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Journal of Materials Science and Surface Engineering



## Tribological and Corrosion Behavior Studies on $\text{Cr}_3\text{C}_2$ -NiCr Powder Coating by HVOF Spray Method- A Review

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### Article history

Received: 02-Feb-2017

Revised: 23-Feb-2017

Available online: 20-Mar-2017

### Keywords:

Wear,  
HVOF,  
Micro structure,  
 $\text{Cr}_3\text{C}_2$ -NiCr,  
Corrosion

### Abstract

High Velocity Oxygen Fuel (HVOF) process is to help to improve the properties of wear and corrosion on various industrial components. Further, the aim of this study is to evaluation of microstructure and mechanical properties in which used in the powder of  $\text{Cr}_3\text{C}_2$ -NiCr sprayed by HVOF method onto different substrate materials. The wear and corrosion resistance has increased due to dispersed components such as Ni and Cr carbide phases present in the coated materials. The HVOF process especially cermet coatings in which powder materials have to accelerate to deposit on substrate materials resulted in high wear and corrosive resistance. Moreover, the electrochemical measurements techniques employed on coated surface is identified in passive surface degradation which is supplied in various potential current is carried out. The several combinations of  $\text{Cr}_3\text{C}_2$ -NiCr powders can produce good results than WC-Co powder coating. The current scenario of review article the thermal spray coating processes has been reported like weight loss and wear rate which is used to different spraying parameters. Electrochemical polarization measurements on coating materials resulted in high corrosion resistance is due to effect of hard phase microstructure revealed in the coated materials.

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### Introduction

This paper reviews the performance, developments and applications of  $\text{Cr}_3\text{C}_2$ -NiCr thermal spray coatings for wear and corrosion under different conditions of environments, and outlines the characteristics of  $\text{Cr}_3\text{C}_2$ -NiCr coatings.  $\text{Cr}_3\text{C}_2$ -NiCr coatings offer greater corrosion and oxidation resistance, also having a high melting point and maintaining high hardness, strength and wear resistance.

### Feedstock powders characterization

HVOF sprayed coatings exhibited more micro-structural alterations than HVOF sprayed ones when compared feedstock powders (Fe-31Cr-12Ni-3.6B-0.6C), (Fe-31 Cr-12Ni-2Mo-3.6B-0.6C) in wt% onto low carbon steel. Precipitate-free particles with high aspect ratio were deposited due to the higher particle temperature during HVOF spraying (~1800°C), compared to the HVOF process (~1400°C), which led to carbide/boride dissolution [1]. Based on SEM analysis the porosity level of the cross section of nc-WC, Ni/MC coating onto St37 steel substrates (ASTM A283 grade B) was measured to be less than 1% (~0.8%), (~0.3%) respectively. It is investigated that the of comprises of ultrafine and nano- sized WC particles, with majority of particle size in the range of ~50~100nm, within the Co(Ni) matrix and no any significant evidences of decarburization was observed in the microstructure [2].

The as-sprayed coating (agglomerated and sintered  $\text{Cr}_3\text{C}_2$ -25(Ni20Cr)) feedstock powder on grid blasted 1.4828 steel substrate yields porosity value below 1% as determined from carefully polished cross-sections by means of optical microscopy

and digital image analysis [3]. The SEM images from the cross section of ST-Glazing are demonstrated that a highly dense glazing layer with negligible porosity of ~0.3% and a thickness of  $208 \pm 32 \mu\text{m}$  was developed onto the 316L stainless steel disk substrate of commercial Stellite 6 (C-1.15W-6.50Si-1.15Ni<3.0Cr25.75Fe<3.0Co-bal. in wt% & size 15-45  $\mu\text{m}$ ) using ST-HVOF (as-sprayed) coating. Besides, the glazed layer was well bonded to the underlying coating and no significant evidences of pores or cracks can be found at their interface [4].

FeBCr alloy coating is less porous below 1% (ASTM B276), than the FeSiNiCr coating alloy on gray cast iron with particle size 15-50  $\mu\text{m}$ . The grains of FeBCr coating are found to the finer size than FeSiNiCr coating. Microstructure of surface and cross section are identical and is replete with uniformly distributed fine grains like powder deposits with prominent wide boundaries, suggesting a consistent coating through HVOF process [5]. Some commercially available feedstock powder like WC-Co, WC-CoCr, WC-12Co, WC-(W,Cr),  $\text{Cr}_3\text{C}_2$ -NiCr, TiC-Based Materials are used for coat the substrate materials. Very high spraying speed of the HVOF spraying and the powder particles staying shortly in flame stream using  $\text{Cr}_3\text{C}_2$ -NiCr based coating, the decarburization may not be occurred [6].

The  $\text{Cr}_3\text{C}_2$ -NiCr alloy coating on steel substrates by HVOF coating has been reported that the fully amorphous ribbons formed can produce good mechanical properties and wear resistance at ambient condition. This paper presents work undertaken in the production of  $\text{Cr}_3\text{C}_2$ -NiCr alloy powders that were designed for use in thermal spraying as shown in Fig.1.

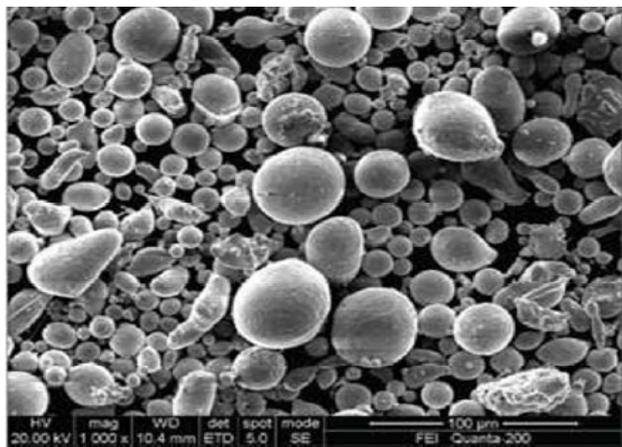


Figure 1: Cr<sub>3</sub>C<sub>2</sub>-NiCr powder image by SEM [59]

### Effect of Coating Performance

HVOF thermal spraying with oxygen and liquid petroleum gas as the fuel gas has been successfully to deposit WC-CrC-Ni alloy coatings on boiler tube steels [7]. However, the quality of coating is closely related to the thermal spraying conditions and feedstock powder size [8]. The level of decarburization of Cr<sub>3</sub>C<sub>2</sub> has also been found to play an important role in relation to both hardness and wear properties of coating, since a high hardness is required in order to improve the coating wear performance [9]. And also the substrate temperature was carefully controlled to avoid over heating of the substrate by using compressive air cooling arrangement and by adopting an inter-pass delay during spray deposition [10].

Therefore, individualized process optimization is necessary for different feedstocks due the extrinsic feedstock characteristics such as density, morphology, heat transfer properties [11]. For better understanding the flame and particle behavior in an HVOF thermal spray process the investigation for gas temperature, gas velocity, gas mach number, gas pressure, gas component were analysed. Usually high hardness corresponds to high abrasive wear and corrosion resistance as well as compact microstructure (low porosity) for liquid fuel HVOF sprayed WC-based coating deposited using WC<sub>12</sub>Co powder [12]. A promising oxidation /corrosion/erosion resistance was achieved by composite coating like HP2 [Cr<sub>3</sub>C<sub>2</sub>-NiCr +25%(WC-Co)] deposited on T22 boiler steel using HVOF spray process [13]. The reduced toughness of the coating surface could be reasonably due to a combination of factors: the environmental interaction, microstructural instability (leading to hardness increase) and the reduction of compressive residual stresses [7]. HVOF Cr<sub>3</sub>C<sub>3</sub>-NiCr coating produced by using high kinetic thermal spray process can be considered a very promising solution for improving fatigue performance of structural steel components in several industrial applications.

### Coating Parameters and Porosity

Flow rates of oxygen (500 L/min) and methane (160 L/min) and corresponding stoichiometry (1.56) at this spray parameter the porosity level was decreased to 1.3% and the hardness increased upto 1286 HV0.3 [8]. The Ni-P coating on ST 37 steel disk achieves extremely low porosity percentage of ~0.3%, while higher porosity level of 1.6 and 1.3% were measured in the case of conventional WC-12Co and WC-17Co coatings [9].

OM observation of cross section coatings depicts that the thickness of SHS9172+Co coating onto 304 stainless steel substrate is thicker than that of SHS9172 coating onto a substrate, under the same operation parameters for HVOF process. It

suggests that adding Co to the Fe-based alloy coating can improve the deposition rate. The minimum average value (ASTM E2109-01) of porosity (~0.8%) for SHS9172+Co is obtained after annealing upto 900°C for 3h [10]. HVOF sprayed carbide coating on stainless steel substrate posses, low porosity less than 1% for WC-17Co (0.81%), WC-10Co-4Cr (0.35%), WC-12Co (0.31%), and Cr<sub>3</sub>C<sub>2</sub>-NiCr (0.65%) due to high impact velocity [11]. WC-10Co-4Cr coatings on naval brass using HVOF spray parameters such as with an oxygen flow rate of 253 lpm, an LPG flow rate of 61 lpm, a spray distance of 227 mm, and a powder feed rate of 35 g/min, yield minimum porosity (1.38 vol.%) [12]. Porosity morphology has revealed by SEM as shown in Fig.2.

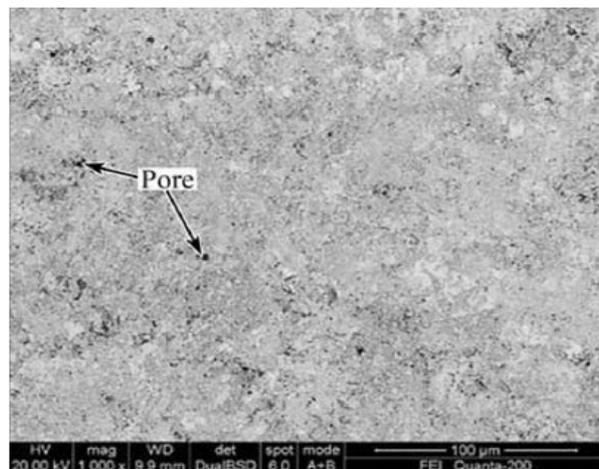


Figure 2: Porosity measurement by using SEM [59]

### Effect of Temperature & Oxidation

Authors showed 88.5% increase in oxidation resistance of Ni/mc WC relative to mc-WC coating, and 89.3% improvement in oxidation resistance of Ni/nc-WC with respect to nc-WC coating after 3 h at 800 °C. The SEM observation of Ni/mc-WC and Ni/nc-WC oxidized at 800 °C revealed very dense and adhesive oxide layers with thickness of ~30–40 µm, whereas highly porous oxide layers with thickness of 210 and 300 µm were produced on the surface of mc-WC and nc-WC coatings. The kinetics analysis showed that oxidation of mc-WC and ncWC coatings obey the linear law, respectively with apparent activation energies of 90.4 and 78.9 kJ/mol [13].

The Cr<sub>3</sub>-25(Ni-20Cr) and Ni-20Cr coatings on AISI 310L sheet were more oxidation resistant compared with WC-20Cr-7Ni coatings, especially at temperatures >800°C. This is due to the higher rate of oxidation of WC in the latter coating. Besides, the oxidation rate of WC also increases forming WO<sub>3</sub>, which promotes cracking and subsequent spalling of the chromium oxide [14]. The HVOF sprayed NiCrAl coating was found to be effective in imparting hot corrosion resistance to Superfer 800 in the coal fired boiler environment as compared to that of Ni-5Al coating. Due to the formation of thin layer of oxides of chromium and nickel in the topmost part of the scale as revealed by the cross-sectional X-ray mapping analysis [15].

The thick protective oxide scale developed on the surface which attributed to a superior oxidation resistance at 800°C of 25% (Cr<sub>3</sub>C<sub>2</sub>-25(Ni20Cr)) + 75% NiCrAlY on Ti-31 alloy substrate. The upper most layer of the oxide scale mainly consisted of continuous film of Cr<sub>2</sub>O<sub>3</sub> which have minimal reaction to air condition [16]. The coating microstructure of the ASTM A182 F51 duplex stainless steel (nominally Fe-25%,Cr-5%Ni-3%Mo-0.14N alloy with less than 0.03%C) is characterized by a low porosity as well homogeneous carbide distribution and no carbide coarsening was observed after aging up to 400°C [17].

## Effect of Hardness

A slight strengthening effect was detected even for the F51 duplex stainless steel. In this case the hardness rises of about 2% and 11% compared to the steel in the as received condition (227±7 HV), respectively after isothermal treatments of 100 h at 350°C and 100 h at 400°C [18]. A maximum microhardness of 1498 HV0.3 was measured for WC-F coating, whereas WC-C and WC-N coatings revealed lower values of 1305 and 1254 HV0.3 [19]. The iron based alloy coatings have shown maximal hardness in the range of 800 to 900 HV. Furthermore, the micro-hardness of the coatings varies with the thickness of the coating- gray cast iron substrate interface [20].

The significant improvement in microhardness (726 HV0.1) TiO<sub>2</sub> coated on mild steel is due to the phase uniformity of the coating, i.e., tetragonal hard rutile phase, which is dominating the amorphous anatase phase [21]. Great significance of stabilized hardness about 920 HV0.1, as it enhances the wear resistance capabilities of the FeBCr coating compared to the wear that can be achieved in a system of gradient hardness. The greater hardness of the coating was attributed to solid-solution strengthening by the B and the Cr in Fe phase [22]. However, FeBCr (980 HV) coating exhibited superior hardness (6.5% higher) compared to FeSiNiCr (920 HV) coating as shown in Fig.3. Due to the low porosity accompanied by very fine grained structure [23].

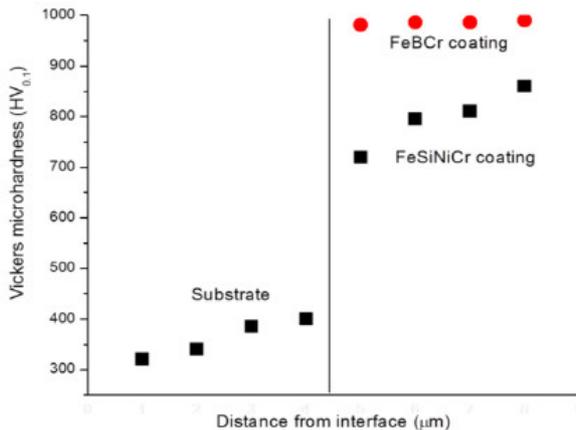


Figure 3: Microhardness profile of FeSiNiCr based alloy coating along cross section [29]

In prior to the coating deposition of submicron-sized (~300 nm) WC particles were mechanically blended with agglomerated and sintered WC-12 wt%Co powder on 304 stainless steel plates. XRD spectra suggest, WC particle leads to increase in microhardness (18.39% increases), from 1153 HV for the coating without of WC addition to 1365 HV for the coating with 5 wt% WC addition [24]. For lower indentation loads (below 10N), the indentation mark was small, close to the thickness of layer. So, the micro-hardness was mainly affected by intrinsic hardness of TiN coating and elastic modulus of crystals inside the splats [25]. The contribution of high hardness (>1000 HV0.1) and high toughness (>80MPa) of HVOF sprayed carbide coating on stainless steel substrate, caused probably by less plastic deformation and fatigue due to the repeated action of the abrasive particles followed by the undermining of the carbide particles resulting in their eventual pullout [26].

## Effect of Wear Mechanism

An agglomerated and sintered WC-12Co powder exhibits different wear behaviors and is improves wear resistance with the uniform and homogeneous distribution of metal binder and carbides [27]. Whereas, this paper a laminar splat-like microstructure was found in the as-sprayed coating, where the

WC-Co phase was nearly uniformly distributed into the Cr<sub>3</sub>C<sub>2</sub>-NiCr matrix. The composite carbide coating Cr<sub>3</sub>C<sub>2</sub>-NiCr on ductile iron has good wear resistance associated with the effect of plasticity of the coating addition of soft, metallic particles to the base ceramic powder. In addition, better wear properties are obtained as the decarburisation degree decreases [28]. The SEM image showed (Fig.4) two body grooving morphology on Fe based coating materials.

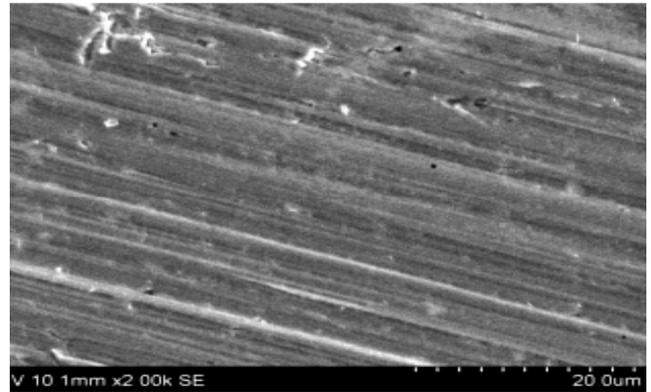


Figure 4: Wear groove of Fe based alloy coating [28]

It evident for the resistance against low-stress abrasive and high-stress abrasive wear of coatings heat treated for 8h at 800°C was reduced by roughly 10% and 30% respectively, compared with as-sprayed state. As a result of their tougher binder matrix, the wear tracks of the aged coatings are basically free of micro-cracks and thus exhibit less wear was exhibited [29]. In terms of the practical application of Cr<sub>3</sub>C<sub>2</sub>-NiCr coatings for high temperature wear resistance, which the formation of a very dense coating with high inter-splat adhesion is of greater importance than the formation of a coating with minimal carbide dissolution, as long as it does not occur at expense of excessive carbon loss. It appears that in-flight carbide dissolution can be tolerated in coatings for use at high temperature because precipitation of the carbide grains. The significance of this effect increases with increasing temperature, particularly above 700°C [30]. Coefficient of friction profile of Cr<sub>3</sub>C<sub>2</sub>-NiCr coating at different elevated temperature as shown in Fig.5.

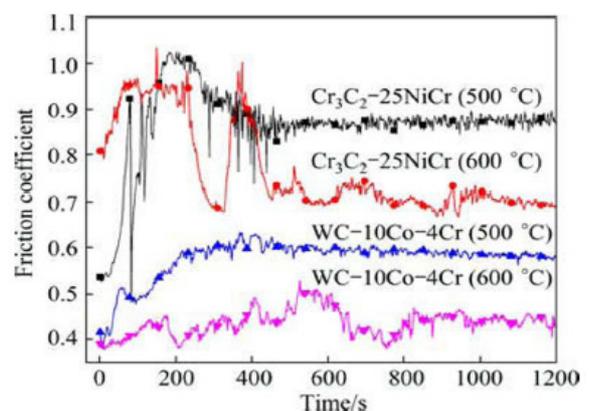


Figure 5: Coefficient of friction profile of Cr<sub>3</sub>C<sub>2</sub>-NiCr coating at elevated temperatures [59]

Despite the high coefficient of friction, HVOF Fe(Mo) coating exhibited the lowest sliding wear rate accompanied by the lowest counterpart wear [31]. Under dry sliding condition, HVOF sprayed FeSiNiCr alloy coating exhibit higher weight loss in this test duration at room temperature. The higher weight loss of as

sprayed coating was associated with removal of slurry particles [32].

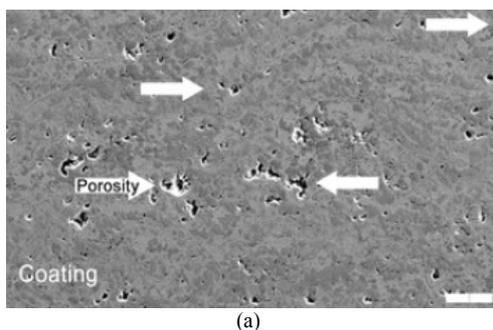
A major role of wear takes place in testing that indicates the diamond abrasive particles on gray cast iron. An irrespective of change in the characteristic behavior of the subsurface at higher loads. Thus, above the 0.05 N load, the coating performs with consistently less wear resistance [33]. The wear rate was unaffected by sliding speed, while the properties of stainless steel substrate with WC-(W,Cr)<sub>2</sub>C-Ni coating have some influence only at the highest test temperature of 750°C. Wear rate values increase gradually from ~10<sup>-7</sup> mm<sup>3</sup>/(Nm) at room temperature to 1×10<sup>-5</sup> mm<sup>3</sup>/(Nm) at 750°C [34].

F-Cr-Ni-Si-b-C alloy coatings, pure and strengthened with 20 wt% and 40 wt% WC-12 wt% Co, were deposited onto carbon steel substrates by HVOF thermal spray process. The sliding wear performance of the Fe-based coating is almost always superior to that of the HVOF sprayed [35]. HVOF sprayed NiMoAl-Cr<sub>3</sub>C<sub>2</sub>-Ag composite coating that was composed of γ-Ni, orthorhombic Cr<sub>3</sub>C<sub>2</sub> and Ag phases exhibits a highly dense structure and well bonds with the stainless steel substrate (ASTM C633-79). The addition of Cr<sub>3</sub>C<sub>2</sub> effectively increases the wear resistance of the coating while silver plays an important role in reducing friction coefficient [36].

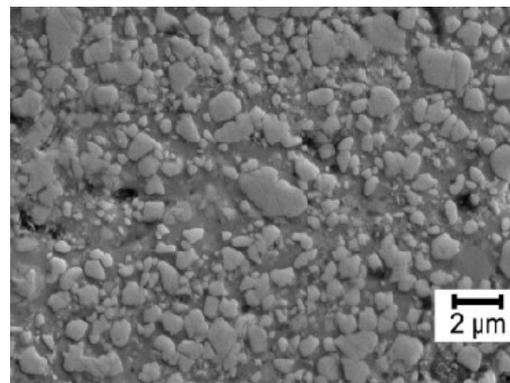
The wear rate of Ni-P modified coating on ST 37 steel disk was ~3.2×10<sup>-4</sup> mg/m indicating approximately 68 and 72% improvement in wear resistance, with respect to the conventional WC-12Co and WC-17Co coatings [37]. Based on dry sand testing, the best anti-wear properties are obtained when cobalt is added to HVOF SHS9172 coatings and annealed at a high temperature of 700°C. Firstly, the wear volume loss for both SHS9172 and SHS9172+Co coatings decrease at less than 500°C. It suggests that there are precipitates of α-Fe in amorphous / disordered phase. Secondly, the increasing trend of the wear volume loss probably is related to the B<sub>2</sub>Fe<sub>15</sub>Si<sub>3</sub> metastable phase precipitate at more than 500°C. The wear loss was due to more carbides, borides and silicides (i.e., Fe<sub>3</sub>Si) [38].

### Characterization of Coating

The study is about the fact that possibility of higher weight due to pores, voids, splat boundaries present in the coating microstructure [39]. Especially in the boiler environment, coal fired plant even after 1000h of exposure, the prevention of corrosion was by preventing the penetration of oxygen into the substrate. Due to the formation of oxides on the surface and the splat boundaries was due to penetration of oxygen develop a weight gain [40]. To avoid the defects, change of properties and behavior of hard metal, the coating technique is recommended. Accordingly, there was a development in spray coating process, ie, HVOF method. It is reported that the HVOF process exhibits lowest porosity (Fig.6) due to the high impact velocity compared to other spraying techniques such as electric arc, flame, plasma spraying, and detonation gun [41]. To reduce extent of decomposition, proper optimization of the HVOF flame jet is recommended.



(a)



(b)

Figure 6: Surface morphology of NiCr coating [14]

The decomposition process is limited, for higher velocity flame and lower flame temperature [42], as well as a good candidate for hard chrome replacement on sealing and bearing surfaces in fluid power components. The Fe-based alloy powder coatings will meet the thermal stability criteria for automotive applications. The coating is stable up to 900°C, without any phase transformations. TGA-DTA curves shows that negligible (0.2%) weight loss could be due to the formation of small amount of oxides. So, it was clear that no significant weight loss in coated substrate [43]. Whereas, WC-10Co-4Cr coating has a more dense structure which forms W<sub>2</sub>C phase and Cr<sub>7</sub>, Cr<sub>23</sub>C<sub>6</sub> phase form in the Cr<sub>3</sub>C<sub>2</sub>-25NiCr coating mainly due to the decarburization during spraying agreed with XRD results [44].

Figure 7 shows the XRD pattern of the coating. Some broad diffraction peaks appearing at 2θ = 45° and 52.5° indicate the presence of an amorphous phase. However, the sharp peaks due to crystalline phases are also observed. The major crystalline phases are compounds CrB, Cr<sub>2</sub>B, Fe<sub>3</sub>B, FeB and solidification α-Fe (Cr). And the peaks of CrB and Cr<sub>2</sub>B are less sharp, which implies the increasing of the formation ability of the crystalline phase. The major factor in determining the strength of the adhesion was the development of bonding strength between the substrate (Fe based alloy coated gray cast iron with Ra=0.6μm) and FeBCr based coating [45].

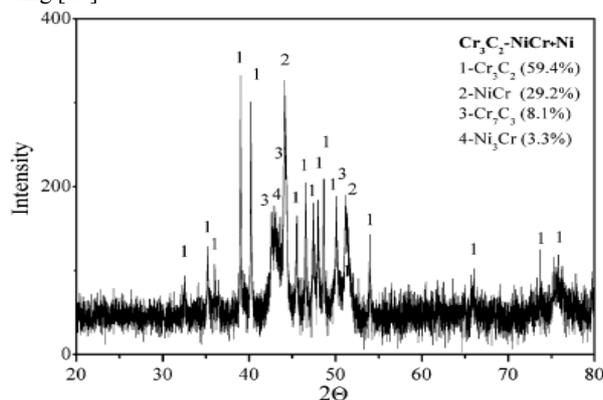


Figure 7: XRD analysis of Cr<sub>3</sub>C<sub>2</sub>-NiCr powder coating [60]

The addition of a thin immediate layer of NiCrAl coating could also be effective to enhance the bonding strength. The FeSiNiCr coatings on gray cast iron exhibit excellent ability to resist localized corrosion when treated with 20 wt% H<sub>2</sub>SO<sub>4</sub>, due to the presence of high chromium content, it was suitable for automotive application [46]. A NiCrBSiWFeCoC alloy coating with a thickness of 200 μm was prepared onto AISI 1045 steel substrate by using HVOF thermal spraying process a alternative for corrosion application due to the presence of amorphous phase and

low porosity [38]. TiN-matrix composite coating on medium carbon steel, it was found that its corrosion resistance was strictly dependent on coating porosity [47]. NiMoAl-Cr<sub>3</sub>C<sub>2</sub>-Ag composite coating that performs an extremely dense structure, high bonding strength as well as excellent lubrication function and wears resistance has a potential to be used as a high performance protective coating in harsh environments such as elevated temperature, high speed and heavy load [48].

The added Fe-based alloy powders transformed into the amorphous alloy, thus the composite coating comprise WC and Fe-based amorphous phases. To protect the nuclear fuel cladding, the dense Cr<sub>3</sub>C<sub>2</sub>-NiCr coating was fabricated using HVOF spraying on Zr-2.5Nb alloy. The as-prepared were examined in high temperature environment and autoclave. During exposure to high temperature air and steam, the Cr<sub>3</sub>C<sub>2</sub>-NiCr coating could provide protection for the zirconium alloy coating. After heat treatment, the coating was still well-bonded on the substrate [49]. The minimum carbon loss is obtained for WC-F (WC-FeCrAl) (16%), while WC-C (WC-Co) and WC-N (WC-NiMoCrFeCo) coatings undergo more severe decarburization of 30% and 36% respectively. Besides, no crystalline peaks related to the binder phases can be observed in the XRD patterns of the coatings [50]. WC particles with bright contrast and the metallic binder phases with dark contrast of two phases with different contrast are visible on the cross sectional BSE images of powder particle at high magnification. It is also obvious that the carbide grains are completely surrounded by metallic binders [51].

TiNi powder particles deposited on a Q235 steel substrate by HVOF technique. The TEM image shows the deformation of the particle and the substrate increased, the adiabatic shear instability happened, as a result, the grain was heavily deformed. In this condition of high strain rate, subgrains with large angular grain boundary were developed and local grain boundary migration driven by differences in dislocation energy occurred at this stage [52]. The addition of Al<sub>2</sub>O<sub>3</sub>-13% TiO<sub>2</sub> nanoparticles on mild steel as the reinforcing materials significantly improved the quality of the HVOF coatings and the overall coating microstructure was found to be homogeneous and uniform long with the lamella boundaries [53].

### Effect of Corrosion Behavior

The composite coating (Wt% of WC-10Co-4Cr) on the mild steel, achieved a higher corrosion resistance (pitting and corrosion cracks) in simulated sea water than WC coating. However, there was no any change / improvement in the wear resistance of composite and WC coating [54]. EPMA and EDAX analysis along the cross-section of the corroded coating reveal that only the external surface of the coating has been oxidized to form a thick oxide scale and below this, coating remains unoxidised [55]. HVOF system with gas fuelled gun is used for coat TiO<sub>2</sub> on the mild steel substrate, which attributes an excellent corrosion resistance in salt spray tests compared to the uncoated mild steel substrate. The hard TiO<sub>2</sub> coating offers better resistance to the impinging slurry particles avoiding loss of material [56].

The composite coating (Fe<sub>48</sub>Mo<sub>14</sub>C-r<sub>15</sub>Y<sub>2</sub>C<sub>15</sub>B<sub>6</sub> Fe-based amorphous powder) on 316L stainless steel exhibited, higher corrosion weight loss than the monolithic amorphous coating [57]. Based on electrochemical testing, the best anti-corrosion properties in 5% NaCl solution are obtained when cobalt was added to HVOF SHS9172 as-sprayed coatings [58].

### Conclusions

From the summarized results and discussion part of the HVOF coatings that have been the subject of published work like microstructure, wear and corrosion reviewed in this paper. Overall

there are relatively many papers reporting research into the wear and corrosion coatings, but, of those authors reviewed, thermally sprayed HVOF coatings are the most common being the subject of corrosion and sliding wear investigations while HVOF coatings have also received some attention for sliding wear-corrosion applications. Most experiments test existing coatings that have been developed for either wear resistance or corrosion resistance. Sometimes, all HVOF coating deposit parameters and compositions reviewed, is the need for improve the quality and fully dense coatings to reduce low porosity and improve the hardness and corrosion influences to improve coating life. The review has identified the key interactions between wear and corrosion mechanisms that occur on a wide range of coating systems along with some two body and three body abrasion techniques that aim to inform coating selection and predict performance. Above literatures focused on Cr<sub>3</sub>C<sub>2</sub>-NiCr coating substrates characterized like microstructure, wear and corrosion behavior by HVOF sprayed coating. The authors were concluded that the powder of Cr<sub>3</sub>C<sub>2</sub>-NiCr combinations produced good results compared to other feedstock materials. Therefore, the coated structure is achieves greater wear resistance and good corrosion resistance employed with an influence of both amorphous/or crystalline microstructure induced in the coated materials.

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