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Tribochemical behavior of alumina coatings deposited by high-velocity oxy fuel spraying

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Abstract

Alumina is one of the most versatile coatings applied on tools whose working life is reduced due to high wear rate, high temperature, and highly corrosive environments. High-velocity oxy fuel (HVOF) methods are industrially used to deposit this type of coatings. In this study, the effect of the hydrochloric acid concentration on the wear behavior of an HVOF alumina coating was investigated via room-temperature and 60 °C pin-on-disk wear experiments. The results showed that the corrosive environments up to 5% acid did not meaningfully affect the wear damage rate, as compared to the dry condition, due to a contest between friction coefficient and corrosion damage. Nevertheless, the wear rate significantly increased at higher acid concentrations and higher temperatures, since the corrosion effect prevailed over the friction coefficient effect. Also, the predominant wear mechanism was recognized to be adhesive.

Keywords: A. Films; C. Wear resistance; D. Al_2O_3

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1. Introduction

Nowadays, thermal spray coatings are vastly used due to their good adhesion, economic cost, and acceptable wear resistance. In these methods, the powder or coating wire is heated and then sprayed via a highly accelerated stream to the substrate [[1-3]]. The thermal spray methods are divided into electrical and flame heating methods, based on the heating method of the powders or coating wire. Since the electric heating method is more expensive, the flame heating methods are more common in some applications [[2-6]]. The flame can be produced using acetylene, hydrogen, home gas, or hydrocarbon fuels. One of the most common methods of flame heating is high velocity oxy fuel (HVOF) method, due to its high performance, low cost, and acceptable coating-substrate adhesion. In this method, the fuel acts as the heating source. The coating powder is then carried via carrier gases. The high temperature of the flame expands the gas and subsequently increases its velocity to a value higher than the sound velocity [7-11]. As a result, the semi-fused powder strikes the substrate and produces a homogenous thick coat on the substrate surface [[1, 2, 4, 7]]. The HVOF coating can be applied via pulse or continuous methods. In the pulse HVOF, an spark plug produces a pulse gas explosion. This explosion accelerates the carrier gas and powder, thereby impacting the powder towards the substrate. On the contrary, in the continuous method, a gun is designed and utilized in such a manner that accelerates the carrier gas to high velocities and subsequently coats the substrate. The first method is more common due to its higher velocity, more homogeneous coating, less porosity, and higher coating efficiency [[1, 8-12]].

Aluminum oxide (alumina) is one of the first coatings which have been applied in thermal spray methods. Alumina is attractive to engineers due to its high wear resistance, acceptable corrosion resistance, and good thermal insulating behaviors. The certain disadvantages of alumina coatings (particularly its brittleness) restrict its use due to the

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increased damage probability during maintenance and handling. However, the alumina coating is commonly applied on devices used in severe situations [[13-15]].

Many studies have focused on the effect of HVOF alumina coatings on the wear, high temperature wear, and corrosion behavior. Nevertheless, to the best of our knowledge, little studies have focused on the effect of spontaneous wear and corrosion on the working life of these coatings. In this study, the corrosive wear of an alumina coating deposited on 4340 hot-worked tool steel at room temperature and 60°C was investigated via pin-on-disk wear tests in dry and watery hydrochloric acidic environments. For further studies, the surfaces were studied via scanning electron microscope and energy dispersive spectroscopy.

2. Experimental Procedures

A rod of AISI 4340 (DIN 1.6565) tool steel with the diameter of 18 mm and the nominal composition of 0.4 C-0.85 Cr-1.7 Ni-0.3 Mo-0.15 Si (wt%) is cut into disks with the height of 2 mm. Afterwards, the sample surfaces is ground to No. 1000 emery paper to reach a smooth surface for coating. The surfaces were then coated by alumina (the mean powder particle size is ~ 20 μm) using the HVOF method. The HVOF coating conditions are listed in Table 1.

The samples were then studied using a scanning electron microscope (SEM VEGA\ TESCAN). This examination was performed on both the coating surfaces and the cross-section of the coatings. It was clarified from the SEM micrographs that the coating thicknesses were approximately 240 μm. Also, the coating was analyzed by energy dispersive spectroscopy (EDX VEGA\ TESCAN).

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Wear tests were carried out using a pin-on-disk wear tester using steel pins with the hardness of 68 HRC, based on ASTM G99-05 [[16]]. The wear tests were done at room temperature (25±5 ºC) in four environments, including air with 30±10% humidity and watery hydrochloric acidic medium with 5, 10 and 15 vol.% acid. The wear tests were also conducted at 60 ºC in 10 vol% hydrochloric acid to evaluate the effect of high temperatures on the corrosion rate of the alumina coating. The wear tests were conducted under the load of 2 N and the sliding velocity of 0.05 m/s. The sliding distance was 800 m and the weight loss was calculated via an electronic balance with an accuracy of 0.0001 gr. 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, the weight loss in gr, ρ, the steel density in gr/cm^3; L, the wear distance in meter; and F_N, the load in Newton. The worn-out surface of the samples was analyzed by SEM to study the extent of the wear damage and topography of the surface.

3. Results and discussion

The SEM image and EDX analysis of the sample surface are shown in Fig. 1. According to this analysis, a homogenous and crack-free coating, essentially containing aluminum and oxygen, i.e. alumina, has been deposited on the tool steel, which is indicative of the merit of the coating procedure.

The corrosion resistance of the coated sample was qualitatively analyzed by immersing in the different environments, including watery hydrochloric acid with the acid concentrations of 5, 10 and 15 vol.%. After 3 h, the sample surface was cleaned by ethanol

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and then analyzed using SEM and EDX (Fig. 2). As clear in this figure, the increase of the acid concentration enhances the corrosion rate, via producing a more porous and damaged surface. Indeed, the corrosion products of the surface can be delaminated from their initial places, so that the sample surface comparatively shows a rough feature in the more corrosive environments. On the other hand, the EDX analysis shows that the corrosion rate is not too high to reveal the iron element which is present in the substrate. Also, the amount of chlorine in the surfaces increases with increasing the acid concentration, since chlorine is trapped in the surface pores and completely does not remove even after washing. Indeed, the increase of the acid concentration leads to an increase in the sample porosity and thereby in the value of trapped chlorine. In order to study the effect of temperature on the corrosion behavior of the alumina coating, one group of the samples was immersed in the 5 vol% acidic environments at 60 °C. The SEM image and EDX analysis of these samples (Fig. 3) show a highly damaged surface with the higher contents of trapped chlorine, as compared to the lower temperature experiments, via local dissolution or weakening of adhesion.

The wear test results show that the wear rate of the samples tested in air is almost equal to that tested in the wet environment of 5% acid (Fig. 4), despite the higher corrosive rate of the latter environment, as indicated in Fig. 2. A consideration to other tribological results demonstrates that, due to the lubricating effect of the wet environment, the friction coefficient is significantly decreased from 0.9 in the dry environment to below 0.3 in the wet 5% acid environment. A contest between the corrosion rate and friction coefficient in the two mentioned environments dictates that the wear rate meaningfully does not change by using 5% acid solution, as compared to the wet condition. Nonetheless, the increase of the acid concentration to 10 and 15 % enhances the wear rate by 16 and 44%, respectively, as depicted in Fig. 4. The increase of the acid concentration increases the corrosiveness of the

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environment, thereby increasing the instability of the coating. In other words, the coating is locally dissolved or weakened in adhesion and thereby can be delaminated more easily during the wear test. This delamination and instability increase the wear rate at the higher acid concentrations (Fig. 4). Indeed, in contrast to the tests conducted in the 5 % acid solution, the positive effect of the friction coefficient on the erosion behavior cannot balance the deleterious effect of corrosion in the higher concentrations of acid.

The SEM micrographs of the worn-out surface show that the wear mechanism is adhesive and the surface damages are similar in the dry and 5% acid environments. Furthermore, as the acid concentration increases, the surfaces of the samples show more severe wear features (Fig. 5). The EDX analysis of the worn-out surface of the samples shows that a higher concentration of iron is detected on the sample surfaces which were tested in the higher acid concentrations (Fig. 6). This situation is a consequence of a more damaged coating in the more severe environments.

Further wear tests were conducted at 60 °C in wet environments with 5% acid. The results show that the enhancement of temperature remarkably increases the damage rate by 16.65 times, as compared with the same samples tested at room temperature (Fig. 7). This behavior can be explained via the significant increase of corrosion damage at high temperatures. The SEM micrograph of the worn-out surfaces shows a very porous coating, which is a consequence of the high damage rate at the high temperature (Fig. 8). The EDX analysis of the sample shows a higher degree of chlorine remaining in the surface porosity. Furthermore, the higher contents of iron are observed as the result of higher erosion rate in this sample (Fig. 8).

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4. Conclusions

In this study, the tribochemical wear behavior of an alumina coating was investigated via pin-on-disk wear tests in dry and wet 5, 10 and 15 vol % hydrochloric conditions, at room temperature and 60 °C. The following conclusions could be drawn from this study:

1. At high acid concentrations (>10 vol%), the acid corrodes the coating and makes an unstable layer which is not resistant to wear.
2. The wear rates of the dry and wet 5% hydrochloric acid environments were not vividly different.
3. Compared to the 5% acidic environment, the increase of the acid concentration to 10 and 15% increased the corrosion rate by 16 and 44%, respectively.
4. The increase of temperature from room temperature to 60 °C increased the wear damage rate by 16.65 times, due to a more unstable layer produced as a result of concurrent effects of corrosive environment and high temperature.
5. The predominant wear mechanism was the adhesive wear.

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Table:

Table .1. HVOF coating process parameters.

Parameter	Fuel	Fuel flow rate	Powder feeding rate	Spray distance	Oxygen flow rate	Oxygen pressure	Oxygen and fuel temperature
Value	Kerosene	280 ml/min	70 g/min	50.8 cm	835 l/min	2 MPa	Room temperature

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Figure:

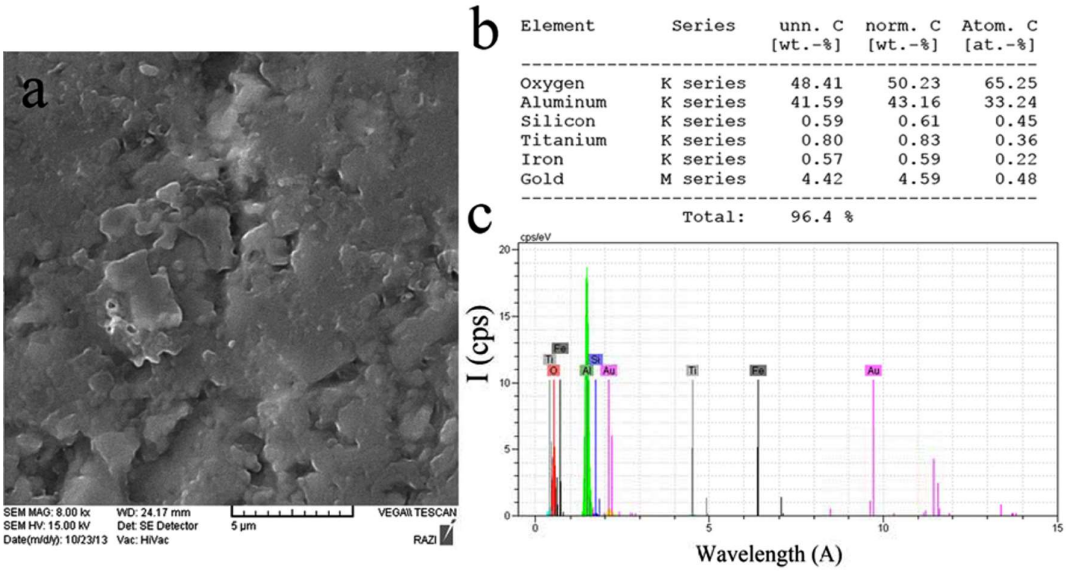

Fig. 1. SEM micrograph (a) and EDX analysis (b) and (c) of the coated surface.

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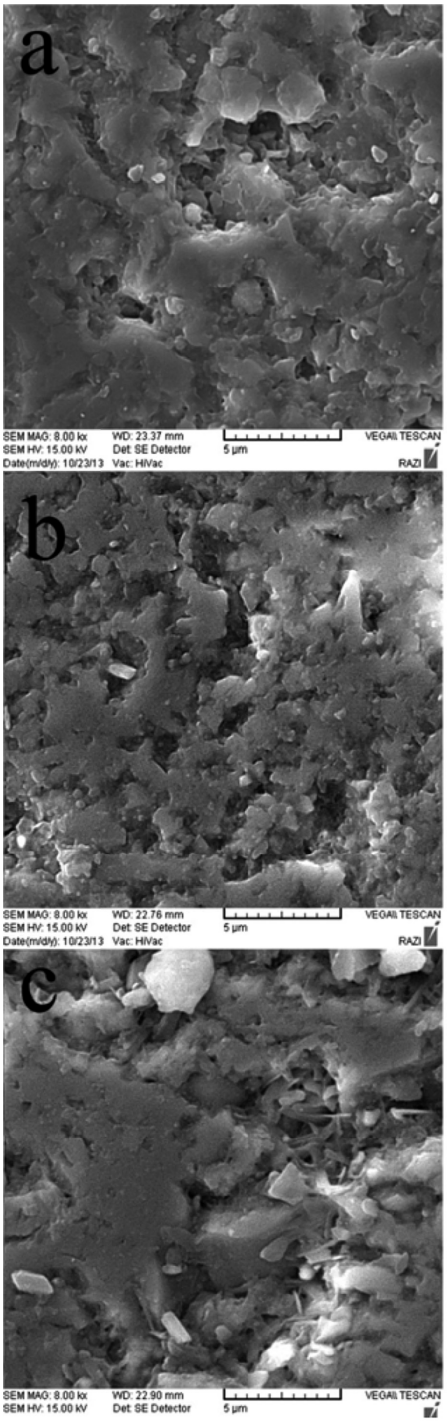

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	49.94	50.61	65.12
Aluminum	K series	43.64	44.23	33.75
Chlorine	K series	0.27	0.27	0.16
Titanium	K series	1.41	1.43	0.61
Iron	K series	0.00	0.00	0.00
Gold	M series	3.41	3.46	0.36
	Total:	98.7 %		

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	49.91	49.80	64.64
Sodium	K series	0.39	0.39	0.35
Aluminium	K series	44.11	44.01	33.88
Silicon	K series	0.24	0.24	0.18
Chlorine	K series	0.37	0.37	0.21
Titanium	K series	0.59	0.59	0.26
Gold	M series	4.61	4.60	0.48
	Total:	100.2 %		

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	49.70	51.11	65.49
Sodium	K series	0.62	0.64	0.57
Aluminium	K series	41.93	43.12	32.76
Chlorine	K series	0.78	0.80	0.46
Titanium	K series	0.80	0.82	0.35
Gold	M series	3.41	3.51	0.37
	Total:	97.2 %		

Fig. 2. SEM image and EDX analysis of the sample surface after 3 hours of immersion in the watery hydrochloric acid with the different concentrations of 5% (a), 10% (b), and 15% (c) at room temperature.

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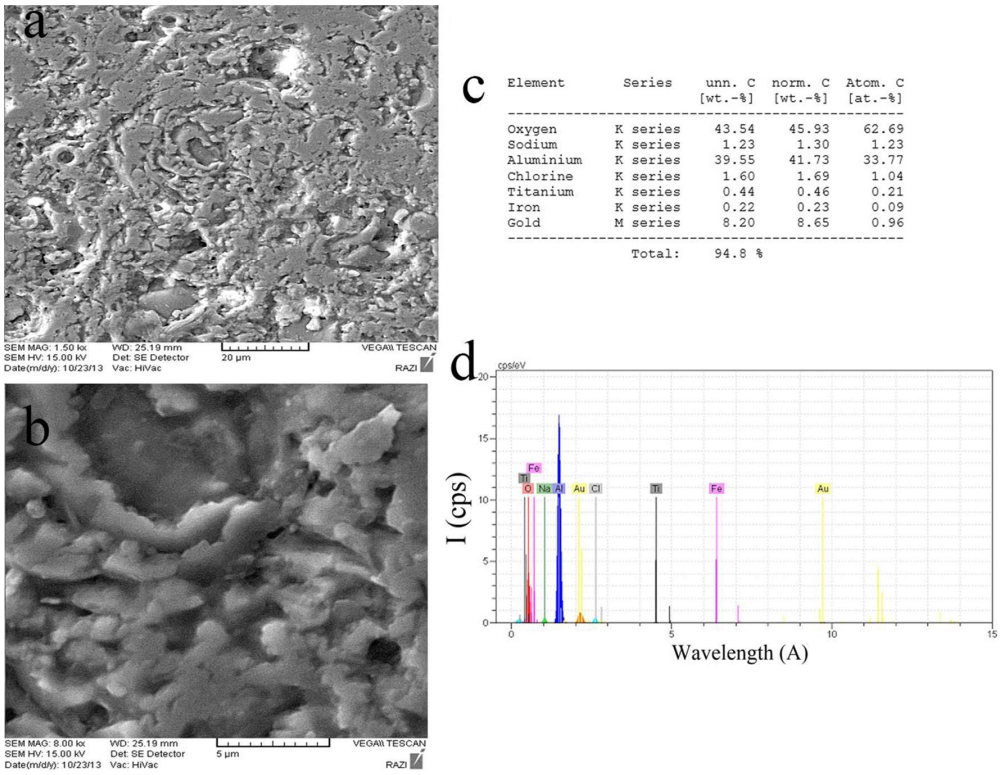

Fig. 3. SEM image (a and b) and EDX analysis (c and d) of the sample surface after 3 hours of immersion in the 5 vol% watery hydrochloric acid at 60 °C.

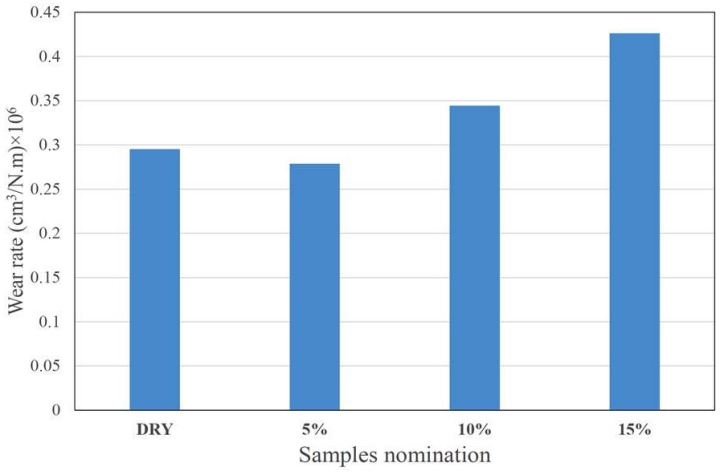

Fig. 4. Wear rate of the samples under the load of 2 N after 800 meter sliding in the different environments at room temperature.

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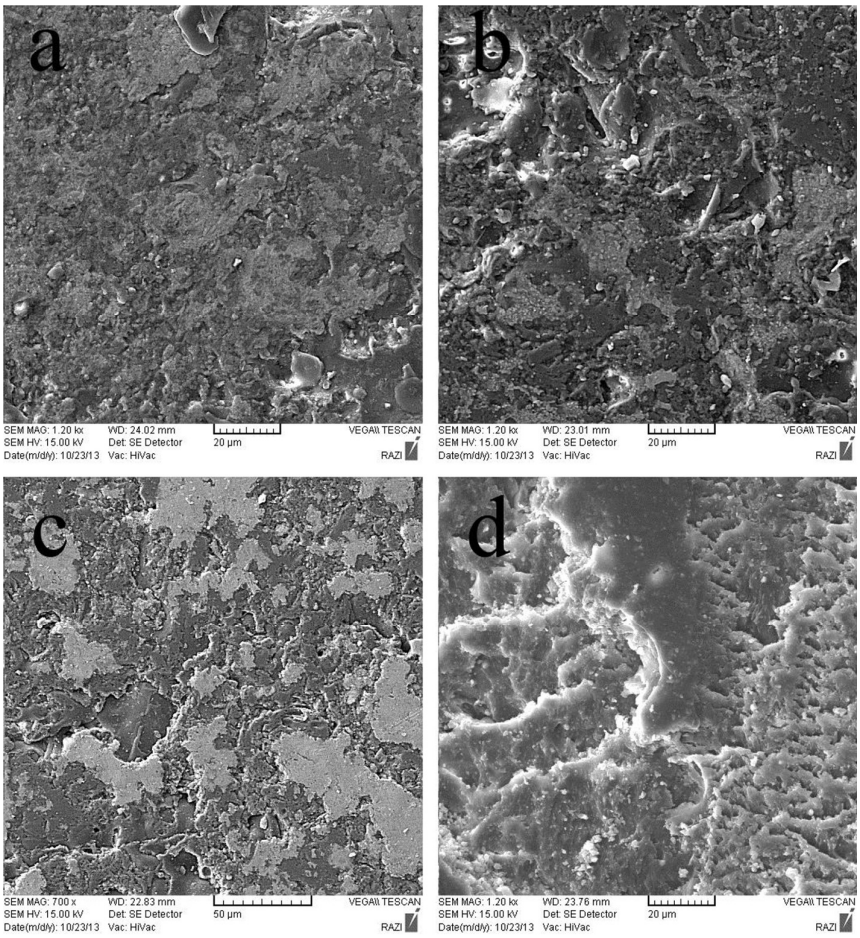

Fig. 5. SEM micrographs of the worn-out surface of the samples after 800 meter sliding in the dry (a), 5% (b), 10% (c), and 15% (d) hydrochloric acid environments at room temperature.

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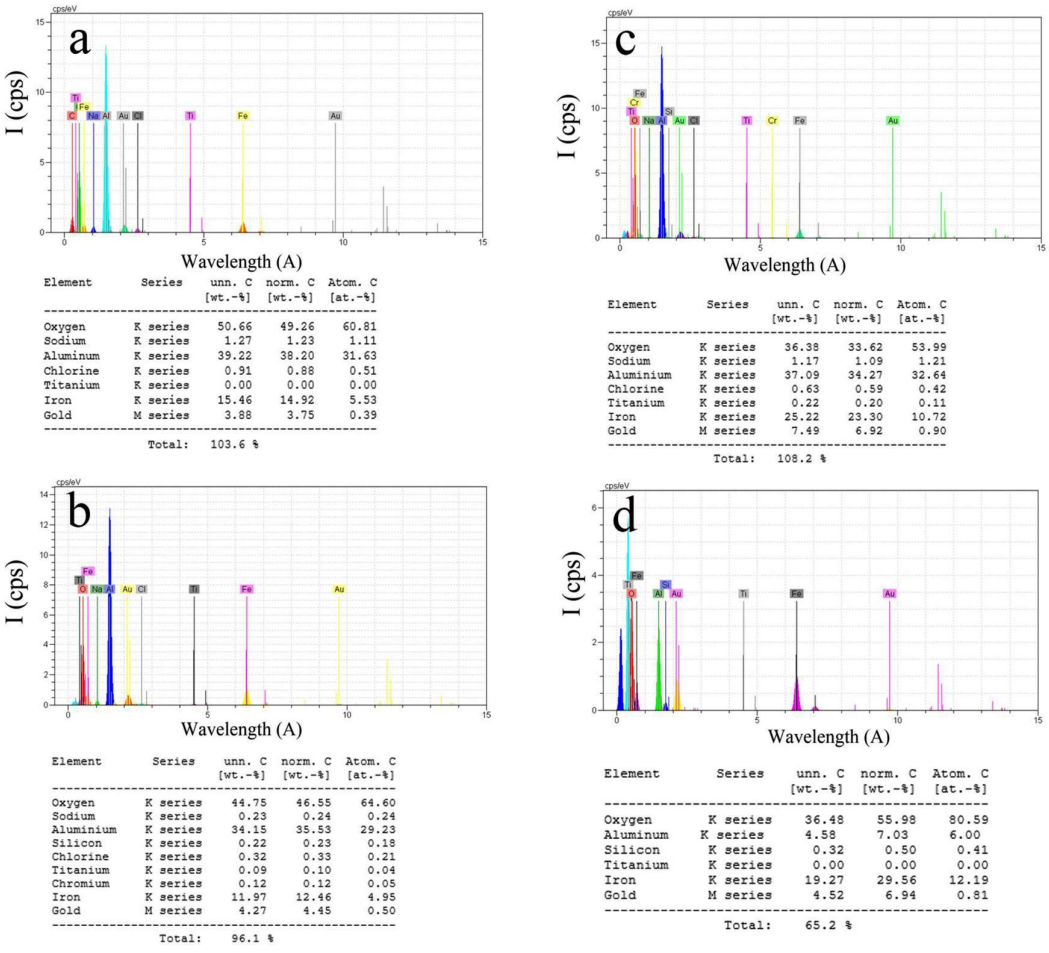

Fig. 6. EDX analysis of the worn-out surface of the samples in the dry (a), 5% (b), 10% (c), and 15% (d) hydrochloric acid environments at room temperature.

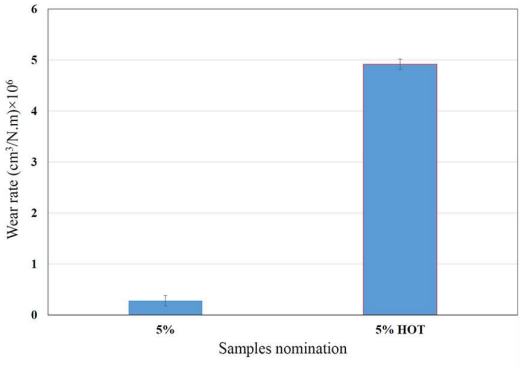

Fig. 7. Wear rate of the samples in the 5% hydrochloric acid environment at room temperature and 60°C (hot).

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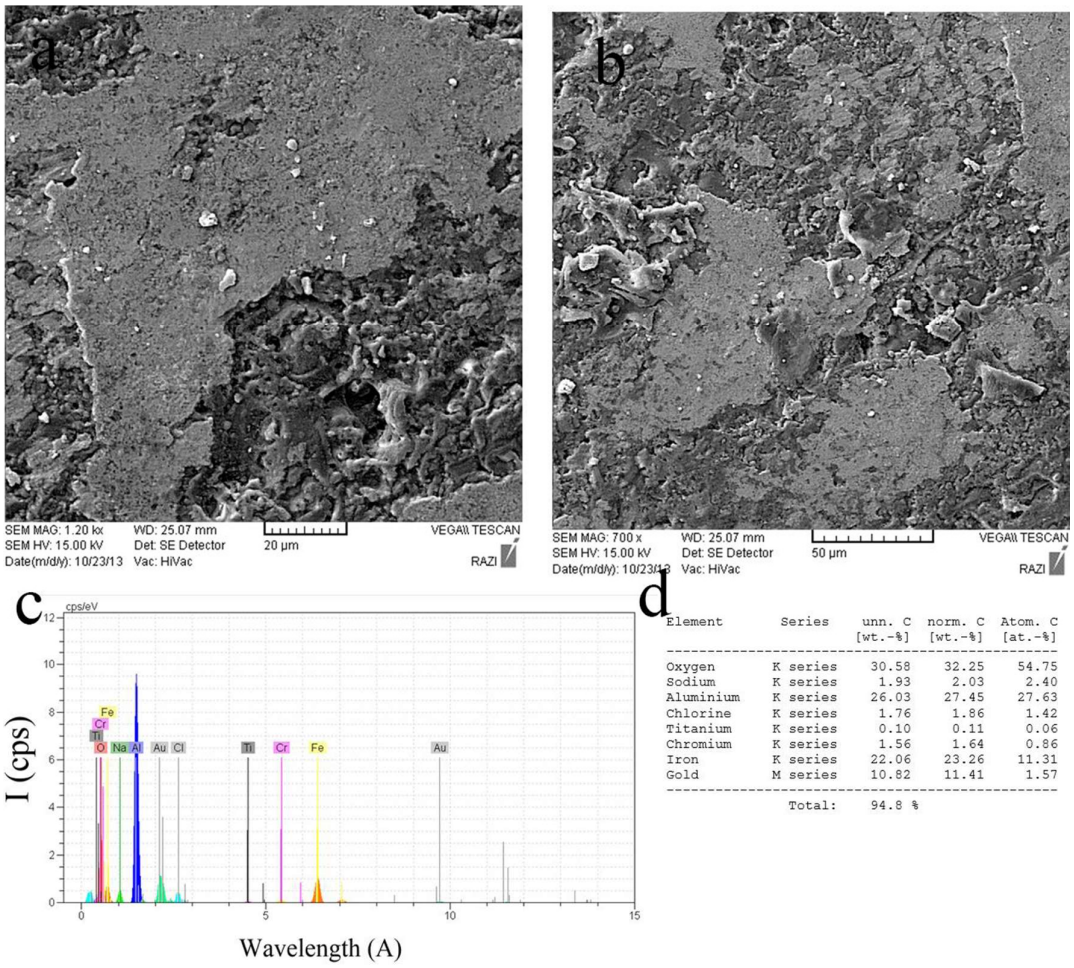

Fig. 8. SEM micrograph (a and b) and EDX analysis (c and d) of the worn-out surfaces of the sample in the 5% hydrochloric acid at 60°C.