JTTEE5 6:205-210
©ASM International

Wear and Corrosion Properties of Plasma Sprayed Al_2O_3 and Cr_2O_3 Coatings Sealed by Aluminum Phosphates

E.M. Leivo, M.S. Vippola, P.P.A. Sorsa, P.M.J. Vuoristo, and T.A. Mäntylä

Plasma-sprayed aluminum oxide (Al_2O_3) and chromium oxide (Cr_2O_3) coatings were sealed by aluminum phosphates. Phosphates were formed throughout the coating, down to the substrate, and were verified by scanning electron microscopy and hardness measurements. The sealing increased the hardness of the coatings by 200 to 300 Vickers hardness (HV) units. Abrasion and erosion wear resistances were increased by the sealing treatment. Sealing also substantially closed the open porosity, as shown in electrochemical corrosion tests. The sealed structures had good resistance against corrosion during 30 days of immersion in both acidic and alkaline solutions with pH values from 0 to 10. No decrease in abrasion wear resistance was observed after immersion.

Keywords alumina, chromia, corrosion properties, sealed coatings, wear resistance

1. Introduction

PLASMA-SPRAYED aluminum oxide and chromium oxide coatings are widely used to improve the resistance of metallic components against various types of wear and corrosion. Alumina is mainly used as a wear resistant coating in mechanical applications and as a corrosion resistant coating. Alumina coatings consist of metastable γ-phase instead of the stable α-phase, which has superior mechanical properties. The γ-phase is formed during the rapid solidification of molten particles. Chromia coatings have better corrosion and abrasion resistance than alumina, but they are more expensive. Chromia has excellent hardness and does not react with most alkalis and acids (Ref 1 and 2).

Plasma-sprayed coatings are composed of layers that are formed when liquid droplets flatten and solidify on the surface of the substrate (Ref 3). Because of their lamellar structure, the coatings have varying amounts of pores. Pores and incomplete bonding between lamellae decrease the strength, wear resistance, and corrosion resistance of the coatings (Ref 4).

The density of plasma-sprayed coatings can be increased by optimizing plasma parameters and spraying powders or by using post-treatments. These post-treatments include different kinds of sealing treatments, which can be completed with organic or inorganic sealants. Although sealing with organic sealants is a common practice in everyday spraying, the use of inorganic sealants is far less frequent (Ref 5 to 8). Sealing treatment decreases the number of open pores, which are linked together by channels. Open pores destroy corrosion protection because they allow a path for the electrolyte from the outer surface to the substrate (Ref 3).

Aluminum phosphates are used as a binder material in refractory ceramics. Phosphate-bonded refractories have improved green strength, high-temperature stability, and improved abrasion resistance. Phosphates are formed by the chemical reaction of phosphoric acid and metal oxides at elevated temperatures (Ref 9 to 11). Phosphate-based materials can also be used as sealants for thermally sprayed ceramic oxide coatings to improve strength and to close the open porosity of the coatings. Recently, it was reported that aluminum phosphate sealing treatment improves the wear resistance and corrosion resistance of oxide coatings (Ref 6 to 8).

According to Ref 6 to 8, aluminum phosphate sealing treatment is an effective sealing method for oxide coatings. This study is a continuation of previous studies and includes more extensive wear and corrosion testing of aluminum phosphate sealed, plasma-sprayed alumina and chromia coatings.

2. Experimental Procedure

Aluminum oxide and chromium oxide coatings were plasma sprayed using the Plasma-Technik A3000S system (Sulzer Metco AG, Wohlen, Switzerland). Spray powders were Amperit 740.1 (Al_2O_3) and Amperit 704.1 (Cr_2O_3) (both by H.C. Starck GmbH & Co. KG, Dusseldorf, Germany). Ni-20%Cr bond coatings (Amdry 4540; Sulzer Metco AG, Wohlen, Switzerland) were used for Cr_2O_3 samples, except for samples that were made for electrochemical corrosion tests and acidic liquid immersion tests. The bond coating was also used for Al_2O_3 coatings that were immersed in tap water and basic liquids. The coatings were 350 to 400 μm thick.

The substrate material was Fe 37 (St 37) low alloy steel for most of the coatings. AISI 316 stainless steel substrates were used for the coatings that were immersed into 0-water in paper processing, tap water and NaOH solution, and SS2377 (AISI 321) duplex steel was used for samples that were immersed in acidic solutions.

2.1 *Sealing Treatment*

The coatings were sealed by an $Al(OH)_3$-H_3PO_4 solution. The ratio $Al(OH)_3$:H_3PO_4 was 1:4.2 by weight, and 20 wt% deionized water was added to the solution. The solution was im-

---

E.M. Leivo, M.S. Vippola, P.P.A. Sorsa, P.M.J. Vuoristo, and **T.A. Mäntylä,** Tampere University of Technology, Institute of Materials Science, FIN-33101 Tampere, Finland.

pregnated into the coatings at room temperature under normal pressure. The impregnation time was more than 12 h and was followed by heat treatment of the specimens in three steps: 2 h each at 100 °C and 200 °C and 2 h at 400 °C. The time-temperature cycle for the heat treatment is shown in Fig. 1.

2.2 *Microstructure, Hardness, and Phase Analysis*

Microstructures of the coatings were studied using a Philips SEM 515 (Philips Export B.V., Eindhoven, The Netherlands) scanning electron microscope from the cross sections of the coatings. Hardness values were also measured for the cross sections at four distances (0.05, 0.10, 0.15, and 0.20 mm) from the top of the coatings. Vickers hardnesses were measured using a weight of 0.3 kg. Phase analyses were made with Siemens D-500 (Siemens, Karlsruhe, Germany) x-ray diffraction equipment to determine the different crystalline phases in the coatings, especially the phases formed in sealed coatings and phases formed after the corrosion tests.

2.3 *Wear Tests*

Wear resistance of the sealed and unsealed coatings was studied by a rubber wheel abrasion test and a solid particle erosion test. The rubber wheel abrasion test equipment is a modified version of the equipment described in standard ASTM G65-85. The samples (20 by 20 by 50 mm) were pressed against the rubber wheel with a force of 13 N. Quartz sand (0.1 to 0.6 mm) was used as an abrasive, and the total wear length was 5904 m.

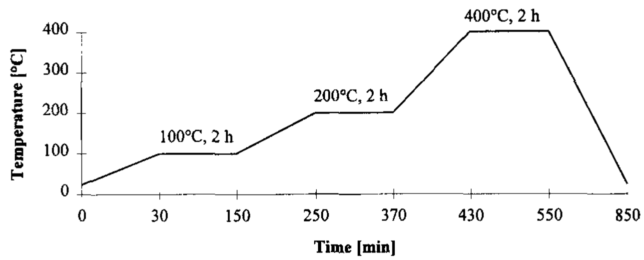


Fig. 1 Time-temperature cycle of heat treatment, in which the impregnated liquid is transformed to aluminum phosphate

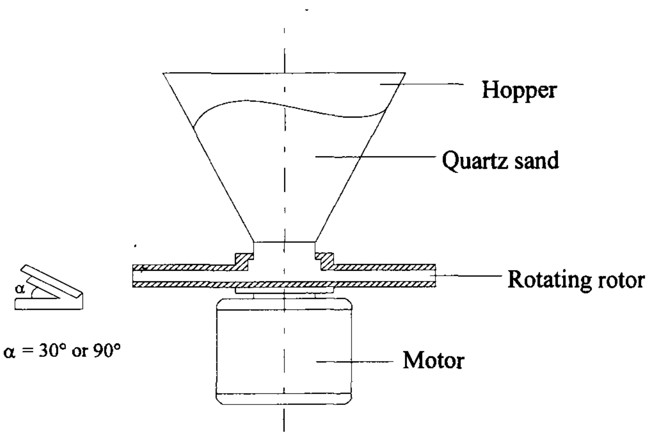


Fig. 2 Schematic presentation of the particle erosion wear tester

Particle erosion tests were conducted with a centrifugal accelerator using quartz sand (particle size 0.1 to 0.6 mm) as an erodent. In the test, sand particles impacted on the coating surface with a velocity of 80 m/s, impingement at angles of 90° and 30° (Fig. 2). Dimensions of the samples were 25 by 15 by 4 mm.

2.4 *Corrosion Tests*

Corrosion behavior was studied by electrochemical potentiodynamic polarization measurements and liquid immersion tests. Potentiodynamic polarization curves were measured by the EG&G Model 273A potentiostatic device (EG&G Instruments, Princeton, NJ 08543). The sample was placed in a special sample holder with only the surface of the coating in contact with the electrolyte. The polarized area was 2.3 cm^2. A 3.5% NaCl solution was used as the electrolyte, and the tests were performed at room temperature. The open porosity from the surface down to the substrate can be detected using the potentiodynamic measurements. Low current densities indicate that the coating has little open porosity. The reference electrode was Ag/AgCl, and the counter electrode was platinum.

In liquid immersion tests, 5 different liquids were used. Liquid compositions are given in Table 1.

The immersion time was 30 days. To determine if corrosion had weakened the structure of the coatings, rubber wheel abrasion tests were performed after the immersion. The wear test parameters were given previously.

Table 1 Composition of the liquids used in liquid immersion tests

Liquid	Composition	pH
L1, a process liquid used in chemical process industry	$FeTiO_2$ 150 to 300 g/l $H_2SO_4 \approx 200$ g/l $TiOSO_4 \approx 200$ g/l $Ti^{3+} \approx 0.5$ g/l $Fe^{2+} \approx 100$ g/l water	0
L2, 0-water in paper processing	NaCl 0.49 g/l Na_2SO_4 0.89 g/l CH_3COOH (to adjust the pH to 4.5) deionized water	4.5
L3, tap water	...	7.8
L4, NaOH solution	NaOH (to adjust the pH to 10) deionized water	10
L5, NaOH solution	NaOH (to adjust the pH to 14) deionized water	14

Table 2 Vickers hardness values of the as-sprayed and aluminum phosphate sealed (AP) Al_2O_3 and Cr_2O_3 coatings

Distance from the top of the coating, mm	Al_2O_3	Al_2O_3 +AP	Cr_2O_3	Cr_2O_3 +AP
0.05	...	1240	...	1410
0.10	...	1000	...	1320
0.15	...	1210	...	1290
0.20	...	1020	...	1240
Mean value	920	1120	1010	1320

3. Results and Discussion

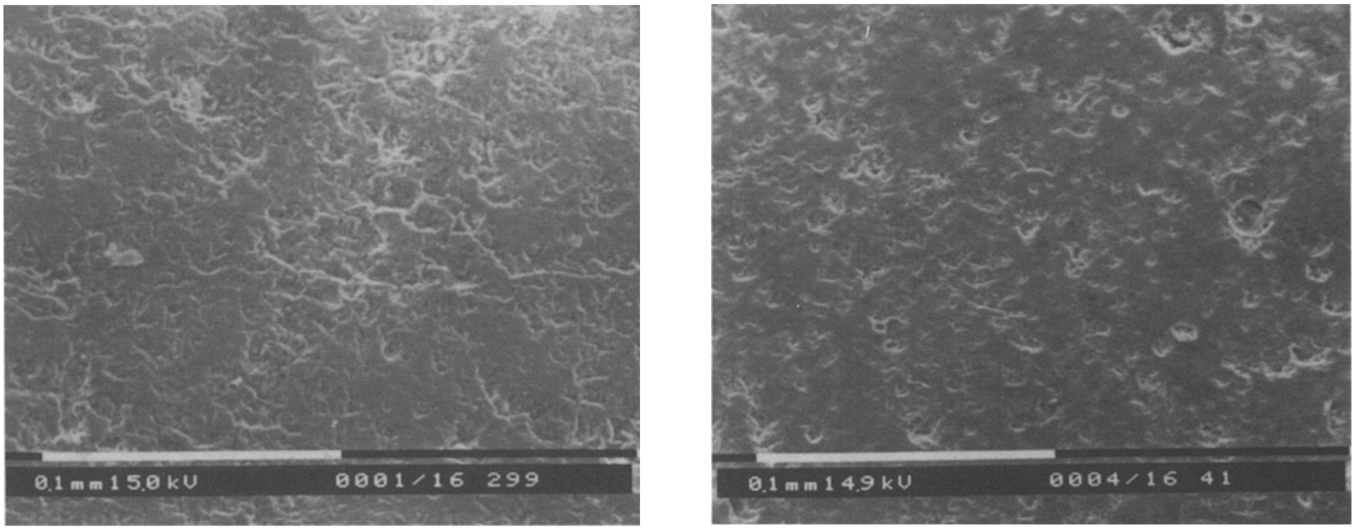
3.1 *Microstructure and Hardness*

Aluminum phosphate treatment densified both Al_2O_3 and Cr_2O_3 coating microstructures (Fig. 3 and 4). The structure is denser after sealing. Aluminum phosphates formed during the sealing treatment were aluminum orthophosphate, $AlPO_4$, and aluminum metaphosphate, $Al(PO_3)_3$. These phases were detected by x-ray diffraction analysis.

The $Al(OH)_3$-H_3PO_4 solution penetrated deeply into the pores of the coatings and was verified by increases in Vickers hardness. Hardnesses at different depths of the sealed coatings were higher than the hardnesses of comparable unsealed coatings. This also reflects a chemical reaction between the sealant and the ceramics. The sealing treatment increased the hardness of the plasma-sprayed alumina from 920 $HV_{0.3}$ to 1120 $HV_{0.3}$ and the hardness of the plasma-sprayed chromia from 1010 $HV_{0.3}$ to 1320 $HV_{0.3}$. The hardness value of the unsealed alumina is typical of an atmospheric plasma spraying (APS) alumina coating, but the hardness of the unsealed chromia was lower than usual. Table 2 shows the measured Vickers hardness values.

3.2 *Wear Resistance*

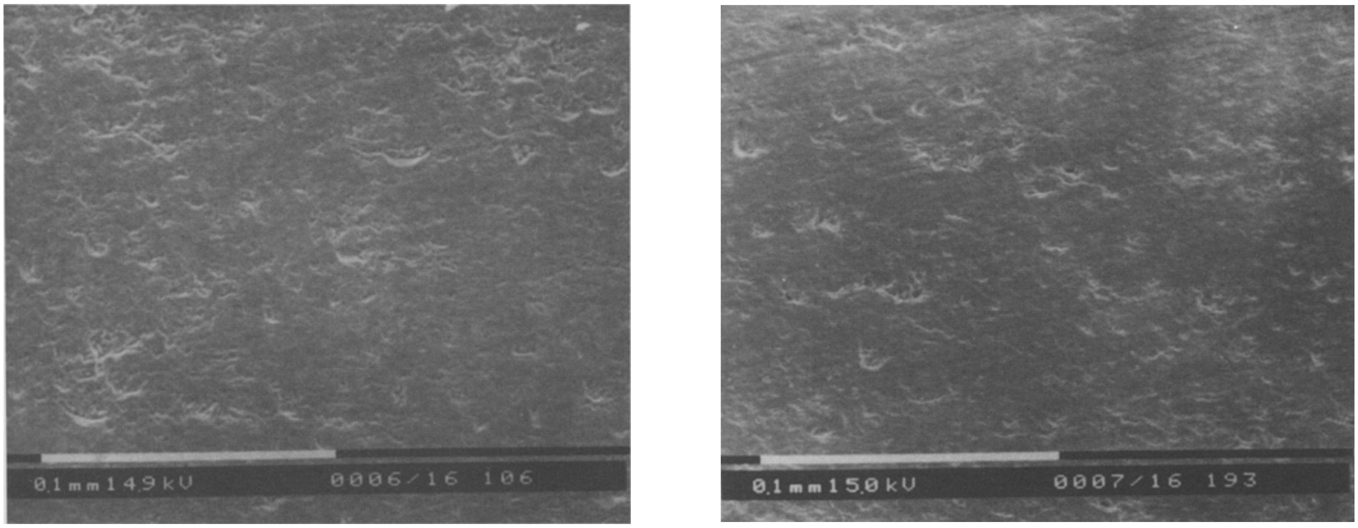
Abrasive wear resistance was significantly increased by the aluminum phosphate sealing treatment for all coatings studied (Fig. 5). Abrasive weight losses of the alumina coatings decreased from 302 to 41 mg by sealing, and the weight losses of



(a)

(b)

Fig. 3 Microstructures of plasma-sprayed Al_2O_3 coatings: (a) as-sprayed Al_2O_3 coating and (b) aluminum phosphate sealed Al_2O_3 coating



(a)

(b)

Fig. 4 Microstructures of plasma-sprayed Cr_2O_3 coatings: (a) as-sprayed Cr_2O_3 coating and (b) aluminum phosphate sealed Cr_2O_3 coating the chromia coatings decreased from 135 to 37 mg. Alumina improved 7×, and chromia improved 4×. Wear traces of the as-sprayed coatings were very rough, which indicates that the material was removed in large pieces the size of a lamella. The sealed coatings reacted differently. They wore smoothly, possibly because the aluminum phosphate treatment bound and glued the lamellae together. Wear traces were featureless and smooth, so the particles removed were very fine. Wear traces of abrasive wear tested Al_2O_3 and Cr_2O_3 coatings are shown in Fig. 6 and 7, respectively.

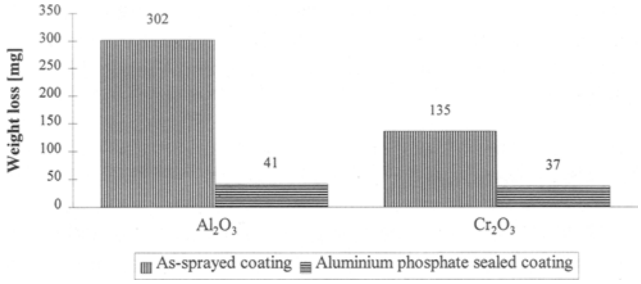
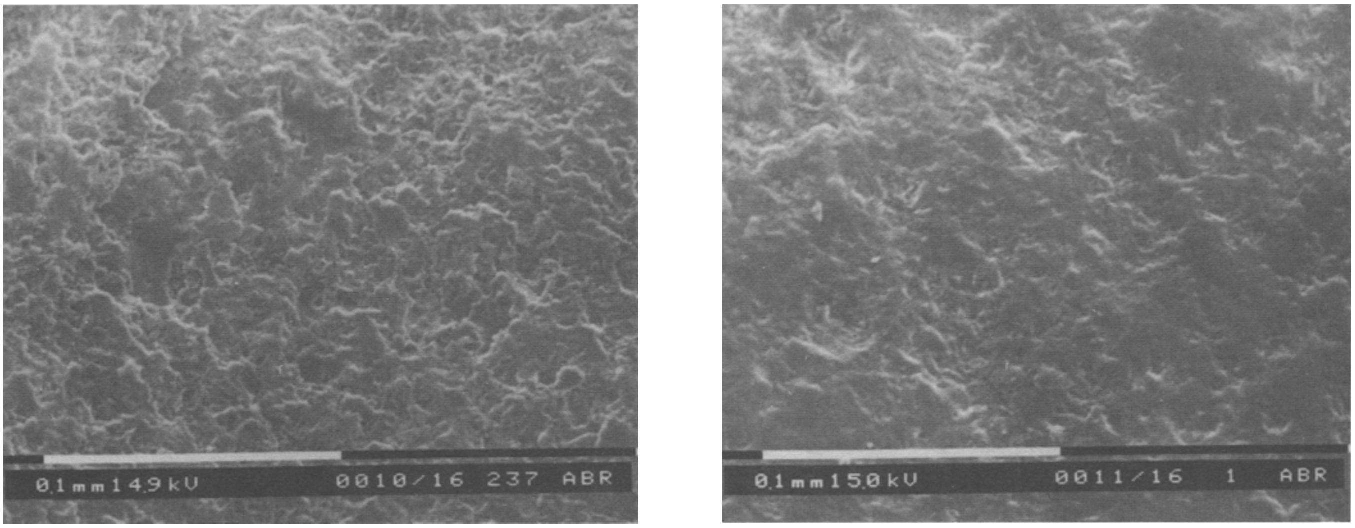


Fig. 5 Results of the rubber wheel abrasive wear test for the as-sprayed and the aluminum phosphate sealed Al_2O_3 and Cr_2O_3 coatings

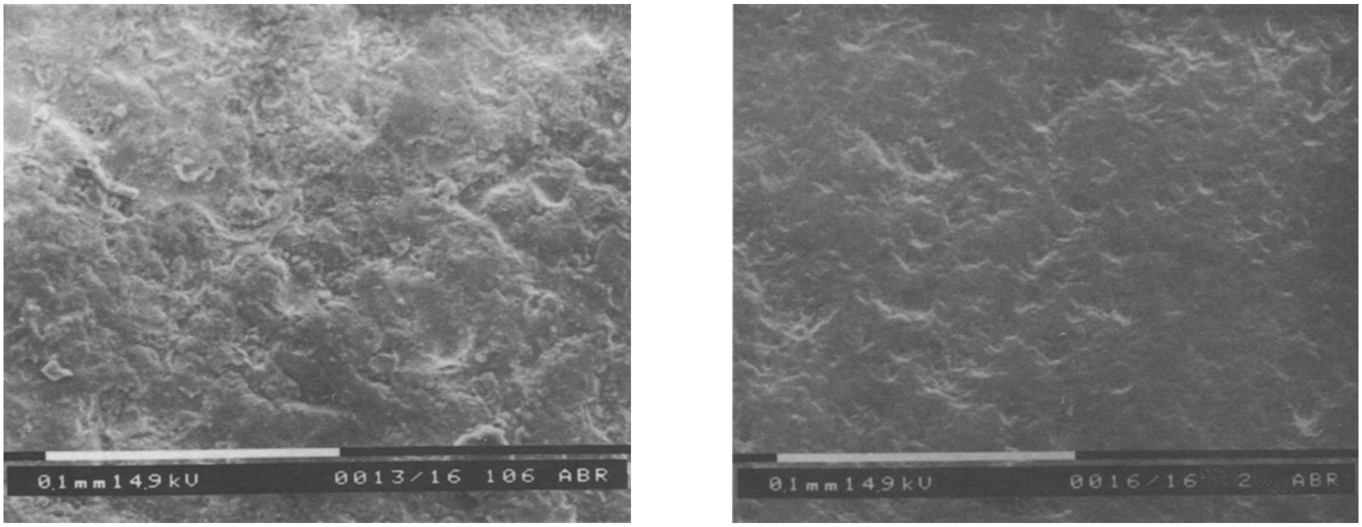
Erosion wear resistance also increased after sealing (Fig. 8). Chromia has good erosion resistance without sealing; thus, sealing did not increase erosion resistance for chromia as much as for alumina. When the angle of impingement was 90°, wear resistance improved more than when the angle was 30°. This indicates that the coatings were toughened by sealing. Brittle materials tend to wear more at the impingement angle of 90° than at 30°. The reverse is true for tough or ductile materials (Ref 12).

Observed improvements in the abrasive and erosive wear resistance are similar to those reported earlier for plasma and deto-



(a) (b)

Fig. 6 Wear traces of abrasive wear tested Al_2O_3 coatings: (a) as-sprayed and (b) aluminum phosphate sealed Al_2O_3 coatings



(a) (b)

Fig. 7 Wear traces of abrasive wear tested Cr_2O_3 coatings: (a) as-sprayed and (b) aluminum phosphate sealed Cr_2O_3 coatings nation sprayed alumina coatings (Ref 6 and 7). The greatest improvements can be obtained with coatings that have higher open porosity and a less dense structure. Therefore, the wear resistance of the detonation sprayed coatings showed less improvement after the sealing treatment than that of plasma-sprayed coatings. This also indicates that during heat treatment there are chemical reactions between the sealant solution and sprayed coatings that improve the cohesive strength of the coatings.

3.3 *Corrosion Resistance*

Aluminum phosphate treated Al_2O_3 and Cr_2O_3 coatings show significantly smaller current densities than unsealed coatings in potentiodynamic polarization tests (Fig. 9 and 10). The current density of the alumina coating decreased more than one order of magnitude by the sealing treatment and an even two orders of magnitude for the chromia coating. This indicates that the aluminum phosphate densifies the structure of the coatings. Sealed coatings have less open porosity but are not fully dense.

Due to their structural heterogeneity, the sprayed coatings behave differently in corrosive environments than sintered bulk ceramics. Sprayed ceramic coatings always contain open porosity, and the corrosion resistance of bond coatings or the substrate need to be considered. These materials should be selected to resist crevice or pitting corrosion in the environment.

Rapidly solidified metastable phases, such as γ-alumina, also differ from stable phases in chemical stability. These phases may have less corrosion resistance in severe environments. Thus, in the case of alumina, the chemical stability of the sprayed material depends on the stability of the predominant γ-phase, which is lower than the stability of the stable α-phase (Ref 13). Considerable corrosion is expected in sprayed alumina coatings in very acidic and basic solutions. In the case of chromia, the sprayed structure is more chemically stable, and it resists most alkalis and acids (Ref 1 and 2).

The abrasion wear resistance of sealed alumina coatings was still good after immersion in 0-water, tap water, and NaOH solution (pH 10). But very acidic (pH 0) and basic (pH 14) solutions attacked alumina coatings, which wore away totally at the beginning of the abrasion test because alumina coatings are chemically unstable in these environments.

The sealed Cr_2O_3 coatings showed good corrosion resistance in all test solutions in the pH range of 0 to 10. No corrosion induced weight decreases were found in the subsequent abrasion wear test. The high basic solution, pH 14, weakened the structure because of corrosion of aluminum phosphate in these environments. This was verified by XRD analysis, which indicated that the peaks of aluminum phosphates disappeared after immersion in the solution with pH 14 (Fig. 12).

4. Conclusions

Aluminum phosphate sealing significantly improved the abrasive and erosive wear resistance of Al_2O_3 and Cr_2O_3 coatings. Aluminum phosphates act as a glue by binding the lamellae together. Wear traces of sealed coatings were smoother than

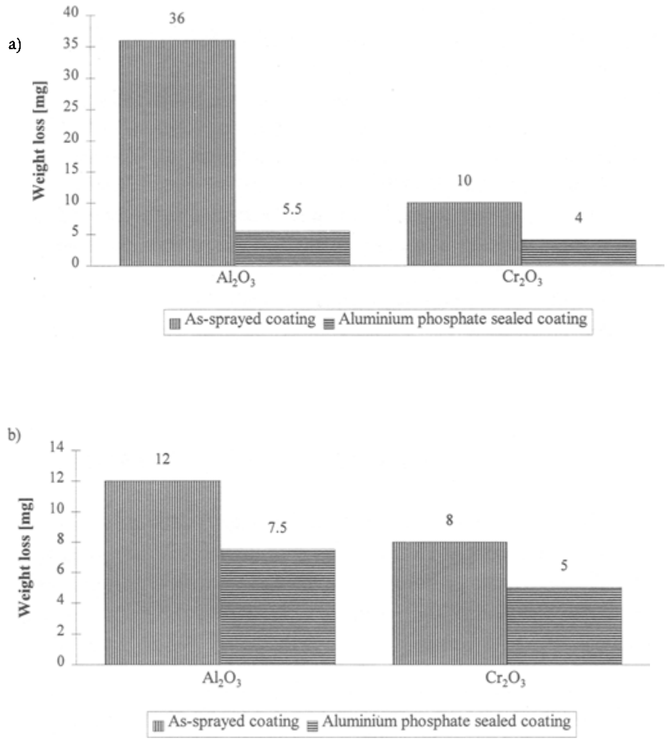


Fig. 8 Results of the particle erosion test for the as-sprayed and the aluminum phosphate sealed Al_2O_3 and Cr_2O_3 coatings. The angles of impingement were: (a) 90° and (b) 30°

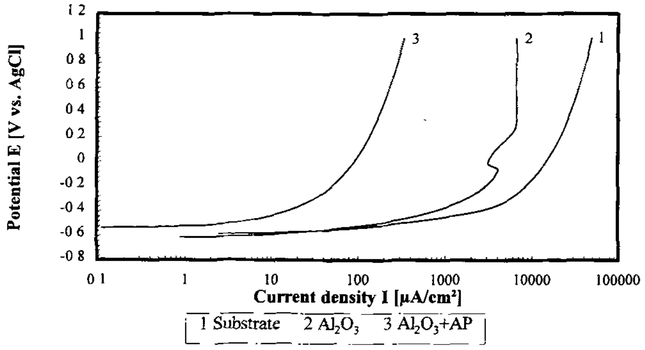


Fig. 9 Potentiodynamic anodic polarization curves of the substrate material (1), the Al_2O_3 coating (2), and the aluminum phosphate sealed Al_2O_3 coating (3)

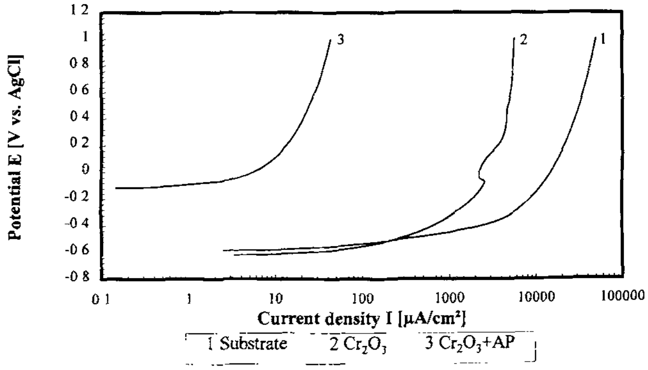


Fig. 10 Potentiodynamic anodic polarization curves of the substrate material (1), the Cr_2O_3 coating (2), and the aluminum phosphate sealed Cr_2O_3 coating (3)

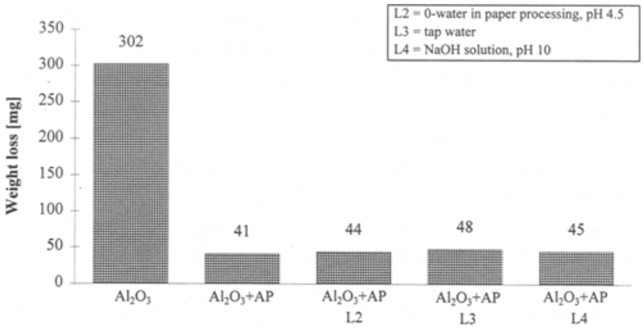


Fig. 11 Rubber wheel abrasion test results of the Al_2O_3 coating, the aluminum phosphate sealed Al_2O_3 (AP) coating, and the aluminum phosphate sealed Al_2O_3 coatings (AP), which were immersed for 30 days in different liquids

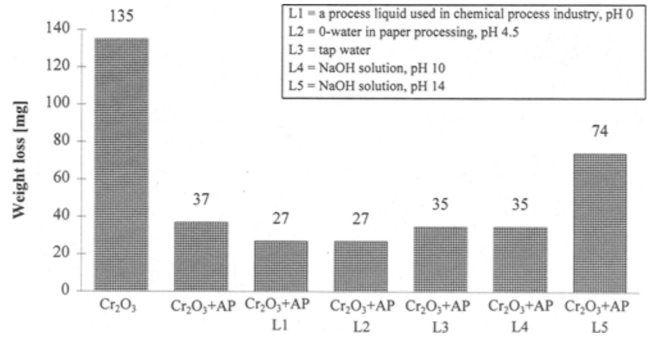


Fig. 12 Rubber wheel abrasion test results of the Cr_2O_3 coating, the aluminum phosphate sealed Cr_2O_3 coating (AP), and the aluminum phosphate sealed Al_2O_3 coatings, which were immersed for 30 days in different liquids

those of unsealed coatings. Hardness values were increased by the sealing treatment.

Aluminum phosphates sealed the structures of Al_2O_3 and Cr_2O_3 coatings, as seen in SEM micrographs and corrosion tests. The abrasive wear resistance of sealed coatings did not decrease after immersion tests of 30 days in liquids of pH 0 to 10, except for the Al_2O_3 coating, which corroded in pH 0 and pH 14 solutions. No corrosion was found with aluminum phosphates in very acidic solutions. Aluminum phosphate is a good candidate to seal oxide coatings that are exposed in corrosive environments, excluding high basic environments of approximately pH 14.

Aluminum phosphate treatment seals and strengthens the structures of plasma-sprayed ceramic oxide coatings. Improvements are the greatest for the coatings that have high open porosity.

References

1. H.G. Schutz, T. Gössmann, D. Stöver, H.P. Buchkremer, and D. Jäger, Manufacture and Properties of Plasma Sprayed Cr_2O_3, *Mater. Manuf. Process.*, Vol 6 (No. 4), 1991, p 649-669
2. D. Chuanxian, H. Bingtang, and L. Huiling, Plasma-Sprayed Wear-Resistant Ceramic and Cermet Coating Materials, *Thin Solid Films*, Vol 118, 1984, p 485-493
3. R. McPherson, The Relationship between the Mechanism of Formation, Microstructure and Properties of Plasma-Sprayed Coatings, *Thin Solid Films*, Vol 83, 1981, p 297-310
4. V. Wilms and H. Herman, Plasma Spraying of Al_2O_3 and Al_2O_3-Y_2O_3, *Thin Solid Films*, Vol 39, 1976, p 251-262
5. A.L. Borisova and A.A. Tkachenko, Structure and the Properties of Oxide Coatings Densified with Phosphate Binders, *Sov. Powder Metall. Met. Ceramic.*, Vol 26 (No. 11), 1987, p 888-892
6. K. Niemi, P. Sorsa, P. Vuoristo, and T. Mäntylä, Thermally Sprayed Coatings with Strongly Improved Wear and Corrosion Resistance, *Thermal Spray Industrial Applications*, C.C. Berndt and S. Sampath, Ed., ASM International, 1994, p 533-536
7. K. Niemi, P. Vuoristo, E. Kumpulainen, P. Sorsa, and T. Mäntylä, Recent Developments in the Characteristics of Thermally Sprayed Oxide Coatings, *Thermal Spraying - Current Status and Future Trends*, A. Ohmori, Ed., Pub. High Temperature Society of Japan, Osaka, Japan, 1995, p 687-692
8. E. Kumpulainen, M. Vippola, K. Niemi, P. Sorsa, P. Vuoristo, and T. Mäntylä, Characteristics of Aluminum Phosphate Sealed Chromium Oxide Coatings, *Thermal Spray Science and Technology*, C.C. Berndt and S. Sampath, Ed., ASM International, 1995, p 579-582
9. J.H. Morris, P.G. Perkins, A.E.A. Rose, and W.E. Smith, The Chemistry and Binding Properties of Aluminum Phosphates, *Chem. Soc. Rev.*, Vol 6, 1977, p 173-194
10. T.A. Taylor, C.G. Bergeron, and R.A. Eppler, Ceramic Coating, *Metals Handbook*, 9th ed., Vol 5, ASM International, 1990, p 532-537
11. R.B. Hudson and M.J. Dolan, Phosphoric Acids and Phosphates, *Encyclopedia of Chemical Technology: Kirk-Othmer*, 3rd ed., Vol 17, M. Grayson, D. Eckroth, A. Klingsberg, L. Spiro, G. Wachsen, A. Klingsberg et al., Ed , John Wiley & Sons, 1978-1984, p 426-472
12. I.M. Hutchings, Transitions, Threshold Effects and Erosion Maps, *Erosion of Ceramic Materials*, J.E. Ritter, Ed., Trans Tech Publications, Zurich, Switzerland, 1992, p 75-92
13. Handbook of Chemistry and Physics, 55th ed., R.C. Weast, Ed., CRC Press, 1974, p B-64