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Investigation of Hardness, Morphology and Structural Analysis of NiCrBSi Composite Coating on Plain Carbon Steel

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ABSTRACT

High velocity oxy-fuel (HVOF) is one of the emerging technologies among the thermal spraying techniques, for producing uniform and dense coatings, having high hardness and very low porosity. A NiCrBSi alloy coating was prepared with approximately 400µm thick, on the A516 steel by means of HVOF and was analyzed with regard to its detailed microstructures, phase formation, thickness, roughness and microhardness. The obtained coating was crack-free, mechanically bonded to the substrate and had very low porosity. A microhardness tester was used so as to determine the mechanical properties of the coating. The microstructure of the coating and its phase transformations was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS), respectively. The major crystalline phases involve Cr3NiB6, Ni31Si12, Ni4B3, Ni3B compounds and Ni-γ solid solution. Also, amorphous phase was obtained in the coating. The results indicated that coating microhardness values were in the range of 700-800 Hv and a uniform distribution of different elements was observed.

1. Introduction

Thermal spray is a technique that produces a wide range of coatings for many industrial applications. The thermal spray technique is based on the melting of feedstock, and impact on a substrate where rapid solidification and deposit build-up happens [1]. Thermal spraying uses two principal energy sources, chemical energy of the combusting gases which the flame spray torches (e.g. HVOF spraying), and electric currents providing energy for the plasmatons (e.g. Atmospheric Plasma spraying) [2]. The flame velocity could be increased in modern HVOF equipment to values near 5 Mach and the temperatures achievement were limited to approximately 2800–3300 K. One of the most usual techniques for Nickel-based alloy coatings is thermal spraying which enhances properties such as hardness, toughness, corrosion and wear resistance to meet many functional requirements in corresponding engineering applications [3-6]. Chromium element is responsible for oxidation, corrosion and wear resistance due to its passivation ability and the hard phases formation such as chromium carbides and borides. In addition, boron and silicon elements create glass formation ability and would reduce the melting point by promoting eutectic transformations. These elements stabilize the super-cooled liquid against crystallized state. Also, it is reported that the formation of hard intermediate phases can be improved with the existence of boron [6-8]. Nickel-base coatings are widely utilized in the chemical, petroleum and glass mould industries with self-fluxing compositions on the substrate of plain carbon steels. They are also used in valves, punches, blades and mud purging elements [9]. Due to the industrial problems, many researchers have studied the microstructure and mechanical properties of nickel-based alloy coatings and their applications. These days, there is no extensive knowledge about the microstructures of HVOF sprayed nickel-based alloy coatings. In this study, the detailed microstructures and phase composition of HVOF sprayed NiCrBSi alloy coating

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have been investigated. Analysis was performed on both the feedstock powder and the as-sprayed coating using X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS). The aim was to show the mechanisms of microstructure formation of the nickel-based alloy coating with a specific composition during HVOF thermal spraying.

2. Experimental Procedure

2.1. Feedstock material

A commercially available nickel-based alloy powder was used in this study. Its morphology and size distribution are listed in Table 1. Powder chemical composition and weight percentage of elements were characterized by XRF. A 516 steel plates were used as the substrate.

2.2. Coating preparation

Before the spraying process, the substrates were degreased with acetone, dried by hot air and then grit-blasted with 24 meshes SiC, 5 bar pressure, 20-25 cm distance and angel of 90^o. The samples were coated until they reached the thickness of 400 µm. Nickel-based alloy coating was obtained using an industrial spray system (Metjet 4L Model, Metallistion Company). The spraying parameters are listed in Table 2.

2.3. Coating Characterization

The microstructure of the coating was evaluated on the cross section by optical microscope (OIYMPUS, BH2-UMA, BHM, U-PMTVC, JAPAN) and scanning electron microscope (SEM, FRI Quanta 450, America) after polishing.

The elemental composition of fine deposits in Ni-based coating was obtained by an energy dispersive spectroscopy (EDS, Bruker, XFlash6l10) attached to the SEM.

The phase composition of the original powder and HVOF as-sprayed coating was investigated by means of X-ray diffraction (XRD, Bruker D8-Advanced, Germany) with Cu Ka radiation (λ = 1.5406 Å) and stepsize 0.06/s operated at 40 kV, 40 mA.

Table 2. HVOF spraying parameters

Parameter	Value
Oxygen flow (l/min)	370
Fuel (l/min)	835
Nozzle (cm)	10
Carried gas (l/min)	91
Spray distance (cm)	35
Powder Feed Rate (gr/min)	60

The surface roughness was measured by Taylor-Hobson, Surtronic 201P, according to DIN EN ISO 4287 (4 mm sampling length and 0.8 mm cut-off distance). The reported values were the average of at least five measurements. The coating microhardness measurements were carried out at 50 g using MMT-7 microhardness tester Buehler in the cross section of the coating. The reported values were the average of 10 measurements. The set of 60 indents in coated sample, in defined position was designed to evaluate the changes of microhardness across the coating thickness.

3. Results and Discussion

Fig. 1 shows the SEM morphology of the feedstock powder in two magnification scales (Fig. 1). It can be seen that the powder was nearly spherical shape with a size distribution in the range of 15-45 µm, which was convenient for HVOF thermal spraying [10].

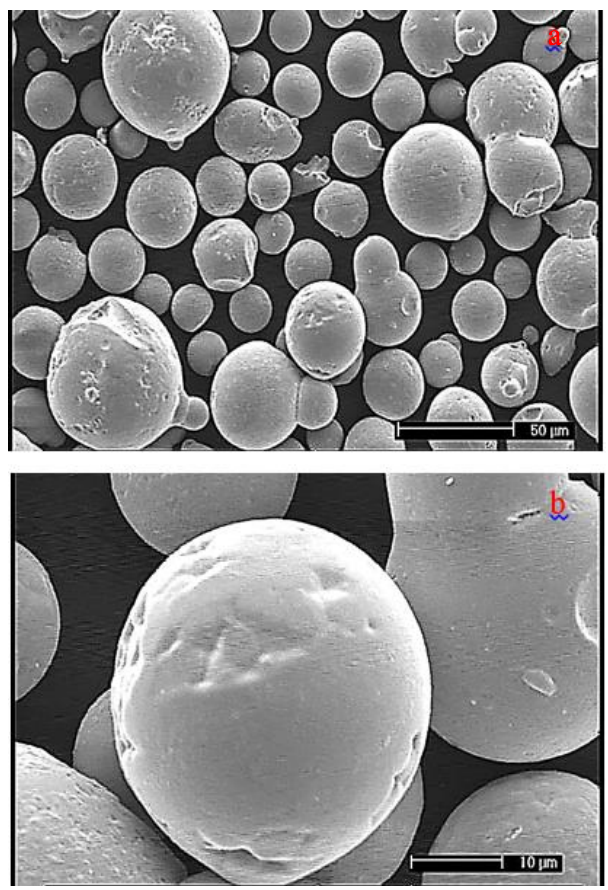

Fig. 1. SEM micrographs of the powder morphology at a magnification of (a) 500x and (b) 2000x.

3.1. Microstructure

The optical microscopy (OM) images revealed the microstructure of cross sections of as-sprayed NiCrBSi coating, deposited by HVOF (Fig. 2). It is clear that the coating and the interface between coating and substrate were crack-free. The as-sprayed HVOF coating contained small precipitates, distributed in eutectic matrix. The coating microstructures did not differ across the coating thickness — they consisted of individual particles, containing small hard precipitates surrounded by eutectic structure of gamma nickel, splat boundaries, and pores. The photograph shows that HVOF coating is nearly not porous and the splats are well flattened.

Fig. 3 depicts a selected region from the coating cross section, where the coating and the substrate are shown. It reveals that the as-sprayed coating has a dense layered structure with a thickness of approximately 400μm (Fig. 3a). The same studies have shown similar morphology [11–12]. No considerable voids or cracks could be observed in the interface between coating and substrate which verifies the high quality of coating. Fig. 3b shows the distribution of splates in the main structure that uniformly spreaded in the substrate, which is in agreement with a previously reported manuscript [13]. Furthermore, few pores are visible since very dark regions demonstrated in SEM photo.

The SEM features and the corresponding EDS spectra of the coating are shown in Fig. 4. Coatings were etched with a dissolution of 80HCl:20HNO3 which eliminated the matrix preferentially, making the precipitates observation easier (Fig. 4a). Some areas of the coatings did not contain these precipitates because of their dissolution during thermal spray. This phenomenon was promoted by high flame temperature and exposing the particles in flame. The EDS analysis of the coating indicated that the coating had an inhomogeneous composition. The matrix contained Ni as major constituent along with considerable amount of Cr and small contribution of other elements like Si and Fe. This means that the matrix had γ-Ni (with Cr, Si, etc. in solid solution), which can be shown in the XRD pattern according to the ref. [14].

It is a good agreement on the fact that the atomic radius and mixing enthalpy were the most important factors affecting the glass formation [15]. In this area, some studies indicated that the reason of addition of Fe, Cr, C, Si and B was the differences inatomic size as follow: Si (1.34 Å) > Cr (1.27 Å) > Fe (1.27 Å) > Ni (1.24 Å) > B (0.95 Å) > C (0.86 Å) [16], decreasing the atomic diffusivity because of the formation of the packed local structure in the super cooled liquid [17, 18].

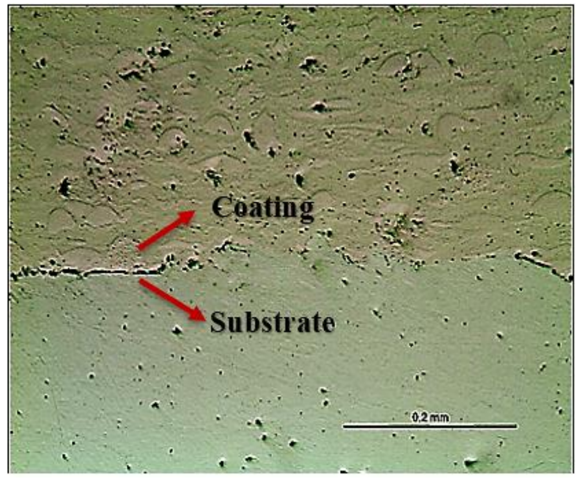

Fig. 2. Optical micrographs of polished cross sections

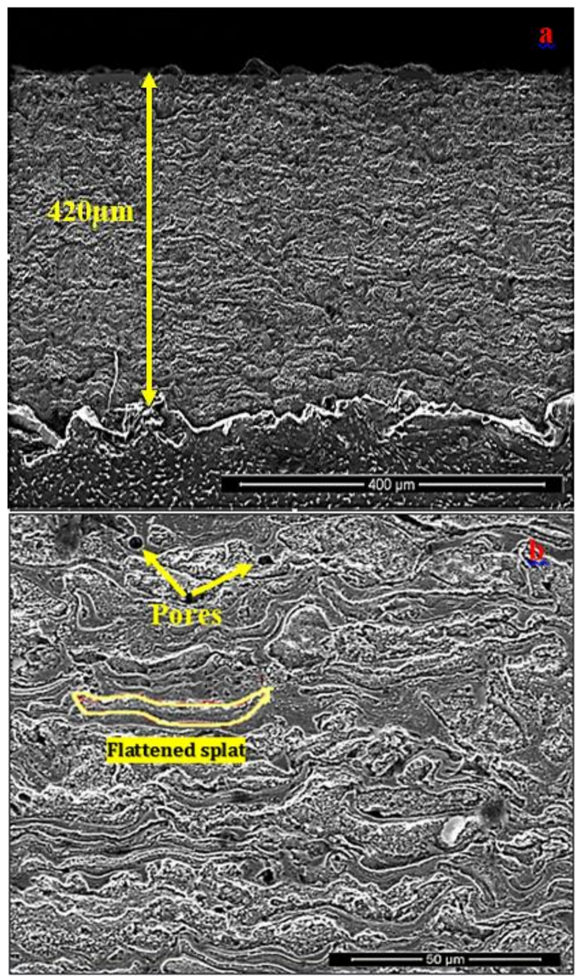

Fig. 3. SEM images of a transverse section of the as-sprayed coating: (a) a lamellar morphology; and (b) pores

On the other hand, the mixing enthalpy valued for Fe–Cr, Ni–B, B–Si, Cr–B, and Ni–Si atomic pairs were -1, -9, -14, -16, and -23 kJ mol^{-1}, respectively [16]. Therefore, the nickel-based alloy system is compatible with Inoue experimental rule that had three conditions: [16], i.e. (1) multi-component, (2) significant atomic size mismatches, and (3) suitable negative heats of mixing among the constituent elements. It was concluded that, the splats were cooled at an average rate of about 10^6 K s^{-1} during HVOF technique [19], which was a key factor for glass formation. Roughness parameter of the coatings (as the average of 5 measurements) is reported in Table 3 and is equal to 13µm. Highest velocity of the powder particles combined to a perfect matrix melting during HVOF spraying enhanced its better lamellar deposition, for this reason, coating roughness decreased.

3.2 Coating structural phases

The X-ray diffraction patterns for the composition phase of the feedstock powder and the as-sprayed coating are shown in Fig. 5.

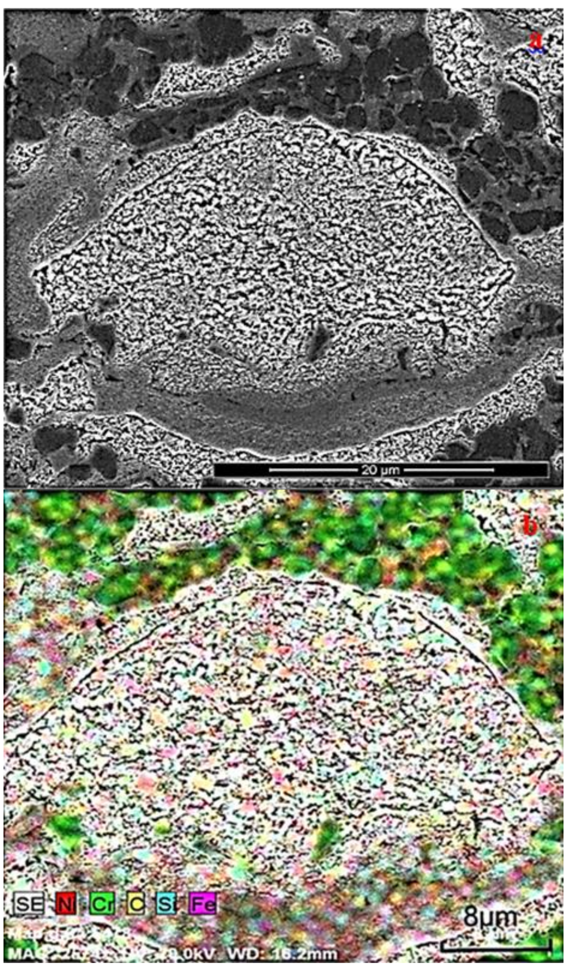

Fig. 4. SEM images showing (a) the morphology of the coating and (b) the corresponding map spectra

Table 3. Properties of the NiCrBSi coatings

	Roughness(Ra, µm)	Thickness(µm)
NiCrBSi	13	420

The XRD analysis revealed a considerable amount of possible phases due to the complexity of the NiCrBSi alloy coating. The complexity of the NiCrBSi alloy was able to create different types of borides, carbides and silicides. The main identified phases include Ni, CrB and NiB were in agreement with previous reported results [20, 21]. In contradiction to the literature [21, 22], the silicides appeared in our case, but no carbide-based phases were identified. In fact, the proximity between Ni, Cr and Fe in the periodic table of chemical elements made it difficult to find the real structure of this coating. Finally, some compositions were consistent with the suggested data. Furthermore, XRD pattern of the NiCrBSi sample revealed that the microstructure of the coating consisted of Ni-γ solid solution as main phase and Cr3NiB, Ni31Si12, Ni4B3, Ni3B which is in agreement with those reported in the literature [23,24,25] for this kind of nickel-based alloy coatings. In addition, it is obvious that silicides appeared in our case. It can be noticed from Fig. 5 that the XRD data of the coating was more intense, and almost diffraction peaks of the coating were broader and weaker than that of the powder. It presents an amorphous background for NiCrBSi sample elaborated by HVOF. Also, a broad diffraction peak appearing at 2Θ of 44° which indicated the presence of an amorphous phase within the coating. This kind of XRD spectra pattern was emblematic of HVOF coating. This amorphous background was due to a reduction of crystallinity. The feedstock powder was sprayed as droplet and solidification appeared very quickly. The feedstock powder used for spraying NiCrBSi sample had a good crystallinity, but when the powder was sprayed in the HVOF, it was in a semi-liquid state. In addition to the presence of porosity and unmelted particles, there was also an amorphous core of matter in each droplet, in complement to the crystallized atoms. This phenomenon developed a perturbation in the crystallization of the NiCrBSi coating.

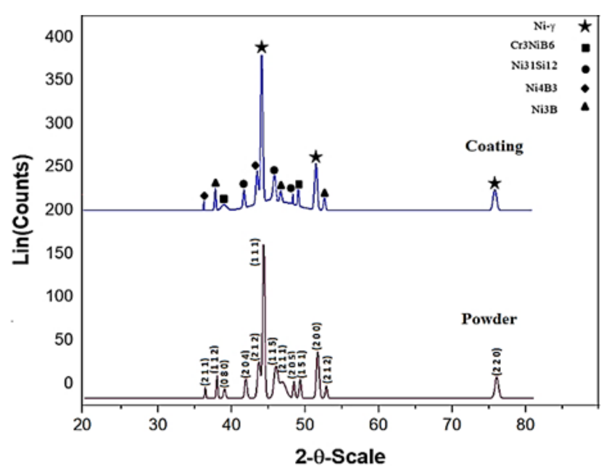

Fig. 5. XRD patterns of the feedstock powder and as-sprayed coating.

3.3. Hardness Values

The change of cross-section microhardness in consequence of spraying technology is shown in Fig. 6. Two factors affected the hardness evolution of the HVOF sprayed coatings: the coatings inner stress and microstructure. In the as-sprayed coating, the compressive residual stress, typical for HVOF coatings, could be expected [20]. The microhardness of the coatings was found to be variable with the distance from the coating-substrate interface. Changes in the microhardness along the thickness of the coatings might be due to the distribution of the hard phase in Ni based alloy coatings [26, 27]. Furthermore, the coatings microstructure changes were responsible for the changes of measured microhardness. HVOF sprayed NiCrBSi showed higher microhardness than substrate, because it combined coating cohesion with a high quantity of small precipitates perfectly distributed in the coating. The low dissolution of the precipitates during the HVOF spraying could lead to a decrease in the microhardness value, but this negative effect was not as important as the benefits given by the good dispersion of the precipitates.

4 Conclusions

In this article, the microstructural, phase formation and microhardness of a Ni-based composite coating on the steel substrate via HVOF technique have been investigated. A NiCrBSiFeC alloy coating with thickness of 400 μm was prepared onto A 516 Gr60 steel substrate using HVOF thermal spraying process. The major crystalline phases were Cr_3NiB_6, $Ni_{31}Si_{12}$, Ni_4B_3, Ni_3B and solid solution Ni-ɣ. Furthermore, amorphous phase was obtained in the coating, due to the high cooling rates of molted droplets and the multicomponent alloy system of feedstock powder. On the basis of the results, it could be concluded that the HVOF sprayed NiCrBSiFeC alloy coating may become a very interesting alternative for coatings with high wear resistance coatings due to the high hardness and low porosity.

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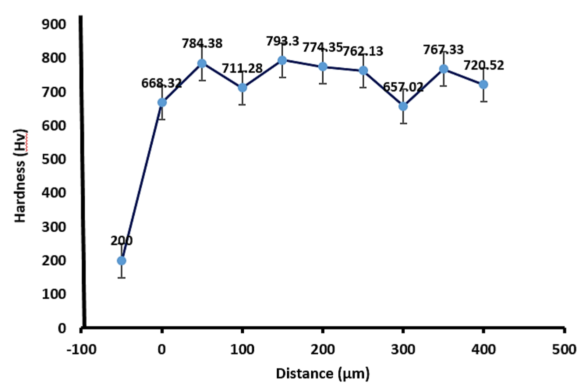

Fig. 6. Microhardness profiles for HVOF sprayed NiCrBSi coatings on the carbon steel

Table 1. Chemical composition (wt %) of spray powders and the substreat by XRF

	Chemical composition (wt %)								
Element	Ni	Cr	B	Si	Fe	C	Mn	P,max	S,max
Powder (NiCrBSi)	Bal	17	3.5	4	4	1	-	-	-
Substreat (A 516 Gr60)	-	-	-	-	-	0.21	0.6-0.9	0.035	0.00035
Powder (NiCrBSi)	Morphology Spherical	Particles size distribution Ranging from 45 to 15 μm (average 30 μm)							

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