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High-Temperature Corrosion Behaviour of HVOF Sprayed Cr_3C_2-25NiCr Coated on Alloy X22CrMoV12-1 at 600°C

P. Akshay Prasanna[1] . P. Subramani[1] . V. Sreenivasulu[1-2] . N. Arivazhagan[1] . Duoli WU[3] . M. Manikandan[1]

[1] Sai Surface Coating Technologies, Hyderabad-502307. India.
[2]School of Mechanical Engineering, VIT, Vellore-632014, India.
[3]College of Mechanical Engineering, Yangzhou University, Yangzhou 225127, PR China.

ABSTRACT
The present study investigates the hot corrosion behaviour of high-velocity oxy-fuel sprayed alloy X22CrMoV12-1 with Cr_3C_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_2O_3 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_2O and spinel oxide $NiCr_2O_4$ 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 upto 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 unpredictably 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 spraying 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 most economical and cost-effective as compared to the other thermal spray coating techniques.
The most commonly used coating powders are Cr_3C_2-NiCr, WC-Co, and WC-CoCr in HVOF. Cr_3C_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_3C_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_3C_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_3C_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_2SO_4-82$Fe(SO_4)_3$. The bare metal was found to be extensive spallation and a higher rate of

Corresponding Author: M.Manikandan, Tel: +91-9944681416
Email: mano.manikandan@gmail.com

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degradation compared to coated steel. The authors concluded that coating enhances the high-temperature resistance of the steel.

Sidhu et al. [16] investigated the performance of HVOF sprayed coatings on Fe based superalloy in Na_2SO_4-60%V_2O_5 molten salt environment at 900°C. Authors deposited the various coating powders NiCrBSi, Cr_3C_2-NiCr, Ni-20Cr, and Stellite-6. Authors found that hot corrosion resistance of all the coatings are better than the uncoated alloy. Authors observed that Ni-20Cr and Cr_3C_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.

Amrendra 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_3C_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_3C_2-NiCr and uncoated alloy X22CrMoV12-1 in the air and molten salt environment (Na_2SO_4+60%V_2O_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_2O_3 (grit 24). The grit blast specimen further coated with commercially available Cr_3C_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 operating environment of ATF fuel and oxygen to generate 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_3C_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_2SO_4-60%V_2O_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_2SO_4-60%V_2O_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 upto 10 cycles the color changed into grey color and further, the color was changed into brown color upto the end of the cycles.

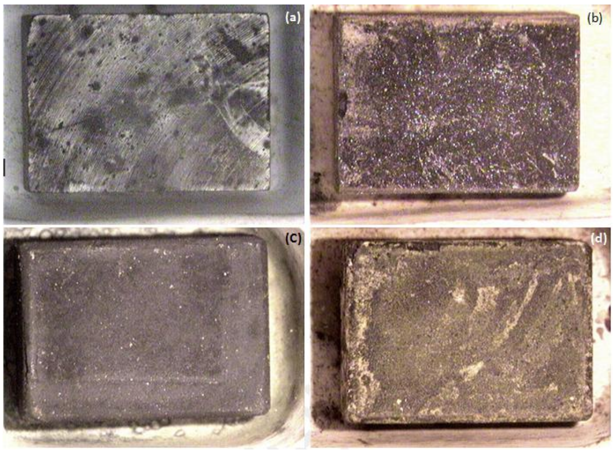

Figure 1: Macrograph of alloy X22CrMoV12-1 subjected to cyclic hot corrosion at 600°C after 50th Cycle (a) Alloy X22CrMoV12-1 air oxidation; (b) Alloy X22CrMoV12-1 Molten Salt; (c) Cr_3C_2-25NiCr HVOF coated air Oxidation and (c) Cr_3C_2-25NiCr HVOF coated molten salt environment

Table 1: Chemical Composition (weight %) of substrate and coating powder

Substrate and Coating Powder	Chemical Composition (Wt %)										
	Fe	Cr	C	Ni	Mo	P	S	Mn	Si	V	Other
Alloy X22CrMoV12-1 substrate	Bal	11.0	0.18	0.3	0.8	0.02	0.015	0.4	0.50	0.20	0.2
Cr_3C_2 -25NiCr coating powder	20.60	Bal.	9.6	0.15							

Table 2: Process parameters employed in the HVOF spray coating technique to coat Cr_3C_2 -25NiCr powder in the alloy X22CrMoV12-1

Process Parameter	Cr_3C_2 -25NiCr Powder
Oxygen Flow (LPM) & Pressure (Bar)	840 & 10
Fuel(ATF) Flow (LPM) & Pressure (Bar)	20 & 7
Argon (Carrier) Flow (LPM) & Pressure (Bar)	8 & 2.5
Powder Feed Rate (Grams / Min)	35
Coating Angle	90°
Stand-Off distance (mm)	365

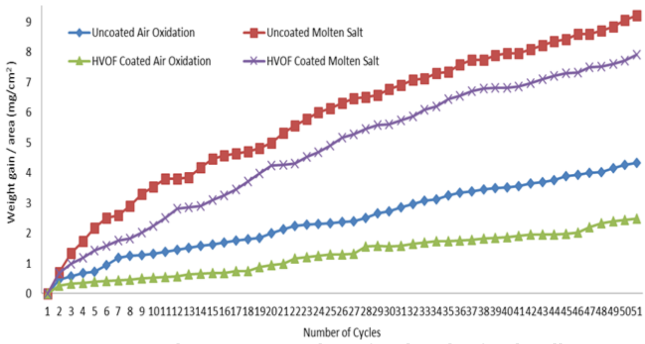

Figure 2: Weight gain Vs. Number of cycles plot for the alloy X22CrMoV12-1 substrate uncoated and coated with Cr_3C_2-25NiCr powder subjected to cyclic oxidation for 50 cycles in air and molten salt environment at 600°C

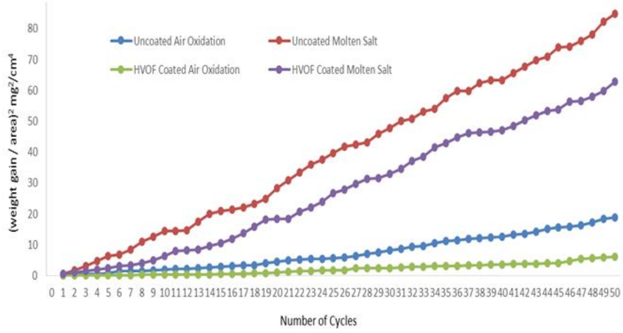

Figure 3: (Weight gain/area)² Vs. Number of cycles plots for the alloy X22CrMoV12-1 substrate uncoated and coated with Cr_3C_2-25NiCr powder subjected to cyclic oxidation for 50 cycles in air and molten salt environment at 600°C

Figure 2 and Fig. 3 shows the weight gain versus a number of cycles for the uncoated and HVOF coated alloy X22CrMoV12-1 with air and molten salt environment. It is observed from the plot that HVOF coated alloy shows less weight gain compared to the uncoated alloy. Table 3 list the overall weight gain. It is observed from the Table 3 that the weight gain in the air oxidation both coated and uncoated alloy is less compared to their molten salt environment and also weight gain is linearly increased from the initial cycle to the 50th cycle in air oxidation environment. The weight gain plots infer that the oxidation process follows the parabolic rate law in both uncoated and HVOF coated substrates. The values of the parabolic rate (K_P) was calculated by using linear least-square algorithm function. The equation is

$$(\Delta W/A)^2 = K_P \times t \qquad (1)$$

Where ΔW is the weight gain per unit area, t is the oxidation time in seconds. The K_P values obtained from the linear least square algorithm is listed in Table 3.

Table 3: Total weight gain and parabolic rate constant (K_P) for uncoated and HVOF coated alloy X22CrMoV12-1 with Cr_3C_2-25NiCr powder with air oxidation and molten salt environment subjected at 600°C

Sample	Total Weight gain (mg / cm²)	Parabolic rate law constant (K_P) $g^2/cm^4/s^1$
Uncoated alloy X22CrMoV12-1 bare metal Air oxidation	4.33	0.00000956
Uncoated alloy X22CrMoV12-1 bare metal Molten salt environment	9.21	0.0000418
Alloy X22CrMoV12-1 bare metal_ HVOF coated with Cr_3C_2-25NiCr powder Air oxidation	2.49	0.00000292
Alloy X22CrMoV12-1_ HVOF coated with Cr_3C_2-25NiCr powder_ Molten salt env.	7.92	0.0000294

It is observed from the table 3 the molten salt environment both uncoated and coated shows higher values of overall weight gain and Kp. HVOF coated substrates shows lesser overall weight gain compared to the uncoated substrates in both air and molten salt environment. It is inferred from the Table 3 HVOF coating protect the surface substrate of alloy X22CrMoV12-1 compared to the uncoated substrates in both molten salt and air environment.

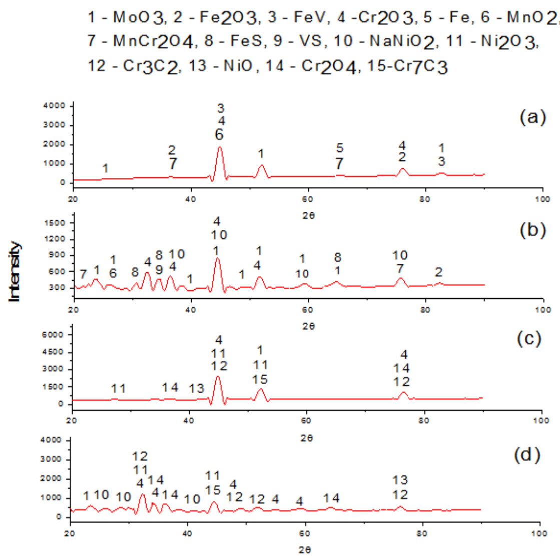

Figure 4: XRD pattern (a) Alloy X22CrMoV12-1 air oxidation; (b) alloy X22CrMoV12-1 molten salt; (c) Cr_3C_2-NiCr coated air oxidation; (d) Cr_3C_2-NiCr coated molten salt

Figure 4 shows the XRD analysis of uncoated and HVOF coated alloy X22CrMoV12-1 with Cr_3C_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_2O_3 was observed in all the substrates and Ni_2O_3 is observed in the coated substrate. During the initial cycle, Cr_2O_3 and Ni_2O_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 the air and

Table 4: XRD analysis identified by the major and minor phases for uncoated and HVOF spray coated alloy X22CrMoV12-1 with Cr_3C_2-25NiCr powder with air oxidation and molten salt environment subjected at 600°C

Sample	Major Phases	Minor Phases
Uncoated alloy X22CrMoV12-1 bare metal Air oxidation	Cr_2O_3, MnO_2, FeV	$MnCr_2O_4$, Fe_2O_3, MoO_3
Uncoated alloy X22CrMoV12-1 bare metal Molten salt environment	MoO_3, Cr_2O_3, FeS, $NaNiO_2$	Fe_2O_3, $MnCr_2O_4$, VS,
Alloy X22CrMoV12-1 bare metal_ HVOF coated with Cr_3C_2-25NiCr powder_Air oxidation	Cr_2O_3, Ni_2O_3, Cr_3C_2,	NiO, $NiCr_2O_4$
Alloy X22CrMoV12-1 _ HVOF coated with Cr_3C_2-25NiCr powder_ Molten salt environment	Cr_2O_3, Ni_2O_3, Cr_3C_2, Cr_7C_3	$NaNiO_2$, NiO

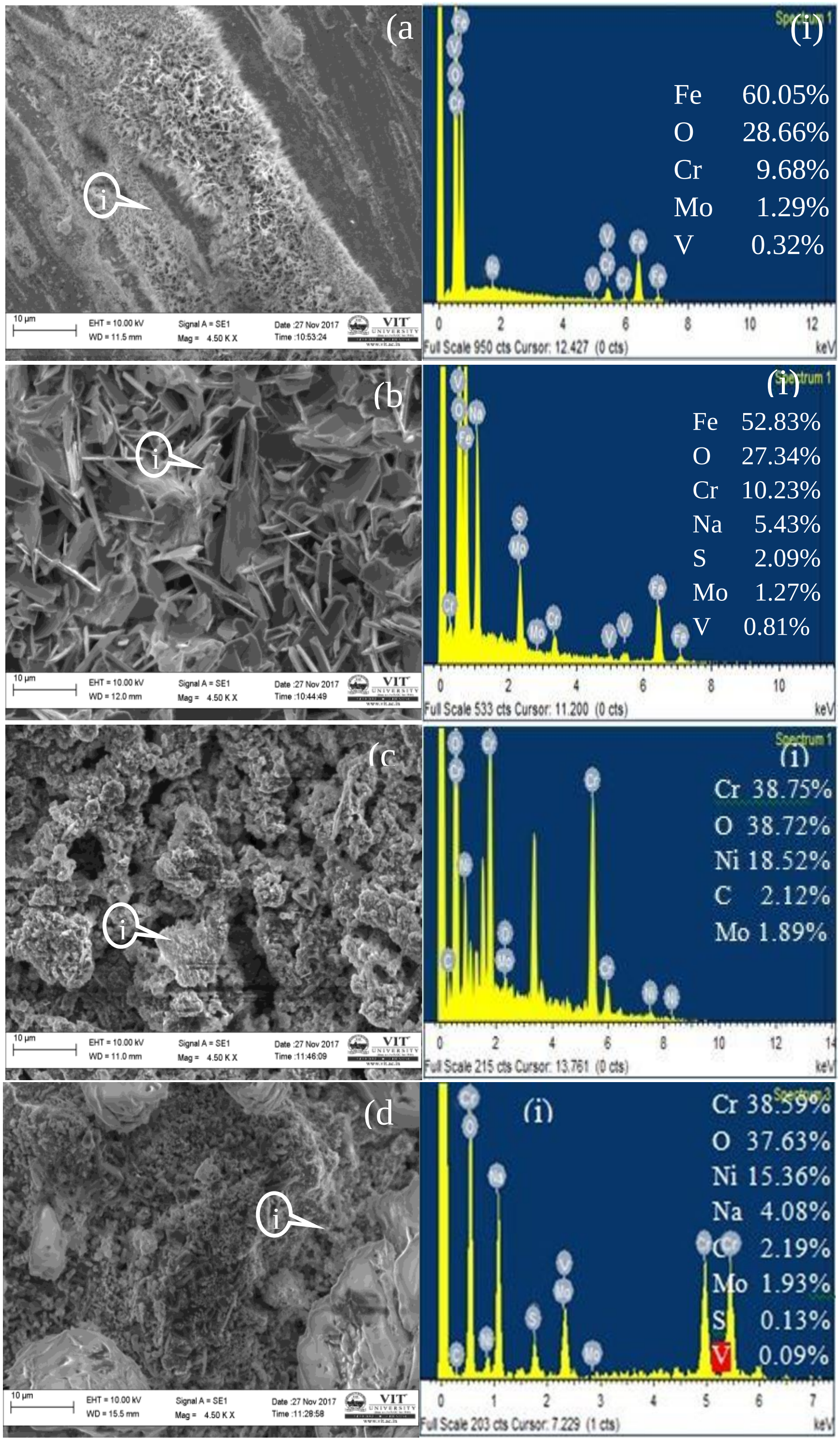

Figure 5: SEM/EDS analysis of 50th cycle cyclic hot corroded alloy X22CrMoV12-1 in air and molten salt environment at 600°C. (a) alloy X22CrMoV12-1 air oxidation ;(b) alloy X22CrMoV12-1 molten salt ; (c) HVOF coated alloy X22CrMoV12-1 ar oxidation and (d)HVOF coated alloy X22CrMoV12-1 molten salt environment

molten salt environment. XRD analysis shows the presence of MnO_2 as a major phase and $MnCr_2O_4$ 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 $MnCr_2O_4$ in his study on the oxidation behavior of Ni-based alloys [18, 19]. The presence of Fe_2O_3 and MoO_3 observed in uncoated alloy subjected to air and molten salt environment. The formation of Fe_2O_3 and MoO_3 is the mostly responsible for the higher weight gain in the uncoated alloy X22CrMo12-1 in both air and molten salt environment. Fe_2O_3 and MoO_3 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 Fe_2O_3 & MoO_3 in air molten salt environment of the uncoated substrate.

The applied fused salt (Na_2SO_4 - 60%V_2O_5) 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 ($NaNiO_2$) 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 Cr_3C_2-NiCr coated sample exposed to molten salt environment formed Cr_2O_3 Phase and this phase inhibited sulfidation and also reduced severity of basic flux mode hot corrosion. The hot corrosion mode occurred in HVOF Cr_3C_2-NiCr coated sample is basic flux mode type only. The chemical inertness of Cr_3C_2 & Cr_7C_3 Phases of Cr3C2-NiCr coating also helped to reduce severity of hot corrosion of molten salt.

Along with Ni_2O_3, Cr_3C_2 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 $NiCr_2O_4$ provides the excellent resistance to corrosion in the air and molten salt environment along with other protecting layers.

Conclusions

1. Cr_3C_2-25NiCr powders were successfully coated in the alloy X22CrMoV12-1 using HVOF technique.
2. The formation of Fe_2O_3 & MoO_3 in the uncoated alloy in both air and molten salt environment reduces the hot corrosion resistance
3. Formation of spinel oxide $NiCr_2O_4$ and Ni_2O_3 oxide provides the good resistance to corrosion in the coated substrates.

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