

Characterization of Coatings Produced by Thermal Spray and Hard Chrome

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Abstract

In this work, tests of micro adhesive wear and corrosion by potentiodynamic polarization in chromium-based coatings produced by thermal spray (HVOF - Cr₃C₂-NiCr alloy) and hard chromium (electrolytic) were performed. The electrolyte used in the tests was natural sea water (Riviera - Bertioga beach / São Paulo - Brazil). In the wear and potentiodynamic polarization curves of the Cr₃C₂-NiCr layers produced by thermal spraying and electrolytic Cr, there was a higher resistance to wear and corrosion for the material obtained by thermal spraying. Therefore, the Cr₃C₂-NiCr layer, having a higher resistance to wear and corrosion, when compared to the electrolytic Cr layer, allows the substitution of this highly polluting and carcinogenic process due to the presence of the Cr⁺⁶ ion and with increasing restriction manufacturing.

Keywords: Coatings; Thermal spray; Hard chrome; Micro adhesive wear test; Potentiodynamic Polarization

Introduction

The progressive deterioration due to the wear and corrosion of the components leads to deterioration and loss of efficiency of the same, with high losses due to the stops, replacements and fuel consumption. Therefore, the production of coatings with characteristics superior to those of the substrate constitutes a constant challenge to the designers [1].

Currently, there are surface coating techniques that allow the production of layers with resistance to wear and/or corrosion resistance superior to that of the substrates. Among the processes used in the metallurgical industries to obtain layers, we highlight the thermal spraying and the coating process with hard chromium [2].

Thermal spraying is the generic term used for the set of coating processes in which the coating material is heated or fused rapidly by combustion, electric arc or plasma and simultaneously designed by gases under pressure at high speeds on a previously prepared substrate [3]. When struck against the surface, the molten or semi-molten particles flatten and adhere to the base material or onto the already existing particles, thus giving rise to a typical layer of structure. These layers consist of small particles flattened parallel to the substrate, with a lamellar structure containing inclusions of oxides, voids and porosity, presenting a structure different from those obtained by the other metal coating processes [4].

Functionally, due to its good combined characteristics of corrosion and wear resistance, the hard chromium coating process is associated with the manufacturing and maintenance operations in aircraft, vehicles and ships, civil or military, as well as several other applications in the industry, such as hydraulic actuator rods, bearings, lip seals, graphical cylinders, among others. Hard chrome has been used for more than 70 years, and has provided, because it is relatively inexpensive, an effective solution. Environmentally, the problem with such a coating is not the chromium itself, but the coating process which uses a solution of chromic acid which is released into the air during the process in the form of a fine mist. This mist contains chromium ions in the hexavalent state, which is carcinogenic in addition to causing

various other health problems such as perforation of the airways and skin rashes. As a result, the US Environmental Protection Agency (EPA) has enacted new and more restrictive laws to limit the release of hexavalent chromium into the environment. In addition, the US Department of Occupational Safety and Health Administration (OSHA) has set exposure limits for hexavalent chromium in the workplace to levels of 0.1mg/m³. Recent studies indicate that the risk of cancer is still significantly high at this level, so it can be anticipated that OSHA will set a substantially lower level than the current value. This should increase the cost of the operation of hard chromium coatings making its use prohibitive in certain applications [5,6]. This is one of the main motivations for the development of chrome substitutes.

The intrinsic wear and corrosion resistance of NiCr alloys, associated with high hardness of the chromium carbides and the lower cost of the Cr₃C₂-NiCr alloy for thermal spraying, compared to the high-content of sputtered materials, were predominant factors in the choice of the same for the present work, aiming at the substitution of electrolytic chromium [5-7]. The tribological and chemical study of the coatings produced is a subject of great technological relevance. The objective of this work was to produce and characterize layers of Cr₃C₂ (75%) - NiCr (25%) by the flame process HVOF (High Velocity Oxy Fuel) or electrolytic chromium produced in an AISI 52100 steel. Tribological pairs in terms of wear resistance, as well as in potentiodynamic polarization corrosion tests.

Material and Methods

The nominal chemical composition of the AISI 52100 steel used in this work is 1.00%C - 1.45%Cr - 0.35%Mn - 0.25%Si, using samples with dimensions of 100x100x5 mm. All samples were tempered (850 °C and cooled in oil) and tempered (150 °C for 40 min) prior to the production processes of the layers. The hard chromium layer was obtained by the electrolytic process in chromic acid solution (CrO₃ + H₂SO₄). The sprinkling of the Cr₃C₂ (75%) - NiCr alloy (25%) was performed by the HVOF process.

A metallographic analysis of the cross sections of the samples was performed to evaluate the constituted layers. The samples were characterized by optical and scanning electron microscopy and Vickers microhardness test (obtaining the hardness profile and average hardness of the layers produced). Fifteen measurements were made on the layers produced and on the substrate to obtain the hardness.

The wear resistance was evaluated using micro adhesive wear tests using a fixed ball (calotest type). Two trials were carried out in each case. SAE 52100 steel balls with a diameter of 25.4mm and a hardness of 60HRC were used, with a rotational speed of 300rpm and a load of 1,6N applied to the sample. The tests were performed with times of 5; 10; 15; 20 and 40 minutes (equivalent to 120, 240, 360, 480 and 960 m relative slip). The mean diameters of the worn caps were measured by optical microscopy and, with this value, the

volume of material removed (V) was calculated using Equation (A). The depth of the shell produced (h) was calculated by Equation (B). Where: d is the average diameter of the caps and R is the radius of the sphere (12.7mm).

$$V = \frac{\pi \cdot d^4}{64 \cdot R}; \text{ for } d \ll R \quad (\text{A})$$

$$h = \sqrt{\frac{v}{\pi \cdot R}}; \text{ for } h \ll R \quad (\text{B})$$

Wear graphs were obtained by plotting the volume removed (mm³) by the slip distance (m). The wear tests were performed at 26 °C and 60% relative humidity, under dry slip friction, in the air and without lubrication.

Potentiodynamic polarization curves, according to ASTM G59 (2014), covering the cathodic and anodic regions, were obtained using a natural solution of sea water (Riviera-Bertioga beach / Sao Paulo / Brazil). An electrochemical cell, used to obtain the curves, was composed of a reference electrode of saturated calomel, an auxiliary electrode of platinum and the working electrode (own sample to be analyzed). The experiments were carried out at room temperature with a scanning speed of 1mV/s from -1.0 to +1.0 V. For each corrosion test 50ml of aerated electrolyte was used, measuring the pH of the solution during the procedure. The polarization curves were obtained by plotting the applied potential (mV) as a function of the logarithm of the current density (A.cm⁻²).

Results and Discussion

Optical micrographs of the cross sections of the layers produced in AISI 52100 steel are shown in Figure 1. Figure 1(a) demonstrates that the chromium electrodeposition treatment produced a uniform layer with a thickness of approximately 30μm, featuring microcracks perpendicular to the substrate and a flat interface, which are characteristic of the process. The average hardness of the layer obtained was 1095.2 ± 18.3HV_{0.5}. Similar results were observed in other studies with hard chromium [5-8]. During the layer production, the decomposition of chromium hydrides occurs, accompanied by a volume reduction of up to 15%, favoring the appearance of residual tensile stresses at the layer/substrate interface, resulting in the formation of microcracks [8].

The uniformity and high hardness of the electrolytic chromium layer highlight its effectiveness in providing a hard and durable coating. However, the presence of microcracks, due to residual tensile stresses, can potentially compromise the integrity and longevity of the coating under mechanical stresses.

Figure 1(b) shows that the thermal spraying process produced a dense Cr₃C₂-NiCr layer with a thickness of 480μm, with few pores and a flat interface with the substrate. The adhesion of the layer to the substrate is due to mechanical anchoring, a mechanism that occurs through forces resulting from the liquid retraction during solidification [3,4]. The average hardness of the sprayed layer was 746.9 ± 21.7 HV_{0.5}.

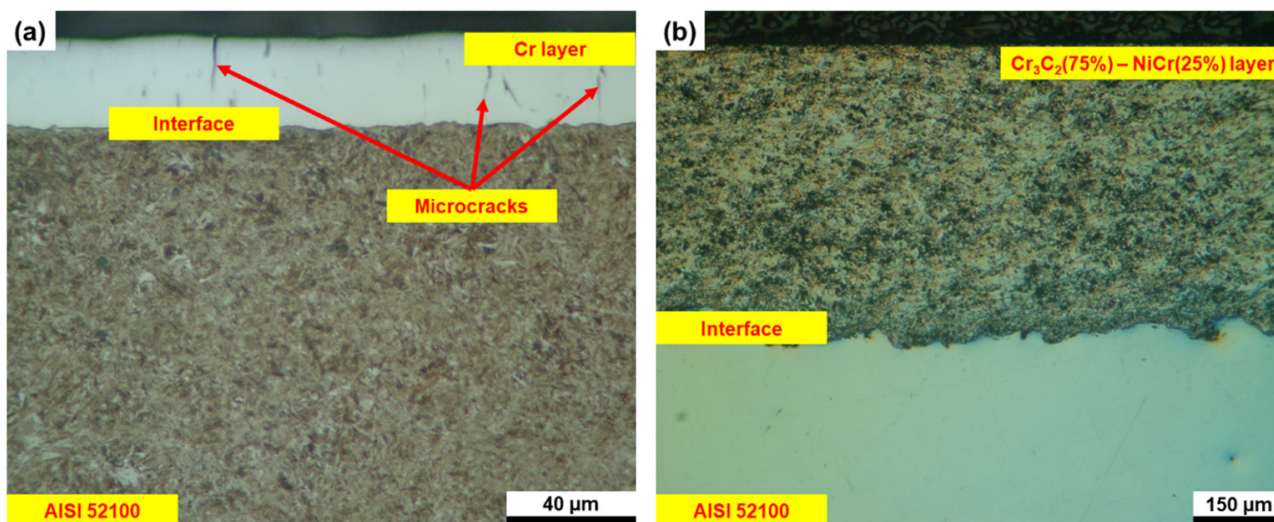


Figure 1: Optical micrographs of the cross sections of the layers produced. (a) Electrolytic Cr and (b) HVOF Spray.

The thermal spraying process produced a significantly thicker and dense layer with a lower hardness compared to the electrolytic chromium layer. The mechanical anchoring enhances the adhesion of the coating, contributing to its durability and performance under stress.

Figure 2 shows the Vicker microhardness profile performed in the cross-section of the hard chromium sample. It is evident

that the hardness remained constant between the surface and near the interface, indicating that the electrolytic chromium treatment produced a uniform layer. A sharp transition in hardness between the layer (approximately 1100HV_{0.5}) and the substrate (approximately 500HV_{0.5}) suggests that the treatment did not produce a chromium diffusion interface.

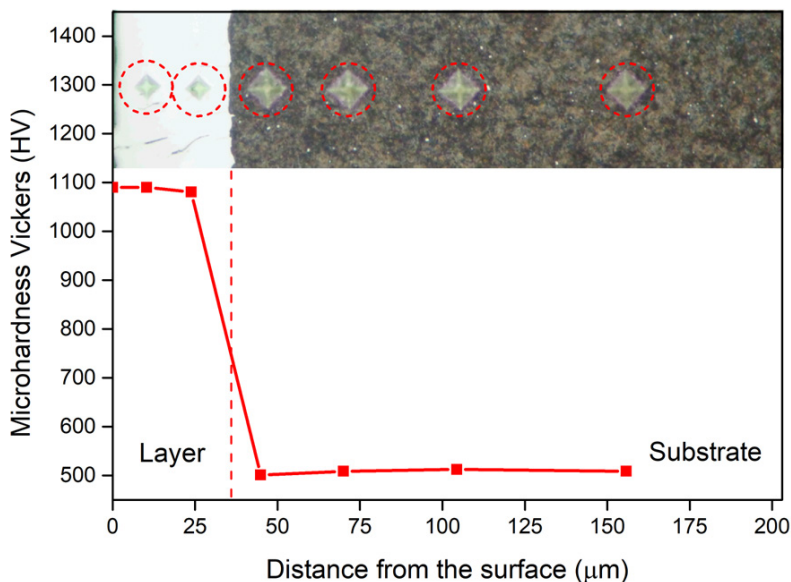


Figure 2: Vickers microhardness profile of the electrolytic chromium layer produced in AISI 52100. Test load applied 0.5N.

The constant hardness across the electrolytic chromium layer signifies a uniform deposition process. The sharp transition to the substrate hardness indicates a lack of diffusion at the interface, which could be a point of weakness under certain conditions,

potentially leading to delamination or other failure modes.

Wear plots for the produced layers and AISI 52100 steel are shown in Figure 3.

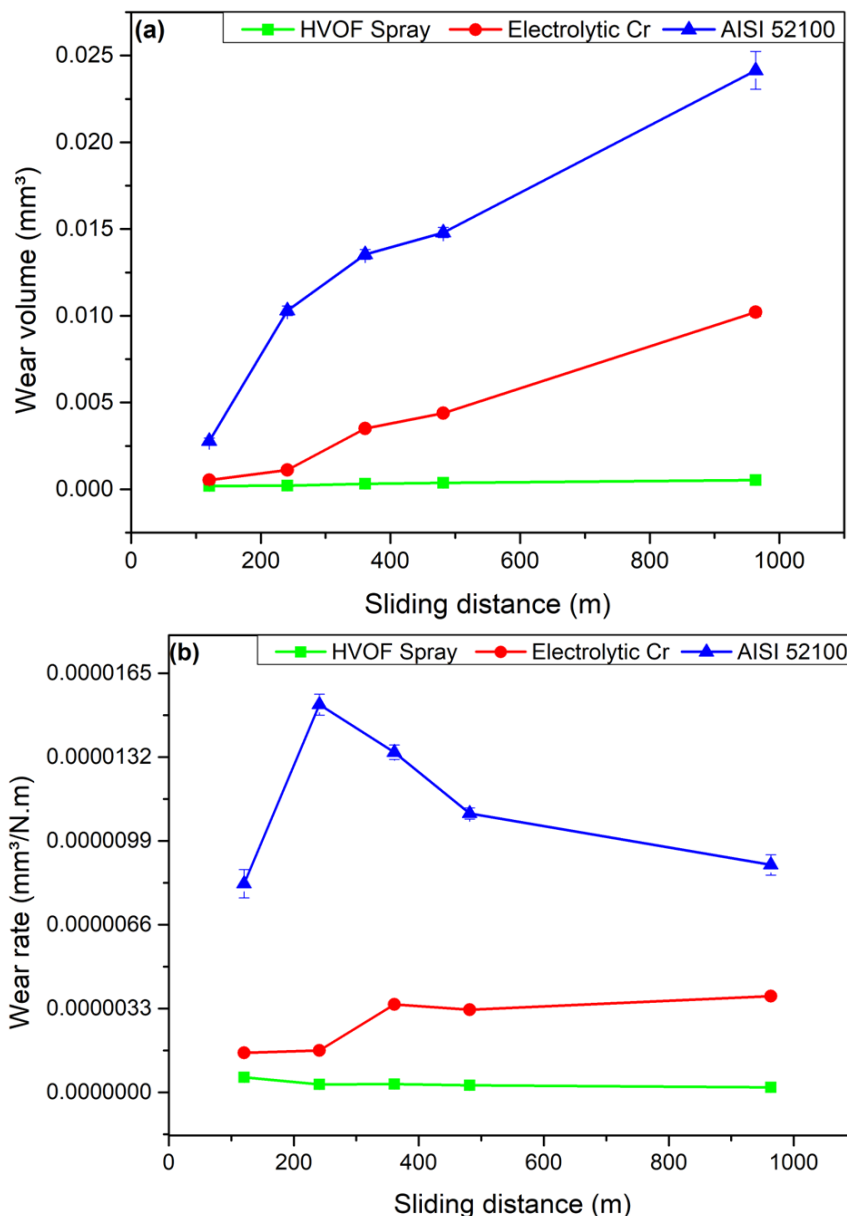


Figure 3: (a) Worn volume graphs and (b) wear rates for the layers produced and the substrate.

It is confirmed that AISI 52100 steel exhibited the lowest wear resistance compared to the produced layers. The Cr_3C_2 -NiCr spray-coated layer showed wear resistance about 18 times higher than the electrolytic Cr layer and 42 times higher than the substrate. The depths of the wear caps produced in the final wear test time (40 minutes - 960m) are summarized in Table 1, calculated using Equation (B).

Table 1: Depth of the caps produced in the last time of the micro adhesive wear tests.

Wear test	h - Cap height (μm)		
	HVOF Spray	Electrolytic Cr	AISI 52100
Test 1	3.4	16.1	24.9
Test 2	3.8	15.8	24.1

The wear resistance results clearly show the superiority of

the Cr_3C_2 -NiCr spray-coated layer. Its resistance to wear, being significantly higher than both the electrolytic Cr layer and the AISI 52100 substrate, can be attributed to its dense microstructure and effective mechanical anchoring. The depth measurements confirm that the wear tests did not breach the coating, indicating robust performance under prolonged wear conditions.

The potentiodynamic polarization curves for AISI 52100 steel, along with the produced electrolytic Cr and HVOF spray-coated layers, are presented in Figure 4. Table 2 provides the electrochemical parameters derived from the polarization curves. Similar corrosion current (I_{corr}) values were found for AISI 52100 steel and the Cr_3C_2 -NiCr spray-coated layer (order of $10^{-9}\text{A}\cdot\text{cm}^{-2}$). For the electrolytic Cr layer, a higher current density of the order of $10^{-7}\text{A}\cdot\text{cm}^{-2}$ was observed, indicating a higher corrosion rate for the chromium layer.

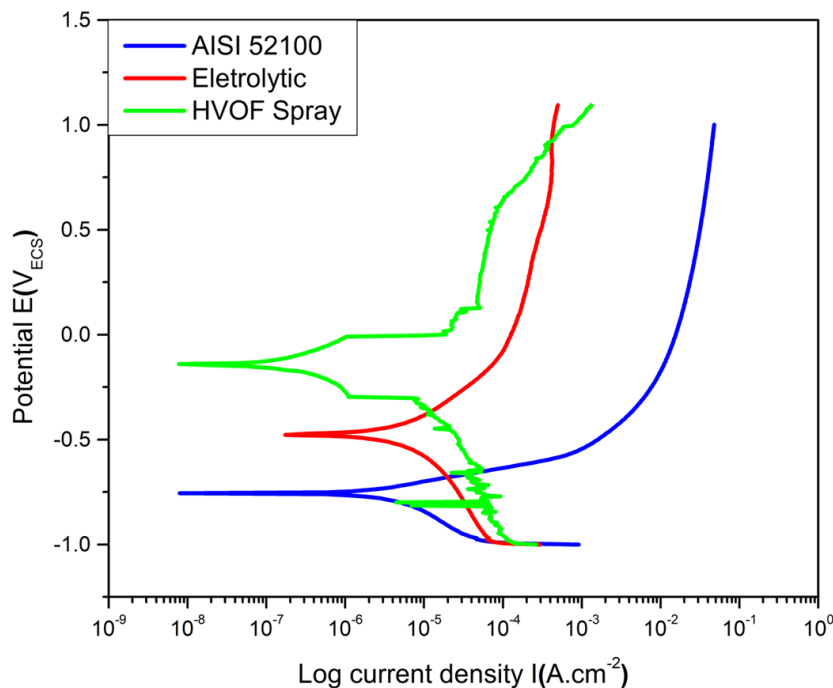


Figure 4: Potentiodynamic polarization curves for AISI 52100 steel, together with the produced layers of electrolytic Cr and HVOF spray.

Table 2: Electrochemical parameters for AISI 52100 steel, together with the produced layers of electrolytic Cr and thermal spray.

Material	E_{corr} (mV)	I_{corr} (A.cm ⁻²)	R_p (Ω.cm)
AISI 52100	-756	7.93×10^{-9}	1.689×10^4
Electrolytic Cr	-478	1.73×10^{-7}	1.992×10^4
HVOF Spray	-141	7.81×10^{-9}	3.125×10^5

Similar corrosion current (I_{corr}) values for AISI 52100 steel and the sprinkled Cr_3C_2 -NiCr layer (order of 10^{-9}A.cm^{-2}) are found. For the electrolytic Cr layer, a higher current density was observed, of the order of 10^{-7}A.cm^{-2} , indicating that the chromium layer had a higher corrosion rate.

In relation to the corrosion potential (E_{corr}) and the aggressiveness of the medium (R_p), it is observed that the asperged layer presented the best result, followed by the electrolytic Cr layer and the substrate, respectively.

The corrosion resistance data indicates that the Cr_3C_2 -NiCr spray-coated layer exhibits the highest resistance to corrosion, as evidenced by its lower current density and higher polarization resistance compared to the electrolytic Cr layer. The higher corrosion potential also suggests a greater resistance to oxidative environments. This superior performance makes the Cr_3C_2 -NiCr coating a more suitable alternative for applications requiring both wear and corrosion resistance, providing a more environmentally friendly solution compared to the traditional electrolytic chromium coating.

The combined results of wear and corrosion resistance clearly demonstrate that the Cr_3C_2 -NiCr spray-coated layer outperforms the electrolytic Cr layer and the AISI 52100 substrate. The thermal

spraying process, while producing a layer with lower hardness, provides significant advantages in terms of wear resistance and corrosion protection. The dense microstructure and effective mechanical anchoring of the Cr_3C_2 -NiCr layer contribute to its superior performance. Additionally, the environmental benefits of avoiding Cr^{+6} ions in the manufacturing process further advocate for the adoption of Cr_3C_2 -NiCr thermal spray coatings in industrial applications.

Conclusion

The Cr_3C_2 -NiCr coating exhibited wear resistance that was approximately 18 times greater than that of the electrolytic Cr layer. This remarkable improvement is attributed to the dense microstructure and effective mechanical anchoring provided by the thermal spraying process. The increased wear resistance of the Cr_3C_2 -NiCr layer makes it a viable option for applications subjected to high-wear conditions, extending the lifespan of components and reducing maintenance costs.

The potentiodynamic polarization curves further validated the superior corrosion resistance of the Cr_3C_2 -NiCr layers produced by thermal spraying. The corrosion potential (E_{corr}) of the sprayed layer was more than 300mV higher than that of the electrolytic Cr layer, indicating a significantly enhanced resistance to oxidation. Additionally, the current density (I_{corr}) of the Cr_3C_2 -NiCr coating was 22 times lower than that of the electrolytic Cr layer, reflecting a much lower rate of corrosion. The high polarization resistance (R_p) also underscores the material's excellent resistance to the saline environment studied.

The findings highlight the Cr_3C_2 -NiCr layer's potential to replace the traditional electrolytic chromium process, which is

not only highly polluting but also carcinogenic due to the presence of Cr^{+6} ions. The environmental regulations are increasingly stringent regarding the use of Cr^{+6} , and the Cr_3C_2 -NiCr coating offers a sustainable and compliant alternative. By adopting this thermal spray coating, industries can significantly reduce their environmental footprint while maintaining or even enhancing the performance of their products.

The Cr_3C_2 -NiCr thermal spray coating presents a compelling case for its adoption in various industrial applications. Its superior wear and corrosion resistance, combined with environmental benefits, make it an ideal choice for components that are exposed to harsh conditions. This study not only provides a technical foundation for the substitution of electrolytic Cr but also aligns with the global shift towards more environmentally friendly and more sustainable manufacturing practices.

In conclusion, the Cr_3C_2 -NiCr layer, produced by thermal spraying, offers a high-performance and environmentally friendly alternative to electrolytic chromium coatings. Its adoption could lead to significant advancements in the durability and sustainability of industrial components.

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