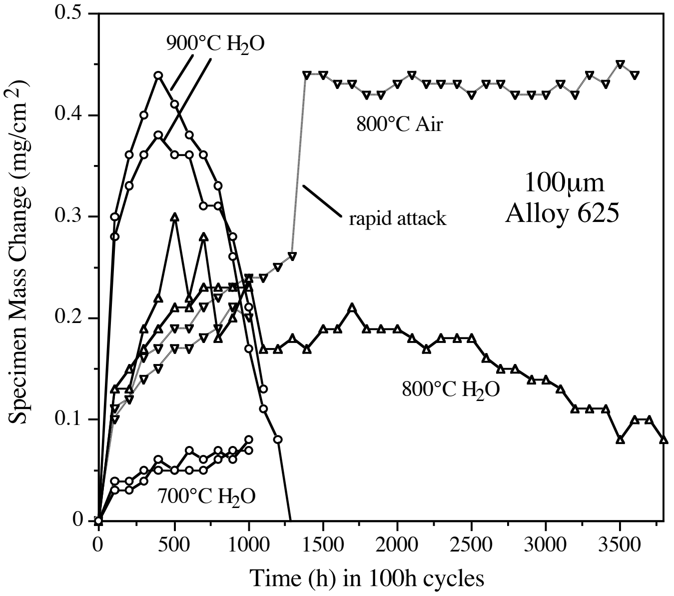

Figure 2. Oxidation data for 100 μm (4mil) thick alloy 625 foil at 700°C-900°C using laboratory air and air+10vol.%H_2O (marked H_2O) and 100h cycles. At 700°C, the mass gain was very low, while at 900°C, high mass gains were followed by mass losses. At 800°C, a sharp increase in mass gain was observed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

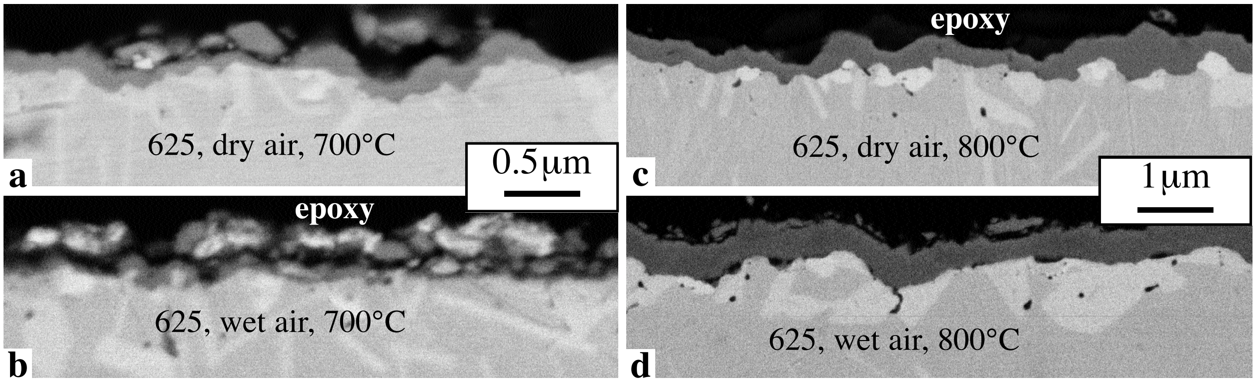

Figure 3. SEM back-scattered electron images of polished cross sections of the scale formed on alloy 625 after 100h at (a,b) 700°C and (c,d) 800°C in (a,c) air and (b,d) air plus 10% water vapor. The round precipitates in the metal are rich in Mo and the acicular precipitates are rich in Nb.

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

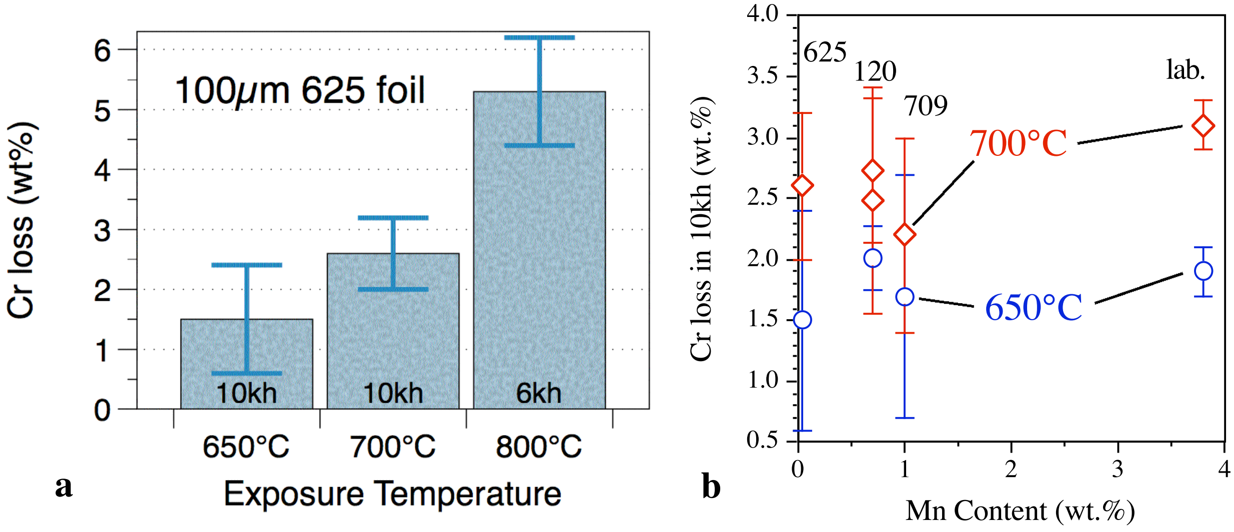

Figure 4. Measured Cr depletion from 100μm foil specimens (a) as a function of exposure temperature in wet air for alloy 625, and (b) as a function of alloy Mn content for 625, 120 (Fe-35Ni-25Cr), 709 (Fe-25Ni-20Cr) and a lab.-made Fe-20Cr-20Ni-4Mn alloy [18].

natural gas is the fuel, the exhaust gas can contain ~20 vol.%H_2O 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 ~1500h 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 ~350 bar (5,000 psi) 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 17 bar steam at 800°C. Unlike the wet air environment, little free O_2 is available to form $CrO_2(OH)_2$. 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

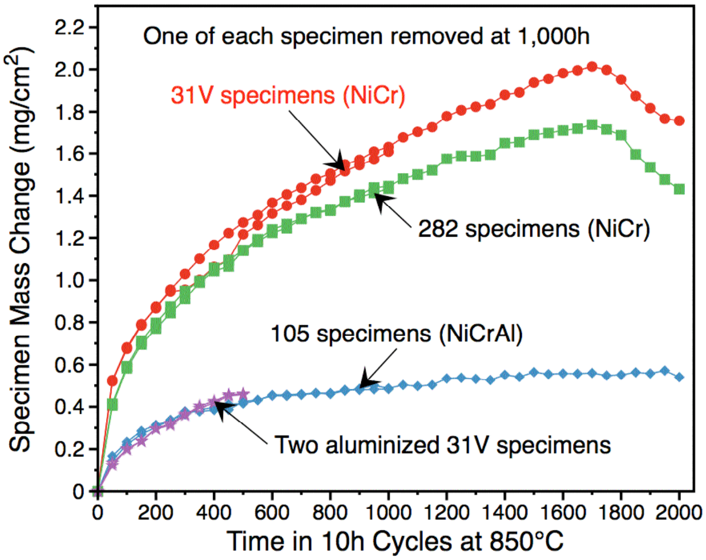

Figure 5. Specimen mass gain as a function of exposure time in 10h cycles at 850°C for specimens of alloys 31V, 105, 282 and aluminized 31V exposed in air with 10 vol.%H_2O.

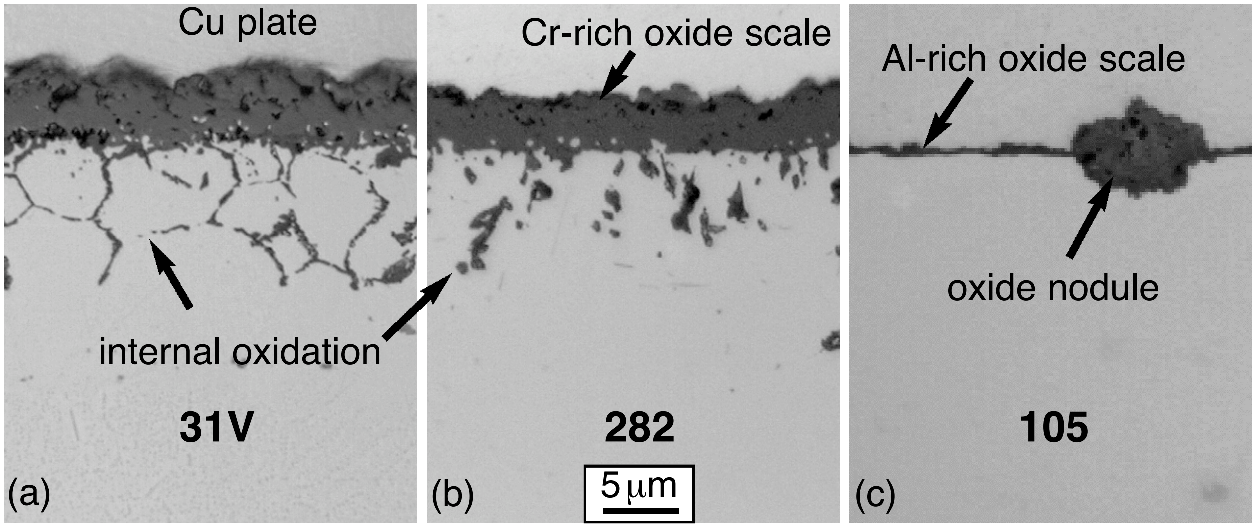

Figure 6. Light microscopy of polished cross-sections of coupons exposed to air+10 vol.%H_2O for 1,000h at 850°C (a) alloy 31V, (b) alloy 282 and (c) alloy 105.

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

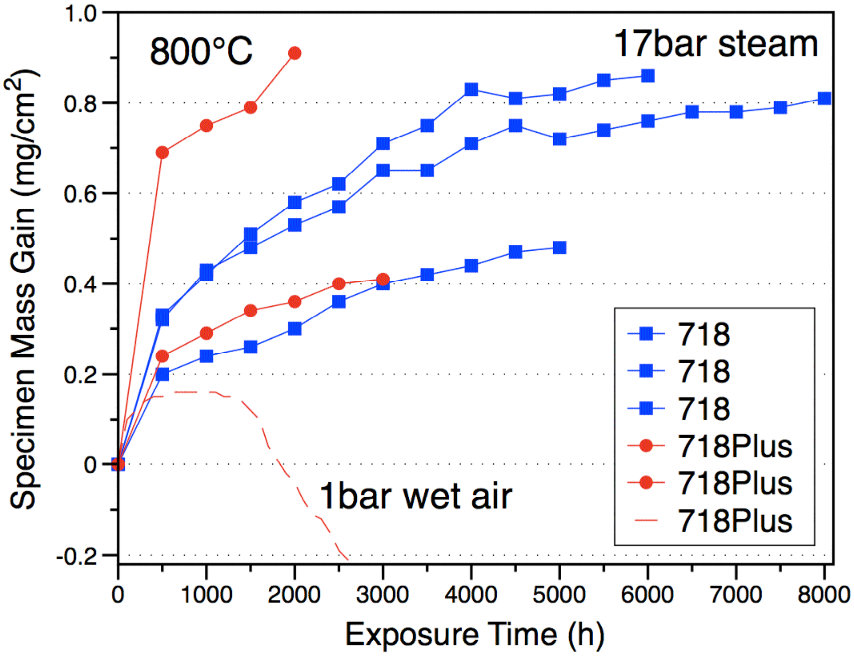

Figure 7. Specimen mass gain as a function of exposure time in 500h cycles at 800°C in 17bar steam.

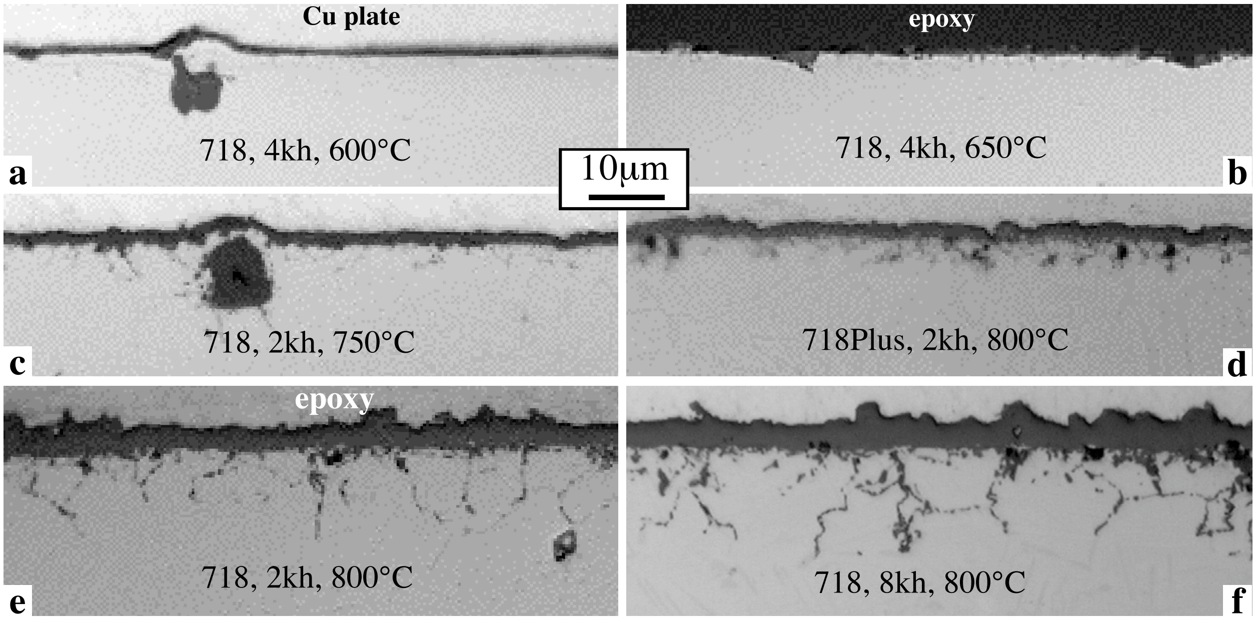

Figure 8. Light microscopy of polished cross-sections of alloy 718 and (d) 718Plus after exposure to 17bar steam (a) 4kh, 600°C, (b) 4kh, 650°C, (c) 2kh, 750°C, (d) 718Plus 2kh, 800°C, (e) 2kh, 800°C and (f) 8kh, 800°C.

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

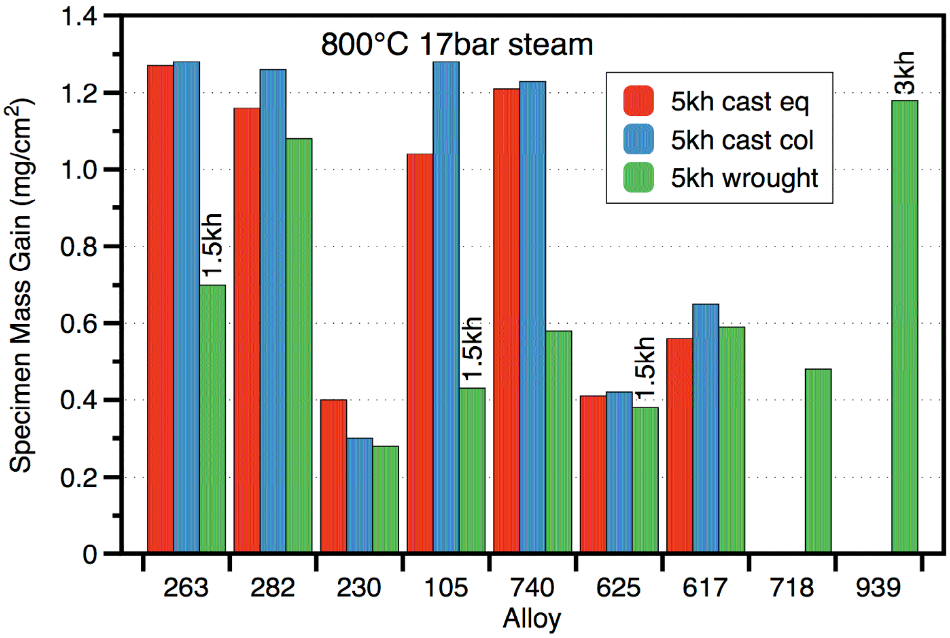

Figure 9. Specimen mass gain of various alloys after 5kh at 800°C in 17bar steam. Wrought and cast microstructures were evaluated with specimens cut from the castings in equiaxed (eq) and columnar (col) grain regions. In some cases where the time is noted, the test is in progress.

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_2O 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_2O causes H injection into the metal as OH^- 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

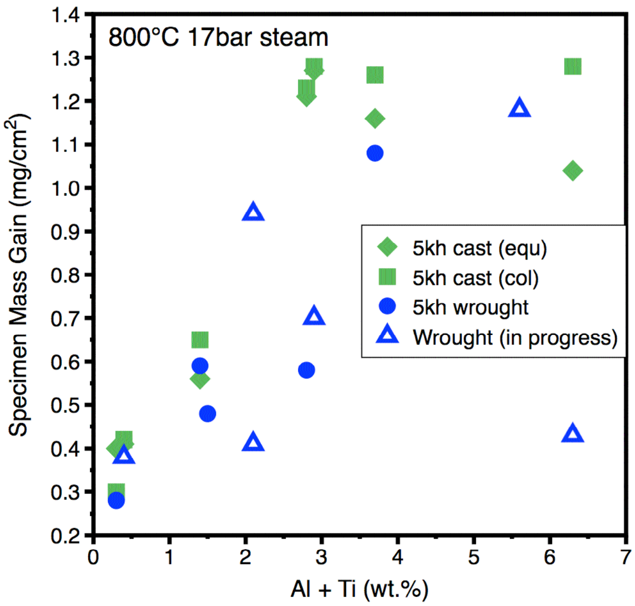

Figure 10. Specimen mass gain from Figure 9 plotted as a function of the alloy Al + Ti content. Some of the wrought experiments are still in progress and have not reached 5kh.

(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_2 and the role of CO_2 in altering corrosion mechanisms, particularly in the presence of other oxidants, is poorly understood [41,45]. However, the role of CO_2 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

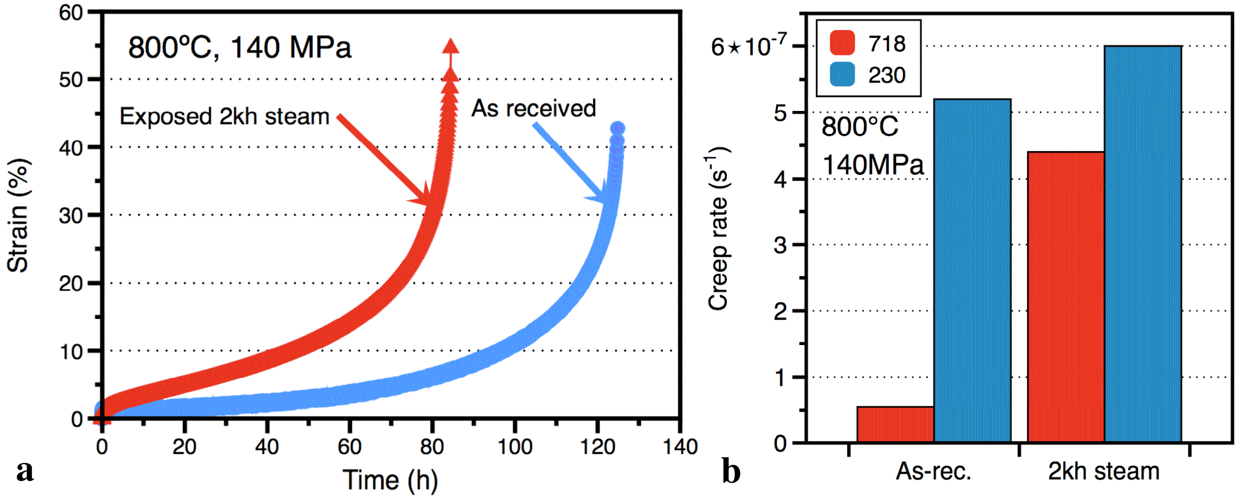

Figure 11. (a) Strain as a function of time at 800°C for 718 specimens with a stress of 140MPa, as-rec. and after the specimen was oxidized for 2kh in 17 bar steam at 800°C. (b) Steady state deformation rate for specimens of alloy 718 (from (a)) and alloy 230.

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_2O 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

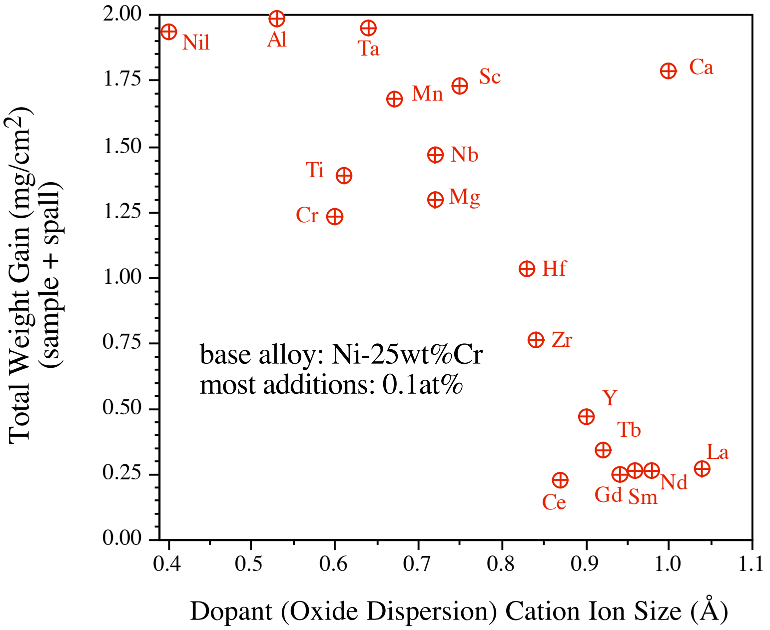

Figure 12. Total mass gain (specimen + spalled oxide) after 100h at 1000°C for various oxide dispersed Ni-25Cr alloys plotted versus the cation size of the dispersed oxide.

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_2O 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_2 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.

Acknowledgments

The authors would like to thank P. F. Tortorelli and P. J. Maziasz at ORNL for comments on the manuscript. At ORNL, G. Garner, T. Brummett, M. Stephens and H. Longmire assisted with the experimental work. This paper was assembled with support from the U.S. Department of Energy, Office of Coal and Power R&D, Office of Fossil Energy, (R. Dennis program manager).

References

[1] R. Viswanathan and W. Bakker, "Materials for Ultrasupercritical Coal Power Plants–Boiler Materials: Part I," *J. Mater. Eng. Perf.*, 10(1) (2001), 81-95.
[2] R. Viswanathan and W. Bakker, "Materials for Ultrasupercritical Coal Power Plants–Turbine Materials: Part II," *J. Mater. Eng. Perf.*, 10(1) (2001), 96-101.
[3] "FutureGen — A Sequestration and Hydrogen Research Initiative," U. S. Department of Energy, Washington, DC 2003. www.fossil.energy.gov/programs/powersystems/futuregen/futuregen_factsheet.pdf.
[4] P. Chiesa, et al., "Co-Production of Hydrogen, Electricity and CO_2 from Coal with Commercially Ready Technology. Part A: Performance and Emissions," *Inter. J. Hydrogen Energy*, 30 (2005), 747-67.
[5] P. Chiesa, G. Lozza and L. Mazzocchi, "Using Hydrogen as Gas Turbine Fuel," *J. Eng. Gas Turbines & Power*, 127 (2005), 73-80.
[6] G. C. Wood, T. Hodgkiess and D. P. Whittle, "A Comparison of the Scaling Behaviour of Pure Iron-Chromium and Nickel-Chromium Alloys in Oxygen," *Corr. Sci.*, 6 (1966), 129-147.
[7] D. L. Douglass and J. S. Armijo, "The Effect of Silicon and Manganese on the Oxidation Mechanism of Ni-20Cr," *Oxid. Met.*, 2 (1970), 207-231.

[8] H. M. Hindam and D. P. Whittle, "Microstructure, Adhesion and Growth Kinetics of Protective Scales on Metals and Alloys," *Oxid. Met.*, 18 (1982), 245-284.

[9] T. A. Ramanarayanan and R. Petkovic-Luton, "Investigations on the Growth Mechanisms of α-Cr_2O_3 on Ni-Base Alloys with and without Y_2O_3 Dispersions," *Berichte der Bunsen-Gesellschaft fur Physikalische Chemie*, 89 (1985), 402-409.

[10] B. Jönsson and C. Svedberg, "Limiting Factors for Fe-Cr-Al and NiCr in Controlled Industrial Atmospheres," *Mat. Sci. Forum*, 251-254 (1997), 551-558.

[11] D. L. Douglass, “A Critique of Internal Oxidation in Alloys During the Post-Wagner Era,” *Oxid. Met.*, 44 (1995), 81-111.

[12] C. S. Giggins and F. S. Pettit, “Oxidation of Ni-Cr-Al Alloys Between 1000° and 1200°C,” *J. Electrochem. Soc.*, 118 (1971), 1782-90.

[13] G. C. Wood, I. G. Wright, T. Hodgkiess, D. P. Whittle, "A Comparison of the Oxidation of Fe-Cr, Ni-Cr and Co-Cr Alloys in Oxygen and Water Vapor," *Werk. Korr.*, 21 (1970), 900-910.

[14] H. Asteman, J.-E. Svensson, M. Norell and L.-G. Johansson, “Influence of Water Vapor and Flow Rate on the High-Temperature Oxidation of 304L; Effect of Chromium Oxide Hydroxide Evaporation,” *Oxid. Met.*, 54 (2000), 11-26.

[15] E. J. Opila, “Volatility of Common Protective Oxides in High-Temperature Water Vapor: Current Understanding and Unanswered Questions,” *Mater. Sci. Forum*, 461-464 (2004), 765-74.

[16] D. J. Young and B. A. Pint, “Chromium Volatilization Rates from Cr2O3 Scales Into Flowing Gases Containing Water Vapor,” *Oxid. Met.*, 66 (2006), 137-153.

[17] B. A. Pint, P. J. Maziasz, J. Schauer and V. Levin, (2008) “Protective Aluminide Coatings for NiCr Alloys in Combustion Environments,” (NACE Paper 08-443, Houston, TX, presented at NACE Corrosion 2008, New Orleans, LA, March 2008).

[18] B. A. Pint, “The Effect of Water Vapor on Cr Depletion in Advanced Recuperator Alloys,” (ASME Paper #GT2005-68495, presented at the International Gas Turbine & Aeroengine Congress & Exhibition, Reno-Tahoe, NV, June 6-9, 2005).

[19] B. A. Pint, R. Peraldi and P. J. Maziasz, “The Use of Model Alloys to Develop Corrosion-Resistant Stainless Steels,” *Mater. Sci. Forum*, 461-464 (2004), 815-822.

[20] K. Onal, M. C. Maris-Sida, G. H. Meier and F. S. Pettit, “Water Vapor Effects on the Cyclic Oxid. Resistance of Alumina-Forming Alloys,” *Mater. High Temp.*, 20 (2003), 327-337.

[21] B. A. Pint, et al., “The Effect of Water Vapor on the Oxidation Behavior of Ni-Pt-Al Coatings and Alloys,” *Surf. Coat. Technol.*, 201 (2006), 3852-3856.

[22] H. Ghonem and D. Zheng, “Depth of Intergranular O Diffusion During Environment-Dependent Fatigue Crack-Growth in Alloy-718,” *Mater. Sci. Eng. A*, 150 (1992), 151-160.

[23] R. Molins, G. Hochstetter, J. C. Chassaigne and E. Andrieu, “Oxidation Effects on the Fatigue Crack Growth Behavior of Alloy 718 at High Temp.,” *Acta Mater.*, 45 (1997), 663-674.

[24] D. A. Woodford, “Environmental Damage of a Cast Nickel-Base Superalloy,” *Met. Trans.*, 12 (1981), 299-308.

[25] U. Krupp, “Dynamic embrittlement - time-dependent quasi-brittle intergranular fracture at high temperatures,” *Inter. Mater. Rev.*, 50 (2005), 83-97.

[26] A. Pineau and S. D. Antolovich, “High temperature fatigue of nickel-base superalloys - A review with special emphasis on deformation modes and oxidation,” *Eng. Failure Analysis*, 16 (2009), 2668-2697.

[27] K. A. Unocic, R. R. Unocic, B. A. Pint and R. W. Hayes, “Effect of Microstructure and Environment on the High-Temperature Oxidation Behavior of Alloy 718Plus,” these proceedings.

[28] J. Kesseli, T. Wolf, J. Nash and S. Freedman, “Micro, Industrial, and Advanced Gas

Turbines Employing Recuperators," (ASME Paper #GT2003-38938 presented at the International Gas Turbine & Aeroengine Congress & Exhibition, Atlanta, GA, June 2-5, 2003).

[29] I. Stambler, "Mercury 50 rated at 4600kW and 38.5% efficiency with 5ppm NOx," *Gas Turbine World*, Feb-Mar (2004), 12-16.

[30] J. M. Rakowski and C. P. Stinner, "The Use and Performance of Wrought 625 Alloy in Primary Surface Recuperators for Gas Turbine Engines," (NACE Paper 05-447, Houston, TX, presented at NACE Corrosion 2005, Houston, TX, April 2005).

[31] B. A. Pint, J. R. DiStefano and I. G. Wright, "Oxidation Resistance: One Barrier to Moving Beyond Ni-Base Superalloys," *Mater. Sci. Eng. A*, 415 (2006), 255-263.

[32] F. Tholence and M. Norell, "High temperature corrosion of cast alloys in exhaust environments. II-Cast stainless steels," *Oxid. Met.*, 69 (2008), 37-62.

[33] I. G. Wright and R. B. Dooley, "A review of the oxidation behavior of structural alloys in steam," *Inter. Mater. Rev.*, 55 (3) (2010), 129-167.

[34] C. T. Fujii and R. A. Meussner, "The Mechanism of the High-Temperature Oxidation of Iron-Chromium Alloys in Water Vapor," *J. Electrochem. Soc.*, 111 (1964), 1215-21.

[35] J. Zurek et al., "Growth and Adherence of Chromia Based Surface Scales on Ni-base Alloys in High- and Low-pO_2 gases," *Mater. Sci. Eng. A*, 477 (2008), 259-70.

[36] G. Calvarin-Amiri, R. Molins and A. M. Huntz, "Coupling Between Oxidation and Mechanical Stresses. Application to the Oxidation of Ni-20Cr Foils," *Mater. Sci. Forum*, 369-72 (2001), 467-74.

[37] P. J. Ennis and W. J. Quadakkers, "Corrosion and Creep of Nickel-Base Alloys in Steam Reforming Gas," *High Temperature Alloys, Their Exploitable Potential*, ed. J. B. Marriott, M. Merz, J. Nihoul and J. Ward (London: Elsevier, 1985), 465-474.

[38] P. Dawson and C. P. Stinner, "The relationship of stress and temperature on high-temperature corrosion fracture mechanism of waspaloy in various catalyst environments," *Mater. High Temp.*, 18 (2001), 107-118.

[39] S. Dryepondt and B. A. Pint, "Determination of the DBTT of Aluminide Coatings and its Influence on the Mechanical Behavior of Coated Specimens," submitted to *Surf. Coat. Technol.*.

[40] M. R. Wootton and N. Birks, "The Oxidation of Nickel-Chromium Alloys in Atmospheres Containing Sulphur Dioxide," *Corr. Sci.*, 15 (1975), 1-10.

[41] C. S. Giggins and F. S. Pettit, "Corrosion of Metals and Alloys in Mixed Gas Environments at Elevated Temperatures," *Oxid. Met.*, 14 (1980), 363-413.

[42] G. Y. Lai, "Sulfidation Resistance of Various High-Temperature Alloys in Low Oxygen Potential Atmospheres," High Temperature Corrosion in Energy Systems, ed. M. F. Rothman (Warrendale, PA: TMS, 1985), 227-236.

[43] R. A. Rapp, "Chemistry and Electrochemistry of Hot Corrosion of Metals," *Mat. Sci. Eng.*, 87 (1987), 319-327.

[44] C. B. Alcock, M. G. Hocking and S. Zador, "The Corrosion of Ni in O_2 + SO_2 Atmospheres in the Temperature Range 500-750°C," *Corr. Sci.*, 9 (1969), 111-22.

[45] H. E. McCoy, "Type 304 Stainless Steel vs Flowing CO_2 at Atmospheric Pressure and 1100-1800°F," *Corr.*, 21 (1965), 84-94.

[46] M. J. Bennett, et al., "Crevice Corrosion of Cr_2O_3 and Al_2O_3 Forming Alloys in Mixed Nitrogen-Oxygen Environments," *Mater. High Temp.*, 19 (2002), 117-25.

[47] F. H. Stott, et al., "The Oxidation Performance of Superalloys in Gaseous Environments at Very High Temperatures," *High Temperature Materials for Power Engineering*, Vol I., ed. Bachelet, et al. (Dordrecht, Netherlands: Kluwer Academic Publishers, 1990), 213-226.

[48] R. P. Rubly and D. L. Douglass, "Internal Nitridation of Nickel-Chromium Alloys," *Oxid. Met.*, 35 (1991), 259-278.

[49] C. Cabet, et al., "Comparison of the High Temperature Surface Reactivity in Impure Helium of Two Materials for Gas Cooled Reactors," *Mater. Sci. Forum*, 595-598 (2008), 439-448.

[50] F. Di Gabriele, et al., "Study of the Metal Dusting Behavior of High-Temperature Alloys," *Mater. Corr.*, 54 (2003), 854-859.

[51] D. P. Whittle and J. Stringer, "Improvement in Properties: Additives in Oxidation Resistance," *Phil. Trans. Royal Soc. London, Serial A,* 295 (1980), 309-29.

[52] Y. Saito, T. Maruyama and T. Amano, "Adherence of Oxide Scale Formed on Ni-20Cr-1Si Alloys with Small Additions of Rare Earth Elements," *Mater. Sci. Eng.*, 87 (1987), 275-280.

[53] J. G. Smeggil, N. S. Bornstein and M A DeCrescente, "The Importance of Interfacial Chemistry in Protective Oxide Scale Adherence," *Oxid. Met.*, 30 (1988), 259-266.

[54] P. Y. Hou and J. Stringer, "The Effect of Reactive Element Additions on the Selective Oxidation, Growth and Adhesion of Chromia Scales," *Mater. Sci. Eng.*, A202 (1995), 1-10.

[55] B. A. Pint, "Experimental Observations in Support of the Dynamic Segregation Theory to Explain the Reactive Element Effect," *Oxid. Met.*, 45 (1996), 1-37.

[56] B. A. Pint, "Progress in Understanding the Reactive Element Effect Since the Whittle and Stringer Literature Review," *Proc. John Stringer Symposium on High Temperature Corrosion*, ed. P. F. Tortorelli, I. G. Wright, and P. Y. Hou (Materials Park, OH: ASM International, 2003), 9-19.

[57] R. F. Decker and J. W. Freeman, "Mechanism of beneficial effects of boron and zirconium on creep properties of complex heat-resistant alloy," *Trans. Met. Soc. AIME*, 218 (1960), 277-285.

[58] W. J. Quadakkers, H. Holzbrecher, K. G. Briefs and H. Beske, "Differences in Growth Mechanisms of Oxide Scales Formed on ODS and Conventional Wrought Alloys," *Oxid. Met.*, 32 (1989), 67-88.

[59] N. R. Lindblad, "A Review of the Behavior of Aluminide-Coated Superalloys," *Oxid. Met.*, 1 (1969), 143-170.

[60] T. C. Totemeier, W. C. Gale and J. E. King, "Fracture Behaviour of an Aluminide Coating on a Single Crystal Nickel Base Superalloy," *Mater. Sci. Eng.*, A169 (1993), 19-26.

[61] T. C. Totemeier and J. E. King, "Isothermal Fatigue of an Aluminide-Coated Single-Crystal Superalloy: Part I," *Met. Trans.*, 27A (1996), 353-61.