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Abstract:

The aim of this work is to present the corrosion behavior of three different coatings sprayed using High Velocity Oxy Fuel (HVOF) technology. The mild steel samples were coated with tungsten carbide/cobalt WC-12%Co, chromium carbide/nickel, chromium Cr₂C₃-25%NiCr and nickel chromium boron silicon NiCrBSi. Powders were sprayed on the substrate using the HVOF process. The specimens were tested in 3.5%NaCl aqueous solution with P^H adjusted to 10 by adding potassium hydroxide and the polarization curves were obtained using the Potentiodynamic polarization system of GILL AC units. The coatings were characterized with regard to coating thickness, porosity, microhardness, bond strength and microstructure. The bond strength of coatings was measured with the pull-off test method according to ASTM C-633-01 standard. The porosity of the specimens was determined by using the optical microscope. The coating morphology was studied by Scanning Electron Microscopy (SEM) and EDAX. The phase identification was performed by the X-ray diffraction technique (XRD). The corrosion behavior of the coatings has been compared with polarization curves. The overall corrosion resistance of NiCrBSi was found to be superior among the trio and then followed by Cr₃C₂-NiCr and the worst was WC-Co.

Key words: Corrosion resistance; thermal spray; HVOF; adhesion; potentiodynamic polarization.

Introduction:

One of the most serious problems of industries is corrosion which causes damage in billions of dollars each year. Materials are very often exposed to environments wherein the metallurgical reaction between the environment and the materials that are corrosive can affect the lifetime of the components and produce high maintenance costs [1, 2]. Though much research and experimentation is going on and there is much to be known. It is recognized that mechanical and chemical properties of HVOF sprayed coatings such as wear resistance; corrosion resistance; microhardness and bond strength are controllable by selecting proper materials[3].

The bonding between particles and substrates has been a chief concern to engineers ever since thermal spray processes were introduced to various manufactures to assure the quality of coatings. Debonding and cracking of the coating from the substrate are two major types of coating failures. The structure integrity evaluation of the coatings is important, which can promise the safety and reliability of coating materials. This is because the procedure cannot be effectively used for engineering applications if the covering does not tie well to a substrate [4-10]. These coatings are selected mainly for applications calling for improved wear resistance and surface hardness, and to a lesser extent, their corrosion resistance [11].

The authors previously reported the corrosion behavior of WC-Co, WC-Co-Cr coatings in Na₂SO₄ solution and found that the resistance of WC-Co-Cr was superior to the other and some worked on Cr₃C₂-NiCr [12, 13].

In the present work HVOF technique is chosen from all the available thermal spray operations, because it is one of the most promising methods. At higher gas jet velocities and lower flame temperatures, HVOF spraying enables to create refined, wear resistant cermet coatings with very low porosity, low oxidization and low carbide decomposition or carbide-matrix dissolution, resulting in high hardness and high abrasion resistance [13, 14].

Materials and Methods:

Three types of commercially available powders were evaluated in the present work. The powders were sprayed onto the specimens of 20x20 mm surface and 10 mm height.

Table 1 presents the general overview of powder characteristics.

Powder	Trade Name	Grain size (μm)	Supplier
88% WC-12% Co	Amperit-518	-38+10	C&M Technologies
NiCrBSi	ISN Diffusion	-53/15	Collomony
75% Cr ₂ C ₃ -25% NiCr	Amperit-584	-45/10	H.C.Starck

Substrate preparation is done by pre-cleaning the specimens in isopropyl alcohol for 5min and all the coatings were deposited on grit blasted (coarse Al₂O₃-24mesh) mild steel substrates using HVOF DJ2700 gun. The parameters employed in spraying the coatings are presented in table 2.

Table 2 HVOF spray process parameters

Gas	Flow (SLPM)	Operating Pressure
Oxygen	200-300	10.0 Kg/Cm ²
LPG	60 - 80	07.0 Kg/Cm ²
Air	450 -600	07.0 Kg/Cm ²

And the operating parameters are as follows:

Flame temperature: min. 2500°C -3160°C

Flame velocity 2200 m/s

Particle velocity 650 m/s

Spray rate/ powder feed rate 25-38 gm/min

Spray distance 6 to 8 inches

Deposition Efficiency 60-70%

Critical orifice No. Flow meter 01

Traverse rate (m/sec): 0.0028-0.0030m/sec.

Mechanical Properties:

The mechanical properties of the coatings for microstructural evaluation like porosity, thickness were evaluated using the optical microscope and the tensile strength was evaluated by using Tensile testing machine and the microhardnes of the coatings by Vickers micro indentation hardness indenter as discussed below. The chemical property corrosion was measured by using the pitting corrosion test using GILL AC unit.

Adhesion:

The adhesive strength of the coatings was measured according to the ASTM C633-01 standard. The commercially available epoxy resin adhesive (FM 1000) was applied. Each test specimen is an assembly comprises of a substrate fixture, to which the coating is applied, and a loading fixture. The substrate and loading fixtures taken are each be circular solid cylinders of 1.5 inch diameter. One end of each fixture shall be adapted for attachment to the self-aligning loading devices of the tensile testing machine. Both ends of each fixture shall have faces parallel to each other and normal to the loading axis. Epoxy is FM1000 an adhesive bonding agent used for Tensile Bond Strength Testing is cured at a temperature of 350 °F to 385°F. A chosen number of substrate fixtures and coated fixtures were prepared and a tensile load to each test specimen at a constant rate of cross-head travel between 0.030 in. /min (0.013 mm/s) and 0.050 in./min (0.021 mm/s) was applied until rupture occurs.

The maximum load applied is recorded and the bond strength of that area is calculated. For each coating three test samples were employed and the average value was applied as the index of the adhesive force. The porosity, thickness, bond strength and microhardness of the respective coatings are tabulated in table 3.

Microhardness:

The microhardness of the coated samples at their cross sections were measured using a calibrated Vickers micro indentation hardness indenter, dwell time 15s, indenter speed of 60µm/sec, and the angle between two faces is maintained as 136° under a test load of 50 grams. The reported values are averages of 5 measurements.

Microstructural Evaluation:

The coating characterization included optical microscopy of metallographically prepared cross-sections where the porosity and thickness of the coatings was measured.

Corrosion behavior of the coated specimens:

In Most of the metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. Here the pitting corrosion test was done by using GILL AC unit.

Potentiodynamic polarization tests: A software based PAR weld electrochemical system of the GILL AC unit was used to conduct the potentiodynamic polarization tests for studying the pitting corrosion behavior of coated steel surfaces. A saturated calomel electrode (SCE) and

carbon electrode were used as reference and auxiliary electrodes respectively. All experiments were conducted in aerated 3.5% NaCl solution with P^H adjusted to 10 by adding potassium hydroxide. The potential scan was carried out at 0.166 mVs^{-1} with the initial potential of -0.25 V (OC) SCE to the final pitting potential. The exposure area for these experiments was 1 cm^2 . The potential at which anodic and cathodic current is equal was considered to be the corrosion E_{corr} . The specimens exhibiting relatively more positive potential (or less negative potentials) were seen to have better pitting corrosion resistance.

Results and discussion:

The mechanical properties obtained from the above experiments are tabulated in table 3.

Table 3 Mechanical Properties obtained from the experimentation of the coatings

Coating	Porosity	Micro Hardness $HV_{0.5}$	Thickness of the coating (μm)	Bond strength (Psi)
88%WC-12%Co	0.855	1290	150-180	11,495
NiCrBSi	0.922	1079	150-180	8,444
75% Cr_2C_3 - 25%NiCr	1.4946	999	150-180	11,434

As observed the microhardness and bondstrength of WC-Co is greater than the other coatings.

The polarization curves of the deposited coatings obtained from the Gill Ac Electrochemical System are as shown in figure 1. In this the NiCrBSi coating exhibited relatively more positive potential (or less negative potentials) to have better pitting corrosion resistance. Cr_3C_2 -NiCr showed little better positive potential and then WC-Co was least corrosion resistance.

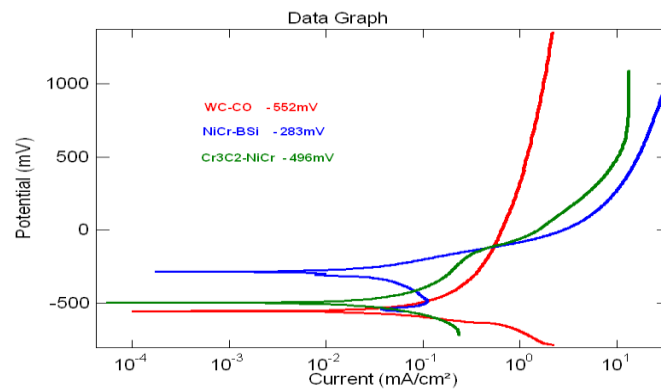


Fig 1 Polarization curves of the deposited coatings

The parameters from the polarization curve are as presented in table 4.

Table 4 Parameter values of the corrosion test in 3.5%NaCl solution

Coating	Corrosion potential $U_{\text{corr}}(\text{mV})$	Current density $I_{\text{corr}}(\text{mA}/\text{cm}^2)$
88WC-12Co	-552	3.5
NiCrBSi	-283	0.075
75Cr3C2-25NiCr	-496	0.4

Structural investigations and properties evaluation of the cross sectional images of the samples are showed in figure 2 that reveal that all the three coatings are dense (porosity less than 2 %).

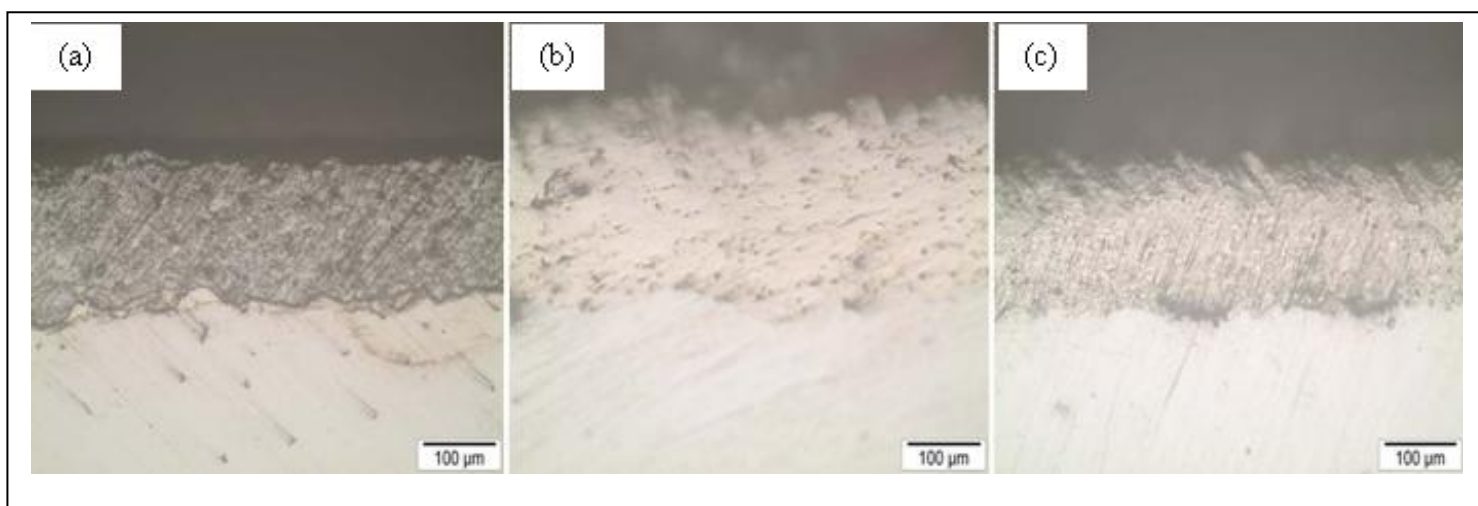


Figure 2 Microstructures of (a) WC-Co (b) NiCrBSi (c) Cr₃C₂-NiCr

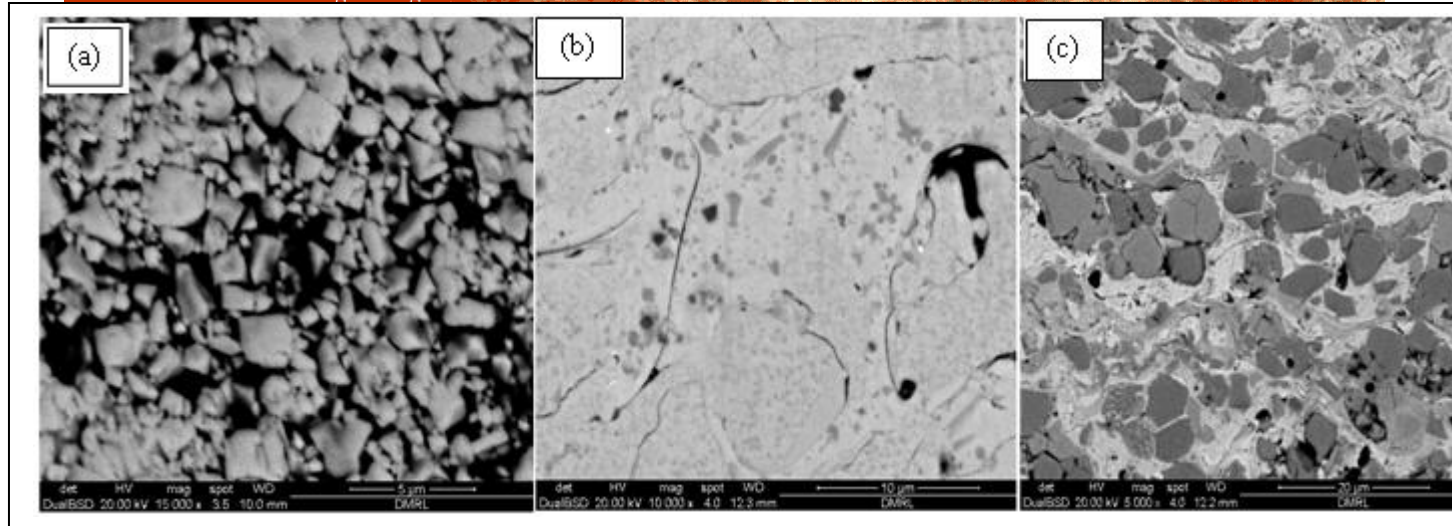


Figure3 SEM of (a) WC-Co (b) NiCrBSi (c) $\text{Cr}_3\text{C}_2\text{-NiCr}$

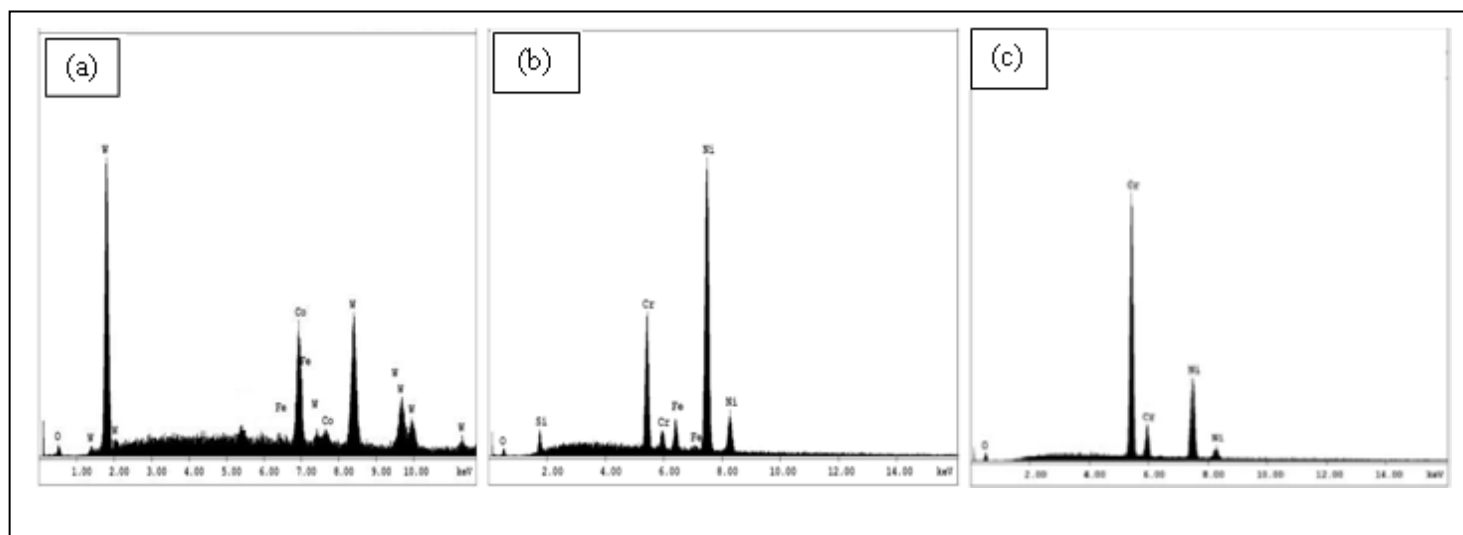


Figure 4 EDAX of (a) WC-Co (b) NiCrBSi (c) $\text{Cr}_3\text{C}_2\text{-NiCr}$

Cross sectional images of the samples SEM/EDAX of the three coatings sprayed using HVOF technique are provided in figures 3 exhibit that the coatings are compact and without defects and cracks. The concentration and distributions of elements in the interface between the coating and substrate were analyzed by energy dispersed X-ray analysis (EDAX) and are shown in figure 4.

The various compounds formed in the powders are tested with X-ray Diffraction (XRD).

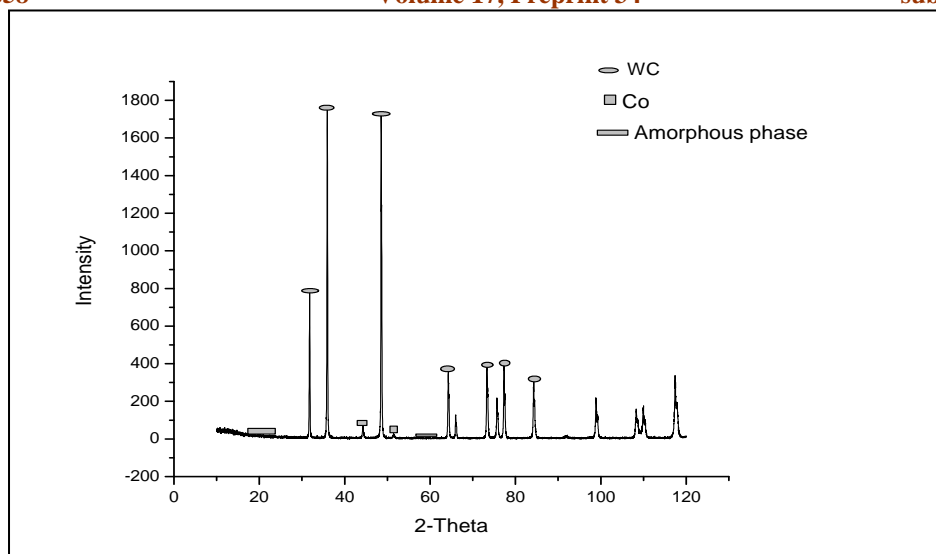


Figure 5 XRD of WC-Co

From the XRD of WC-Co as in figure 5 the peaks of WC are of high intensity and some dissolved peaks of Co are also observed.

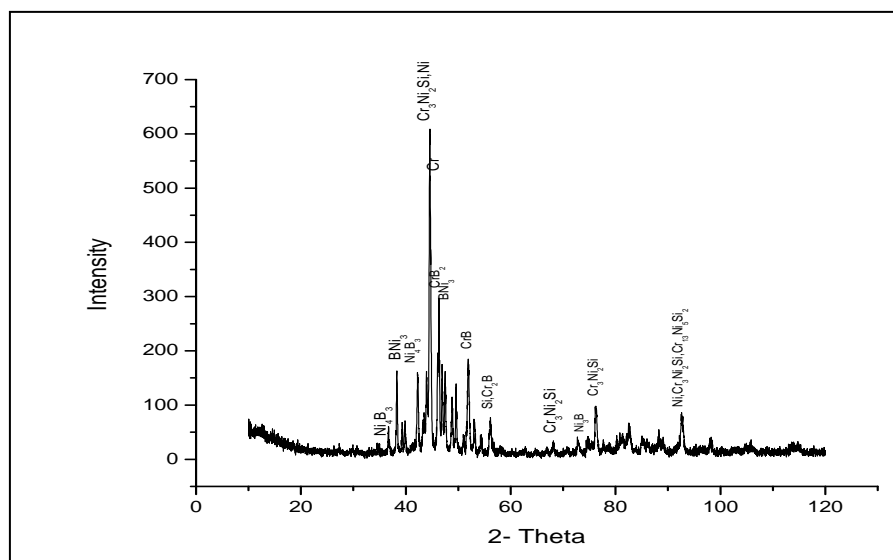


Figure 6 XRD of NiCrBSi

As observed in figure 6 many new compounds are seem to be formed which may be the reason for the high corrosion resistance of this coating.

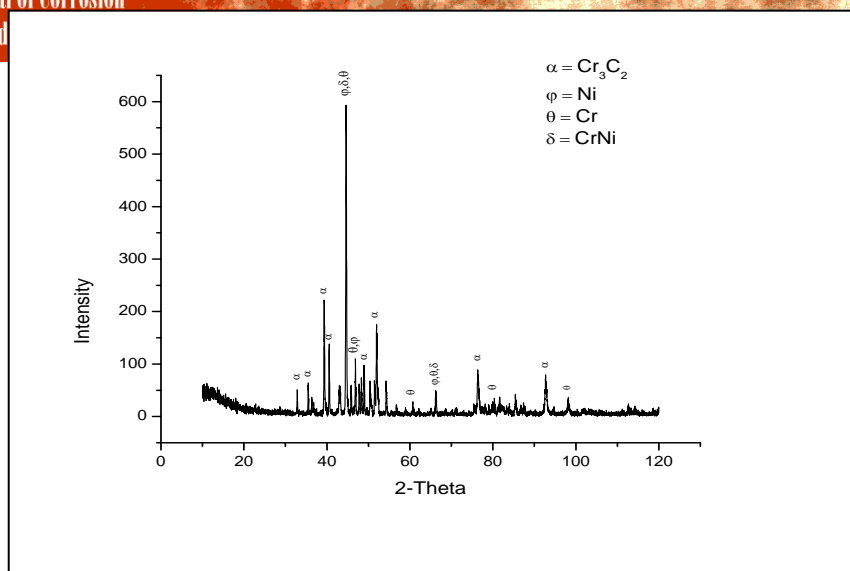


Figure 7 XRD of $\text{Cr}_3\text{C}_2\text{-NiCr}$

In figure 7 the highest intensity peaks are of Ni, Cr and Cr_3C_2 .

From the XRD results of all the three coatings the compounds formed in NiCrBSi are very much suitable for corrosion resistance.

Conclusion:

1. HVOF thermal spraying process was applied for depositing the three cermet coatings WC-12%Co, NiCrBSi and $\text{Cr}_3\text{C}_2\text{-25%NiCr}$.
2. Corrosion test was conducted in aerated 3.5% NaCl solution revealed that the corrosion resistance of the NiCrBSi was higher than of the $\text{Cr}_3\text{C}_2\text{-NiCr}$, WC-Co exhibited inferior corrosion properties.
3. This better corrosion behavior is influenced by the chemical composition differences of the metallic matrix.
4. Microstructural examination and evaluation of properties showed that the three coatings are dense (porosity less than 2%), packed in and without defects and fractures.
5. Poorest corrosion resistance of WC-Co was recognized might be possibly due to partial sintering between the WC matrix and the binder Co during the spraying process.

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