

Cyclic Oxidation and Hot Corrosion Behaviour of Nimonic Series Superalloy at an Elevated Temperature Range of 700 °C -800 °C

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Abstract

Structural materials are usually operated under extreme circumstance of temperature, `problem in steam power plant. Super alloy have been meet the condition of high corrosion resistance and high temperature oxidation resistance. Super alloys have good mechanical property such as, creep ,fatigue strength and surface stability. The present analysis aims to calculate the high-temperature oxidation and hot corrosion behavior of Ni-based super alloy. Oxidation damage has been characterized through weight change data from thermo gravimetric analysis at temperatures from 700 °C to 800 °C and cyclic oxidation testing at 700 °C and 750 °C. The samples were examined at the end of each cycle and subjected to weight change measurements. The parabolic rate constants calculated for the super alloys show that the corrosion rate is minimum in air as compared to molten salt environment. Aggregate Weight gain analysis for 50 hours considered more severe in turbines and boilers and aircraft engines at land base power plants. , high chloride manner salts and fine sulphate bearing sands are consumed in the engines. The species can pass through the engine to the hot gas path of the HP turbine, and can result in deposits being formed on areas of the blades, vanes and the disc rim by particle and vapors deposition. The presence of sulphur dioxide, a by-product of combustion contributions the formation of sodium sulphate (Na₂SO₄) rich deposits. At temperatures in excess of 650°C, these Na₂SO₄deposits react with the Ni alloy components to form low melting point eutectics that attack the component surface. This mode of hot corrosion is known as type II sulphidation. .XRD analysis and SEM surface morphology of hot

corroded super alloy shows the formation of NiO Cr₂O₃ and spinel (NiCr₂O₄) as major phases. Surface morphology and composition analysis of super alloys oxidized in air shows Fe₂O₃, NiO and Cr₂O₃ as foremost phases. The formation of scale rich in Cr₂O₃, NiO and spinel (NiCr₂O₄) has contributed for the better oxidation and hot corrosion. The presence of these elements at the surface will decrease oxygen availability in the underlying alloy and favours the formation of most thermodynamically stable oxide (Cr₂O₃). These studies of Nimonic 80A at 750 °C proves its better resistance to oxidation and hot corrosion as compared to some other super alloys of same series.

Keywords: Oxidation, Hot corrosion, super alloys ,XRD analysis, SEM, parabolic rate constant.

1. Introduction

High-temperature alloys that suffered hot corrosion attack were generally found to exhibit both oxidation and sulfidation. The hot corrosion morphology is typically characterized by a thick, porous layer of oxides with the underlying alloy matrix depleted in chromium, followed by internal chromium-rich sulfides. It is generally believed that the molten sodium sulfate deposit is required to initiate hot corrosion attack. The temperature range for hot corrosion attack, although dependent on alloy composition, is generally 800 to 950 °C (1470 to 1740 °F). The lower threshold temperature is believed to be the melting temperature of the salt deposit, and the upper temperature is the salt dew point. When temperature reached beyond the melting point of these deposit these compounds starts depositing on turbines blades. Liquid phase is ideal condition for corrosion to takes place because of faster transport phenomenon. Oxidation and hot corrosion are turn out to be the solemn problem in such devices which are usually operated under high temperature range such as land based power plant ,aircraft ,marine gas turbines. . Hot corrosion is considered more severe in aircraft engines that are used for air travel near coastal areas, and over deserts and volcanic regions. During these flights, high chloride bearing salt sand fine sulphate bearing sands are ingested in the engines. The species can pass through the engine to the hot gas path of the HPTurbine, and can result in deposits being formed on areas of the blades, vanes and the disc rim by particle and/or vapour deposition. The presence of sulphur dioxide, a by-product of combustion, assists the formation of sodium sulphate (Na₂SO₄) rich deposits. At temperatures in excess of 650°C, these Na₂SO₄deposits react with the Ni alloy components to form low meltingpoint eutectics that attack the component surface.

2. Material Used

Super alloy nimonic80A procued from manher metals Mumbai India, in the form of hot rolled bars.

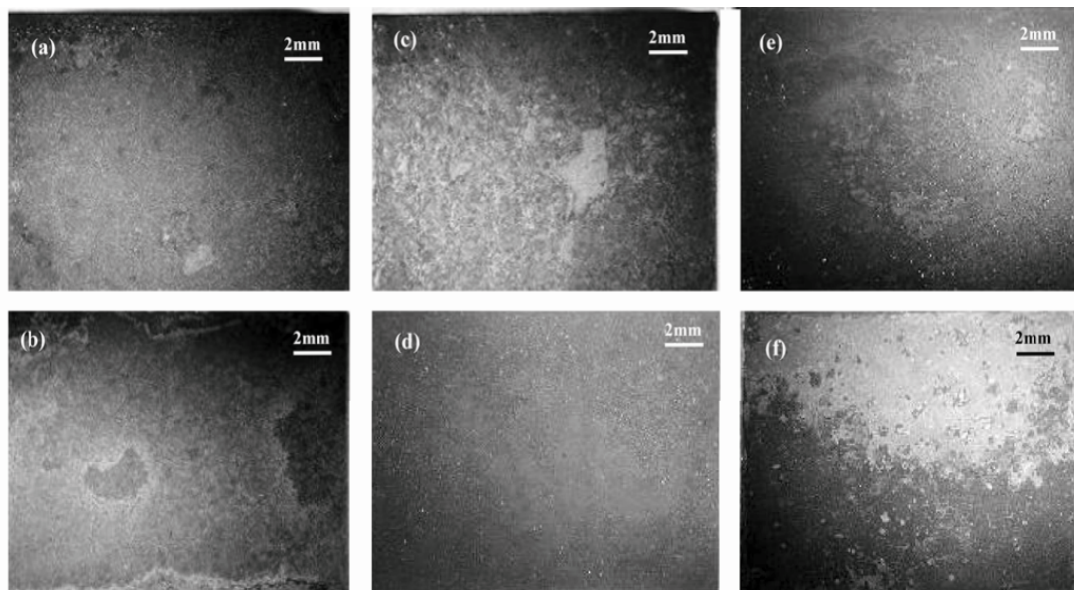
2.1 Sample preparation

Specimen cut in the form of rectangular shape of size 20mm into 50mm. the thickness of the sample has been reduced 2-3 mm using surface grinder. The specimen then mirror polish down to alumina using emery papers of 220,320,800,1200grit sizes followed by cloath polishing using diamond paste, then sample was washed with water and cleaned with acetone.

3. Studying Oxidation of Super Alloys

Hot corrosion degradation process of the super alloys usually consists of two stages, namely an initiation stage and a propagation stage. According to Pettit and Meier, it is a fact that all corrosion resistant alloys degrade via these two stages and it is the result of using selective oxidation to develop oxidation or corrosion resistance. They further elaborated that the conditions causing hot corrosion therefore do nothing more than shortening the time for which the super alloys can form protective alumina or chromia scales via selective oxidation. During the initiation stage of hot corrosion, super alloys are being degraded at rates similar to those that would have prevailed in the absence of the deposits. Elements in the alloy are oxidized and electrons are transferred from metallic atoms to the reducible substances in the deposit. Consequently, the reaction product barrier that forms beneath the deposit on the alloy surface usually exhibits primarily those features resulting from the gas–alloy reaction (Pettit and Giggins). Up to 800 °C, the lower oxidation rates for Na₂SO₄ 80A and 90 Cr₂(SO₄)₃, for nimoinic 80A NiSO₄ or coated alloys were attributed to a scale morphology CoSO₄ additions, consisting of inner scales of Cr₂O₃ acting as a protec-650-1000 °C oxide film and external scales of NiO. This morphology was observed to be maintained at high temperatures (Malik and Ahmad,).

High temperature cyclic oxidation and hot corrosion behaviours of super alloys



3.1 X-ray mapping

The hot corroded samples were cut across the cross-section and mounted in transoptic mounting resin, mirror-polished and gold coated to facilitate X ray mapping by FE-SEM/EDAX of the different elements present across the scale. X-ray mapping analyses of the scale formed on the Superni718 after hot corrosion in Na_2SO_4 -60% V_2O_5 environment at 750°C for 100 cycles reveals that the surface scale mainly consists of soft Ni and Fe in the upper most part of the scale, presence of oxygen in that scale shows the formation of NiO and Fe_2O_3 layer. In the sub scale region, there is a thick band of chromium (Cr) which indicates the formation of relatively dense scale of Cr_2O_3 , minimum amount of Si penetrated deep into the substrate.

For 8 h so that their weight would remain constant during the course of high temperature cyclic study. The weight of boat loaded with specimen was measured at the end of each cycle using an electronic balance (model 06120) with a sensitivity of 1 mg. corrosion. SEM, XRD and EPMA techniques were used to analyse the corrosion products after subjecting the specimens to oxidation and hot corrosion tests

3.2 X-ray diffraction analysis (XRD) of scale

The XRD patterns for the super alloys is subjected to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C after 100 cycles. The major phases identified for Superni75 are NiO, TiO_2 , NiFe_2O_4 , Cr_2O_3 , $\text{Ni}(\text{VO}_3)_2$, V_2O_4 and NiCr_2O_4 , whereas in the scale of Super ni718, an additional phase, γ - Fe_2O_3 except V_2O_4 is noticed. Similarly, for Superfer 800H, the scale has all the above phases, but without V_2O_4 .

3.3 Surface morphology of scale: FE-SEM/EDAX

Micro graphs with EDS spectrum of the super alloy specimen after cyclic oxidation in air and hot corrosion in molten salt (Na_2SO_4 -60% V_2O_5) environment for 100 cycles at 900°C are shown in, respectively. Air oxidized super alloys clearly indicate the formation of NiO as a major oxide phase formed on Superni75 (figure 4a); but in case of Superni718, Cr_2O_3 is the major oxide phase formed on the air oxidized surface. In Superfer 800H (figure 4c), the formation of hemispherical shaped protrusion was observed, which mainly consists of Fe_2O_3 , MnO and Cr_2O_3 as the predominant phases. All the three hot corroded super-alloys in molten salt (Na_2SO_4 -60% V_2O_5) environment show the oxides scale of three different chemical compositions on the surface. For example, superalloy Superni 75 (figure 5a) shows NiO (96%) in the form of fine irregular shaped crystals as a sparse dominant phase, but superalloy, Superfer 800H and Superni718 show a massive scale with NiO, Cr_2O_3 and Fe_2O_3 . Mainly consists of Ni and Fe in the upper most part of the scale, presence of oxygen in that top scale shows the formation of NiO and Fe_2O_3 layer. In the sub scale region, there is a thick band of chromium (Cr) which indicates the formation of relatively dense scale of Cr_2O_3 , mg of Si penetrated deep into the substrate.

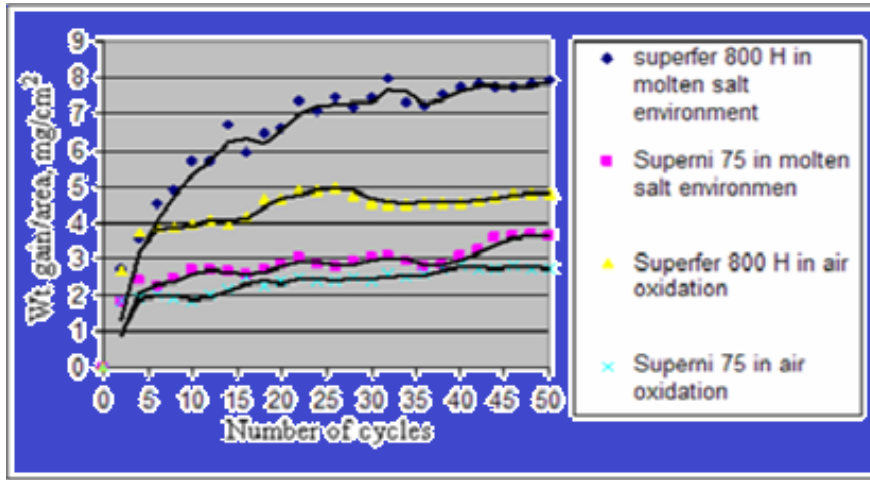
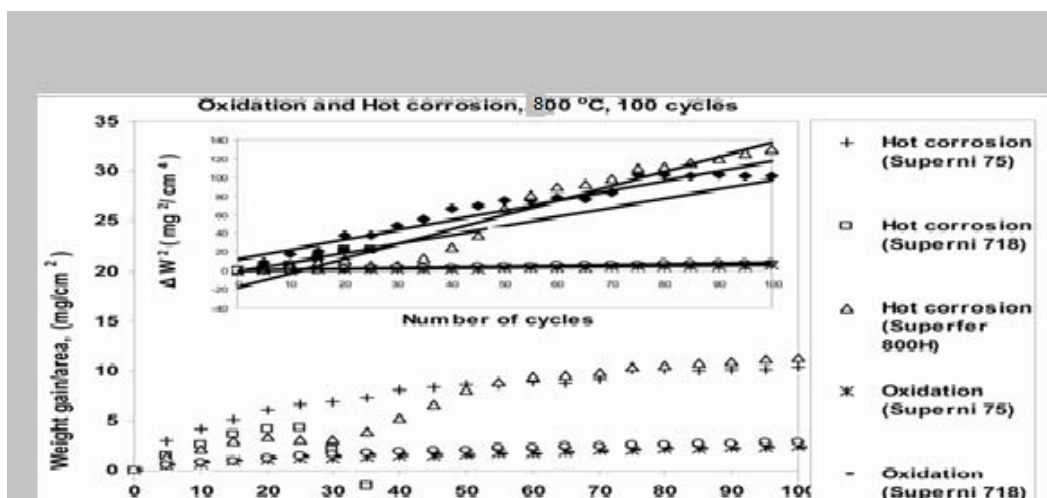


Fig. 1: Weight gain/area versus number of cycles plot for the Superni 75 and Superfer 800H Super alloys subjected to air and molten salt (Na₂SO₄-25% NaCl) environments for 50 cycles at 750°C.

4. Discussion

The weight change data for Super alloys subjected to oxidation and hot corrosion test in air and molten salt environment, respectively are plotted in figure 2. It indicates that all air oxidized super alloys followed a parabolic rate law up to 100 cycles, whereas hot corroded super alloys show a larger increase in weight. Superni 75 followed the parabolic rate law whereas Superfer 800H deviates from parabolic law between 30 and 50 cycles, and for the remaining cycles it followed parabolic rate. A small deviation from the parabolic rate law might be due to cyclic scale growth. Superni 718 (figure 2) has shown a sputtering behaviour between 25 and 70 cycles; during these cycles, the corrosion products started falling out-side.



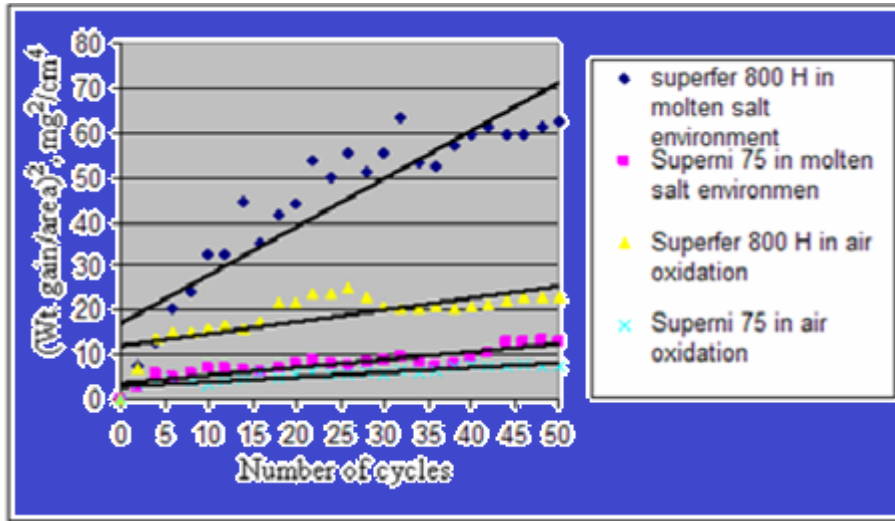


Fig. 2: (Weight gain/area)² versus number of cycles plot for the Superni 75 and Superfer.

The higher weight gain of the specimens during the first few cycles might be due to the rapid formation of oxides at the boundaries and within the open pores due to the penetration of the oxidizing species; afterwards, the subsequent increase in weight is gradual. Values of parabolic rate constant, K_p ($10^{-10} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$), were obtained from slope of the linear regression fitted line and are tabulated in table 2. The nature of fit, parabolic rate law, for oxidation and hot corrosion of super alloys are shown in figure 2. The parabolic rate constant for the hot corroded super alloys is found to be greater than the air oxidized.

800H super alloys subjected to air and molten salt ($\text{Na}_2\text{SO}_4\text{-25\%NaCl}$) environments for 50 cycles at 750C.

Table 2: Values of Parabolic rate constant, k_p for bare super alloys.

Sample	k_p ($\text{g}^2 \text{ cm}^{-4} \text{ sec}^{-1}$)
Superfer 800 H in presence of molten salt	9.8×10^{-10}
Superni 75 in presence of molten salt	71.4×10^{-10}
Superfer 800 H in presence of air oxidation environment	36.3×10^{-10}
Superni 75 in presence of air oxidation environment	22.78×10^{-10}

5. Conclusions

1. All the super alloys are resistant to oxidation and hot corrosion at 900°C for 100 cycles Super alloy, nimonic 80A, has higher oxidation and hot corrosion resistance properties as compared to other two super alloys.
2. These super alloys are found to be more resistant to oxidation as compared to that of hot corrosion.

3. The parabolic rate constants (K_p) for the air oxidized Superni 75, Superni 718, and Superfer 800H super alloys are 0.16, 0.147 and 0.237, respectively.
4. The K_p for the hot corrosion of super alloys is 2.29, 2.1 and 4.312, respectively.
5. The formation of protective oxide scales such as NiO, Cr₂O₃ and Fe₂O₃ is responsible for imparting resistance against high temperature oxidation and hot corrosion of super alloys investigated in the present work.

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