



TECHNICAL NOTE

STUDY OF MOLTEN SALT CORROSION OF SUPERNI-75 USING THERMOGRAVIMETRIC TECHNIQUE

T.S. Sidhu, S. Prakash and R.D. Agrawal

Metallurgical and Materials Engineering Department, Indian Institute of Technology Roorkee, Roorkee-247667 (UA) India,
E-mail: tssidhu@rediffmail.com

Abstract

The present study aims to evaluate the hot corrosion behaviour of the Ni-based alloy Superni-75 in the molten salt environment of $\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$ at 900°C under cyclic conditions. The thermogravimetric technique was used to establish the kinetics of corrosion. X-ray diffraction, scanning electron microscopy/energy-dispersive analysis and electron probe microanalysis techniques were used to analyse the corrosion products. Superni-75 has successfully provided the hot corrosion resistance to the given molten salt environment. The hot corrosion resistance of the Superni-75 has been attributed to the formation of uniform, homogeneous and adherent thick layer of the scale consisting mainly of oxides of nickel and chromium, and refractory $\text{Ni}(\text{VO}_3)_2$. These oxides and refractory nickel vanadates have blocked the penetration of oxygen and other corrosive species to the substrate.

Keywords: Hot corrosion, nickel-based alloy, superalloy, molten salt environment

1. Introduction

No alloy is immune to hot corrosion attack indefinitely, although there are some alloy compositions that require a long initiation time at which the hot corrosion process moves from the initiation stage to the propagation stage (Provenzano and Cocking, 1987). The alloys used for blades and vanes in high performance gas turbine engines operated in marine environment are, in general, optimized with regard to their mechanical properties and resistance against corrosive environment (Sidhu *et al.*, 2005).

The iron- and nickel- base superalloys are commonly used for high-temperature applications involving aggressive environment such as gas turbines and boilers for marine applications, aircraft, energy generation systems etc. However, the presence of combustion gases constitutes an extreme environment and the hot corrosion is inevitable when these alloys are used at high-temperatures for longer periods of time (Goebel *et al.*, 1973). The corrosion resistance of superalloys can be improved by adding fair amounts of Al and Cr (Wang *et al.*, 1989). However, these elements can be added only up to a limited extent as their higher concentrations adversely affect the mechanical properties of the alloys (Eliaz *et al.*, 2002 and Pomeroy, 2005).

Due to depletion of high-grade fuels and for economic reasons, use of residual fuel is well known. Residual fuel oil contains sodium, vanadium and sulphur as impurities, forming $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$ complex and sodium-vanadates mixtures (Luthra & Spacil, 1982 and Reid, 1971). A mixture of Na_2SO_4 and V_2O_5 in the ratio of 40:60 constitutes a eutectic with a low melting point of 550°C and creates a very aggressive environment for hot corrosion to occur (Tiwari, 1997).

The present investigation is an attempt to evaluate the hot corrosion resistance of the nickel based alloy Superni-75 (similar grade Nimonic-75) in a corrosive environment of molten salt $\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$ at 900°C under cyclic conditions. This alloy is developed by Mishra Dhatu Nigam Limited, Hyderabad (India). They provided this alloy for studying its hot corrosion resistance for high temperature corrosive environment applications such as gas turbine and boiler.

The thermogravimetric technique was used to establish the kinetics of corrosion. X-Ray diffractometer, scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDAX) and electron probe microanalysis (EPMA) techniques have been used to analyse the corrosion products after hot corrosion at 900°C .

2. Experimental Procedure

2.1 Substrate material

The Ni-based superalloys namely Midhani Grades Superni-75 (19.5Cr-3Fe-0.3Ti-0.1C- Balance Ni) was used as a substrate material in the present study. The alloy was provided by Mishra Dhatu Nigam Limited, Hyderabad (India) in the rolled sheet form. The specimen with dimension of approximately 20mmX15mmX5mm was cut from the alloy sheets. The specimen was mirror polished down to 1 μ m alumina on a wheel cloth polishing machine.

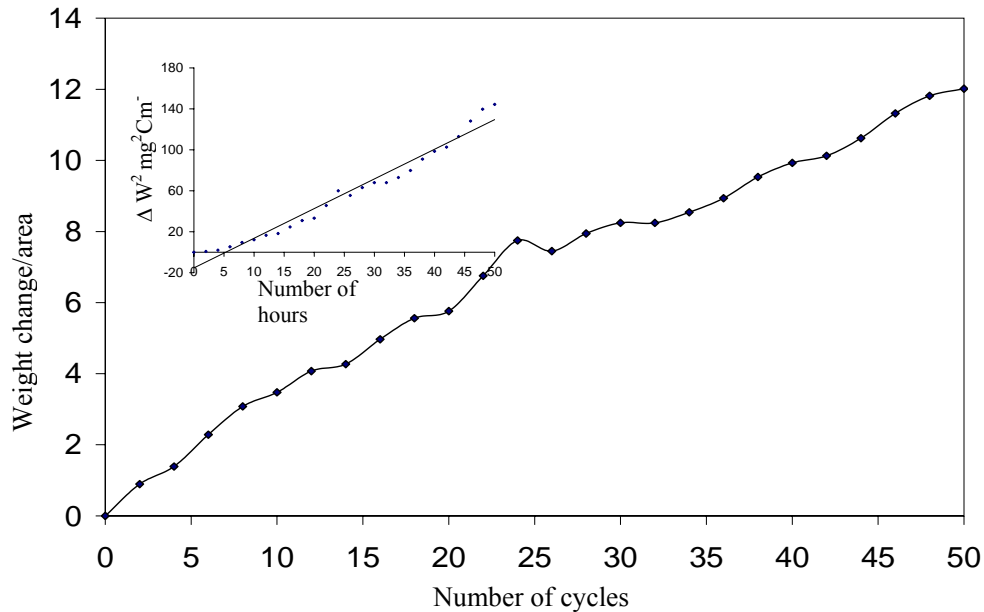


Fig. 1: Weight change vs. time plots for Superni -75 during cyclic study. Insert is fitted for (weight change/area)² vs time plots

2.2. Molten salt corrosion test

Cyclic study was performed in the molten salt (Na₂SO₄-60%V₂O₅) for 50 cycles. Each cycle consisted of one hour heating at 900 °C in a silicon carbide tube furnace followed by 20 minutes cooling at room temperature. A salt mixture of Na₂SO₄-60%V₂O₅ (wt%) was dissolved in distilled water. After washing with acetone, the specimen was heated in an oven to about 200 °C. The heating of the specimen was found necessary for proper adhesion of the salt layer. Thereafter, a layer of Na₂SO₄-60%V₂O₅ salt mixture was applied uniformly on the warm polished specimen with the help of a camel hair brush. Amount of the salt coating was kept in the range of 3.0 -5.0 mg/cm². The salt coated specimen as well as the alumina boat was then kept in the oven for 3-4 hours at 100 °C. Then they were again weighed before exposing to hot corrosion tests in the tube furnace. During hot corrosion runs, the weight of boat and specimen was measured together at the end of each cycle with the help of Electronic Balance Machine Model 06120 (Contech) with a sensitivity of 1 mg. The spalled scale was also included at the time of measurements of weight change to determine the total rate of corrosion. The hot corrosion study on the Superni-75 was repeated two times under the same conditions for establishing the reproducibility of results. Efforts were made to formulate the kinetics of corrosion.

3. Results and Discussions

3.1 Corrosion kinetics

Thermogravimetric data for the hot corroded Superni-75 is compiled in the form of a graph between weight gain per unit area expressed in mg/cm² versus time expressed in number of cycles (Fig. 1). The figure shows that the weight gain of the alloy increases during cyclic study in the given environment. The overall weight gains after 50 cycles of hot corrosion for was found to be 12.015 mg/cm².

A fragile scale appeared on the surface of uncoated superalloy during the initial cycles. Subsequently, cracks were developed in the scale and spalling of the scale was observed during the course of study. However, after 25 cycles, there was no spallation of the scale. The colour of the scale, which was brownish grey during early cycles, turned to dark brownish grey after some cycles.

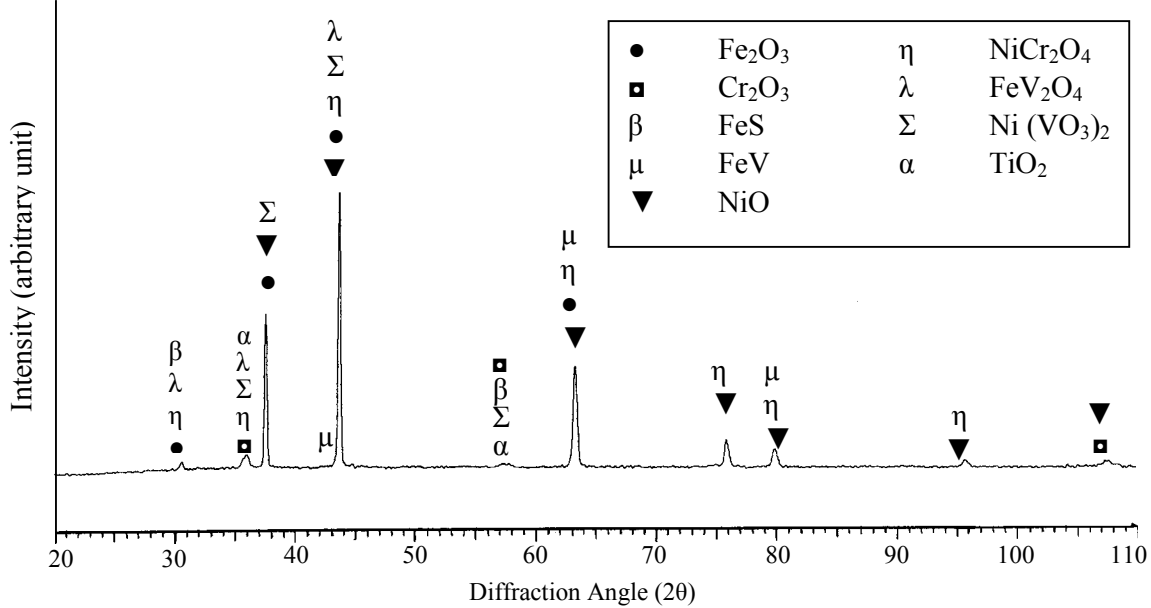


Fig. 2: X-ray diffraction patterns for the Superni-75 subjected to hot corrosion in Na₂SO₄-60%V₂O₅ environment at 900 °C for 50 cycles

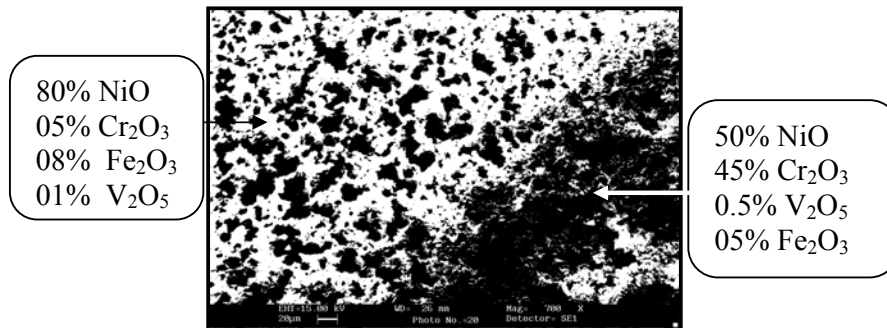


Fig. 3: SEM/EDAX analysis showing elemental composition (wt.%) for the Superni-75 subjected to hot corrosion in Na₂SO₄-60%V₂O₅ environment at 900 °C for 50 cycles.

Further, the weight gain square (mg^2/cm^4) versus time (number of cycles) plot is shown as an insert in Fig. 1 to establish the rate law for the hot corrosion. The plots show some deviations from the parabolic rate law for hot corroded superalloy. On the whole the alloy follows sub-parabolic behaviour up to 50 cycles. The parabolic rate constant k_p was calculated by a linear least-square algorithm to a function in the form of $(\Delta W/A)^2 = k_p \cdot t$, where $\Delta W/A$ is the weight gain per unit surface area (mg/cm^2), t is the hot corrosion time in seconds. The parabolic rate constant, k_p , for the Superni-75 calculated on the basis of 50 cycles is found to be as $9.716 \times 10^{-10} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$.

3.2. X-ray diffraction analysis of the scale

The diffraction pattern for the Superni-75 superalloy after subjecting to hot corrosion for 50 cycles at 900°C is shown in Fig.2. The major phases identified with the XRD analysis are NiO, Fe₂O₃, NiCr₂O₄, Ni(VO₃)₂, and FeV₂O₄, whereas Cr₂O₃, FeS, FeV and TiO are detected as minor phases. The substrate elements such as Fe and Ti diffuse through the protective scale during the hot corrosion of the specimen at 900°C.

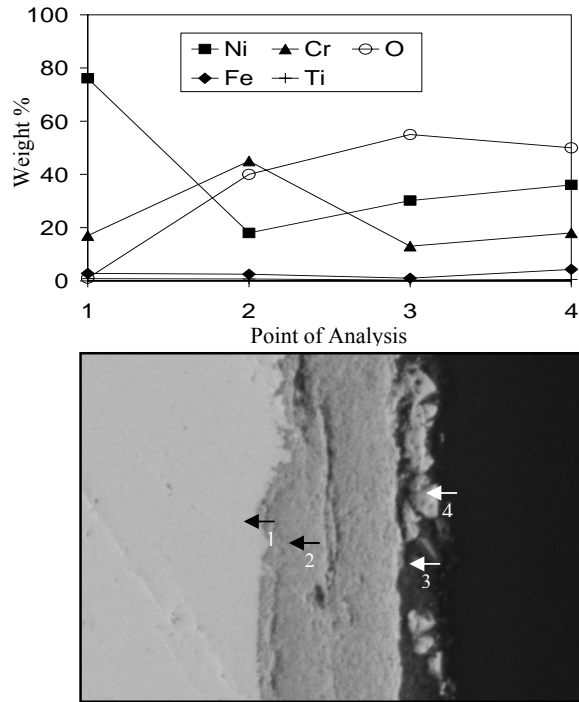


Fig. 4: Oxide scale morphology and variations of elemental composition across the cross section of Superni-75 hot corroded in $\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$ environment at $900\text{ }^\circ\text{C}$ for 50 cycles.

3.3. SEM/EDAX Analysis of the Scale

3.3.1 Surface analysis

SEM micrograph showing surface morphology and EDAX analysis of the Superni-75 superalloy after cyclic hot corrosion at $900\text{ }^\circ\text{C}$ is given in Fig. 3. A granular scale was formed after 50 cycles of hot corrosion. The black areas in the scale are the regions from where scale has spalled during experimentations. The EDAX results indicate that the top most scale (white phase) is rich in NiO along with small amounts of Cr_2O_3 , Fe_2O_3 and unreacted salt V_2O_5 . The subscale (black phase) is found to have almost equal amounts of NiO and Cr_2O_3 along with small amount of Fe_2O_3 and negligible V_2O_5 .

The presence of large number of oxides in the surface scale indicates the occurrence of hot corrosion and fluxing action of the molten salt.

3.3.2 Cross-sectional analysis

Back scattered electron image (BSEI) and elemental variation across the cross-section of Superni-75 corroded in the molten salt at $900\text{ }^\circ\text{C}$ is shown in Fig. 4. A continuous and adherent oxide scale is formed after 50 cycles of hot corrosion. The EDAX analysis at Point 1 shows the existence of very small amount of oxygen indicating the protective behaviour of the scale. At Point 2, the concentration of Cr and O is high and Ni has decreased substantially, whereas at Point 3 and 4 amount of Ni is relatively more. Quantity of oxygen has also increased at Points 3 and 4. Therefore it can be inferred that the scale has relatively more nickel oxide in its upper region, while lower portion of the scale is rich in oxide of Cr.

3.4 EMPA analysis

The hot corroded samples were cut across the cross-sections and mounted in transoptic mounting resin, mirror-polished and carbon coated to facilitate X-ray mapping of the different elements present across the scale. Elemental X-ray mappings at the cross-section of uncoated Superni-75 superalloys after cyclic oxidation at $900\text{ }^\circ\text{C}$ in $\text{Na}_2\text{SO}_4\text{-60}\%\text{V}_2\text{O}_5$ environment for 50 cycles are shown in Fig. 5. The BSE image indicates the formation of a dense, homogeneous, continuous and adherent scale (about $78\text{ }\mu\text{m}$ thick) consisting mainly of nickel and chromium. Titanium and iron show their existence throughout the cross-section. The upper part of the scale is rich in nickel oxide, whereas chromium forms a dense layer of chromium oxide just above the scale-substrate interface. These oxides have blocked the penetration of oxygen and other corrosive species to the substrate and,

therefore, the substrate Superni-75 is found to be free from the internal corrosion attack. Traces of sodium and sulphur are present throughout the scale. The existence of vanadium in the scale indicates the possibility of formation of various vanadates.

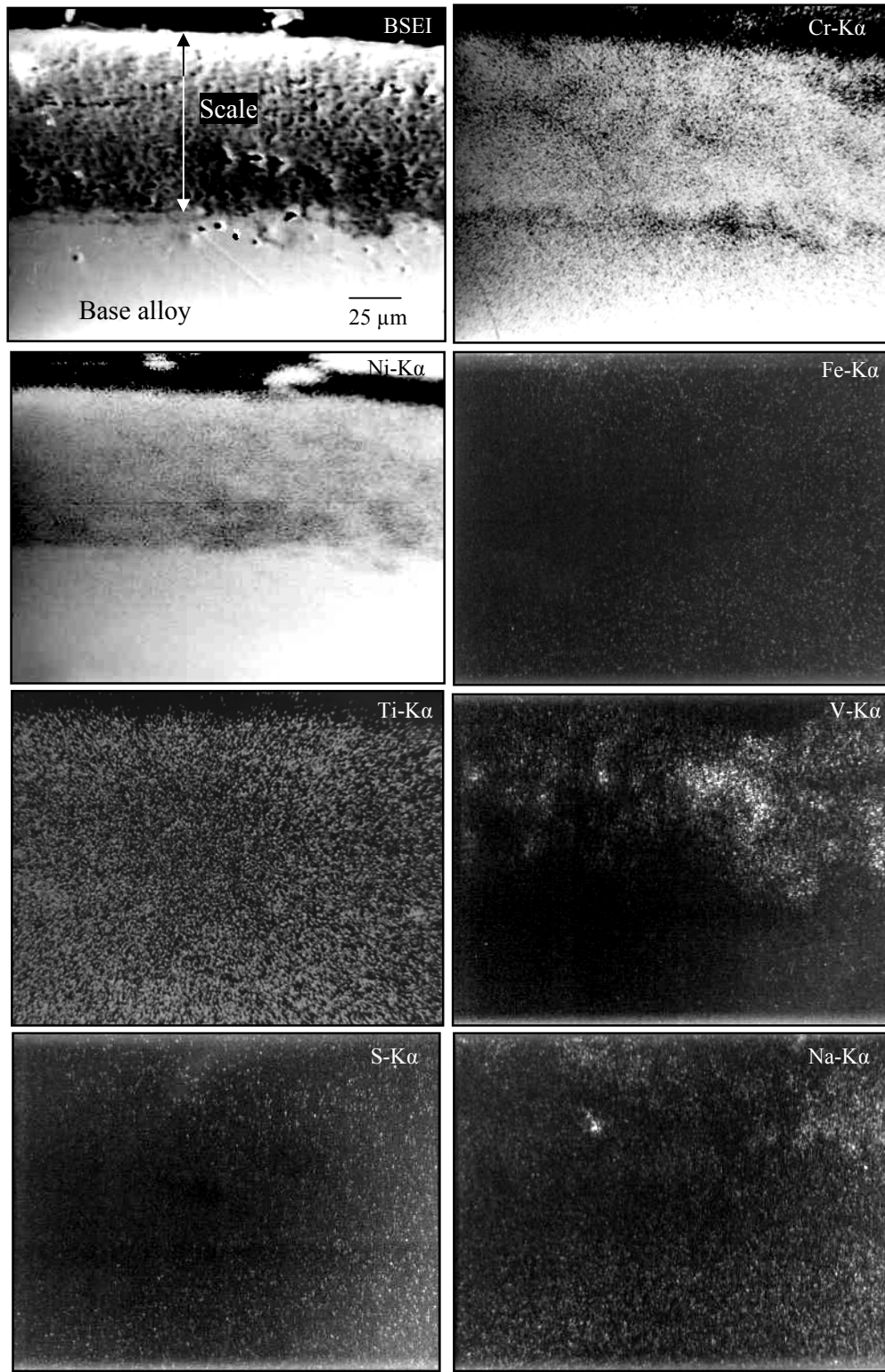


Fig. 5: Composition image (BSEI) and X-ray mappings of the cross-section of the Superni-75 subjected to hot corrosion at 900 °C in Na_2SO_4 -60% V_2O_5 environment for 50 cycles.

4. Discussion

Due to fluxing action of the molten salt, the scale formed on the bare alloy was porous and irregular during the initial cycles. Therefore, the substrate elements such as iron and titanium might have diffused through the scale during initial cycles. The XRD analysis shows the presence of non-protective oxide of iron and titanium. Significant spalling of the scale was observed during hot corrosion experimentation of Superni-75 during initial cycles. The spalling of the scale of Superni can be attributed to severe strain developed due to the precipitation of Fe_2O_3 from the liquid phase during cooling period of thermal cycles, and inter diffusion of intermediate layers of iron oxide (Sachs, 1958). Further in the cooling period of each cycle, the presence of nine different phases might impose severe strain on the surface thin layer which may result in cracking and exfoliation of the scale. The cracks may allow the aggressive liquid phase to reach the metal substrate (Sachs, 1958).

The (weight gain/area)² versus time plot (insert in Fig. 1) shows some deviation from the parabolic rate law of oxidation indicating that spallation of the scale has occurred during hot corrosion of the specimens. After some time, a protective scale of the oxides of chromium and nickel was formed which showed no spallation. Additionally, the formation of a refractory $\text{Ni}(\text{VO}_3)_2$ also acts as a diffusion barrier against the penetration of the oxidizing species (Seiersten and Kofstad, 1987).

Thermogravimetric data, XRD and EDAX analyses of the repeated specimen show similar trend of weight gain and the formation of similar phases in the surface scale, thus reproducibility of results has been established. Being similar, the results of repeated specimens are not shown.

5. Conclusions

The Superni-75 showed some spalling of the scale during testing in the molten salt $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$ at 900 °C, and the oxidation rate was increasing initially. EDAX analysis detected relatively more oxides of nickel in the upper region of the scale, while lower portion of the scale is found to be rich in oxides of Cr. The hot corrosion resistance of the Superni-75 has been attributed to the formation of uniform, homogeneous and adherent thick layer of the scale consisting mainly of oxides of nickel and chromium, and to the presence of refractory nickel vanadate, $\text{Ni}(\text{VO}_3)_2$.

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