Compatibility of Gas Turbine Materials With Steam Cooling

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Introduction

Gas turbines had been traditionally used for peak load plants and remote locations as they offer advantage of low installation costs and quick start up time. Their use as a base load generator had not been feasible owing to their poor efficiency. However, with the advent of gas turbines based combined cycle plants (CCPs), continued advances in efficiency are being made. Coupled with ultra low NO_x emissions, coal compatibility and higher unit output, gas turbines are now competing with conventional power plants for base load power generation. Currently, the turbines are designed with TIT of 2300^0 F and metal temperatures are maintained around 1700^0 F by using air cooling. New higher efficiency ATS turbines will have TIT as high as 2700^0 F. To withstand this high temperature improved materials, coatings, and advances in cooling system and design are warranted. Development of advanced materials with better capabilities specifically for land base applications are time consuming and may not be available by ATS time frame or may prove costly for the first generation ATS gas turbines. Therefore improvement in the

cooling system of hot components, which can take place in a relatively shorter time frame, is important. One way to improve cooling efficiency is to use better cooling agent. Steam as an alternate cooling agent offers attractive advantages because of its higher specific heat (almost twice that of air) and lower viscosity.

Steam cooling can lead to several materials related problems that warrant attention prior to its introduction in ATS. The most deleterious effect steam can have on the gas turbine materials is the hot corrosion aided by deposition of impurity salts from the steam. The solubility of salts in steam generally increase with increasing temperature and increasing pressure of the steam. As the steam flows through cooling passages, the steam pressure will be dropping which may lead to salt deposition from steam. The salt deposits can lead to enhanced corrosion and oxidation problems. Number of cases of hot corrosion by Na_2SO_4 deposits in gas turbines have been reported. The problem can be worse in the case of steam cooling because of presence of the chloride ions in the steam. The other major problem associated is the heavy internal oxidation of Al containing alloys. The extent of internal penetration of oxides and the large γ' depleted zone associated with it may cause severe degradation in mechanical properties. This in combination with hydrogen damage due to dissociation of steam at high temperatures, may pose severe problem.

Objectives

Information on steam/materials interaction is mainly available for materials relevant to steam turbines, boilers and heat exchanger tubes. The effect of steam on superalloys is little known. For the continuous reliable operation of gas turbines this information is very vital, so that alternatives can be considered and allowances can be made. The objective of this research program is to investigate performance of gas turbine materials in steam environment and evaluate remedial measures for alleviating the severity of the problem.

During the first year of this AGTSR funded project the emphasis was on the investigation of the nature and the extent of the problem that may be encountered, if any. This study demonstrated that hot corrosion can be a severe problem in case of steam cooling. In the next two years following issues will be studied.

A.   Long terms effects of low impurity level steam environments.

B.   Studying the effect of variables such as temperature, pressure and stress on the mode and kinetics of attack.

C   Effectiveness of different techniques such as use of protective coatings and inhibitors for mitigating the material degradation in steam environment..

Apart from these technical objectives, important goals from the academic point of view are to educate students about issues relevant to gas turbine industry and to establish a close university-industry relationship.

Project Description:

For the first year of research, the emphasis was on investigating the nature and extent of material degradation and its relation with steam chemistry. For this three superalloys commonly used in gas turbines were exposed to three steam environments containing different impurity levels for periods ranging from two to six months. In this paper, the results of this research has been summarized. In the next phase of the research programs following tasks will be accomplished.

A. Long Term Testing in Low Impurity Steam Environment

Land based gas turbines are designed for long uninterrupted trouble-free operation. Therefore, for the reliable life prediction, long term kinetics data at low impurity levels are required. The typical steam pressures likely to be present in the cooling holes is about 140 psi[1]. The high steam pressure may have a significant effect on deposition of salts as well as on oxide scale morphology. Therefore steam pressure in the planned experiment will be maintained at levels closer to the actual industrial environment. The duration of the tests will be 12 months. this test will be carried out on both aluminide coated and un-coated superalloy specimens.

B. Measures to reduce the severity of problem:

1.   **Coatings**: One possible solution for mitigating the severity of material degradation in cooling hole channels is the use of protective coatings. The two types of protective coatings used in gas turbine industry are MCrAlY and aluminide diffusion coatings. MCrAlY coatings tend to be more hot corrosion resistant than aluminide coatings whereas aluminide coatings tend to provide better resistance to high temperature oxidation. Since aluminide coatings can be formed with a relative ease in the internal cooling holes using CVD, aluminide coatings are likely candidate as internal cooling hole coating material. Therefore, the exposure studies will be

carried out with aluminide coated superalloy specimens to evaluate their effectiveness in retarding the hot corrosion problems in steam environment.

2. **Inhibitors:** Some studies[3] have indicated the beneficial effects of alkaline earth metals particularly Ba on inhibition of hot corrosion of superalloys. Ammonium dichromate is also known to alleviate hot corrosion by providing extra chromium needed for hot corrosion resistance. These water soluble compounds will be added to feedwater and the effect on the steam induced hot corrosion will be evaluated.

C. Effect of other variables

1. **Temperature:** Temperature significantly influences both the kinetics and the morphology of hot corrosion. It is important to investigate the possibility of type II hot corrosion in superalloys in the presence of steam. The existence of type I or II hot corrosion depends on temperature. In this study therefore, depth and morphology of attack will be monitored as a function of time at four different temperatures in the range 1500-1700^0 F.

2. **Stress**: For the turbine blade application, the effect of stress is likely to be critical. The proposed study will aim at understanding whether there is any synergetic effect between stress and salt deposit induced hot corrosion. Five different stress levels will be used at a chosen temperature and the specimens will then be examined metallographically to determine the severity of attack.

3. **Pressure:** The steam pressure can significantly influence the salt deposition process thus affecting the hot corrosion behavior. Also pressure may have some effect on oxide morphology and growth. These effects will be studied by carrying out the experiments at different pressure levels.

Experimental Techniques

The alloys chosen for the study are IN 738, X-45 and IN 617 which are commonly used for blade, vane and transition piece, respectively. The specimen geometry is cylindrical with a 1/4" diameter central bore through which steam is passed. Steam is made to pass through three different samples arranged in a series.

In order to study the effect of impurity contents, three different steam environments are used namely "aggressive", "mild" and "pure". A multiple steam generator was specially designed and fabricated to accomplish this task. Steam is generated by passing water through IN-600 heat exchanger pipes housed in a 5000 Watts radiative furnace. For "aggressive" steam environment, Na_2SO_4 and $NaCl$ salts are added to water. The concentration of each salt is kept at 50 ppm in the water used for "aggressive" steam and 5 ppm each for "mild" steam generation.

In all cases, two types of tests are performed: simple exposure tests and ex-situ EIS. In the latter case, the progress of corrosion/oxidation is monitored as it occurs. All the specimens are housed in two furnaces; one for the Electrochemical Impedance Spectroscopy (EIS) tests and other for the exposure tests. The furnace housing test specimens for EIS studies are opened periodically (biweekly) for performing ex-situ EIS studies on the specimens, following which they are returned to the furnace. The material damage is identified using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and conventional metallography at the end of the test period for exposure tests.

For EIS testing, outer surface of the specimen is soldered to an electrically conducting wire. Since in this case the surface of interest is the inside surface, the outer surface is masked with MICCROSTOP[R] polymer paint. The cylindrical

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specimens are immersed in an aqueous electrolyte containing a highly reversible redox $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$ system at ambient temperatures. The specimen is held horizontal. The potential of the specimen is measured with respect to a Saturated Calomel Electrode (SCE) which was kept at the bore of the specimen. Graphite rods are used as counter electrodes. A sinusoidal voltage perturbation of about 10mV amplitude was applied and the response of the system is measured. The impedance spectrum was measured over a wide frequency range (1 mHz to 100 KHz) using a lock-in amplifier.

Results and Discussion

Microstructural Evaluation

Figure 1a shows scale thickness measurements taken at the end of the test periods. These values are averages of thirty measurements. The figure shows that the oxide thickness observed after two months exposure period in "aggressive" environment is comparable to the thickness observed after four months exposure in "mild" environment for IN 617 and IN 738. The internal penetration depth in the case of "mild" steam environment however is larger than "aggressive" steam environment for all the three alloys. The "mild" steam exposure was four months compared to two months in "aggressive" steam. Thus the results may indicate incubation time for the attack during which salt deposition and protective oxide brekdown are occurring. For IN 617 and X-45 the oxide scale thickness observed for "clean" steam environment is less or similar to what was observed for "aggressive" and "mild" environment even though the exposure time in "clean" steam environment was longest at six months. IN 738 however shows a contrary trend showing very high oxide scale thickness and internal penetration depth of oxides after six months exposure in "clean" steam environment (Figures 1a and 1b). This data may indicate that IN 738 is more

susceptible to oxidation damage in steam environment, whereas IN 617 is more susceptible to hot corrosion attack in the presence of impurities in steam environment.

Figure 2a shows the micrograph of IN 738 cross-section after 6 months exposure in "clean" steam environment. Figure 2b is the x-ray dot map of the area shown in figure 2a broken into six elemental surveys. It shows top oxide layer to be rich in Cr and Ti while beneath the oxide scale there is a severe penetration of Al rich tentacles, indicating heavy internal oxidation of aluminum. As evident from figure 2c, there is a severe depletion of γ' because of this attack. IN 617 also showed similar type of attack. However, the extent of internal penetration of Al rich oxides was much smaller. In X-45, the oxidation damage is smallest for all environments compared to IN617 and IN738. The oxide layer in X-45 was observed to be Cr rich and internal penetration damage was mainly restricted to interdendritic boundaries.

Figure 3 is the electron micrograph indicating the microstructural damage of IN 617 observed in the "mild" steam environment. Locations of compositional microanalysis are labelled on the micrograph. The results from this semi-quantitative micro-analysis are depicted in figure 3. Results show the oxide layer to be Cr rich. Some nickel and aluminum rich sulfur containing particles were also observed. This type of morphology was observed in IN 738 and IN 617 in "mild" as well as "aggressive" steam environments.

Mechanism of Degradation

Oxidation of superalloys in air/oxygen is a well studied phenomenon[4,5]. The growth rates of NiO and CoO are too rapid to permit their presence at steady state in the oxidation of a practical alloy. In superalloys, Al_2O_3 and Cr_2O_3 rich oxide films formed on the surface are responsible for high

temperature oxidation resistance. For a nickel base alloy to form a Cr_2O_3 rich scale in air, it must contain 15% or more chromium and less than about 5% aluminum. Whereas alloys with more than about 5% aluminum form Al_2O_3 scale. It has been suggested that the critical value of Cr/Al ratio seperating Al_2O_3 formers from Cr_2O_3 formers is 4. For Cr/Al ratio higher than 10, there is tendency for a preferential attack on alloy grain boundaries largely because of grain boundary carbide network there. Conventional cobalt base alloys generally do not contain aluminum and are consequently Cr_2O_3 formers. Al_2O_3 formers have scale morphology characterized by a thin continuous layer of Al_2O_3 adjacent to the metal substrate. The Al_2O_3 may be covered by an external layer of another oxide or other oxides may be dissolved in it, depending upon composition. Generally internal oxidation is absent behind the continuous scale. The scale morphology in Cr_2O_3 formers containing considerable aluminum is characterized by a predominantly Cr_2O_3 layer with internal oxidation of aluminum just beneath, resulting in tentacles of Al_2O_3 directed into the alloy as the Al activity is not sufficiently large to form a continuous scale. Other oxides may be dissolved in the Cr_2O_3 layer or may exist below or above of it. Generally higher Al content alloys show better resistance to oxidation owing to better protective properties of the Al_2O_3 scales.

However, the trend observed in steam environment is quite the opposite. IN 738 which has higher Al content and should have shown higher reistance to oxidation shows more oxidation damage than IN 617 in steam environment. To explain this abnormal behavior following mechanism is proposed.

Oxidation in steam environment may take place in two steps

$$H_2O \longrightarrow H_2 + 1/2 \ O_2 \qquad (1)$$

$$M + 1/2 \ O_2 \longrightarrow MO \qquad (2)$$
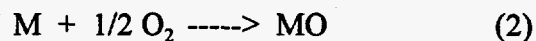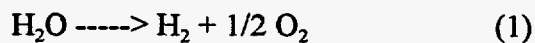
The overall reaction being

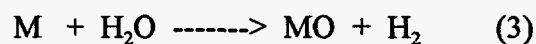$$M + H_2O \longrightarrow MO + H_2 \qquad (3)$$

Figure 4 plots equilibrium partial pressure of oxygen in H_2O-O-H system as a function of temperature using thermodynamic data for equation 1[6]. For most of the elements used in superalloys, free energy change for reaction 3 is negative which indicates that at equilibrium, reaction 3 may go to near completion. In fast flowing steam, conditions are far from equilibrium. Because of low residence time of steam with the alloys, extent of reaction 3 will be limited and oxygen potential in the environment may well be decided by equation 1. As a result, oxidation rates of pure metals in steam would be much lower than in air because of reduced Po_2 levels in steam environment. Aluminum has the most negative free energy of oxide formation and hence can form oxide at lower oxygen partial pressures comapred to other elements such as Ni, Co, Cr and Ti. Therefore it is prone to internal oxidation as the oxygen diffusing into the lattice may be sufficient to selectively oxidize Al. Higher the aluminum content higher will be the severity of internal attack. However at sufficiently large aluminum level, continuous Al_2O_3 scales may form which will provide oxidation resistance.

The compositions of the alloys used in this research program are listed in table 1 . All the three alloys are Cr_2O_3 formers. However these alloys have differing amounts of Ti and Al which make their oxidation response different. IN 738 has higher Al and Ti levels and though they are not sufficient for continuous scale formation, it is high enough to cause damage by internal penetration of Al-rich oxide stringers. IN 617 has lower levels of these elements leading to a lower internal penetration attack. X-45 which has a very large Cr content and no compositional Al shows

the lowest damage.

The low Po_2 in steam environment may have also significant effect on hot corrosion. The lower stability of oxides in this case may lead to increased sulfidation as well. However, this could not be proven conclusively from these experiments because of the uncertainties involved in the onset of salt deposition. The actual time of the onset of salt deposition may affect the kinetics of sulfidation. Therefore hot corrosion in steam environment will be investigated by first coating the superalloy pins with salt and then exposing them to steam.

Electrochemical Testing

The electrochemical impedance behavior of an alloy with an oxide layer over it can be modelled using an electrical analog model (transmission line model) as shown in figure 5a. For a perfect oxide layer the oxide/metal interface will not play any role. The electrochemical impedance spectrum in this case , represented by the Nyquist plot will be perfectly semicircular completely dominated by oxide layer characteristics. However in these studies, the oxide layer is far from perfect. Because of discontinuities or defects present in the oxide film, ionically conducting low resistance paths perpendicular to the coated surface may penetrate to the metallic substrate. As a result, the double layer at the metal/electrolyte interface will also play an important role. Therefore, for an oxide layer with a number of defects, there will be an overlap of the double layer and oxide film characteristics. The equivalent circuit in this case could be represented as shown in figure 5b. This results in flattening of the impedance spectrum. Also, the presence of these defects lead to the depression of the semicircle below the real axis[7]. As the number of defects increases, the spectrum will become more and more complex. This type of behavior is apparent in the case of X-45 and IN 617 alloys shown here after exposure to "clean"

steam environment (figures 6a and 6b). In the case of IN 738, the diameter of semicircle in Nyquist plot appears to be increasing with exposure time till 6 weeks reflecting the increase in thickness of the oxide film with time, without introduction of many defects. After 6 weeks however the trend reverses reflecting the degradation of the oxide film (fig. 5c). Even though "clean" steam exposure studies showed IN 738 to be most susceptible to degradation after six month exposure, at shorter times the oxide film was observed to be thin and uniform. This is reflected in the EIS short term (6-8 weeks) data which indicates IN 738 to be less susceptible than IN 617 or X-45. Thus again the results seem to indicate that the susceptibility of low Al content IN 738 is time dependant and that the internal penetration attack on this alloy become more pronounced with time. In all the three alloys, after long exposure times, the complexities because of heterogeneities induced by a large number of defects have made the estimation of numerical values from the results rather difficult.

Applications

This study has been helpful to understand the steam-superalloy interaction at high temperatures. A mechanism was proposed to explain the oxide morphology of these superalloys in steam environment. Following inferences can be drawn about the oxidation and hot corrosion behavior of nickel and cobalt based alloys in steam environment

1. Cr_2O_3 forming alloys containing considerable amount (1-4 wt. %) of aluminum such as IN 738 are susceptible to heavy internal oxidation of aluminum.

2.   High Al (>5 wt%) alloys in which case continuous Al_2O_3 scale can be formed may not be susceptible to such attack.

3.   Deposition of salts from steam will

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accentuate hot corrosion problems. Alloys with higher Cr content such as X-45 are generally less prone to hot corrosion. The greater damage observed in IN 617 make this alloy less attractive for gas turbine applications with steam cooling.

4.   Electrochemical impedance spectroscopy was found to be a good non-destructive technique to evaluate microstructural damage especially in the early stages of the attack. The technique has the potential of proving very useful in understanding the kinetics and mechanism of attack.

Future Activities

As mentioned earlier in the objectives section, the future rresearch will focus on the following aspects:
1. Long term effects of steam exposure
2.   Evaluation of the efffect of pressure, mechanical stree and temperature on the kinetics of the attack.
3. Understanding the mechanism of the attack and identifying the species responsible for the degeadation.
4. Evaluate the efficacy of protection techniques such as protective coatings and inhibitors.

References

1. Rice I.G., "Steam Cooled Gas Turbine Casings, Struts and Disks in a Reheat Gas Turbine Combined Cycle", Transactions of ASME, Journal of Engineering for Power", Vol. 105, October 1983, pp. 844-858.

2. Arsen'ev L.V., Corsov Yu.G., Khodak E.A., Romankhova G.A., Bazhonov G.V., "A hHighly Efficient Combined Cycle Plant with Steam-Cooled Gas Turbine", ASME Cogen-Turbo, IGTI-Vol.6, 1991, pp. 31-41

3. Saunders S.R.J., "Effect of trace elements and Environmental Impurities on Oxidation and Hot Corrosion Characteristics of Superalloys", Metals Technology, 11(10), 1984, pp. 465-473.

4. Smialek J.L. and Meir G.H., "High Temperature Oxidation" in C.T. Sims, Stoloff N.S. and Hagel W.C. (eds), Superalloys II, Wiley, New York, 1987, pp. 291-326.

5. Whittle D.P., "High Temperature Oxidation", in "High Temperature Alloys for Gas Turbines", proceedings of COST-501 meeting in Liege, Belgium, Sept. 1878, Applied Science Publishers, pp. 109-124.

6.Barin I., Thermochemical Data for Pure Substances, VCH Publications, Germany, 1989.

7. Compere C, Frechette L. and Ghali E., "The Corrosion Evaluation of Painted and Artificially Damaged Painted Steel Panels by A.C. Impedance Measurements", Corrosion Science, Vol. 34, August 1993, pp. 1259-1274.

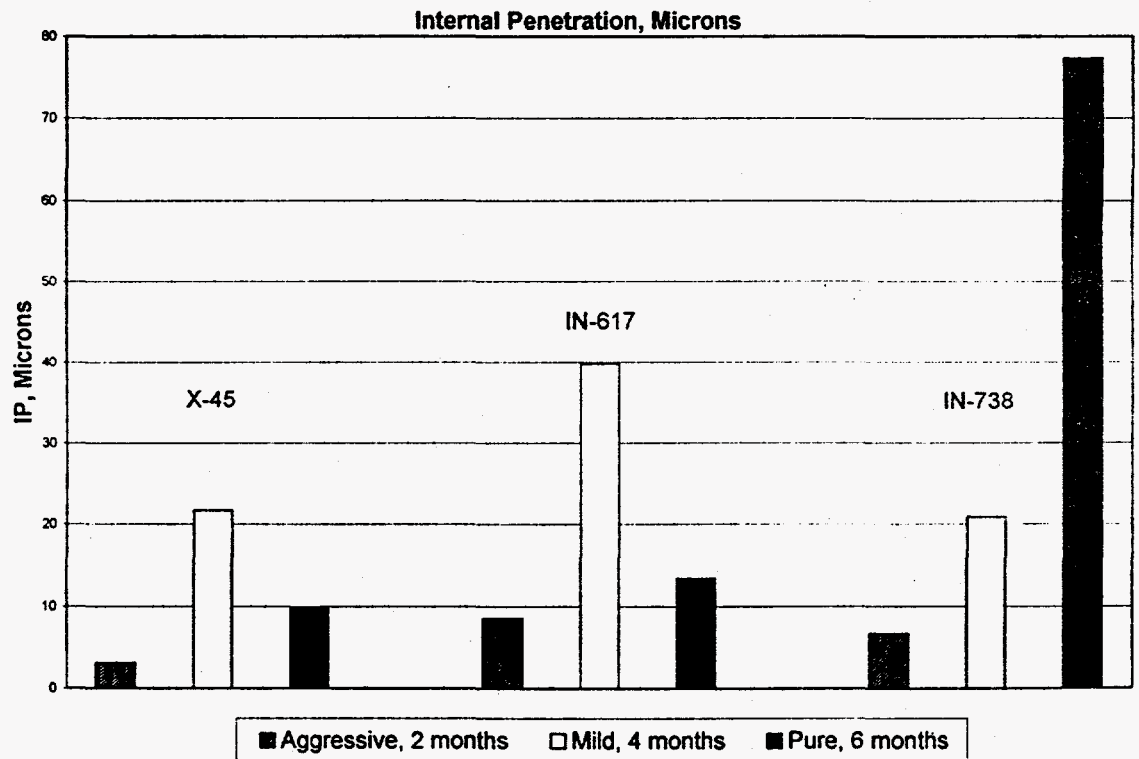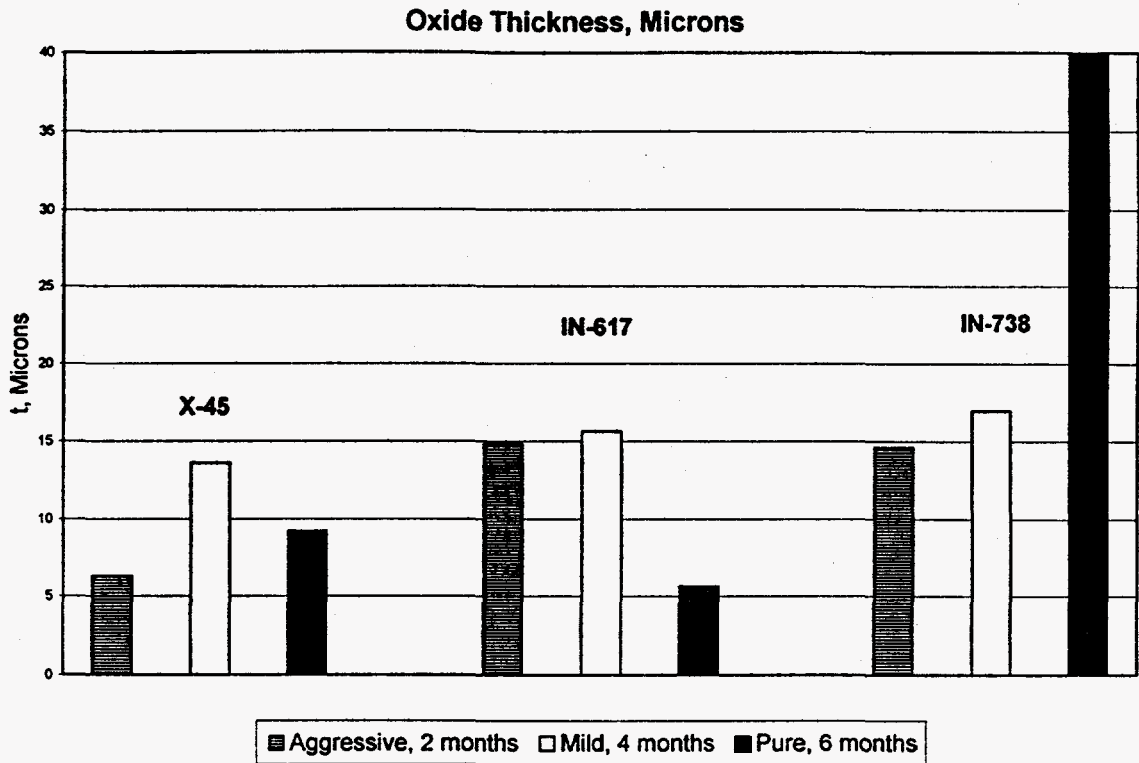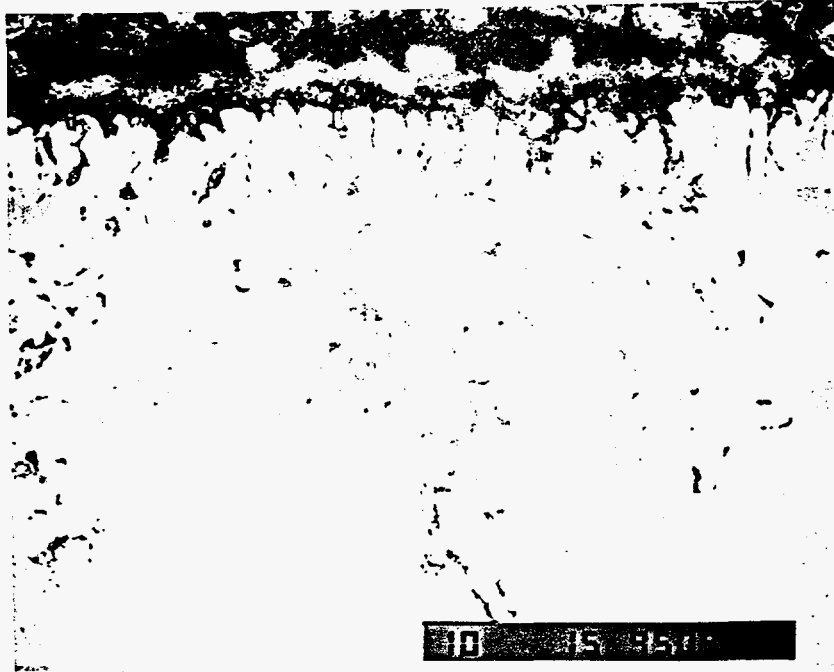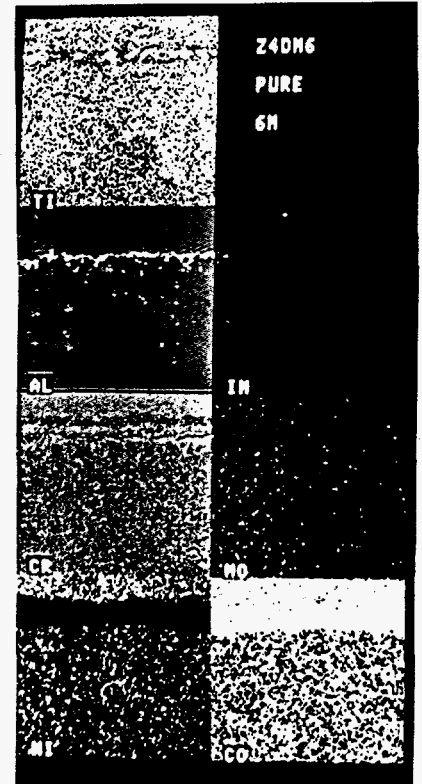**Oxide Thickness, Microns**

Internal Penetration, Microns

Figure 1: Oxide scale thickeness and internal penetration depths at the end of test periods in "aggressive", "mild" and "clean" environemnts at 1600^0F.
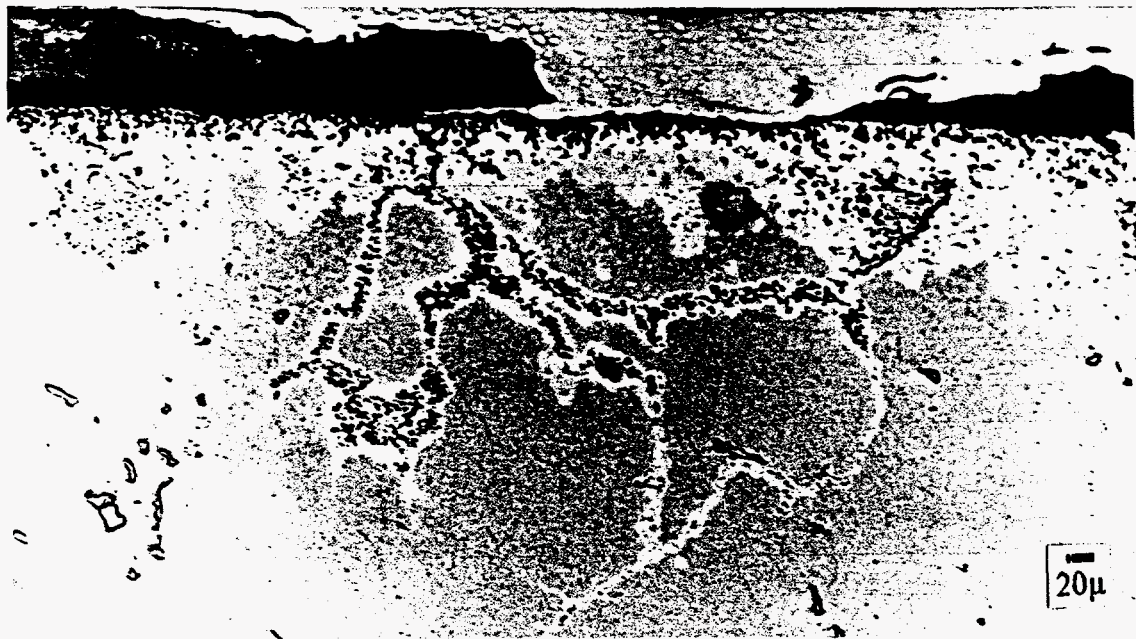 (a)   Oxide scale thickness
  (b)   Internal penetration depth of oxidation or corrosion products.

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(a)

Z40M6
PURE
6M

(b)

20μ

(c)

Figure 2:   Microstructural degradation of IN 738 in "clean" steam environment after six months exposure.

(a)   SEM micrograph showing heavy internal oxidation.

(b)   X-ray dot-map of the area shown in figure 2a. It reveals that while oxide scales are mainly composed of Cr and Ti, the internal oxidation products are mostly Al rich.

(c) γ' depleted zone near the oxidation products revealed by using etchant.

EDS Analysis
IN-617 Exposed to Mild Steam
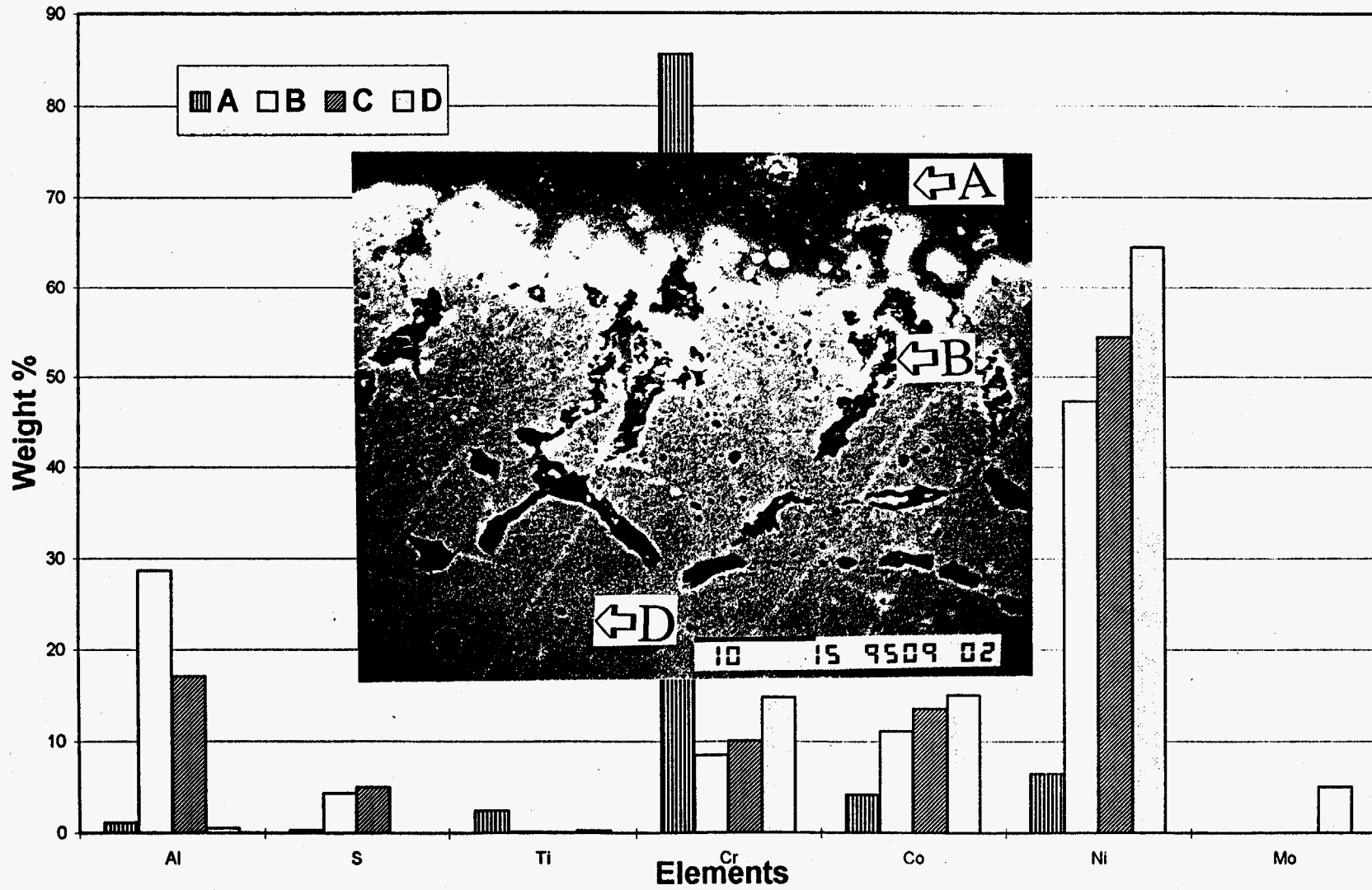
Figure 3: Microstructural damage in IN 617 after four month exposure to "clean" steam environment. SEM micrograph and EDS semi-quantitative analysis performed at different locations labelled in the micrograph are shown.

	C	Mn	Si	Cr	Ni	Co	Mo	W	Ta	Nb	Ti	Al	B	Zr
Inconel 617	0.07	0.5	0.5	22	bal.	12.5	9.0	--	--	--	0.3	1.0	--	--
IN-738	0.11	--	--	16	bal.	8.5	1.7	2.6	1.7	0.9	3.4	3.4	0.01	0.05
X-45	0.5	0.7	0.7	25.5	10	bal.	--	7.5	--	--	--	--	--	--

Table 1: Nominal Chemistry of the alloys
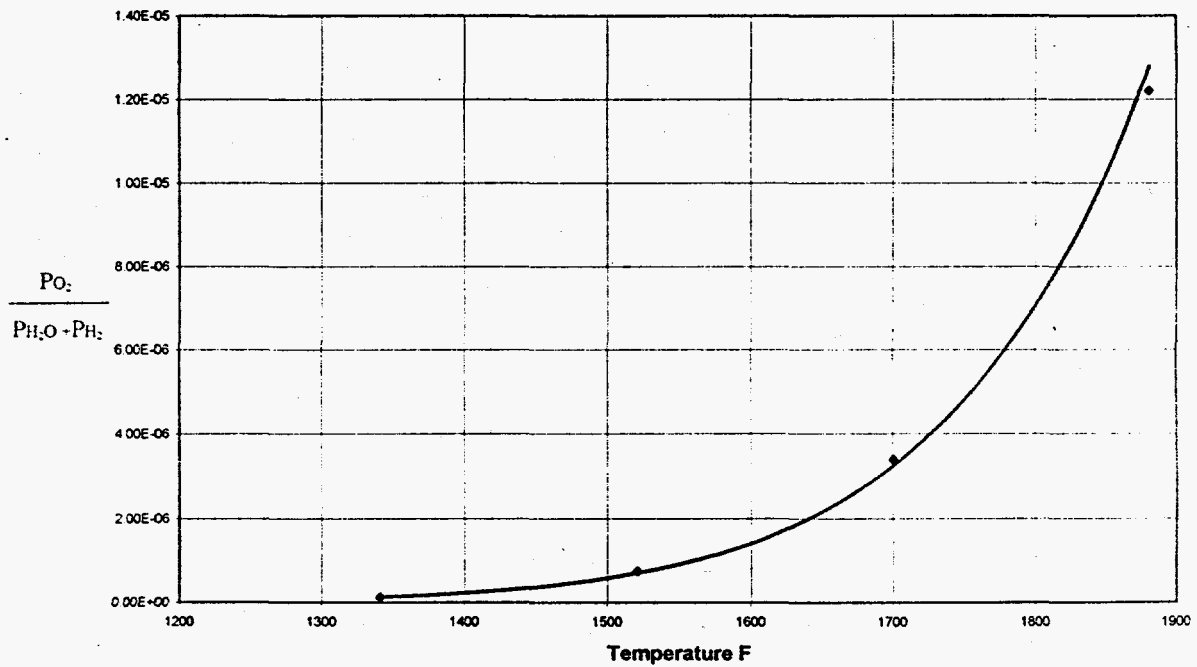
Figure 4:   Equilibrium partial pressure of oxygen in H_2O-O-H system at different temperatures. It shows that oxygen partial pressure is very small in steam environment at temperature of interest. However at higher temperatures the dissociation of steam becomes easier.
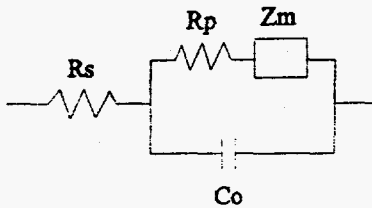
Rs = Solution Resistance
Rp = Oxide Resistance Perpendicular to Surface
Zm = General Impedance Characterizing
   Electrochemical Reactions at Metal / Oxide
   Interface
Co = Oxide Capacitance

(a)
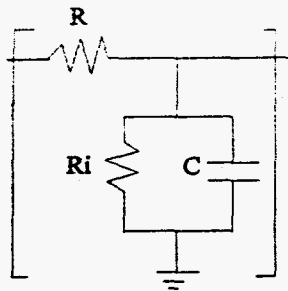
R = Interfacial Reistance Tangential to Surface
Ri = Interfacial Resistance

(b)

Figure 5:   (a) General electric equivalent circuit model for coated metal system. For an ideal oxide layer the value of Zm will be zero.
(b) For the nonideal case where there are a number of short circuit paths are available for ionic conduction through defective oxide layer, Zm can be replaced by n unit cells in series. The unit cell can be represented by the equivalent circuit diagram as shown in figure 9b.
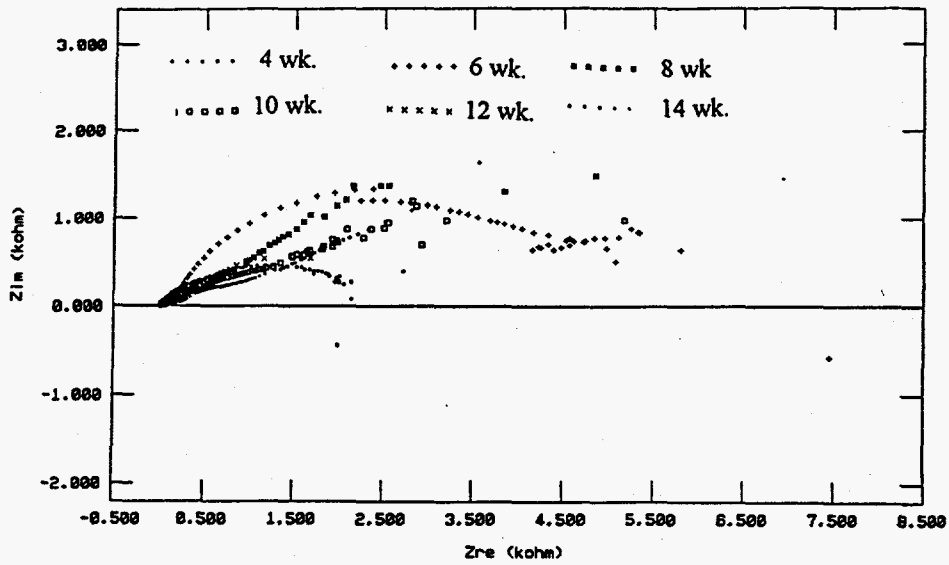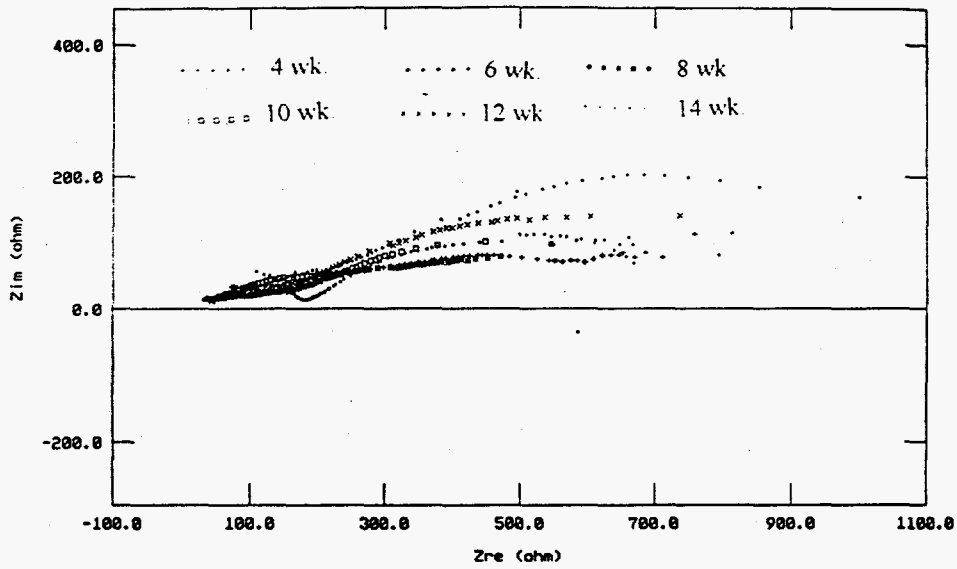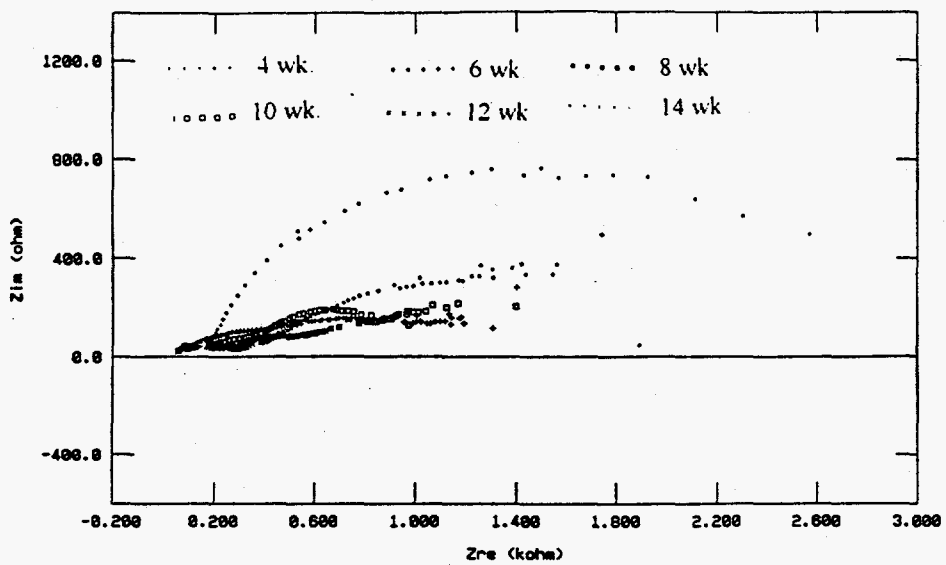
Figure 6:   Electrochemical impedance behavior as a function of exposure time in "clean" steam environment.