Influence of Steam Cooling on Hot Corrosion

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Abstract

Since the efficiency of a turbine is tied to its firing temperature, the Turbine Inlet Temperature (TIT) in the latest Advanced Turbine Systems (ATS) is being increased from 2,200 °F to 2,650 °F. None of the superalloys that are being used commercially are capable of withstanding this increased temperature. This has necessitated improvements in the properties of the superalloys, cooling system design, and thermal barrier coatings technology for the hot section components. Replacement of air with steam as a cooling medium is one of the options being pursued.

The first year of this research study indicated extensive oxidation of IN 738 (common blade material) under steam cooling compared to the other alloys studied. IN 617 (material for transition piece) showed poor hot corrosion resistance in the presence of steam impurities, while cobalt-based alloy X-45 (common vane material) showed evidence of cracking in the stressed regions. The second year of this program focused mainly on the kinetics of oxidation in air and steam. IN 738 exhibited higher weight gain and greater internal oxidation in steam than in air at all the test temperatures. CMSX-4 alloy behaved similar to IN 738 at lower temperatures, but formed a continuous protective oxide layer at higher temperatures, particularly with long exposure times. IN 617 showed better resistance to oxidation in steam than air, but the extent of oxidation increased with an increase in temperature. X-45 showed considerably higher volatilization in steam than in air.

The objectives for the current year are:

- Study the effect of mechanical stress on the material degradation.

- Study the effect of corrosion inhibitors and coatings on the oxidation and hot corrosion protection.

Long-term hot corrosion studies in salt-contaminated steam gave the following results:

- The extent of degradation in IN 738 was found to be substantially higher than that in the first year's study, possibly because of the higher steam pressures used in this study.

Acknowledgment

This research is sponsored by the U.S. Department of Energy's Federal Energy Technology Center, under cooperative agreement no DE-FC21-92MC29601 with South Carolina Research and Development Center, subcontract no. 95-01-SR029 (University of Central Florida).

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Gas Turbine Efficiency

The Efficiency of gas turbines is inversely proportional to the turbine inlet temperature (TIT). Hence, TIT needs to be increased to 2,650 °F to achieve 60-percent efficiency in ATS engines. Currently used commercial turbine alloys are not designed to operate at such high temperatures. Therefore, material and design improvements are necessitated.

The research thrust to meet the greater TIT demand in ATS engines can be summarized as follows:

(a) **Advanced Materials Development:** Use of new generation materials such as single-crystal superalloys, and improvements in thermal barrier coatings.

(b) **Cooling System Design:** Use of a more efficient cooling medium, such as steam; and improvements in the cooling-system design.

Steam Cooling

The **advantages** of steam as an alternate cooling medium are:

- Specific heat twice that of air.
- Lower kinematic viscosity than air.
- Possible to reduce the length of the cooling passage.
- Mixing losses can be eliminated.

The **disadvantages** of steam as an alternate cooling medium are:

- The oxidation mechanism and behavior are unknown.
- Hot corrosion is likely, because of steam impurities.
- Steam dissociation might lead to hydrogen damage.
- Steam-borne particles could lead to erosion (especially in closed-loop cooling).

Summary of Previously Reported First-Year Work

Samples were tested in three different steam environments. The steam was made from de-ionized/distilled water containing 50, 5, and 0 ppm NaCl and Na_2SO_4.

- The test temperature was 840 °C.
- The steam inlet temperature was 150 °C
- The steam outlet temperature was 260 °C
- The steam flow rate was 0.1 Lt/sec
- The test duration was 1,450 hr (at 50 ppm), 2,900 hr (at 5 ppm), and 3,900 hr (at 0 ppm).

Steam Oxidation: Extensive oxidation of IN 738 occurred in steam, compared to other alloys. IN 617 showed a compact and layered protective scale structure. X-45 having large Cr content showed the least damage.

Hot Corrosion in Steam: In the salt containing environments, IN 617 exhibited the highest damage. Sulfidation damage in IN 738 and X-45 was relatively small.

Summary of Previously Reported Second-Year Work

Test temperatures of 845 °C, 875 °C, 900 °C, and 950 °C. The second year of research focused mainly on studying the kinetics of oxidation in uncontaminated steam, and comparing the steam kinetics with that of air.

- IN 738 exhibited higher weight gain and greater internal oxidation in steam than in air at all the test temperatures.
- CMSX-4 alloy behaved similar to IN 738 at lower temperatures, but formed a continuous protective oxide at higher temperatures and longer exposure times.

- IN 617 showed better resistance to oxidation in steam than in air, but the extent of oxidation increased with an increase in temperature.

- X-45 showed considerably higher volatilization in steam than in air.

Objectives of Current Research

- Study the long-term hot-corrosion behavior of superalloys at low levels of steam impurity.

- Study the effect of mechanical stress on the material degradation of superalloys in a steam environment.

- Study the effect of corrosion inhibitors and coatings in the oxidation and hot-corrosion protection of superalloys.

Superalloys	**Ni**	**Cr**	**Co**	**Mo**	**W**	**Al**	**Ti**	**C**	**Others**
IN 617	Bal.	22.0	12.5	9.0	0.0	1.0	0.3	0.07	
IN 738	Bal.	16.0	8.5	1.7	2.6	3.4	3.4	0.11	Ta-1.7, Nb-0.9, B-0.01, Zr-0.05
X-45	10	25.5	Bal.	0.0	7.5	0.0	0.0	0.5	Mn-0.7, Si-0.7
CMSX-4	Bal.	6.5	9.0	6.0	6.0	5.6	1.0	0.5	Ta-6.5, Re-3.0

Summary of Long-Term Hot-Corrosion Results

- **IN 738:** The extent of degradation in IN 738 was found to be substantially higher than that in the first year study, because of the higher steam pressure used. The higher steam pressure was translated into a higher flow rate, which exposed the test specimen to a greater amount of impurities. Large sulfide precipitates were observed as a result of inward diffusion of sulfur.

- **IN 617:** IN 617 showed greater degradation in the higher impurity steam, compared to that in the low impurity steam. The extent of degradation increased with an increase in steam pressure. A tendency for grain boundary attack was observed. Internal oxidation with aluminum stringers penetrating into the substrate was observed.

- **X-45:** X-45 exhibited the greatest sensitivity towards the impurity level and steam pressure difference. A considerable degree of volatilization was observed that resulted in a drastic reduction in the cross-sectional thickness of the sample. The Cr-rich oxide stringers also appeared to follow a preferential grain boundary form of attack.

Summary of Stress Test Results

- **IN 738** exhibited a degradation morphology that was similar to that of an oxidation attack. The extent of oxidation damage in IN 738 was higher than that observed in IN 617 and X-45. There was no evidence of internal stress cracking. The extent of degradation in this case was greater than that observed in the case where unstressed specimens were exposed to uncontaminated steam.

- **IN 617** showed branching cracks in a direction perpendicular to that of the applied stress. The extent of internal oxidation is low because of the alloy's high Cr content. The extent of internal oxidation was lesser in the case of the unstressed IN 617 specimen exposed to uncontaminated steam. There was no evidence of cracking.

- **X-45** exhibited the presence of a large dendritic crack with little evidence of an oxidation-type attack. In the case of the unstressed specimen exposed to uncontaminated steam, there was no evidence of cracks in the substrate.

Gas Turbine Efficiency

Efficiency of Gas Turbines $\propto$ Turbine Inlet Temperature (TIT)

Hence, TIT needs to be increased to 2650 $^\circ$F for achieving 60 % efficiency in ATS engines

Currently used commercial turbine alloys are not designed to operate at such high temperatures. Therefore Materials and Design improvements are necessitated.

ATS Research Thrust

The research thrust to meet the greater TIT demand in ATS engines can be summarized as follows:

a) Advanced materials development

- Use of new generation materials such as single crystal superalloys
- Improvements in Thermal Barrier Coatings

b) Cooling system design

- Use of a more efficient cooling medium such as steam
- Improvements in the cooling system design

Steam Cooling

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SUMMARY OF PREVIOUSLY REPORTED FIRST YEAR WORK

Samples tested in three different steam environments. Steam made from de-ionized/distilled water containing 50, 5 and 0 ppm NaCl and Na_2SO_4

Test Temperature: 840 °C **Steam Flow Rate: 0.1 Lt/sec**

Steam Inlet Temperature: 150 °C **Steam Outlet Temp.: 260 °C**

Test Duration: 1450 hr (50 ppm), 2900 hr (5 ppm), 3900 hr (0 ppm)

a) Steam Oxidation

Extensive oxidation of IN 738 in steam compared to other alloys

IN 617 showed compact and layered protective scale structure

X-45 having large Cr content showed least damage

b) Hot Corrosion in Steam

In the salt containing environments, IN 617 exhibited highest damage. Sulphidation damage in IN 738 and X-45 was relatively small

SUMMARY OF PREVIOUSLY REPORTED FIRST YEAR WORK

Test Temperatures: 845 °C, 875 °C, 900 °C and 950 °C

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- Study the effect of mechanical stress on the material degradation of superalloys in steam environment
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Compositions of the alloys tested

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X-45	10	25.5	Bal.	0.0	7.5	0.0	0.0	0.5	Mn 0.7, Si 0.7
CMSX-4	Bal.	6.5	9.0	6.0	6.0	5.6	1.0	0.5	Ta 6.5, Re 3.0

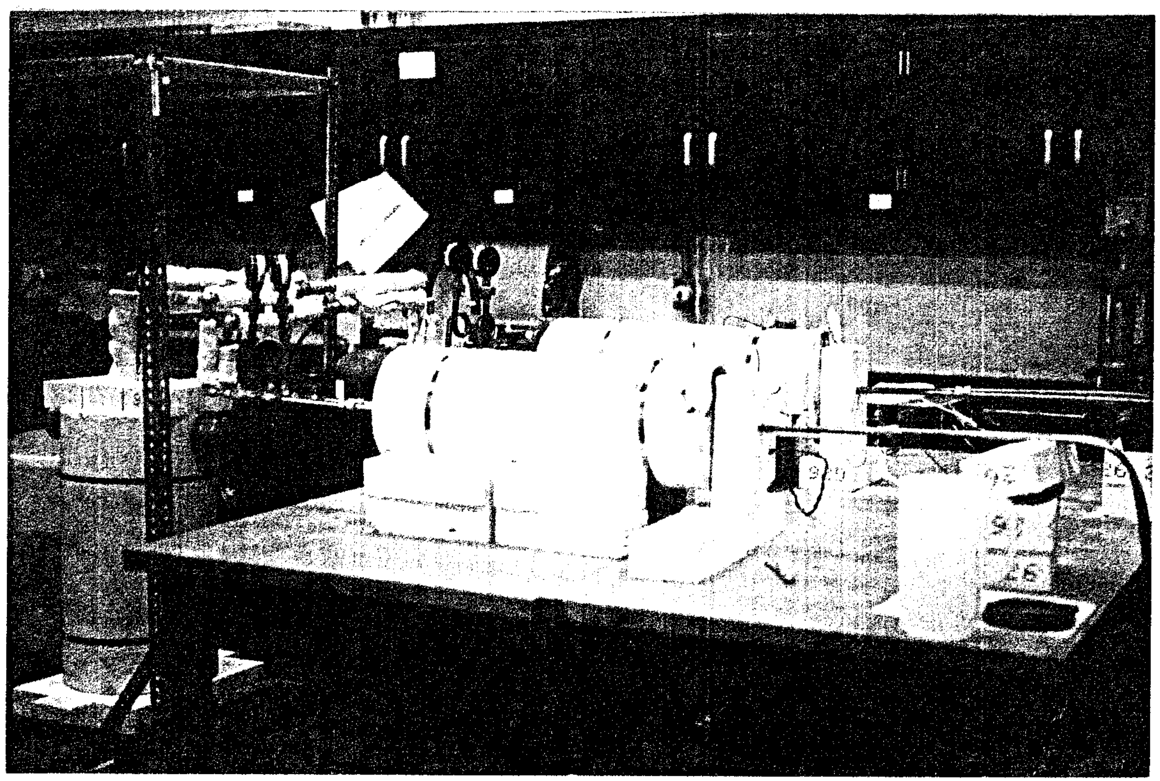
Test Set-up for Long Term Hot Corrosion Testing:

Test Temperature: 875 °C **Steam Pressure: 25 Psi**

Steam Inlet Temp.: 150 °C **Steam Outlet Temp.: 295 °C**

Steam Flow Rate: 1.4 Lt/sec **Test Durations: 1500hr, 3000hr**

In the long term tests, steam produced from de-ionized/distilled water containing 1 ppm and 5 ppm each of NaCl and Na_2SO_4 were used to study the simultaneous effects of oxidation and hot corrosion induced by salts deposited from the steam. These tests are carried out to provide the long term hot corrosion data essential for the gas turbine design.



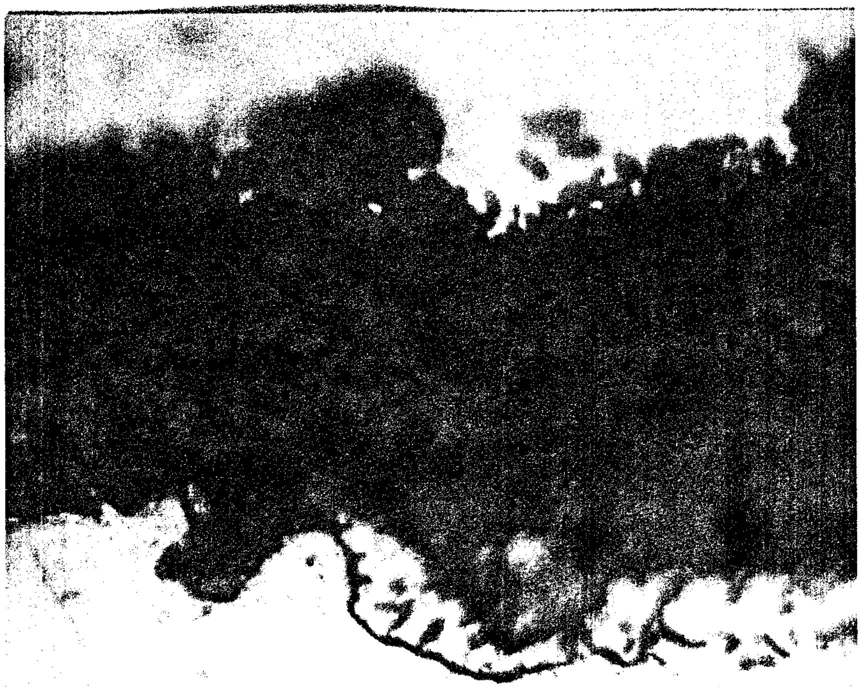
IN 738 specimens exposed to contaminated steam .

Test Temperature: 875 °C **Exposure Time:** 1500 hrs

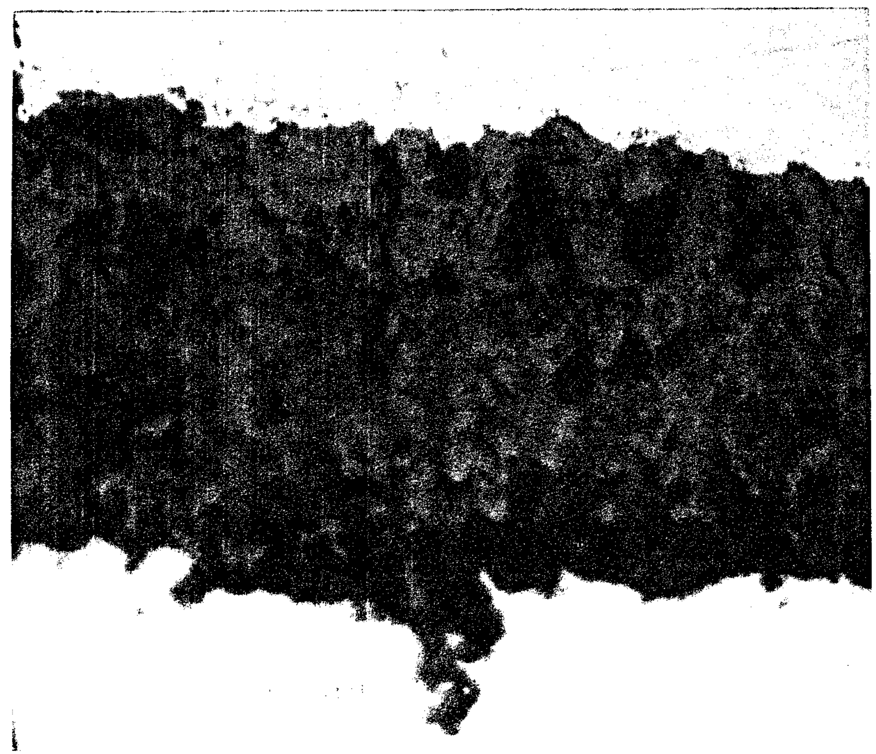
Steam Impurity Level: 1 ppm & 5 ppm **Steam Pressure:** 25 Psi

In the sample exposed to the steam with 5 ppm impurity concentration, the oxide layer is thicker and more continuous than the oxide layer formed in the sample exposed to steam with 1 ppm impurity.

IN 738 (1 ppm impurity steam)
Magnification: 1000 X



IN 738 (5 ppm impurity steam)
Magnification: 1000 X



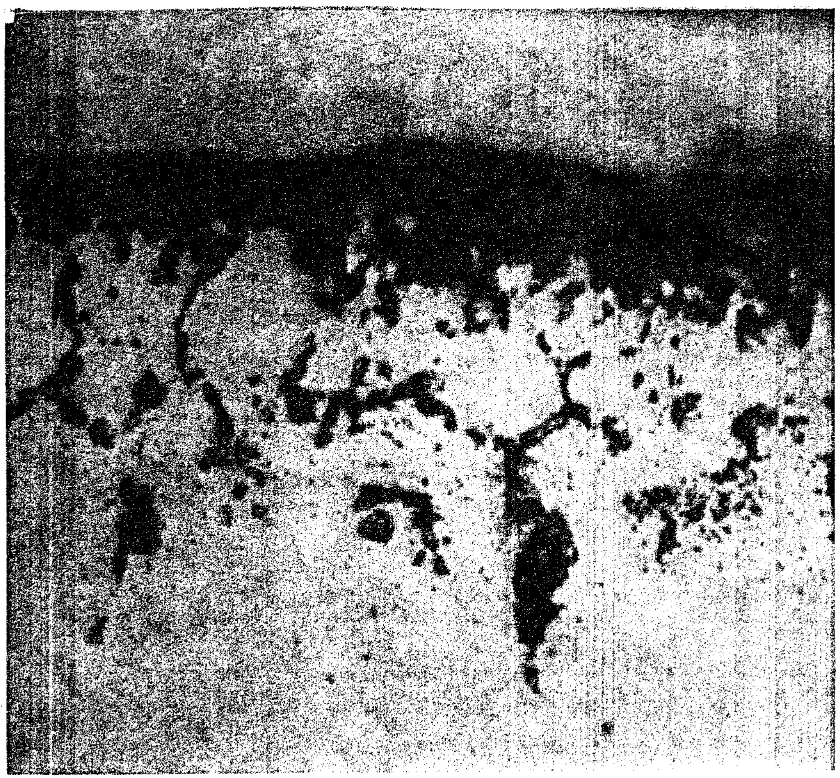
IN 617 specimens exposed to contaminated steam.

Test Temperature: 875 °C **Test Duration:** 1500hrs

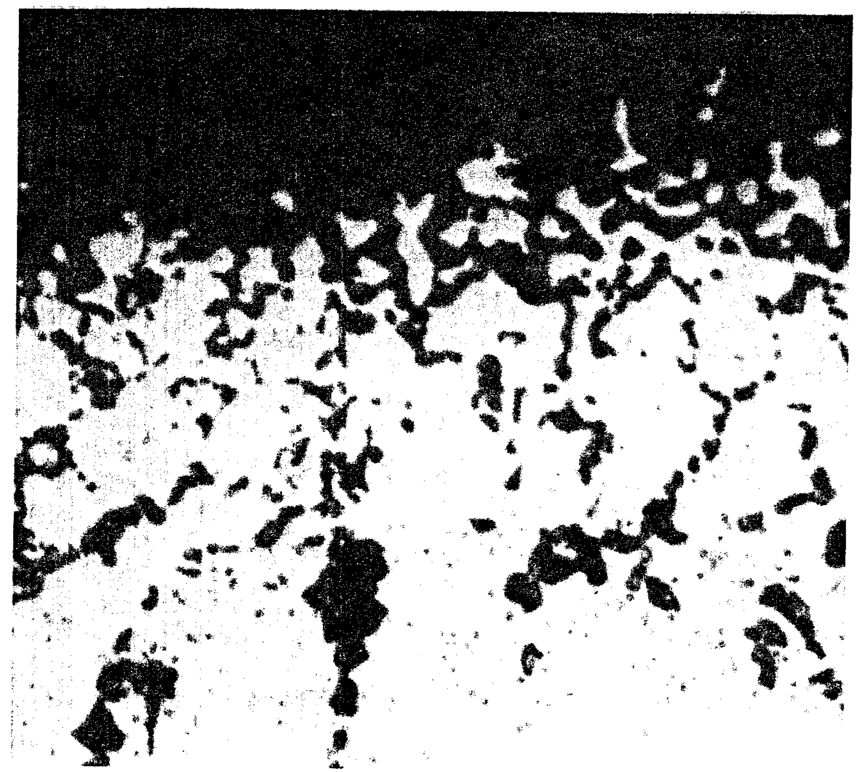
Steam Impurity Levels: 1 ppm & 5 ppm **Steam Pressure:** 25 Psi

From the micrographs shown below, we can see that there is a distinct tendency for preferential grain boundary attack. There is also evidence of internal oxidation in the form of aluminum stringers extending into the substrate. The extent of degradation increases with impurity concentration.

IN 617 (1ppm Impurity Steam)



IN 617 (5ppm impurity Steam)



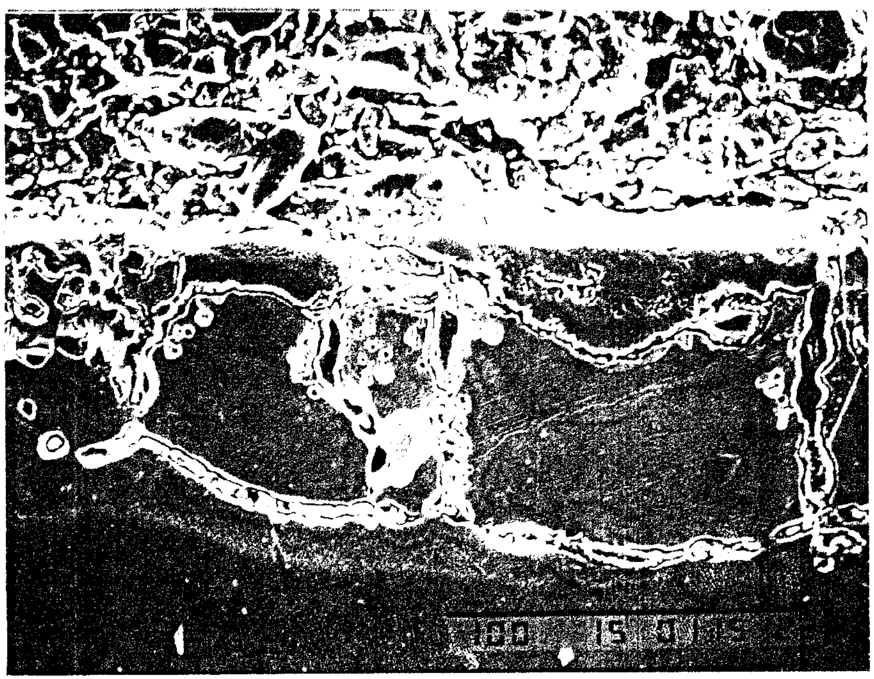
X-45 specimens exposed to contaminated steam.

Test Temperature: 875 °C **Test Duration:** 1500 hrs

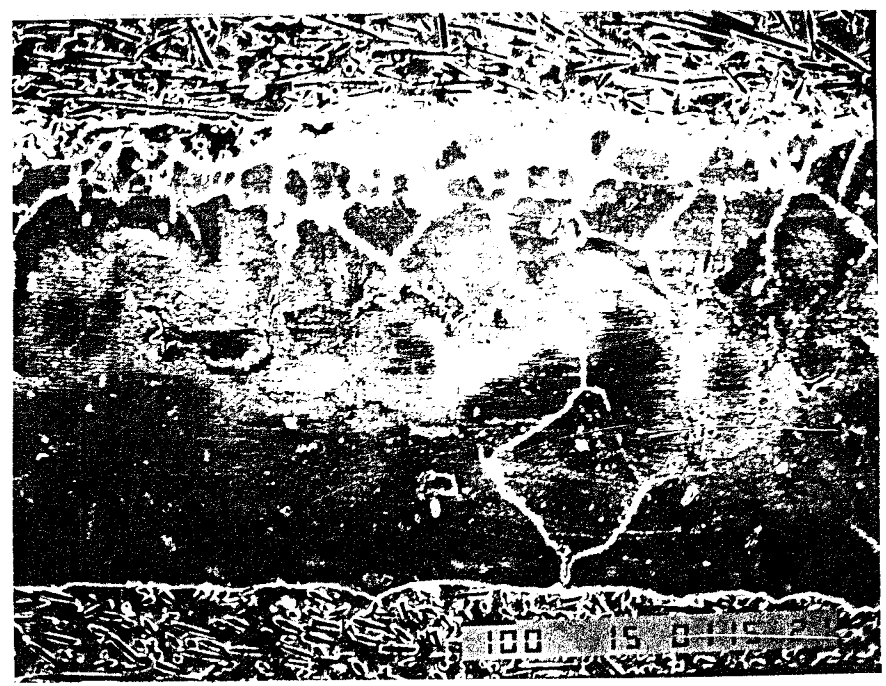
Steam Impurity Levels: 1ppm & 5ppm **Steam Pressure:** 25 Psi

From the micrographs shown below, the effect of impurity concentration is distinctly visible. The sample exposed to the steam containing 5ppm of NaCl and Na_2SO_4 exhibits cracks that run right through the sample, and the reduction in cross-section suggests volatilization of the sample.

X-45 (1ppm Impurity Steam)



X-45(5ppm impurity steam)



Effect of steam pressure on intensity of degradation (comparison of first and third year's results).

Test Temperatures: 840 °C (first year),875 °C (third year)

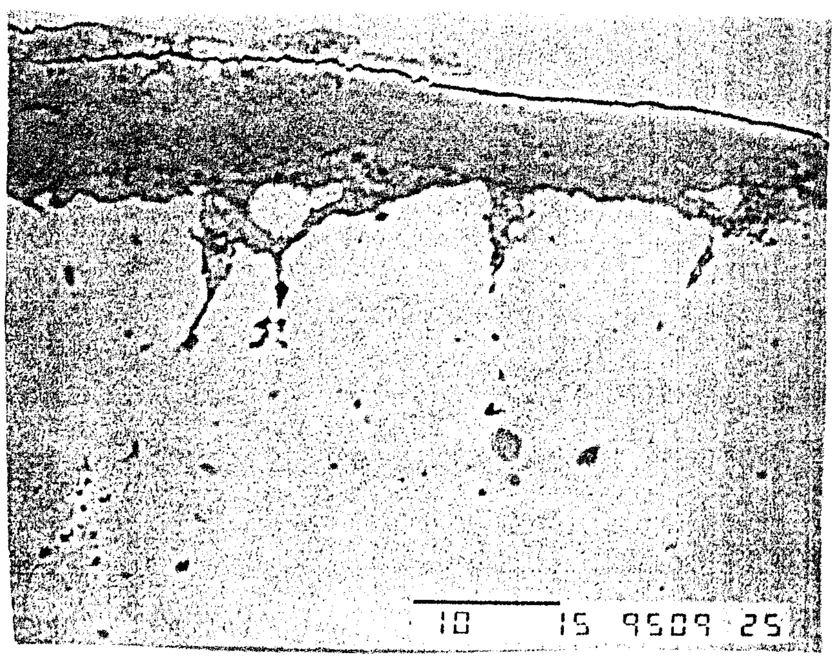
Steam Impurity Level: 5 ppm each of NaCl and Na_2SO_4

Test Duration: 2950hrs (first year), 1500hrs (third year)

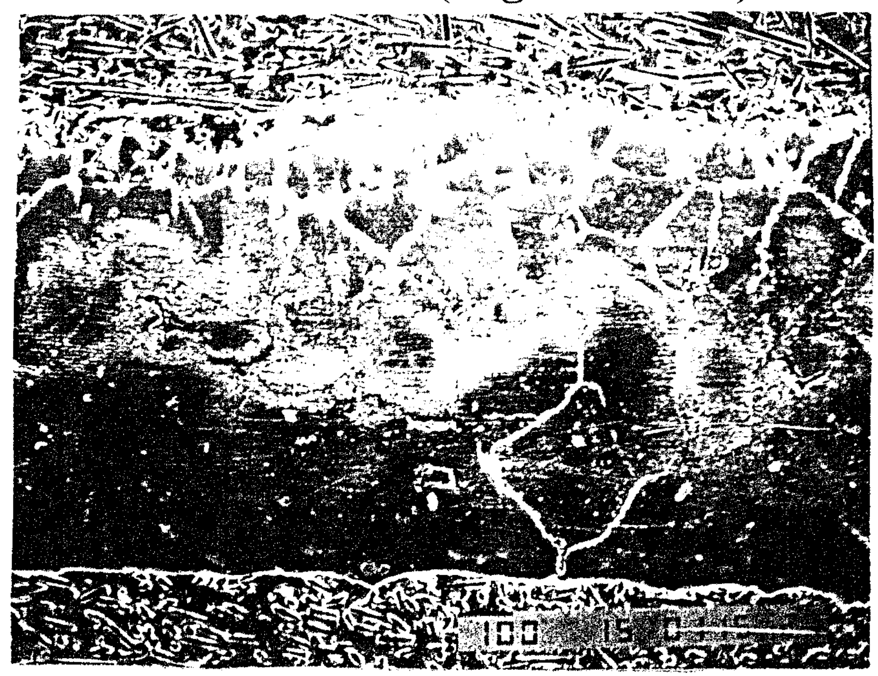
Steam Pressure: 2.5 Psi (first year), 25 Psi (third year)

The degradation is much more for all alloys when exposed to the higher pressure steam. Compared to the lower pressure steam the maximum difference in degradation was observed in the case of X-45. The difference in degradation could be attributed more to the flow rate differences and resultant salt exposures rather than pressure itself.

X-45 (Low Pressure)



X-45 (High Pressure)



Effect of applied stress on Degradation

Test Temperature: 875 °C

Applied Stress: 2 Mpa

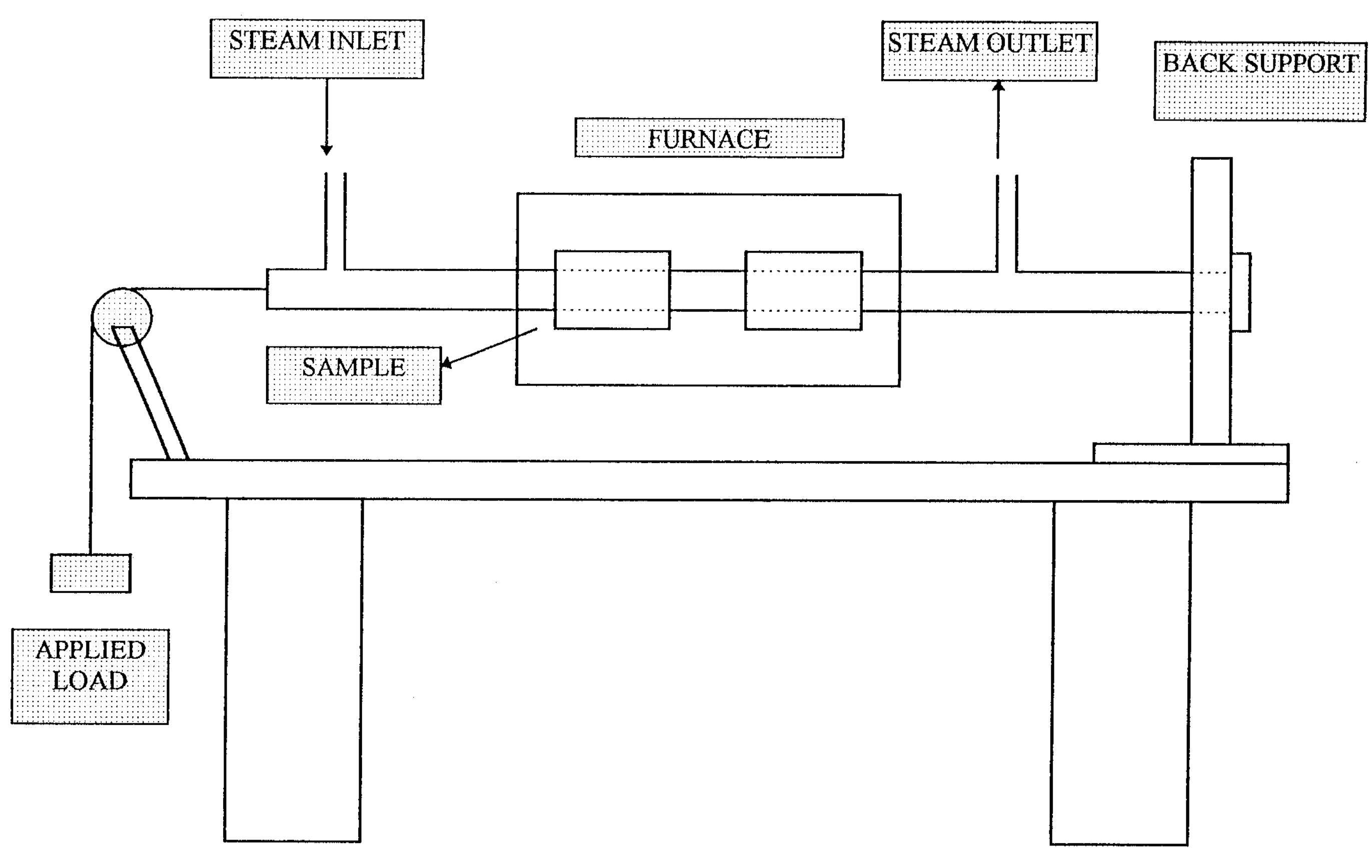
Steam Inlet Temp.: 150 °C

Steam Outlet Temp.:275 °C

Steam Flow Rate: 0.1 Lt/sec

Test Duration: 750 hrs

The samples were stressed in their axial direction using an external constant load. The effect of stress on the superalloy-steam interaction was studied. The steam used in these tests was uncontaminated



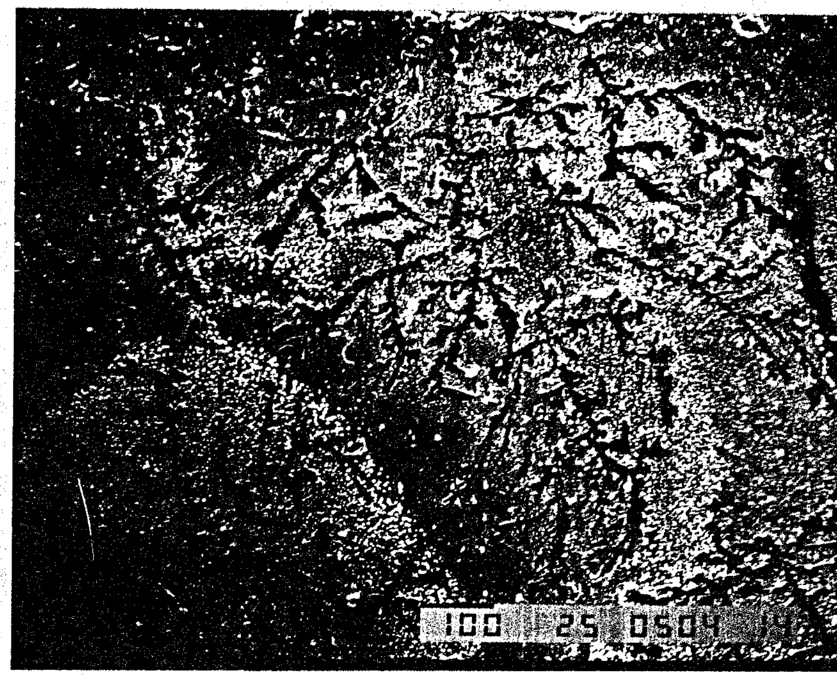
Schematic of Experimental Set-up for Stress Testing

Degradation in the IN 738 exposed to uncontaminated steam under an applied stress of 2 Mpa

Test Temperature: 875 °C **Test Duration:** 750 hrs

<u>Degradation in the IN 617 exposed to uncontaminated steam under an applied stress of 2 Mpa</u>

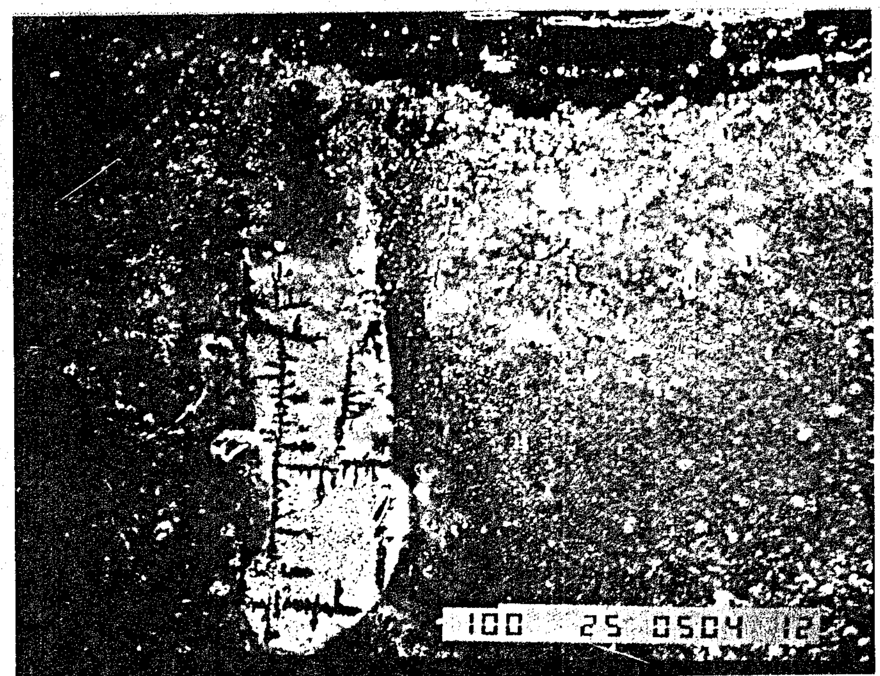
Test Temperature: 875 °C **Test Duration:** 750 hrs



Degradation in X-45 exposed to uncontaminated steam under an applied stress of 2 Mpa

Test Temperature: 875 °C

Test Duration: 750hrs



Long Term Oxidation Behavior of CMSX-4 in Steam

Test Temperatures: 800 °C & 950 °C **Exposure Time:** 1250hrs

After prolonged exposure of upto 1250 hrs in uncontaminated steam, it was observed that the internal oxidation underwent a healing with the formation of a protective film at 950 °C

CMSX-4 (288 hours exposure)
Test Temperature: 950 °C
Magnification: 1000 X

CMSX-4 (1250 hours exposure)
Test Temperature: 950 °C
Magnification: 1000 X