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Effect of Deep Cryogenic Treatment on Hot Corrosion of Nimonic-90 Alloy

By Kailash Narayan Pandey[*] & Raj Saurav[±]

Nimonic-90, a nickel-based super alloy, is widely used in high-temperature and corrosive environments where hot corrosion is a matter of concern. Deep cryogenic treatment (DCT) is a novel technique for improvement of properties of materials where retained austenite is either completely transformed or eliminated, fine carbides are precipitated and redistributed along the matrix. The present study is focused on the effects of DCT on the rate of hot corrosion of Nimonic-90 alloy. In power generation devices such as gas turbines the Na_2SO_4 may present in the intake air or form by reaction between NaCl present in the intake air and sulphur present in the fuel as an impurity, V_2O_5 is formed during the combustion process of the fuel where it is present in the form of vanadium porphyrin. These compounds are responsible for hot corrosion of the components. In the Na_2SO_4-60%V_2O_5 molten salt environment, the rate of hot corrosion significantly decreased for the DCT sample. It has also been noticed that under DCT cycle, the tempering temperature and time also influence the alloy's resistance to environmental degradation under simulated high-temperature corrosive conditions using Na_2SO_4-60%V_2O_5. Thus, DCT significantly improves the lifespan and performance of Nimonic-90 in hot corrosion environments.

Keywords: *deep cryogenic treatment, hot corrosion, oxidation, tempering*

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Introduction

Corrosion and oxidation are irreversible processes that significantly affect the durability, structural integrity, and functionality of metals. These processes, which are chemical or electrochemical in nature, occur when metals interact with their environments [1, 2]. Cryogenic treatment has emerged as a promising technique offering transformative enhancements to the properties of various materials. Deep Cryogenic Treatment (DCT) involves gradually cooling the material to cryogenic temperatures (typical range of temperature is -126°C to -196°C) and holding it at that temperature for an extended duration, often ranging from several hours to several days. It refines the material's microstructure and relieves internal stresses, resulting in enhanced hardness, wear resistance, toughness, corrosion resistance and dimensional stability [3-6].

It has been demonstrated that DCT can significantly reduce the rate of corrosion in a wide range of materials, including ferrous and non-ferrous alloys. The specific mechanisms underlying this corrosion resistance vary depending on the material composition, microstructure, and environmental factors [3-7]. However, common mechanisms include the refinement of the microstructure, the formation of protective oxide layers, and the elimination of vulnerable sites for corrosion initiation [8]. For Nimonic series of superalloys hot corrosion at elevated temperature (700 ºC - 800 ºC) was found to be higher in a Na_2SO_4-60%V_2O_5 environment as compared to air [9, 10]. Hot corrosion processes involve the formation of various compounds on the surface of superalloys, such as NiO, Cr_2O_3, and spinel ($NiCr_2O_4$), impacting their overall performance [3, 9-12].

The effect of DCT is demonstrated on various materials like Nimonic-80A, Nimonic 95, AA7075-RRA alloy, different Ni-Co based superalloys etc. for the corrosion resistance of the materials but the study of effect of DCT on Nimonic-90 alloy for hot corrosion is yet to be performed. Nimonic-90 alloy has less corrosion rate as the base material is Nickel-cobalt but under high temperature corrosion resistance is less as compared to normal temperature. The material is used at high temperatures where the flue gases contain 40-70% V_2O_5, which reacts with Na_2SO_4 (Sodium sulphate) and forms $NaVO_3$, which is a highly corrosive environment to the materials [3, 9, 10].

Material and Sample Preparation

A nickel based super alloy Nimonic-90 is selected for the analysis of effect of DCT on the rate of hot corrosion. The chemical composition of Nimonic-90 super alloy is given in Table 1.

Table 1. *Elements of Nimonic-90 [12]*

Wt %	Ni	Cr	Co	Ti	Al	C	Si	Cu	Fe	Mn	P	S
Nimonic-90	60.380	18.235	15.880	2.380	1.325	0.049	0.536	0.065	0.400	0.433	0.008	0.004

Square samples for hot corrosion were prepared using wire EDM (Electrical Discharge Machining) of make - EX-7732C EXPRESS CUT, with a dimension of 15mm × 15mm × 5mm. Surface area of samples were 7.5 cm^2. After cutting, all surfaces of the samples were cleaned using emery paper of grit 400, 220 and 150 to remove any surface impurities and ensure a smooth and clean surface. The cleaned samples were placed in a ASTM E1379 glass Dewar with a 3.9 litres capacity having liquid nitrogen in it. The temperature within the chamber was -196°C. The slow cooling process was crucial to prevent thermal shock and to ensure uniform temperature distribution throughout the samples. Once the samples reached the target cryogenic temperature of -196°C, they were kept at this temperature for a soaking time of 36 hours. This extended soaking period allowed for the diffusion of the cryogenic temperature throughout the material, facilitating structural transformations at the atomic level. After the soaking period, the samples gradually warmed back to ambient temperature. Similar to the cooling process, the warming phase was performed slowly to prevent thermal shock and minimize the risk of cracking or distortion. Following the cryogenic treatment, the samples underwent a tempering process as per Table 2. This involved heating the samples to a desired temperature and holding them for a predetermined time to relieve residual stresses and further refine the microstructure. The treated samples were subjected to a thorough inspection to assess the effectiveness of the cryogenic treatment. This included XRD and Point Energy Dispersive X-ray Spectroscopy Analysis to identify and analyze the phases present with the elemental composition and distribution in the treated samples.

Table 2. *Tempering Parameters*

Sample No.	Tempering Temperature (°C)	Tempering Time (hrs.)	Number of Tempering (n)
DCT-01	100	1	1
DCT-02	100	1	2
DCT-03	150	2	1
DCT-04	150	2	2

Preparation of Salt for Hot Corrosion Study

The study aimed to replicate the harsh conditions that Nimonic-90 encounters in real-world applications. To simulate a high-temperature corrosive environment, a salt mixture of sodium sulfate (Na_2SO_4) and vanadium pentoxide (V_2O_5) was prepared. The environment simulates conditions common in industrial settings such as gas turbines, boilers, and jet engines due to fuel impurities and combustion processes [11]. Sodium sulphate (Na_2SO_4) and vanadium pentoxide (V_2O_5) were mixed in the ratio of 4:6 by weight respectively. 20g of sodium sulphate was mixed with 30g of vanadium pentoxide is mixed homogenously in a dry beaker for the study of hot corrosion and the prepared salt was stored in an airtight container to prevent contamination and moisture absorption until it was applied on the samples for hot corrosion.

The prepared salt was mixed with acetone. Then it was applied homogeneously on all the faces of the samples for the study of hot corrosion

with the help of camel hairbrush and it is subjected to heating for 30 minutes at 200°C.

For hot corrosion study, the four samples, as per Table 2, and one untreated sample were taken. On these five samples, prepared salt was applied.

Hot Corrosion Studies of DCT Treated Nimonic-90 Alloy in Na_2SO_4 – 60%V_2O_5

For the hot corrosion test, deep cryogenically treated specimens of Nimonic-90 alloy are subjected to cyclic heating in an environment of Na_2SO_4-60% V_2O_5. This specific coating was chosen to simulate aggressive corrosive environments and evaluate the material's resistance with or without DCT under hot corrosion environment. The samples for hot corrosion are subject to a high temperature of 900°C for 50 heating cycles. The temperature was almost 2/3rd of the melting temperature of Nimonic-90.

Cyclic Heating

To study the effect of DCT on oxidation and hot corrosion rates, specimens were subjected to a rigorous cyclic heating protocol using alumina crucibles in the Tribology Laboratory of MNNIT Allahabad on Electrically Heated Thermal Cycling Furnace.

This process involved a total of 50 cycles for hot corrosion, with each cycle comprising a 1-hour heating phase at 900°C, followed by a 20-minute cooling at ambient temperature on. At the end of each cycle weight measurement was carried out and the change weight was observed.

Visual Examination

Upon completion of the initial heating cycle, the specimens exhibited a noticeable change in colouration, transitioning to a blackish-grey hue. This colour change became more pronounced with subsequent heating cycles. Specifically, the specimens labelled DCT-CS-01 through DCT-CS-04 displayed a progressively darker black colouration. Additionally, these specimens developed slight greenish spots in certain areas, indicating localized chemical or structural changes. In contrast, the specimen identified as UT-CS underwent a distinct transformation, turning silver rather than following the blackening trend observed in the other samples. This divergence in colour change suggests a different reaction to the treatment process, possibly due to variations in material composition or initial surface conditions. The visual changes and surface degradation are documented in Figure 1, which provides a comparative visual representation of the treated samples. The images highlight the extent of colour change, surface roughness, and pitting, offering a clear visual correlation.

Figure 1. *Visual Picture of Hot Corroded Samples*

Sample: DCT-CS-01

Sample: DCT-CS-02

Sample: DCT-CS-03

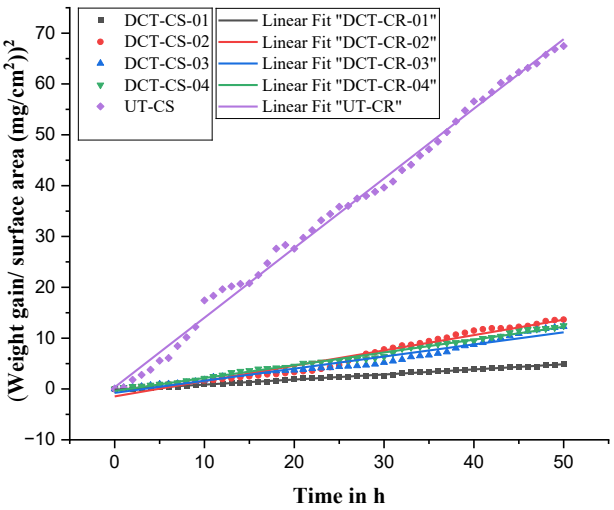
Sample: DCT-CS-04

Sample: UT-CS

Weight Gain Analysis

The weight change data for each specimen was recorded after each heating cycle in the salt environment. The weight gain serves as an indicator of the corrosion rate. The rate of corrosion for the untreated specimen is significantly higher than that of the DCT-treated specimens. Square of weight gain per unit area $(mg/cm^2)^2$ versus number of cycles for the hot corrosion analysis is shown in **Error! Reference source not found.**; it can be seen that the untreated sample has the maximum parabolic rate constant (k_p) as compared to the DCT treated samples. In DCT-treated samples, sample DCT-CS-01 has the least parabolic rate constant.

Figure 2. *Linear Fit Curve for Square of Weight Gain/Surface Area vs no. of Cycles*



The untreated sample has the maximum (k_p) compared to the DCT-treated samples. Initially, the (k_p) is highest for UT-OS 76.08611111 × 10^{-10} (mg^2/cm^4)/s, and DCT-OS-01 achieved the lowest (k_p) of 5.553888889 × 10^{-10} (mg^2/cm^4)/s with a repetitive heating cycle, untreated specimens' oxidation rate increased, for other samples it is given in the Table 3.

Table 3. *Values of Parabolic Rate Constant k_p*

Samples	DCT-CS-01	DCT-CS-02	DCT-CS-03	DCT-CS-04	UT-CS
k_p (10^{-10} $g^2cm^{-4}s^{-1}$)	5.55389	16.74667	13.21944	13.9861	76.0861

High rate of spalling (flaking) of the scale, or molten salt fluxes (such as Na_2SO_4-V_2O_5 mixtures) can cause deviations from the ideal parabolic law, leading to linear kinetics [13].

XRD Analysis of Hot Corroded Samples

XRD analysis was performed on the corroded samples, and the X-ray diffractograms for the hot corrosion study samples are presented in Figure 3 to 7.

Figure 3. *X-Ray Diffraction Pattern of DCT-CS-01*

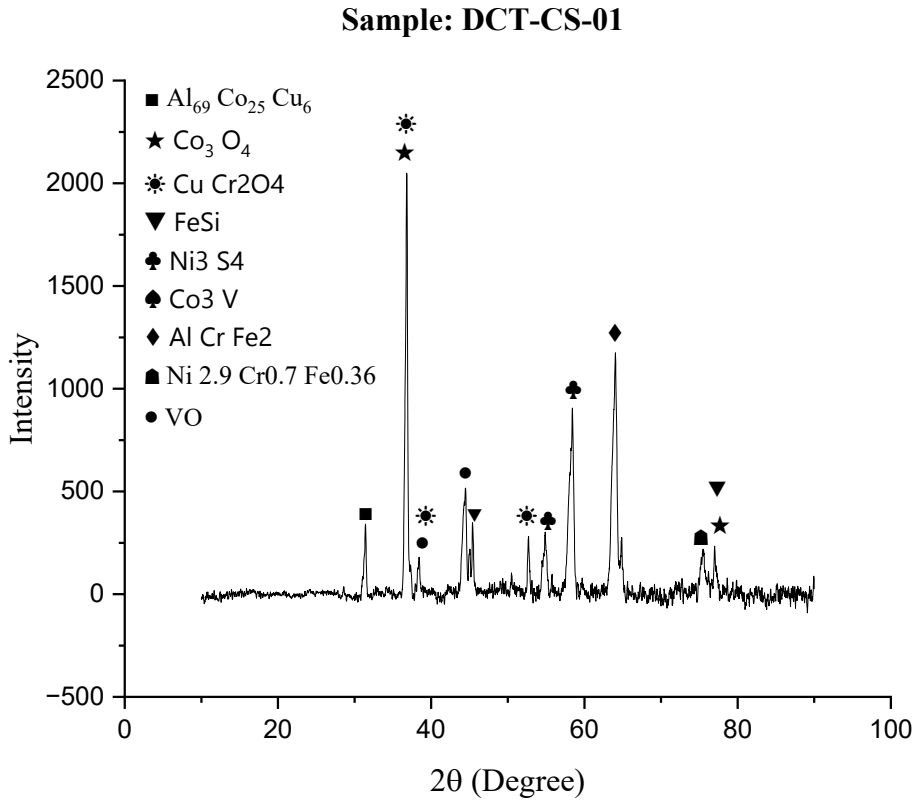


Figure Error! No text of specified style in document.**.** *X-Ray Diffraction Pattern of DCT-CS-02*

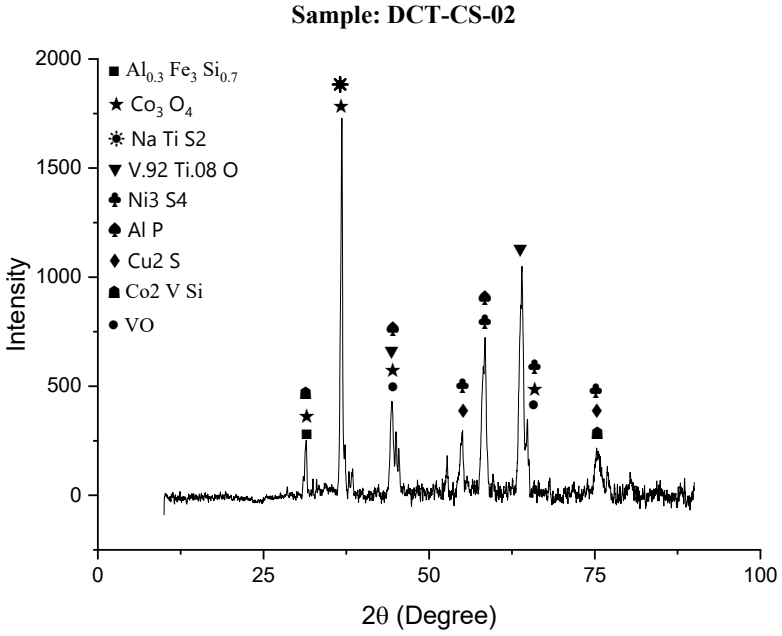


Figure 5. *X-Ray Diffraction Pattern of DCT-CS-03*

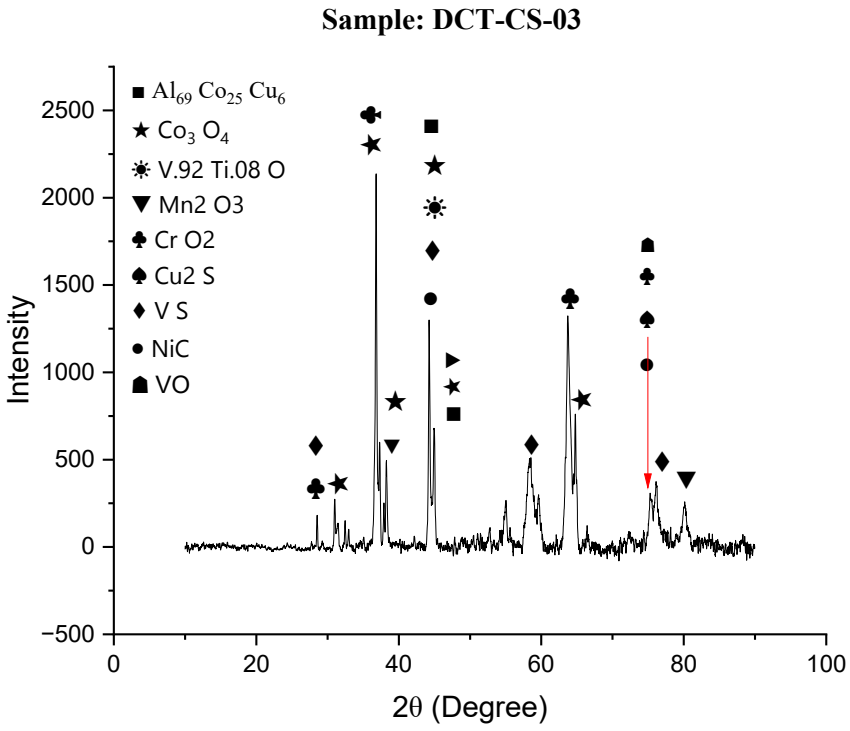


Figure 6. *X-Ray Diffraction Pattern of DCT-CS-04*

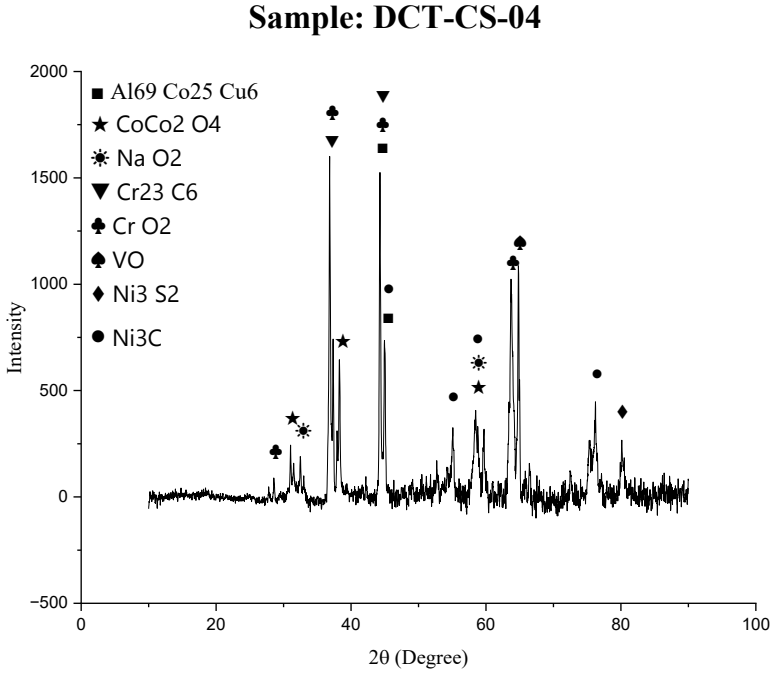
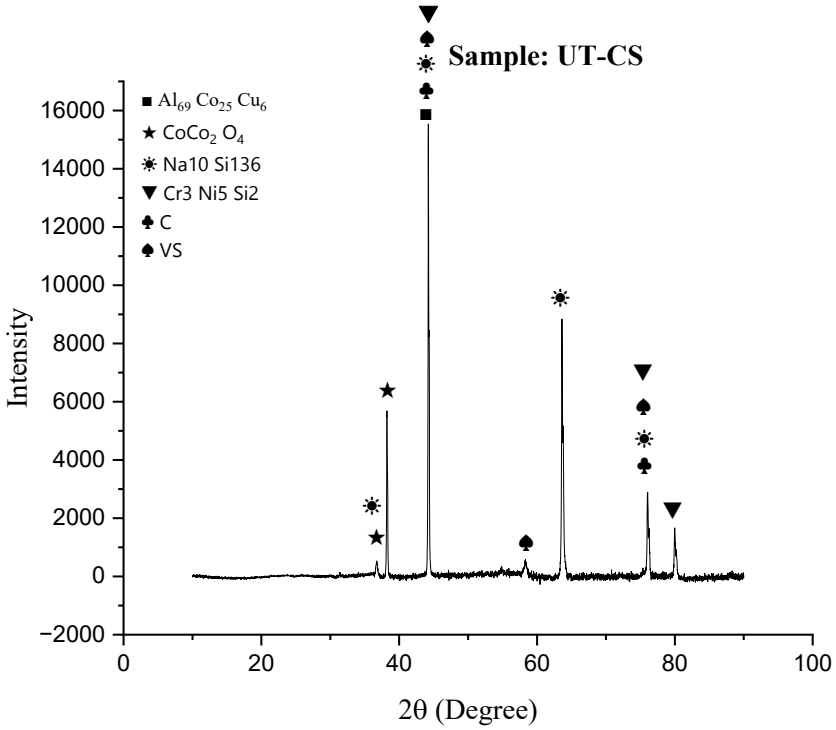


Figure 7. *X-Ray Diffraction Pattern of UT-CS*



Different phases were observed in X-ray diffractograms of the hot corrosion samples. The compounds like $CuCr_2S_4$, Ni_3S_4, Cu_2S, $NaO_2Ni_3S_2$, and VS can have led to the corrosion rate. However, few detected phases can form a protective layer,

and the further corrosion rate can be slower. VO is sometimes used in coatings to improve the corrosion resistance of metals. Stable oxides like Co_3O_4, CrO_2, Mn_2O_3, and AlP can reduce or protect the metal from higher corrosion rates. These oxides can form protective layers on the metal surface as a barrier against corrosive agents.

Conclusions

Corrosion behaviour was assessed under harsh conditions involving a mixture of Na_2SO_4 and 60% V_2O_5 at 900°C. The results from these studies highlight several important aspects:

- Weight gain per unit surface area and thus the hot corrosion is significantly less for the deep cryogenic treated sample with respect to the untreated sample, which indicates enhanced corrosion resistance due to DCT.
- Tempering negatively affects the corrosion resistance. With higher tempering temperatures and a high number of tempering, the rate of corrosion increases. This suggests treating tempering at lower temperatures, or if tempering can be avoided, then it should be completely avoided.
- The formation of a stable protective layer composed of vanadium oxide, cobalt oxide, and chromium oxide was observed during cyclic corrosion tests which decreased the rate of corrosion by creating a barrier between the surface and the corrosive environment.

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