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Corrosive wear behavior of chromium carbide coatings deposited by air plasma spraying

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Abstract

The corrosive wear behavior of chromium carbide coatings deposited by air plasma sparing was studied, through wet pin-on-disk wear experiments. During the wear tests, the samples were immersed in corrosive environments consisting of watery hydrochloric acid with the acid concentrations of 5, 10 and 15 vol.%. The wear tests were performed at both room temperature and 80˚C. The results showed that the wet environment significantly increased the wear rate. In addition, the increase of the acid concentration and temperature considerably deteriorated the wear resistance of the coated samples. It was also realized that, compared to the dry condition, the wear mechanism changed from abrasive to adhesive in the wet environment where a tribochemical wear was observed.

Keywords: A. Films; C. Wear resistance; D. Carbides

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1. Introduction

Some of the common engineering materials are not suitable for working at high temperatures. Tungsten alloys are highly oxidized, a growing oxide layer is produced on iron alloys, nickel and cobalt alloys do not show appropriate mechanical properties, and thallium and niobium are highly solutionized at high temperatures. Hence, coatings with active elements are used as a thermal barrier to overcome high-temperature oxidation. These coatings are metal and ceramic layers that react with oxygen and produce a dense layer against the oxidation of the base metal [1-4].

Alumina is one of the coatings used at elevated temperatures, due to its acceptable corrosion resistance. This is, however, highly brittle and is frequently damaged during installation and thermal cycles [2, 5]. This coating has been substituted by MCrAlY coatings since 60 decade [6]. The next generation of these coatings is chromium carbide coatings. These coatings are good barriers against heat with high hardness and strength, appropriate adhesion to substrate and presenting a stable oxide at high temperatures. One of the most common chromium carbides is Cr_3C_2 [1, 7]. These coatings were applied on surfaces through cladding in the early times and could be hence used in complex parts like turbine blades. Newly developed coating methods like electron beam physical vapor deposition (EB-PDV), air plasma sparing (APS) and high velocity oxy fuel (HVOF) are common methods for chromium carbide coatings [8-11]. The chromium carbide is often mixed with nickel and chromium and the coating phenomenon is performed at high temperatures. In this method, the particles of Cr_3C_2 are substituted in the Ni-Cr layer [9].

Thermal spraying methods have commonly been used for coating of thermal barrier coatings (TBC) since 1933. These methods are based on heating of the coating elements and sparing them on the substrate surface [12-14]. The heating of the powders can be performed

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by electricity or flame heating. In the APS method, the powders are heated through an electric arc and a plasma jet is used for heating and accelerating the semi-molten material to the substrate. In this method, the substrate is not regularly heated up to 150 °C; hence, the metallurgical properties of the substrate do not change after coating. The speed of the outlet material is a function of torch design, powder properties, plasma gas, torch working voltage and many other variables. The applied coatings are denser than those created by electric coating methods and can reach 85-90% of theoretical densities [12, 15].

Many studies have focused on the effect of APS of chromium coatings on wear, high temperature wear and corrosion behaviors. Nevertheless, to the best of our knowledge, a few work has dealt with the effect of spontaneous wear and corrosion on the working life of these coatings. This study focused on the effect of corrosive wear at room temperature and 80 °C on the coating deposited on 4340 hot worked steel through pin-on-disk wear testing in dry and watery hydrochloric acidic environments. For further studies, the sample surface was analyzed through scanning electron microscopy and energy dispersive spectroscopy.

2. Experimental procedures

AISI 4340 (DIN 1.6565) steel disks with a nominal composition of 0.4 C, 0.85 Cr, 1.7 Ni, 0.3 Mo and 0.15 Si wt.% were used as the substrate. The sample surface was first sand-blasted in order to reach a rough surface for thermal spray coating. The samples surface was then coated with Cr_3C_2-NiCr through the air plasma spray (APS) method with the parameters listed in Table 1. The coating powder particle size was examined by SEM, where it was clarified that the powder size is in the range of 10-40 μm (Fig. 1) with a relatively spherical morphology.

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The sample surface was then analyzed using a scanning electron microscope (SEM VEGA\ TESCAN). This observation was performed on the coating surface and the cross-section of the coatings. From SEM micrographs, it was found that the coating thickness was about 1 mm. For more accuracy, the coating was analyzed through energy dispersive spectroscopy (EDX VEGA\ TESCAN). Microhardness tests were also carried out by a COOPA MH1 microhardness tester equipped with a Vickers indenter under a load of 100 gr and a load exertion time (dwell time) of 15 s. The average value of 20 separated measurements made at randomly selected points was reported.

Wear tests were carried out by a pin-on-disk wear tester, based on ASTM G99-05, at room temperature (25±5 ºC) in four environments, including air with 30±10% humidity and watery hydrochloric acid with 5%, 10% and 15 vol.% acid concentration. Also, the wear tests was conducted at 80 ºC in the 10 vol.% hydrochloric acid to evaluate the effect of temperature on the corrosion-wear rate of the Cr_3C_2 coating. The wear tests were performed under a load of 10 N at the sliding velocity of 0.08 m/s with the sliding distance of 500 m. Then, the weight loss was measured by an electronic balance with an accuracy of 0.0001 gr and the wear rate was calculated by Eq. 1:

$$Wr = \Delta m/(\rho L F_N) \times 10^3 \quad (1)$$

where Wr is the wear rate in mm^3/Nm; Δm is the weight loss in gr, ρ is the steel density in gr/cm^3; L is the wear distance in meter; and F_N is the load in Newton [16]. For calibration, the first group of the samples was six times tested and it was found that the variation in the results was less than 10% deviation. Thus, each test was performed two to three times. In addition, the worn-out surface of the samples was analyzed through SEM (Oxford Instrument Stereoscan 120 and VEGA\ TESCAN) to study the extent of wear damage and the surface topography, as well as to clarify the predominant wear mechanism.

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3. Results and discussion

The SEM micrograph of the samples is presented in Fig. 2a, which shows a desirable APS coating. Also, image analyzing of the similar pictures by the Clemex (Vision 4.1) software suggested that about 5% porosity exists in the cross-section of the coating (Fig. 2b). These are indicative of an acceptable coating feature, showing the merit of the coating deposition procedure. The EDS analysis of the samples reveals that chromium and nickel exist in the coating, as shown in Fig. 2c, confirming the composite structure of the coating which consists of Cr_3C_2, nickel and chromium. The presence of nickel and chromium in the coating produced a matrix for the particles of Cr_3C_2, leading to a composite structure for the coating. Attributed to this composite structure, the microhardness value was measured to be about 1117 HV, while the hardness of Cr_3C_2 was 2280 HV and that of the nickel and chromium matrix was about 700 HV. The measured hardness value confirms the results of the SEM/EDS analyses (Fig. 2) and clarifies that the coating consists of nickel and chromium matrix along with the Cr_3C_2 particles.

The results of the room-temperature wear tests conducted in the different environments are presented in Fig. 3. As can be clearly observed, the wear rate significantly increases in the acid environments, as compared to the dry sliding wear. On the other hand, it was realized that the wear rate of the samples slightly increases with enhancing the acid concentration. This increase is 6% and 13% for the acid concentration of 10 and 15%, respectively, as compared with the 5% environment. These are a consequence of the corrosive contribution of the acidic environment to wear damage and thereby wear rate. However, to future clarify the related mechanisms and sources, the tested surfaces were studied by SEM and EDS, as below.

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The SEM micrograph of the sample surface dipped in the 15 % acidic environment, without wear testing, is depicted in Fig. 4, which shows a highly corroded feature due to the corrosive effects of the acid. Moreover, it can be inferred that corrosion deteriorates the coating quality and thus increases the affinity of delamination during the wear tests, thereby contributing to high wear rates in these environments.

As presented in Fig. 5, the worn-out surface of the samples shows that the predominant wear mechanism in the dry sliding test is abrasive. This mechanism changes to adhesive in the wet test (Fig. 5b). The wear test mechanisms are different in the dry and wet tests, due to a decreased friction coefficient in the wet environment, where the friction coefficient changed from 0.4 in the dry test to 0.1 in the wet test. Moreover, corrosion increases the affinity of the coating delamination during the wear test. On the other hand, the EDS analysis of the samples shows that the oxygen content of the worn-out surface in the environments of 15 vol.% hydrochloric acid increases vividly for 4% (Fig. 6). This increase is a consequence of the existence of a tribo-chemical wear mechanism in the wet environment, which is due to significant corrosion in the wet environment [17]. This excessive corrosion can also be observed by a severe decrease of the chromium and nickel contents in the worn-out surface at the wet environments, as compared with the dry condition (Fig. 6).

The results of the wear tests done in the 10 vol.% acid solution and the different temperature are presented in Fig. 7, showing an increase of 860% in the wear rate with increasing the testing temperature. This is a consequence of a severe corrosive ability of the solution at the higher temperature. Fig. 8 demonstrates the SEM micrograph of the worn-out surface of the samples in the 10 vol. % acid solution and at 80°C. As can be observed, a less uniform and more damaged feature was obtained in this condition, compared with the dry and room-temperature wear conditions, confirming the higher wear rate of this sample. However, the predominant mechanism is still adhesive like the samples in the same environment at room temperature.

4. Conclusions

The effect of a corrosive environment (watery hydrochloric acid with the acid concentrations of 5, 10 and 15 vol.%) on the wear behavior of AISI 4340 steel coated with a APS chromium carbide coating at room temperature and 80 °C was investigated. The following results were obtained from this study:

1- The corrosive environment increased the wear rate significantly, as compared to the dry wear test. Despite decreasing the friction coefficient from 0.4 in the dry test to 0.1 in the wet test, the increase of the corrosive ability of the wear environment was essentially responsible for the increased wear rate.

2- The increase of the acid concentration during the wear test enhanced the corrosive ability of the wear environment and thereby increased the wear rate for 6% and 13% in the watery hydrochloric acid with the concentrations of 10 and 15% vol, as compared with the 5% acidic environments.

3- The wear mechanism in the dry sliding was abrasive. This mechanism changes in the wet environments to the adhesive. Moreover, a considerable amount of oxygen was found in the worn-out surface of the wet tested samples, resulting from the tribo-chemical wear.

4- The increase of temperature from room temperature to 80 °C increased the wear rate for 8.6 times, but the wear mechanism did not change from adhesive and tribo-chemical.

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Figures

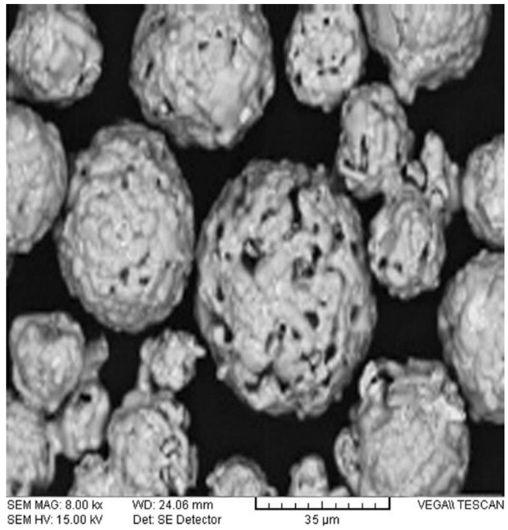

Fig. 1. SEM micrograph of the Cr_3C_2-NiCr particles before coating.

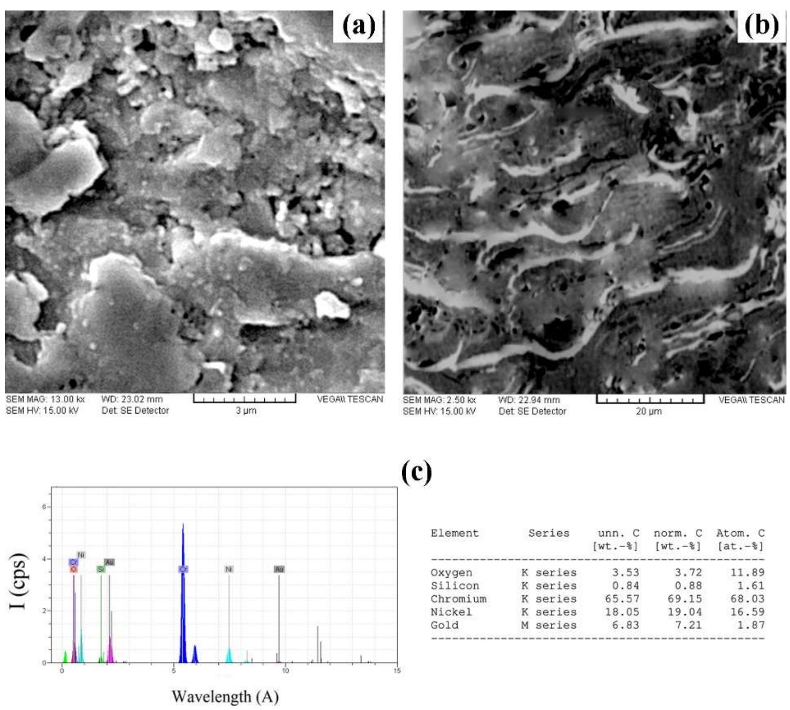

Fig. 2. SEM micrograph of the chromium carbide coating: the top view (a), the cross section (b) and EDS analysis (c).

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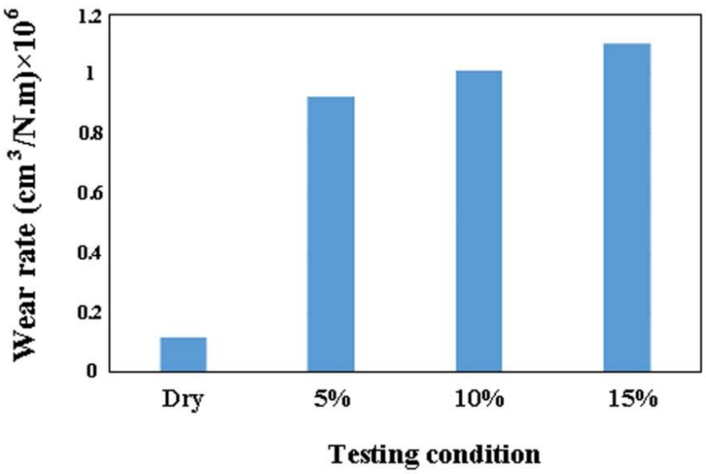

Fig. 3. Wear rate of the samples in the different environments tested at room temperature.

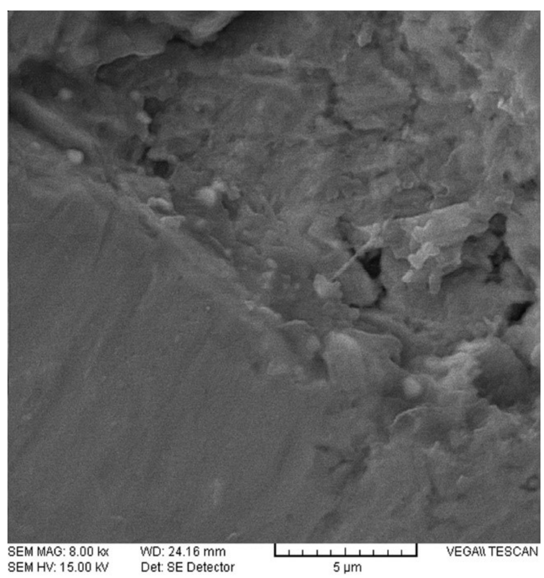

Fig. 4. SEM micrograph of the sample after dipping in the 15% watery hydrochloric acid solution.

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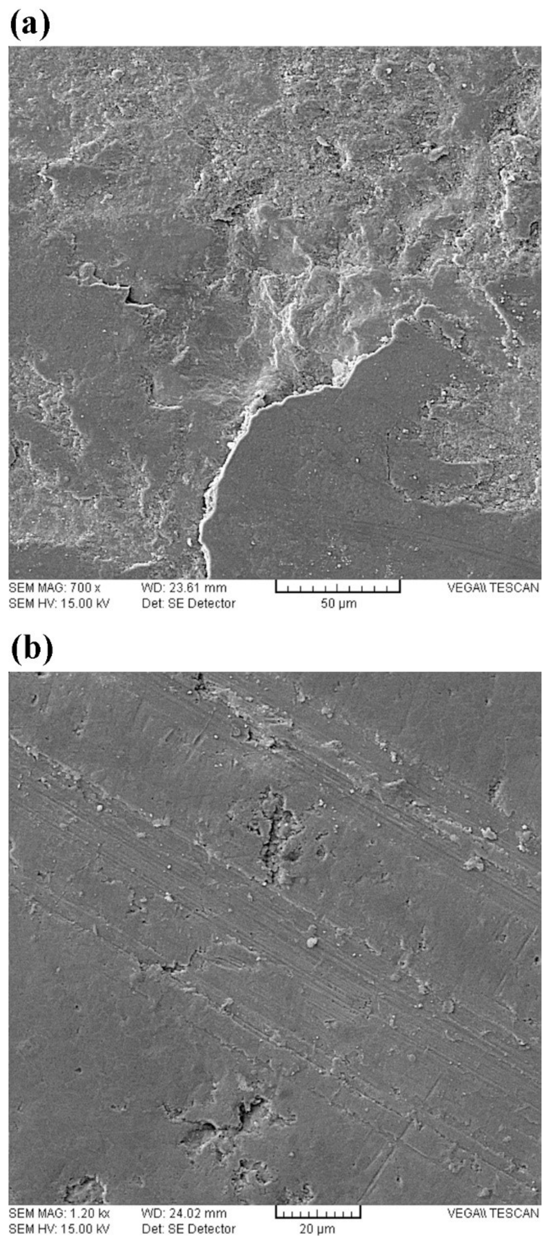

Fig. 5. SEM micrographs of the worn-out surfaces in the dry condition (a) and the watery hydrochloric acid with the concentration of 10 vol.% (b), tested at room temperature.

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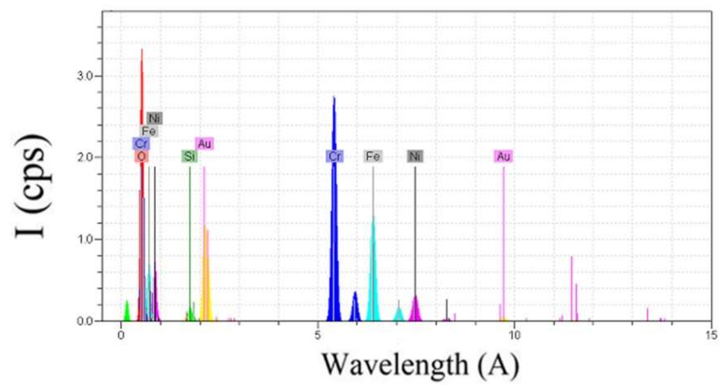

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	14.26	15.36	39.89
Silicon	K series	0.64	0.69	1.02
Chromium	K series	34.09	36.74	29.35
Iron	K series	25.58	27.57	20.51
Nickel	K series	9.50	10.24	7.25
Gold	M series	8.73	9.40	1.98

Fig. 6. EDS analysis of the worn-out of the samples in (a) the dry condition and (b) the 15 % acid solution.

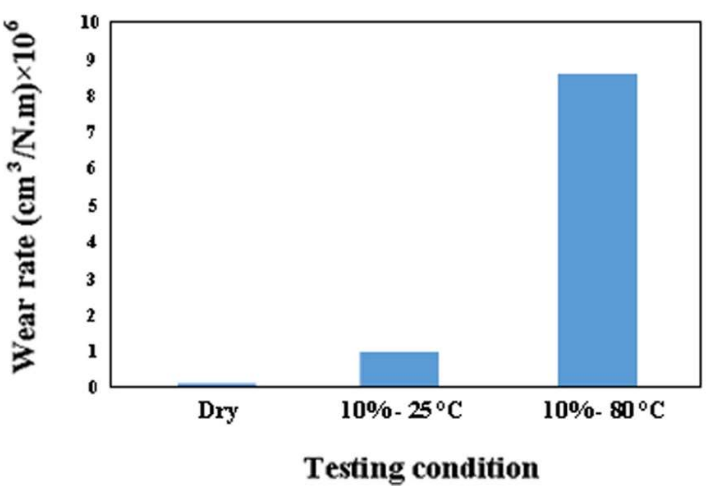

Fig. 7. Wear rate of the samples tested in the different temperatures and environments.

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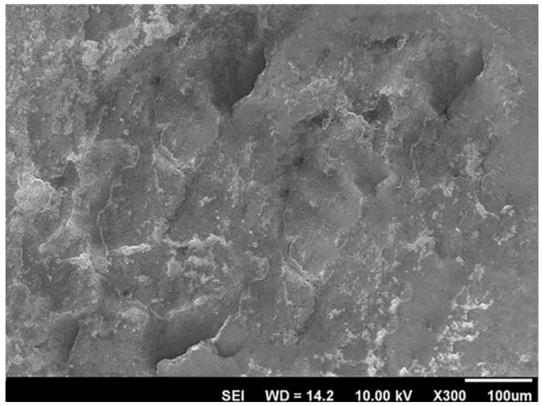

Fig. 8. SEM micrograph of the worn-out surface of the samples tested in the 10 vol. % acid solution and at 80°C.

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Table

Table 1. APS coating conditions.

Current (A)	Voltage (V)	Ar (SPLM)	H_2 (SPLM)	Powder feed rate (gr/min)	Spraying distance (mm)	Gun translation speed (m/min)
600	60	60	5	40	150	75