

Corrosion behavior aspects of Ni-base self-fluxing coatings

C Paulin¹, D L Chicet², B Istrate¹, M Panțuru¹ and C Munteanu¹

¹Mechanical Engineering, Mechatronics and Robotics Department, “Gheorghe Asachi”
Technical University of Iasi, Iasi, Romania

³Materials Science and Engineering, Materials Science Department, “Gheorghe Asachi”
Technical University of Iasi, Iasi, Romania

E-mail: dchicet@tuiasi.ro

Abstract. Due to the development of thermal spray deposition technologies, thus obtained layers have more applications and fields of use. One of the coatings with increased application is the one produced from Ni-based self-fluxing alloys, which besides the good wear resistance, shows a satisfactory corrosion resistance. In this study it was observed the behavior of three types of coatings produced by Flame Spray method, both at wear and especially corrosion in the environment simulating acid rain. As a result of the experiments it was found that these layers became compact enough after applying the self-fluxing heat treatment, so in their structure are not present defects such as pores and micro-cracks, unmelted particles etc., which could be points of corrosion initiation.

1. Introduction

Thermal spray coatings made from self-fluxing Ni-based powders are used in many fields, especially in applications where good resistance to wear is required. Some of these areas are: chemical, oil, plastic hot or cold deformation industry, cement factories etc. [1, 2, 3]. In many of these applications, the operation requirements are combined and according to the working environment it is often necessary also a good corrosion resistance.

A problem regarding the corrosion resistance of coating produced by thermal spray is given by the very way of spraying them: layered deposition of powders heated up to the melting temperature and accelerated by a carrier gas towards the substrate. It is produced a structure with lamellar morphology, adherent to substrate, with variable porosity, possible micro-cracks and oxidized interlayers, which could allow the penetration of corrosive agent to the substrate and its destruction [3, 4].

For this reason, especially in the case of self-fluxing powders it is applied a subsequent heat treatment, leading to a decrease in the porosity degree, the formation of strong metallurgical bond between the coating and substrate, resulting thus increased corrosion resistance.

The literature identifies several studies on the corrosion behavior of coatings deposited by thermal spray, because once with the evolution of deposition technologies will evolve also the fields of application of these layers. For example, Gil and Staia, Dent et al [1, 5] studied the corrosion resistance of Ni-base alloys in NaCl and H₂SO₄ solution, Harvey et al. [1, 5] studied the links between spraying parameters, microstructure and corrosion resistance of the coatings produced from Ni, Co and Fe-based alloys and Lee and Min [1, 5] studied the effect of heat treatment on the microstructure of NiCrWMoB coatings deposited by HVOF.



In this paper is studied the corrosion behavior of some Ni-base self-fluxing coatings previously subjected to wear stress, in order to simulate the operating conditions in corrosive environments and wear requests.

2. Materials and methods

2.1. Materials

The materials which were analyzed inside this paper are three types of coatings produced through thermal spraying using the Flame Spraying (FS) method, onto a lamella type substrate from unalloyed steel (0.34%C). For this purpose there were used three types of commercial powders, which chemical composition is presented in table 1.

Table 1. Chemical composition of powders.

Sample	Powder type	Chemical composition (wt%)							
		Cr	Si	Fe	C	B	Mo	Cu	Ni
A	1355-20	15.8	4.07	2.72	0.54	3.49	2.96	2.95	bal.
M	JK-586	15	4.3	4	0.7	3.1	-	-	bal.
P	1060-00	14.92	4.31	3.82	0.78	3.17	-	-	bal.

The spraying process was realized using oxyacetylene flame, with a gas pressure of 3-4 bar in case of oxygen and 0.7-1.5 bar in case of acetylene, and a spraying distance of 20 cm between the samples and the gun tip. After finishing the coatings, a thermal treatment of fusing by remelting was applied at a temperature of 800°C, by oxyacetylene flame heating for several minutes and slow cooling in air.

2.2. Experimental setup

2.2.1. Dry sliding wear test. Using the micro-tribometer UMTR 2M-CTR was conducted on each of the three samples a linear dry sliding wear test using a grindstone as abrasive element, whose conical peak was approximated spherical, as seen in figure 1.

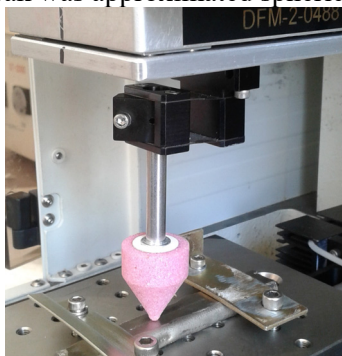


Figure 1. The assembly used for linear dry sliding wear test.

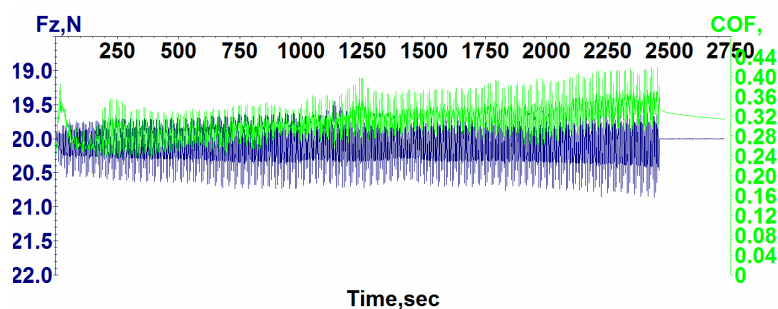


Figure 2. The chart of friction coefficient-time evolution, constant load, in case of A sample.

For each of the three samples, the test was conducted at a constant load of 20N for 40 minutes. It was observed an approximately linear behavior, with a gradual increase in the friction coefficient, as can be seen in figure 2 the representative behavior of sample A.

After these tests the wear degree of the analyzed coatings was assessed by measuring all wear mark profile using Form Talysurf Intra system. In all three cases there were not observed major changes or appearance of clear signs of wear, but only superficial changes of roughness, which confirms good wear resistance of the tested coatings. In figure 3 is presented the profile chart of M sample, considered representative for the three samples.

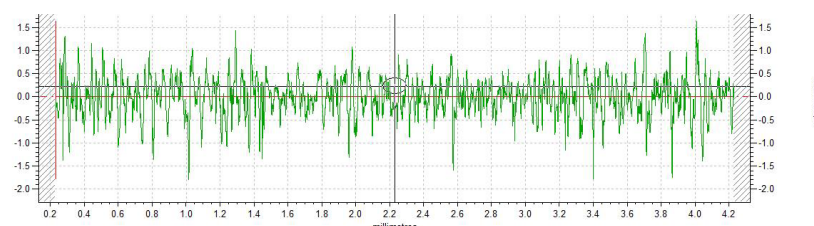


Figure 3. Wear scar profile of M sample after 40 min of linear wear at 20N.

2.2.2. Corrosion test

In order to conduct the corrosion tests, the samples were dimensionally prepared and it was chosen as corrosive environment a solution that simulates the acid rain, which chemical composition is presented in table 2.

Table 2. Chemical composition of corrosive environment.

Chemical composition	pH	SO ₄ ²⁻	Cl ⁻	CH ₃ COO ⁻	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	Ca ²⁺	Mg ²⁺
Natural acid rain (μM)	3.5-5.5	1-150	0.5-1800	1-10	0.3-50	0.1-39	4-2200	2-500	2-160
Simulated solution	4.3	55	1800	5	50	30	2200	480	120

Corrosion tests were carried out electrochemically, at room temperature of about 25° C for 24 hours in glass corrosion cell CA145/170 A 50T110 type. The electrochemical cell is composed of a reference electrode (saturated calomel electrode), an inert auxiliary electrode from platinum and the working electrode represented by the sample itself.

3. Results and discussions

After the corrosion tests were conducted, the samples were analyzed in terms of microstructural morphology using the scanning electron microscope Quanta 200 3D type (FEI Holland, 2008) and in terms of chemical elements using the EDX analysis module (AMETEK Holland 2008), part of the SEM system.

In figures 4-6 are shown microstructural aspects of the samples, both in case of wearing by linear friction tests and in case of electrochemical corrosion tests.

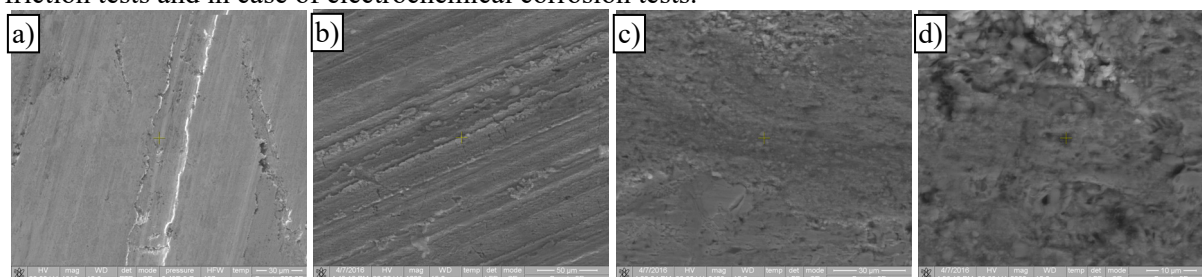


Figure 4. Secondary electrons images of sample A: a) linear wear mark (1516x), b) wear mark after corrosion (1200x), c) corroded surface aspect (2400x), d) corroded surface aspect (5000x).

In figures 4a, 5a and 6a can be seen a light wear mark caused by the dry sliding linear friction test, which is partly caused by the material removal, but also by a gentle material flow in the marginal area of the linear contact. It is easy to note that the sample's surface has a uniform appearance, no defects of pores type, incomplete molten particles, micro cracks, inclusions or lamellar areas, mainly due to remelting heat treatment applied after coating.

In figures 4b, 5b, 6b are presented aspects of wear after the corrosive agent action, at different magnifications. It is noticeable that all three samples behave similar at corrosion. Due to increased

coating density, the corrosive agent did not affect the metal substrate. Instead we observe a uniform layer of intermediate chemical compounds CIMO type resulted from the chemical reactions with the corrosive solution, especially in case of Cl element that could damage the coating.

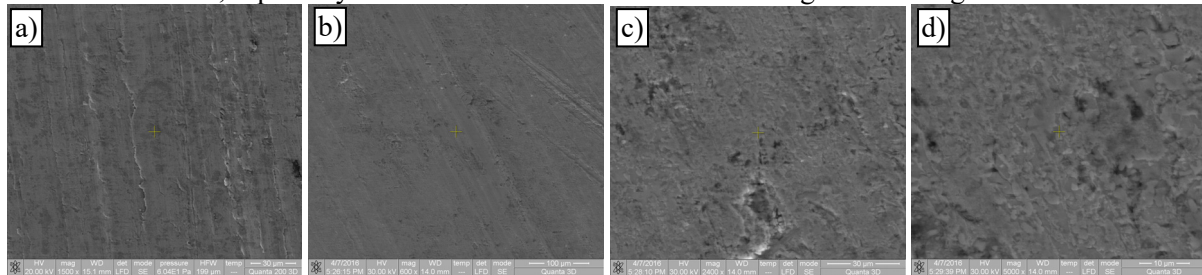


Figure 5. Secondary electrons images of sample M: a) linear wear mark (1500x), b) wear mark after corrosion (600x), c) corroded surface aspect (2400x), d) corroded surface aspect (5000x).

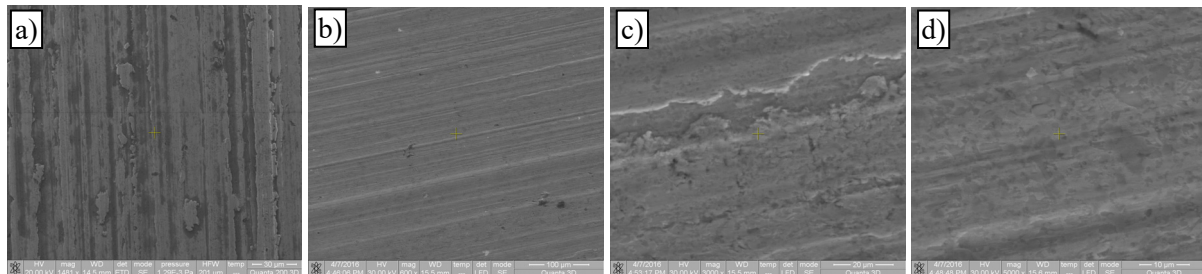


Figure 6. Secondary electrons images of sample P: a) linear wear mark (1481x), b) wear mark after corrosion (600x), c) corroded surface aspect (3000x), d) corroded surface aspect (5000x).

In figures 4, 5, 6 c, d are presented secondary electrons images of corroded surfaces. Thin layers of corrosion products are visible, crowded in some areas with irregular profile, specific to a smooth corrosion process.

Table 3. Chemical elements present on the samples surfaces before and after corrosion process.

Sample	Chemical elements (wt %)								
	O	Si	Mo	Cl	Ca	Cr	Fe	Ni	Cu
A, wear without corrosion	-	3.13	3.8	-	-	23	5.18	60.75	4.14
A, wear with corrosion	2.15	3.98	7.5	0.68	0.57	25.13	4.68	52.52	2.79
M, wear without corrosion	-	3.82	-	-	-	23.71	4.06	68.41	-
M, wear with corrosion	2.05	3.89	-	0.28	0.24	24.08	3.49	65.97	-
P, wear without corrosion	-	3.27	-	-	-	21.3	4.04	71.39	-
P, wear with corrosion	1.85	4.27	-	0.31	0.38	19.73	4.27	69.19	-

The existence of these corrosion products was highlighted by elemental chemical analysis EDX-type performed on the corroded layers, which are presented in table 3 compared to the analysis performed on the surfaces without corrosion. It is observed the presence of elements O and Cl, which in combination with other existing elements of coatings form complex chemical corrosion products. The difference between the chemical composition of the powders presented in table 1 and the one of the surfaces before corrosion (table 3) could be explained based on the wear process, which affected more the Ni matrix (decreased percent of Ni) than the other intermetallic compounds (Cr, Mo).

4. Conclusions

In the case of the thermal spray coating, due to the specific lenticular structure, corrosion can develop along the paths formed by the pores, inclusions, micro-cracks, unmelted particles and lamellar structures. Once with the corrosion development, some coatings parts will gradually separate themselves from the layer, by the action of corrosive environment and by the existence of corrosion products, so that will finally occur the peeling and removing of their structure. Thanks to the compactness of the three samples coatings analyzed in this paper, there were not observed differentiated areas (such as pores, inclusions, micro-cracks, etc.) that could act as initiation of corrosion. Thus, the corrosive agent does not enter inside the deposited layer and there are not observed aspects of advanced corrosion type that could cause the complete destruction of the coating, by laminar flaking or peeling. Good compactness of the deposited layer was obtained after the self-fluxing heat treatment, which consisted from the remelting of the coated particles, being created the premises of a compact layer, with a low percentage of pores, micro-cracks, unmelted particles or lamellas. This aspect is highlighted by the surface appearance in the area of dry sliding linear friction wear, where are not observed any changes in the structure such as a specific wear mark profiles.

5. References

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