Research Article

Experimental Investigation on the Effect of Coating Al₂O₃+70% NiCrBSi Cermets on Ti-31 Superalloy to Combat Hot Corrosion

M. S. Vinod Kumar,¹ R. Suresh,¹ N. Jegadeeswaran,² and Meseret Leta Feyisa³

¹Department of Mechanical Engineering, VTU-CPGS, Mysuru, 570029 Karnataka, India
²School of Mechanical Engineering, REVA University, Bangalore, 560065 Karnataka, India
³Department of Food Process Engineering, College of Engineering and Technology, Wolkite University, Wolkite, Ethiopia

Correspondence should be addressed to Meseret Leta Feyisa; meseret@wku.edu.et

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The superalloys are generally used for high-temperature applications, and since they operate in an aggressive environment, it is required to protect them with an appropriate coating to enhance the life of the superalloy material. In the present study, the superalloy Ti-31 is coated with cermets Al₂O₃+NiCrBSi by high-velocity oxy fuel (HVOF) spray coating technique, and hot corrosion tests were performed on both coated and uncoated samples, in presence of Na₂SO₄+60% V₂O₅ molten salt at a temperature of 700°C, and the corroded samples are characterized using SEM/EDS and XRD techniques. From the thermogravimetric studies, it is observed that total weight gain per unit area for uncoated Ti-31 is very high compared to Al₂O₃+NiCrBSi-coated Ti-31 and parabolic rate constant indicates that corrosion rate is decreased when substrate is coated. The current study's findings clearly show that the coating deposition is effective in protecting the substrate from hot corrosion.

1. Introduction

A superalloy is a type of high-temperature metal that is commonly employed in the hottest parts of jet and rocket engines, where temperatures can exceed 1200–1400°C [1]. Superalloys are composed of nickel, cobalt, and iron with significant quantities of alloying metals to offer high-temperature strength, toughness, and durability [2–4]. The components used in high-temperature conditions suffer severe thermal stresses resulting in reduced life of operation [5]. The cermets is a composite material made up of ceramic (cer) and metal (met) elements; cermets can combine the attractive features of both a ceramic and a metal, such as high-temperature resistance and hardness [6–8]. Coating of cermets on the superalloys can certainly be beneficial in enhancing the life of operation of the components made of superalloys [9–11]. HVOF technique is the most popularly used thermal spray coating technique of deposition of cermets onto the substrates, as it is proved to provide a coating with properties like good bond strength between substrate and coating, less porosity, and laminar structured coating [12–14].

Mahesh et al. in a study reported the high-temperature corrosion behavior of a special alloy Ti-31 in different salt environments of Na₂SO₄=50% NaCl and Na₂SO₄=60% V₂O₅ at 750°C. The thermogravimetric data reveals that corrosion rate is least in air when compared to salt environment [15]. Another research tested NiCrAl-coated superalloys at 900°C in a Na₂SO₄–60 percent V₂O₅ salt environment. According to the findings, uncoated samples gained more weight, and the NiCrAl coating performed better with the SuperNi-750 substrate, which may be linked to the oxide scale’s Al, Cr, and Ni ingredients, which increase hot corrosion resistance [16].

Sidhu et al. reported the hot corrosion behavior of NiCrBSi-coated Ni- and Fe-based superalloys in Na₂SO₄–60% V₂O₅ salt environment at 900°C. From the study, it is observed that the NiCrBSi coating is performing better with Ni-based superalloy when compared with Fe-based superalloy, and the NiCrBSi coating is successful in reducing
corrosion rate in Na₂SO₄–60% V₂O₅ salt environment [17]. Mahesh et al. investigated the performance of Ni–5Al and NiCrAl coating on iron-based superalloy in boiler environment, and the results indicate that NiCrAl coating is performing better in improving resistance to hot corrosion than Ni–5Al coating in the similar test conditions [18].

Reddy et al. investigated corrosion behavior of Ni₃Ti and Ni₃Ti+(Cr₇C₃+20Nicr)-coated Ti-15 and MDN 420 superalloys in Na₂SO₄–40% V₂O₅ salt environment at 650°C. From the thermogravimetric data, it is observed that the hot corrosion resistance of coated superalloys is better than uncoated superalloys [19]. Sidhu et al. have evaluated the oxidation and hot corrosion behavior of WC-NiCrFeSiB-coated Superni-75 and Superfer-800H superalloys in Na₂SO₄–25% NaCl salt environment at 800°C. From the results, it is observed that the coating WC-NiCrFeSiB is effective in protecting both the substrates Superni-75 and Superfer-800H from oxidation and hot corrosion. The protection obtained from coating is attributed to the formation of oxide scale which contains the oxides of active elements of coating. Here, these oxides act as shield against the diffusion of corrosion species through coating [20].

Jegadeeswaran et al. reported a hot corrosion study of the Al₂O₃+CoCrAlTaY coating on substrate Ti-31 and found that resistance to hot corrosion is increased due to major phases of chromium in the coating [21]. From the literature survey, there is minimum work reported on hot corrosion behavior of Al₂O₃+70% NiCrBSi-coated Ti-31; the present work evaluates the hot corrosion behavior of Al₂O₃+70% NiCrBSi-coated Ti-31 superalloy in (Na₂SO₄ +V₂O₅,60%) molten salt environment at 700°C.

2. Experimental Work

2.1. Substrate. The superalloy Ti-31 used in the present study is supplied by MIDHANI, Hyderabad. The supplied material was in sheet form, and it was cut into coupons of size 25 × 25 × 5 mm for experimental purpose. The material has Ti-6Al-4 V constituents, and it is generally used in making of turbine components, marine components, and chemical pumps [22]. The Ti-31 material is of ASTM B338 grade 5 standard; the details of substrate superalloy material as specified by the supplier are shown in Table 1.

2.2. Coating Powder and Its Deposition on Substrate. Based on literature survey, the metals are best suited for plastic deformation situation, and ceramics show high hardness value and are suitable for high-temperature applications. The combination of ceramics and metals performs better for hot corrosion environment [23]. For the current study, 30% Al₂O₃+70% NiCrBSi-fused alumina oxide alloy powder is the cerments chosen for coating; here, the alloy NiCrBSi is the base alloy, and the ceramic alumina is of 30 weight %. The powder particle size is in the range of 45 ± 15 μm and is in spherical shape. The SEM with EDAX examination of the coating powder is shown in Figure 1, which reveals that the coating powder has the phases of Ni, Cr, B, Si, and Al elements which are nearer to the coating composition selected. The detail of cerments as specified by the supplier is shown in Table 2.

To get the microstructure of the substrate materials, a standard metallographic polishing procedure is applied. For substrate material Ti-31, etchant used is 1.5% HF-4%
HNO₃-94% water. The coating powder is deposited on the substrate superalloy Ti-31 using high-velocity oxy fuel (HVOF) thermal spray coating technique. Here, the fuel used is liquefied petroleum gas (LPG) and the process parameters set are as follows: oxygen pressure is 98 × 10⁴ N/m², flow rate of oxygen is 252 liters per minute, spraying distance is in the range of 0.2 to 0.25 m, fuel pressure is 68.02 × 10⁴ N/m², oxygen pressure is 98 × 10⁴ N/m², and pressure of powder carrier gas is 49.02 × 10⁴ N/m². Coating obtained was laminar structured, less porous, and thickness in the range of 250 to 300 μm. The thermal spray coating process is carried out using the equipment METCO DJ2600 at M/s Spray Met Industries, Bangalore, India. Figure 2 shows a cross-sectional micrograph of the coated sample, revealing that the coating deposition is between 270 and 315 microns thick. The porosity of the coating is measured using a metal-lurgical microscope, and the porosity of the coating measured is 1.89%. The microhardness of uncoated and coated samples is measured using a Micro VICKER Hardness tester as per ASTM E384 standards. The hardness value measured for uncoated Ti-31 is in the range of 232 to 303 Hv, and after coating, the microhardness value is in the range of 591-648 Hv. The densities of the uncoated and coated samples were measured using the water immersion method, and the density of the uncoated Ti-31 sample was 4.35 gm/cc and for the Al₂O₃+70% NiCrBSi-coated sample was 4.54 gm/cc.

2.3. High-Temperature Corrosion Study. Uncoated Ti-31 and 30% Al₂O₃+70% NiCrBSi-coated Ti-31 samples were exposed to 50 hot corrosion cycles using the following procedure. Initially, the uncoated sample is polished and washed in acetone to remove dirt particles, and coated sample will not be polished because it will remove the coating deposition. The prepared sample’s initial weight and dimensions are recorded; the molten salt of Na₂SO₄+60% V₂O₅ is applied on the sample with a coating thickness of 3-5 mg/cm². The alumina boat along with salt-coated sample is placed in hot section of silicon carbide tube furnace set at a temperature of 700°C; after one hour of duration, the sample is allowed to cool. The weight change is recorded, and visual observations of oxide scale formation and color changes are recorded which constitutes one cycle of hot corrosion. The test is repeated for 50 cycles.

2.4. Characterization. Thermogravimetric data are recorded to better understand kinetics of hot corrosion; the corrosion products of both uncoated and coated materials were investigated using a scanning electron microscope (SEM), X-ray diffractometer (XRD), and energy dispersive X-ray spectroscopy (EDS) to reveal their microstructural and compositional details, as well as to elucidate the mechanism of corrosion.

3. Results and Discussion

3.1. Thermogravimetric Study. Figure 3 depicts the macrograph of uncoated and 30% Al₂O₃+70% NiCrBSi-coated Ti-31 specimen which have undergone the hot corrosion process in Na₂SO₄ 40% and 60% V₂O₅ molten salt environment for 50 cycles at 700°C. The surface of uncoated Superco-605 initially was grey in color, which persisted throughout the cyclic hot corrosion process. During repeated corrosion tests, there was a severe weight gain observed in uncoated Ti-31, and the oxide scale formed was with cracks, and crack width was growing with the number of heating cycles, and also, the oxide scale was getting peeled off from the surface.

The 30% Al₂O₃+70% NiCrBSi-coated Ti-31 sample was initially grey in color, and the oxide scale formation is observed from the 10th cycle onwards. Here, the weight gain in sample was comparatively very less than uncoated Ti-31. The oxide scale turned to yellowish green color from 20th...
cycle onwards, and it was well adherent to the substrate, and no cracks were developed throughout the hot corrosion test.

Figure 4 depicts the variation of total weight gain for different heating cycles for both uncoated and Al$_2$O$_3$+70 wt% NiCrBSi-coated Ti-31 during corrosion test. The value of total weight growth after 50 cycles of hot corrosion for uncoated Ti-31 is 40.3 mg/cm$^2$, and the weight gain of the Al$_2$O$_3$+NiCrBSi-coated Ti-31 materials is 2.1 mg/cm$^2$. Further, to look at the possibility of parabolic relationship between weight gain and time of exposure, square of weight gain per unit area is plotted against number of cycles as shown in Figure 5. It implies that the oxides scale that has formed on the surface is not protective in the presence of molten salt.

Figure 3: Macrographs of candidate metals exposed to high-temperature corrosion at 700°C of (a) uncoated Ti-31 and (b) 30% Al$_2$O$_3$+NiCrBSi 70%-coated Ti-31.

Figure 4: Plots of weight gain/area V/s No. of cycles for uncoated and Al$_2$O$_3$+NiCrBSi-coated Ti-31 superalloys exposed to high-temperature corrosion at 700°C.
Since the uncoated Ti-31 was undergoing sputtering and severe weight gain which indicates that the hot corrosive environment necessitates the protection of substrates, the parabolic rate constants \( K_p \) for the uncoated Ti-31 are
\[
112.36 \times 10^{-10} \text{g}^2\text{cm}^{-4} \text{s}^{-1} \quad \text{and} \quad 0.28 \times 10^{-10} \text{g}^2\text{cm}^{-4} \text{s}^{-1}
\]
for the \( \text{Al}_2\text{O}_3+\text{NiCrBSi} \)-coated Ti-31, respectively. Both gain weight after 50 cycles of hot corrosion and the parabolic rate constant (\( K_p \)) for coated Ti-31 materials decreases when compared to uncoated Ti-31 materials, implying that the HVOF-sprayed \( \text{Al}_2\text{O}_3+\text{NiCrBSi} \) coatings to the Ti-31 substrate superalloy have provided the necessary protection by slowing down the kinetics of hot corrosion [9]. Uncoated Ti-31 materials acquire more weight than coated Ti-31 materials. This might be attributable to the formation of fractures after the 9th cycle of hot corrosion studies in molten salt environment for 50 cycles, as well as thermal shocks caused by variances in substrate and deposition thermal expansion coefficients [22].

3.2. SEM with EDAX Analysis of Sample Subjected to Studies of Hot Corrosion. Figure 6 depicts SEM with EDAX analysis report of the oxide scale formed on uncoated Ti-31 sample subjected to 50 cycles of hot corrosion test at 700°C. From the figure, it can be observed that there is a discontinuous oxide scale formed which contains a considerable number of cracks, indicating that the scale is nonprotective. EDAX examination at selected points on the scale formed reveals 27.7% of Na, 27.45% of Co, and 22.48% of Cr as major constituents and 10.26% of S, 3.67% of Al, 2.46% of Si, 2.53% of Ti, and 1.89% of Ni as minor constituents observed as the reaction products of hot corrosion.

3.3. XRD Analysis. The XRD pattern of uncoated and \( \text{Al}_2\text{O}_3+\text{NiCrBSi} \)-coated samples exposed to 50 heating cycles of hot corrosion test is shown in Figure 8. The XRD pattern of uncoated Ti-31 indicates the presence of titanium oxide, aluminum, vanadium, and tialite phases; here, the titanium oxide is of major phase on the oxide scale, with few phases of aluminum and vanadium, whereas the XRD pattern of coated samples indicates the presence of nickel vanadium oxide, chromium, and nickel as major phase and with few phases of silicon on the oxide scale.

3.4. Cross-Sectional Analysis. The SEM/EDS analysis along the cross section of uncoated Ti-31 exposed to 50 heating cycles of hot corrosion test is shown in Figure 9. The development of oxide scale on top of the substrate owing to hot corrosion, as well as the existence of pores after hot corrosion near the top of the oxide scale, may be seen on SEM micrographs (Figure 9(a)), and it indicates significant corrosion activity of the substrate. From the EDS examination at chosen points (Figure 9(b)), the presence of major phases

![Figure 5: Plots showing weight gain/area against number of cycles for uncoated and \( \text{Al}_2\text{O}_3+\text{NiCrBSi} \)-coated Ti-31 exposed to high-temperature corrosion at 700°C.](image-url)
of Co, Ni, Si, C, Cr, and Fe and its oxides can be observed at point 4 which is on the oxide scale and at point 1 which is on the substrate material EDS examination confirms the major phases of Ti. Figure 10 shows a SEM micrograph of the Al$_2$O$_3$+70% NiCrBSi-coated sample exposed to 50 cycles of hot corrosion. From Figure 10(a), it can be seen that a thick oxide scale has been formed, which is continuous and has higher thickness as compared to uncoated sample. EDS analysis at the chosen points (Figure 10(b)) reveals the presence of rich phases of Cr, Ni, Co, and Al and their oxides at point 4 which is on the oxide scale formed, and the elements detected are nearer to the active elements of the coating deposited, and it is reported that these elements are successful in improving the hot corrosion resistance, and at point 1 which is on the substrate, the EDS examination indicates major phase of Ti, which is the primary phase of substrate superalloy.

3.5. Discussion. From the plots of weight gain/area and SEM micrograph analysis, observations that can be made are as follows: there is occurrence of slightly more damage to the uncoated Ti-31 samples when compared to coated Ti-31 under similar test conditions, and there is a notable improvement in the resistance to material degradation due to hot corrosion when the substrate is coated with Al$_2$O$_3$+70% NiCrBSi cermet powder. The weight growth plot for
uncoated Ti-31 exhibits severe weight gain of the sample throughout the cyclic hot corrosion test, and it indicates that corrosion rate is very high for uncoated Ti-31 than coated one, which is attributed to the development of nonprotective oxide scale. Mahesh et al. reported a study of hot corrosion on Ti-31; here, the TiO₂ interacts with molten salt and...
increases kinetics of corrosion owing to the peeling of the TiO$_2$ scale, which causes Ti-31 to corrode at a faster pace [15].

The comparison of results of both uncoated and coated Ti-31 superalloy is shown in Table 3. On comparison, it is observed that the weight gain is significantly low in the case of coated samples, and also, the corrosion rate is reduced substantially in the case of coated samples. The resistance to hot corrosion is increased when the sample is being coated which may be attributed to the following. The oxide scale formed is lesser in case of coated sample indicating reduced severity of corrosion, and there were no evident signs of crack formation. Since the coating has higher percentage of Ni, Cr, and Si, all of these elements are beneficial from hot corrosion point of view and oxides that are formed as a result of exposure to salt are capable to withstand the strain that results from hot corrosion [24], and the protective oxide scale helps in preventing the penetration of corroded chemicals into the substrate materials [25].

Table 3: The findings for uncoated and coated alloys exposed to heat corrosion are summarized below.

<table>
<thead>
<tr>
<th>SI no.</th>
<th>Candidate material</th>
<th>Weight gain (mg/cm$^2$)</th>
<th>Parabolic constant $K_p$ in g$^2$cm$^{-4}$s$^{-1}$</th>
<th>XRD phases</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Uncoated Ti-31</td>
<td>40.3</td>
<td>112.36 $\times 10^{-10}$</td>
<td>Al$_2$O$_3$Ti$_1$ Al$_4$O$_7$V$<em>2$ O$</em>{12}$Ti$_9$</td>
<td>(i) Excessive peeling of Ti-31 (ii) Color changes to light grey</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(i) Color changes from grey to light greenish yellow</td>
</tr>
<tr>
<td>2</td>
<td>Al$_2$O$_3$+70 % NiCrBSi-coated Ti-31</td>
<td>2.1</td>
<td>0.28 $\times 10^{-10}$</td>
<td>Ni$_3$O$_8$V$_2$ Cr$_7$ Ni$_3$ B$_3$ Si$_3$</td>
<td>(ii) Oxide scale is well intact with the substrate (iii) Preferential oxidation of Ni has been revealed by hot corrosion (iv) Formation of Ni$_3$O$_8$V$_2$ was also revealed by XRD</td>
</tr>
</tbody>
</table>

Figure 10: (a) SEM micrograph along the metallographic cross section of Al$_2$O$_3$+70 wt% NiCrBSi-coated Ti-31 exposed to cyclic hot corrosion studies at 700°C. (b) EDS analysis at chosen points along the cross section.
4. Conclusions

The superalloy Ti-31 finds application in turbine components, and since it is required to operate in the high-temperature environment to improve the life expectancy of components, it is coated with cerments using HVOF thermal spray technique, and to evaluate the effect of coating, the uncoated Ti-31 and HVOF spray-coated Ti-31 samples are subjected to hot corrosion study at 700 °C; from the results obtained, the following observations are made.

(i) The total weight gain after 50 cycles of hot corrosion for uncoated Ti-31 is 40.3 mg/cm² and for Al₂O₃ +NiCrBSi-coated Ti-31 is 2.1 mg/cm². From this data, it can be observed that with the help of coating, the total weight gain has reduced by 94.78%

(ii) The uncoated Ti-31’s parabolic rate constant $K_p$ is $112.36 \times 10^{-10}$ g² cm⁻⁴ s⁻¹ and for the Al₂O₃+70% NiCrBSi-coated Ti-31 is $0.28 \times 10^{-10}$ g² cm⁻⁴ s⁻¹; this data indicates that the corrosion rate of coated samples is reduced by 98%

(iii) The improvement in the resistance to hot corrosion due to coating may be attributed to the development of protective oxide scale rich in phases of Cr, Ni, and its oxides

(iv) SEM with EDAX analysis indicates that the scale of oxides generated on the surface of coated Ti-31 is more continuous, and a relatively higher percentage of Ni and Cr is confirmed by XRD analysis, which are beneficial in improving the hot corrosion resistance

Data Availability

The data used for this research is included in the manuscript.

Conflicts of Interest

The authors declare that there is no conflict of interest to publish this research article.

References


