High-Temperature Corrosion Behaviour of HVOF Sprayed Cr$_2$C$_2$-25NiCr Coated on Alloy X22CrMoV12-1 at 600°C

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ABSTRACT
The present study investigates the hot corrosion behaviour of high-velocity oxy-fuel sprayed alloy X22CrMoV12-1 with Cr$_2$C$_2$-25NiCr coating at 600°C. The study was carried out by air and molten salt environment for both coated and uncoated substrates for 50 cycles. Thermogravimetry analysis was carried out to evaluate the hot corrosion by calculating the mass changes in each cycle. The results show that coating provides the marginally good corrosion resistance than the uncoated alloy. The formation of Fe$_3$O$_4$ and MoO$_3$ phases in the uncoated substrates in both air and molten salt environments reduces the corrosion resistance at the high-temperature environment. The formation of Ni$_2$O and spinel oxide NiCr$_2$O$_4$ provided good resistance to corrosion in the coated substrates in the air and molten salt environment.

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Introduction
X22CrMoV12-1 is a martensitic alloy developed for the high-temperature application up to 565°C in the high pressure (HP) turbine regions in the sub and supercritical power plants [1]. The alloy X22CrMoV12-1 is having a wide range of applications in Turbine blades, Valve Stems, Valve cone with spindles, Guide Bushes Angle Rings, Threaded Rings, Diffusers, Sleeves, Fasteners in the steam turbine region. The major problems associated with the alloy in the power plant environment is high-temperature oxidation, corrosion, erosion-corrosion due to low-rank coal with the presence of impurities like sodium, sulfur, and vanadium used in the power plant operation. The impurities deposit above the surface of the substrates and form a low melting point compounds and induce accelerated oxidation [2]. Hot corrosion is the major problem encountered in a steam and gas turbines, boilers and internal combustion engines in the coal-fired power plants [3]. Corrosion consumes the structural materials at an unpredictable rapid rate and reduce the load carry ability of the components and end its catastrophic failure [4].

To withstand the corrosion attack and improve the life of the component is a very important consideration. A study reported by Hidalgo et al. [5] high-temperature corrosion and erosion in the structural components is the main cause of downtime in the coal-fired power plant, which could account for 50–75% of their total arrest time. The maintenance cost of replacing components can be estimated up to 54% of the total production costs. It needs to develop a technique to protect the structural components in the aggressive environment. A prominent way to protect the surface of the component is to protect the surface by thermal spray coatings. The coating will act as a protective layer for the surface and enhance the life of the component [6-9]. There are many techniques like air plasma spray, high-velocity oxy-fuel spraying (HVOF), and detonation gun spray technologies widely used to deposit the coatings on the materials in high-temperature applications [10]. In general, HVOF technology is widely used to deposit the coating on boiler and steam turbine material [11]. Also, HVOF coatings offer with high hardness, good bond strength, low porosity, excellent wear resistance and ability to resist high-temperature corrosion environment [12]. HVOF coatings are also more economical and cost-effective as compared to the other thermal spray coating techniques.

The most commonly used coating powders are Cr$_2$C$_2$-NiCr, WC-Co, and WC-CoCr in HVOF. Cr$_2$C$_2$-NiCr coatings are widely used in the applications that required protection against surface degradation due to high temperature corrosion and wear conditions under aggressive environment and load [13]. These coatings are having good tribological properties in the aggressive working environment. In addition to the above-mentioned features, the thermal expansion of Cr$_2$C$_2$ (10.3 x 10$^{-6}$ °C$^{-1}$) is closely comparable to the iron (11.4 x 10$^{-6}$ °C$^{-1}$) and nickel (12.8 x 10$^{-6}$ °C$^{-1}$) that constitute the base of most high-temperature steels [14]. This reduces the stress generation taking place from the thermal expansion mismatch during thermal cycles.

Rakesh Bhatia et al. [15] investigated the hot corrosion studies on HVOF – spray coated on T-91 boiler steel at different temperatures 550, 700, and 800°C. Authors observed that the Cr$_2$C$_2$-NiCr coated steel shows the minimum weight gain at all the operating conditions compared to the uncoated steel. Authors concluded that the formation of oxides and spinel of nickel-chromium act as a protective layer against the hot corrosion. Manpreet et al. [11] investigated the hot corrosion behaviour of HVOF sprayed Cr$_2$C$_2$-NiCr coating on ASTM SA213-T22 boiler steel at 700°C. The authors found that the coating was intact and spallation free in a molten salt environment of Na$_2$SO$_4$-82Fe(50%). The bare metal was found to be extensive spallation and a higher rate of
degradation compared to coated steel. The authors concluded that coating enhances the high-temperature resistance of the steel.

Siddhu et al. [16] investigated the performance of HVOF sprayed coatings on Fe based superalloy in Na$_2$SO$_4$-60%V$_2$O$_5$ molten salt environment at 900°C. Authors deposited the various coating powders NiCrBSi, Cr$_3$C$_2$-NiCr, Ni-20Cr, and Stallite-6. Authors found that hot corrosion resistance of all the coatings are better than the uncoated alloy. Authors observed that Ni-20Cr and Cr$_3$C$_2$-NiCr coating found to be good as compared to the other coatings. Authors concluded that the formation of oxides and spinels of nickel, chromium, cobalt act as a protective medium against the hot corrosion.

Amreendra et al. [17] studied the combined slurry and cavitation erosion resistance of thermal spray coating on martensitic stainless steel (SS 410). HVOF coating was performed on the substrate with 70Ni-30Cr powder. The authors observed that the slurry erosion resistance of SS 410 can be improved by HVOF coating. Authors reported that the HVOF coated specimen showed good and better erosion resistance than the uncoated bare specimen subjected to similar condition.

It is observed from the literature many studies reported on the boiler steels. From the reported literature it is believed that Cr$_3$C$_2$-NiCr coating provides the good resistance to corrosion in a high-temperature environment. Also, the reported literature demonstrate that the coating will improve the resistance to corrosion in the high-temperature environment. However, X22CrMoV12-1 alloys play a significant role in the HP steam turbine in power plant. There is need to study the high-temperature corrosion behavior of alloy X22CrMoV12-1 at the aggressive environment. The aim of the present study is to explore the high-temperature oxidation and corrosion behavior of HVOF coated with Cr$_3$C$_2$-NiCr and uncoated alloy X22CrMoV12-1 in the air and molten salt environment (Na$_2$SO$_4$+60%V$_2$O$_5$) at the temperature of 600°C. The corrosion products were analyzed by using SEM/EDS and XRD analysis.

**Experimental**

**Substrate Material**

Alloy X22CrMoV12-1 was employed as a substrate in the present investigation. The chemical composition of the as received alloy is tested in optical emission spectroscopy and the result is listed in Table 1. The specimen was extracted in the dimension of 20mm X 15mm X 7mm with the help of wire-cut electric discharge machining (EDM) machine. The substrate was polished with 180 grid SiC paper and subsequently followed by the grid blast with Al$_2$O$_3$ (grit 24). The grit blast specimen further coated with commercially available Cr$_3$C$_2$-25NiCr powder.

**Coating Formulation**

The coating was performed at M/s Sai Surface coating Technologies, Hyderabad, India with the help of HVOF machine make: M/s FST, Netherlands make, HV-50 with the help of wire-cut electric discharge machining (EDM)

<table>
<thead>
<tr>
<th>Substrate and Coating Powder</th>
<th>Chemical Composition (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy X22CrMoV12-1 substrate</td>
<td>Fe</td>
</tr>
<tr>
<td>Cr$_3$C$_2$-25NiCr coating powder</td>
<td>20.60</td>
</tr>
<tr>
<td>Bal.</td>
<td>9.6</td>
</tr>
</tbody>
</table>

required combustion energy in the chamber of gun. The process parameters of the coatings were listed in Table 2. The coating was carried out by Cr$_3$C$_2$-25NiCr powder particle size of 45/15 µm. The coating was performed on all the six faces of the substrate in the thickness range of 150 ±10 µm.

**Cyclic Hot Corrosion tests**

Cyclic hot corrosion study was performed at 600°C for 50 cycles in the air and molten salt environment (Na$_2$SO$_4$-60%V$_2$O$_5$) of coated and uncoated alloy. Each cycle of hot corrosion test consists of 1 hour of heating at 600°C in a silicon carbide tube furnace and followed by 20 minutes of cooling to reach room temperature. For the molten salt environment, the substrate is coated with the salt of Na$_2$SO$_4$+60%V$_2$O$_5$ in the range of 3-5 mg/cm$^2$. The salt coating was done with the help of Camlin paint brush. The substrate was kept inside the furnace for 3 hours at the temperature of 200°C to observe the moisture content. Before the sample subjected to hot corrosion test, the substrate and the alumina boat were weighted individually and the combination of both with the help of electrical weight balance sensitivity of 1 mg. During the hot corrosion test, the coated and uncoated substrate weight were monitor along with the boat and scales formed during the test. At the end of the 50th cycle, the hot corrosion kinematics products were analyzed with the help of XRD and SEM/EDS analysis.

**Results and Discussion**

Figure 1(a-d) shows the macrograph of alloy X22CrMoV12-1 subjected to cyclic hot corrosion at 600°C for 50 cycles. At initial cycles up to 10 cycles the color changed into grey color and further, the color was changed into brown color up to the end of the cycles.

![Figure 1](http://www.inscience.in/JTSE.html)
Table 2: Process parameters employed in the HVOF spray coating technique to coat
Cr$_3$C$_2$-25NiCr powder in the alloy X22CrMoV12-1

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Cr$_3$C$_2$-25NiCr Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Flow (LPM) &amp; Pressure (Bar)</td>
<td>840 &amp; 10</td>
</tr>
<tr>
<td>Fuel (ATF) Flow (LPM) &amp; Pressure (Bar)</td>
<td>20 &amp; 7</td>
</tr>
<tr>
<td>Argon (Carrier) Flow (LPM) &amp; Pressure (Bar)</td>
<td>8 &amp; 2.5</td>
</tr>
<tr>
<td>Powder Feed Rate (Grams / Min)</td>
<td>35</td>
</tr>
<tr>
<td>Coating Angle</td>
<td>90°</td>
</tr>
<tr>
<td>Stand-Off distance (mm)</td>
<td>365</td>
</tr>
</tbody>
</table>

Figure 2: Weight gain Vs. Number of cycles plot for the alloy X22CrMoV12-1 substrate uncoated and coated with Cr$_3$C$_2$-25NiCr powder subjected to cyclic oxidation for 50 cycles in air and molten salt environment at 600°C.

Figure 3: Weight gain/area Vs. Number of cycles plots for the alloy X22CrMoV12-1 substrate uncoated and coated with Cr$_3$C$_2$-25NiCr powder subjected to cyclic oxidation for 50 cycles in air and molten salt environment at 600°C.

It is observed from the Table 3 HVOF coating protect the surface substrate of both air and molten salt environment. It is inferred from the Table 3 HVOF coating protect the surface substrate of both air and molten salt environment. It is inferred from the Table 3 HVOF coating protect the surface substrate of both air and molten salt environment. It is inferred from the Table 3 HVOF coating protect the surface substrate of both air and molten salt environment. It is inferred from the Table 3 HVOF coating protect the surface substrate of both air and molten salt environment. It is inferred from the Table 3 HVOF coating protect the surface substrate of both air and molten salt environment.

Table 3: Total weight gain and parabolic rate constant ($K_p$) for uncoated and HVOF coated alloy X22CrMoV12-1 with Cr$_3$C$_2$-25NiCr powder with air oxidation and molten salt environment subjected at 600°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Weight gain (mg/cm$^2$)</th>
<th>Parabolic rate law constant ($K_p$) g/cm$^2$/s$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated alloy X22CrMoV12-1 bare metal Air oxidation</td>
<td>4.33</td>
<td>0.000000956</td>
</tr>
<tr>
<td>Uncoated alloy X22CrMoV12-1 bare metal Molten salt environment</td>
<td>9.21</td>
<td>0.00000418</td>
</tr>
<tr>
<td>Alloy X22CrMoV12-1 bare metal, HVOF coated with Cr$_3$C$_2$-25NiCr powder Air oxidation</td>
<td>2.49</td>
<td>0.00000292</td>
</tr>
<tr>
<td>Alloy X22CrMoV12-1, HVOF coated with Cr$_3$C$_2$-25NiCr powder, Molten salt env.</td>
<td>7.92</td>
<td>0.00000294</td>
</tr>
</tbody>
</table>

Figure 4 shows the XRD analysis of uncoated and HVOF coated alloy X22CrMoV12-1 with Cr$_3$C$_2$-25NiCr powder in both air and molten salt at the end of the 50th cycle. The major and minor peaks are listed in Table 4 for the reference. It is inferred from the Fig. 4, Cr$_2$O$_3$ was observed in all the substrates and Ni$_2$O$_3$ is observed in the coated substrate. During the initial cycle, Cr$_2$O$_3$ and Ni$_2$O$_3$ forms an oxide layer and protect the surface of the alloy and act as a diffusion barrier of species. EDS analysis (Figure 5) also further evident the Ni and Cr rich elements are a presence in the both uncoated and coated substrates in both air and molten salt environment.
Table 4: XRD analysis identified by the major and minor phases for uncoated and HVOF spray coated alloy X22CrMoV12-1 with Cr₃C₂-25NiCr powder with air oxidation and molten salt environment subjected at 600°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major Phases</th>
<th>Minor Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated alloy X22CrMoV12-1 bare metal Air oxidation</td>
<td>Cr₂O₃, MnO₂, FeV</td>
<td>MnCr₃O₇, Fe₃O₄, MoO₂</td>
</tr>
<tr>
<td>Uncoated alloy X22CrMoV12-1 bare metal Molten salt environment</td>
<td>MoO₃, Cr₂O₃, FeS, NaNiO₂</td>
<td>Fe₂O₃, MnCr₃O₇, VS,</td>
</tr>
<tr>
<td>Alloy X22CrMoV12-1 bare metal, HVOF coated with Cr₃C₂-25NiCr powder Air oxidation</td>
<td>Cr₂O₃, Ni₂O₃, Cr₃C₂, NiO</td>
<td>NiO, NiCr₂O₄</td>
</tr>
<tr>
<td>Alloy X22CrMoV12-1, HVOF coated with Cr₃C₂-25NiCr powder, Molten salt environment</td>
<td>Cr₂O₃, Ni₂O₃, Cr₃C₂, Cr₃C₂, NaNiO₂</td>
<td>NaNiO₂, NiO</td>
</tr>
</tbody>
</table>

Figure 5: SEM/EDS analysis of 50th cycle cyclic hot corroded alloy X22CrMoV12-1 in air and molten salt environment at 600°C.
(a) alloy X22CrMoV12-1 air oxidation; (b) alloy X22CrMoV12-1 molten salt; (c) HVOF coated alloy X22CrMoV12-1 air oxidation and (d) HVOF coated alloy X22CrMoV12-1 molten salt environment.
molten salt environment. XRD analysis shows the presence of MnO2 as a major phase and MnCr2O4 as minor phases in the uncoated air and molten salt environment. During the hot corrosion study the Mn diffusion towards the outward of the surface and form the top oxide layer in the coating. This forms white spots on the top surface of the substrates. This is also well evident from the Figure 1. It is also reported that the few white spots observed on the top surface of the specimens as MnO or MnCr2O4 in his study on the oxidation behavior of Ni-based alloys [18, 19]. The presence of Fe2O3 and MoO3 observed in uncoated alloy subjected to air and molten salt environment. The formation of Fe2O3 and MoO3 is the mostly responsible for the higher weight gain in the uncoated alloy X22CrMo12-1 in both air and molten salt environment. Fe2O3 and MoO3 induces the strain on the oxide layer which results in easy spallation of fine-grained scales on the substrates. Further EDS analysis also evident for the formation of Fe2O3 & MoO3 in air molten salt environment of the uncoated substrate. The applied fused salt (Na2SO4 - 60%VsO3) on uncoated alloy acted as a barrier for growth of protective oxide scale formation and reacted with initially formed thin NiO oxide scales and formed as non protective (NaNiO2) salt compounds (2). Further, the fused salt reacted with Fe and V elements in the alloy and formed VS and FS phases. The formation of VS and FS phases are evident for sulfidation in uncoated alloy subjected to molten salt environment. The basic flux mode (formation of NaNiO2) corrosion and Sulfidation occurred in uncoated alloy subjected to molten salt environment because of the same, the overall weight gain was higher than all other samples. The high presence of Chromium element in HVOF Cr3C2-NiCr coated sample exposed to molten salt environment formed Cr2O3 Phase and this phase inhibited sulfidation and also reduced severity of basic flux mode hot corrosion. The hot corrosion mode occurred in HVOF Cr3C2-NiCr coated sample is basic flux mode type only. The chemical inerts of Cr3C2 & Cr-C2 Phases of Cr3C2-NiCr coating also helped to reduce severity of hot corrosion of molten salt. Along with NiO2, Cr2O3 phases in the coatings protect the good corrosion resistance in both air, and molten salt environment of HVOF coated substrates. Further, the presence of spinel oxides in the minor amount NiCr2O4 provides the excellent resistance to corrosion in the air and molten salt environment along with other protecting layers.

Conclusions

1. Cr3C2–25NiCr powders were successfully coated in the alloy X22CrMoV12-1 using HVOF technique.
2. The formation of Fe2O3 & MoO3 in the uncoated alloy in both air and molten salt environment reduces the hot corrosion resistance
3. Formation of spinel oxide NiCr2O4 and Ni2O3 oxide provides the good resistance to corrosion in the coated substrates.

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References

