Microstructure and wear behaviour of self-fluxing alloy coatings reinforced by WC-Co

I L Conciatu¹, C R Ciubotariu¹*, E R Secosan¹, D Frunzaverde¹ and C V Campian²

¹Faculty of Engineering and Management, Department of Mechanical Engineering and Management, Eftimie Murgu University of Resita, Resita, Romania
²Center for Research in Hydraulics, Automation and Thermal Processes, 1-4 Traian Vuia Sq., 320085, Resita, Romania

E-mail: r.ciubotariu@uem.ro

Abstract. The wear behaviour of Ni-base self-fluxing alloys, thermally sprayed as protective layers on martensitic stainless steel substrates, is affected by several factors, such as the microstructure of the coatings and their adhesion to the substrate, the porosity and the hardness of the surface. In this study, the mechanical wear properties of thermally sprayed self-fluxing alloys with different additions of Cermet powders (10, 20 and 30% WC-Co) were investigated using the pin-on-disk method. Moreover, it was highlighted that after the flame fusion process the morphology of the layers has been greatly improved. Based on scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis the evolution of the metallic matrix reinforced by ceramic phases consisting of carbides, borides and silicide’s was pointed out. Micro-hardness measurements were carried out as well, in order to evaluate the influence of flame fusion process on the coating hardness. The investigations revealed that the addition of up to 30% Cermet powder to self-fluxing alloys leads to the improvement of the wear resistance of the protective coatings, extending the range of practical applications of self-fluxing layers.

1. Introduction

High Velocity Oxygen Fuel (HVOF) is a technology which involves the deposition of molten or semi-molten droplets of powder onto a substrate to form a coating with small porosity [1-2] and high adhesion strength [3-4]. A wide range of HVOF coatings applied in almost all industrial fields with different combinations of coating substrate materials is used for applying protective layers to material surfaces [5-13].

For the limitation of maintenance costs and obtaining the coatings for components exposed to high wear intensities or thermal stability, hard surfaces containing Tungsten Carbide (WC) are usually used. During the spraying process, WC with their high melting temperatures do not melt and become included in the sprayed coating as hard particles and combined with the relatively ductile binder lead to excellent mechanical properties [14-15]. Cobalt acts as a binder to form a ductile, dense tribofilm on the worn surface to protect the underlying surface from further wear, resulting in a very low wear rate [16]. WC–Co hard materials can be densified by liquid phase sintering and the mechanical properties of these materials depend on their composition and microstructure (especially on the grain size of the carbide phase [17]).
The purely mechanical bonding between the coating and the substrate, cracks and porosity are disadvantages in detrimental to the performance of the coatings [18]. In many researches solutions are being sought with regarding to possibility of including hard ceramic particles into metal alloys using several deposition techniques in order to increase wear resistance, mechanical stability and corrosion especially at high temperatures [19-22].

The aim of the present study was to improve the resistance to sliding wear of NiCrBSi self-fluxing alloys coatings by reinforcement with WC-Co powder thermally sprayed followed by secondary processing through remelting, in order to enhance their as-sprayed properties. WC-Co particles were added to the NiCrBSi powder at various ratios with the purpose of obtaining coatings with optimum hard materials content.

In order to evaluate the effect of the WC-Co content in the mixture, the wear experiments were performed with different mixing ratios. Following the wear tests, the worn surfaces were investigated by means of scanning electron microscopy (SEM) with the scope to determine the effect of WC-Co particles on the wear mechanism of the coatings.

2. Experimental procedure

2.1. Materials and processes
Coatings consisting of self-fluxing alloys (NiCrBSi) with different additions of cermet powders (10, 20 and 30% WC-Co) were deposited by flame spraying on martensitic stainless steel substrates. The powder mixtures used for the layers were obtained following a mechanical mixing process. Table 1 presents the sample codes and the compositions of the coating powders. In the sample codes, the first 2 numbers represent the percentage of self-fluxing powder (in wt. %), while the last 2 figures represent the percentage of the cermet powder content (in wt. %). For example, the coating produced using a powder mixture with 80% NiCrBSi – 20% WC-Co (wt. %) was stated as 80/20 coating. Prior to spraying, a sand-blasting machine was used to roughen the working surface of the stainless steel substrate. Because during the thermal spraying process the powder becomes liquid and deforms to impact, a remelting treatment with oxyacetylene flame is applied, also resulting in refining the morphology of the layers and enhance of the coating/substrate adhesion. After spraying and remelting, the coatings were examined in cross-section with a scanning electron microscope (SEM/Philips XL30 ESEM), combined with energy dispersive X-ray analysis (EDX/Company) at magnifications between 50× and 1000×, in order to characterize the microstructure of the layers and the quality of the coating/substrate interface.

| Sample code | Coating powder (in wt. %) |
|-------------|--------------------------|
| 90/10       | 90% Ni–Cr–B–Si + 10% WC-Co |
| 80/20       | 80% Ni–Cr–B–Si + 20% WC-Co |
| 70/30       | 70% Ni–Cr–B–Si + 30% WC-Co |

2.2. Measurement of wear resistance
The wear tests were realized in accordance with the ASTM G99 standard. For most accurate results, the sample surfaces were specially prepared by grinding and polishing, and finally degreased with acetone. Air with a humidity of 50% was used as test medium and the temperature did not exceed 20°C.
The CSM Pin-on-Disk tribometer consists of a flexible arm that has a ball of WC-Co on the tip, with a diameter of 6 mm, which actuate on the sample surface with a force of 10 N (F). The trajectory radius was 8 mm with 16 cm/s linear speed, while the number of laps was 10,000. The width (s) and depth (h) of the wear track were measured using a digital microscope, in order to calculate the area of the cross section (A – relationship 1). The quantification of the wear rate (K - relationship 2) was realized using the values for the amount of material lost (V - relationship 3), the applied load (F) and the length of the trajectory (d).

\[ A = \frac{h}{6} \left(3 \cdot h^2 + 4 \cdot s^2\right) \]  \hspace{1cm} (1)

\[ K = \frac{V}{F \cdot d} \]  \hspace{1cm} (2)

\[ V = 2\pi \cdot A \]  \hspace{1cm} (3)

### 3. Results and discussion

#### 3.1. Coatings characterization

The microstructure of the layers concerning the morphology and the distribution of the different phases was examined by scanning electron microscopy (SEM) and the chemical composition of the different structural elements was determined by energy dispersive X-ray spectroscopy (EDX). The EDX analysis was used in order to evaluate the chemical composition of the phases, differing by shape, distribution and the shade of grey. The micrographs and the results of the EDX analysis are shown in the figures 1 to 4.

**Figure 1.** SEM micrographs for sample 90/10:
(a) – magnitude 50x and (b) – magnitude 1000x.

Based on the results of the EDX analysis (see figure 2) performed for each shade of grey or white corresponding to a particular phase in the microstructure, the following can be concluded:

- areas with the shade of grey corresponding to the point marked with EDX 1 represent the metal matrix which is containing mainly elements such as Ni, Cr and Fe;
- particles marked with EDX 2 (very light grey to white) correspond to a phase rich in tungsten carbide (WC);
- areas marked with EDX 3 (dark grey) are rich in Cr (chromium carbides and chromium borides).
Figure 2. EDX analysis of microstructural components for sample 90/10.

As the micrographs in figure 3 and figure 4 reveal, the coatings consisting of self-fluxing alloys in combination with 20%, respectively 30% hard particles of WC-Co consist of the same phases as the layer which contains 10% WC-Co. The only difference is the proportion between the phases (metal matrix, carbides, borides and silicide).

Figure 3. Microstructural analysis in cross section for sample 80/20: (a) – magnitude 50x and (b) – magnitude 1000x.
3.2. Hardness tests

The hardness measurements were performed on mounted samples using a Zwick tester of type Z3.2A. In order to determine the Vickers hardness, a 0.3 kgf load was applied for 15 seconds. Figure 5 shows the values calculated as average of 10 measurements, after the highest and the lowest values were removed. One could observe that the 10 measurements for each type of coating conduced to very different values of the hardness, determined by the inhomogeneous phase distribution in the layers. As the size of the indenter track is directly associated with the hardness of the structural element, the traces obtained in the layer areas with a higher content in hard phases had small values of diagonals, whereas the phases with lower values of hardness conduced to higher values of diagonals generated by the indenter. As shown by figure 5, for amounts up to 30% hard particles added to the self-fluxing alloy, the increase of the cermet content leads to the increase of the hardness, but in relation to the NiCrBSi coating, the WC-Co content added does not conduce to higher values of the hardness, as it was expected.

![Figure 4. Microstructural analysis in transversal section for sample 70/30: (a) – magnitude 50x and (b) – magnitude 1000x.](image)

![Figure 5. Average values of hardness in the cross section of the deposited layers.](image)
3.3. Sliding wear testing
The friction coefficients for the four coatings with different chemical composition (NiCrBSi and mixture: 90/10, 80/20, 70/30) obtained by Pin-on-Disk sliding wear determinations can be seen in figure 6. In case of the NiCrBSi layer, the values for the friction coefficient has stabilized relatively late, after about 4000 laps, in comparison with the values for the mixed coatings, which were stabilized much faster (after 3000 laps 90/10 and 80/20; after 1000 laps 70/30). As shown in figure 6, the reinforcement of the self-fluxing alloys with WC-Co hard particles conduces to considerable increases of the friction coefficient values, especially for the mixed coatings with 10 %, respectively 20 %.

![Figure 6. The variation of the friction coefficients value](image)

The micrographs of the wear traces captured with the Keyence digital microscope were used for the calculation of the wear rate of the layers. For example, figure 7 shows the topography of the wear trace for the mixture 70/30.

![Figure 7. Topography of the wear trace for mixed coating 70% NiCrBSi + 30% WC-Co](image)
The results presented under the form of a histogram in figure 8 show the wear resistance of the investigated coatings. Thereby the layer of self-fluxing alloy has the highest value of the wear rate in comparison with the mixed coatings (90/10, 80/20, 70/30). One can see that the increase of the hard component (WC-Co) content in the coatings leads to increased wear resistance.

![Figure 8. The values of sliding wear rate on the surfaces of coatings](image)

4. Conclusions
The investigations carried out within this study showed that the reinforcement of self-fluxing alloys coatings by WC-Co cermets leads to significant increase in the sliding wear resistance. In this regard, the addition of 10%, 20% and 30% WC-Co to NiCrBSi layers conducd to a decrease of the wear rate of 17%, 31% and respectively 38%. Starting from these considerations, one may conclude that the addition of hard materials to self-fluxing alloys extends their applicability to domains in which also better wear resistance is required.

On the other hand, the results regarding the friction coefficient correspond to those obtained for the wear resistance, while the hardness values of the tested layers cannot be directly associated with, since the phenomena appearing on the interface between the test layer and the WC-Co ball of the Pin-on-Disk Tester are of a more complex nature. One has to consider that the values of friction coefficients are, among other things, a result of the topography, the morphology and the chemical composition of the tribofilm generated along this interface.

5. References
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