



Microstructural Study of Aluminum Phosphate-Sealed, Plasma-Sprayed Chromium Oxide Coating

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Microstructural characterization of aluminum phosphate-sealed, plasma-sprayed chromium oxide coating was carried out in order to study the strengthening mechanisms of the aluminum phosphate sealant in the coating. Characterization was performed using x-ray diffractometry, scanning electron microscopy, and analytical transmission electron microscopy. The structure of the sealed coating was lamellar with columnar α - Cr_2O_3 grains extending through the lamella thickness. Amorphous aluminum phosphate sealant had penetrated into the structural defects of the coating such as cracks, gaps, and pores between the lamellae. The relative composition was 25 at.% aluminum and 75 at.% phosphorus for the sealant in the coating, giving the molar ratio P/Al of 3, which corresponds to that of metaphosphates $\text{Al}(\text{PO}_3)_3$. There is no indication of reaction products from the chemical reactions between the sealant and the coating. Thus, the aluminum phosphate sealing in the chromium oxide coatings can be explained mainly by adhesive binding resulting from the formation of the condensed phosphates with the appropriate adhesive properties to the coating, and not by chemical bonding resulting from the chemical reactions between the sealant and the coating.

Keywords aluminum phosphate sealing, chromium oxide coatings, energy dispersive spectrometry, plasma spraying, scanning electron microscopy, transmission electron microscopy, x-ray diffractometry

1. Introduction

Plasma-sprayed chromium oxide coatings are used especially for wear and corrosion-protective applications.^[1,2] After the coating is sprayed, it consists of lamellae, which are formed when molten droplets flatten and solidify onto the substrate.^[1-5] The lamellar structure always has some structural defects, such as pores and cracks due to entrapped gas, shadowing of the previously solidified droplets, and incomplete bonding between the lamellae.^[3,4] Because of these structural defects, coatings always have some open porosity, which decreases the protection ability. To obtain coatings with sufficient protection, sealing of the open porosity is necessary.^[6,7] The open porosity can be sealed by various means.^[7] Laser or electron-beam surface melting can be used to close the surface porosity. Hot isostatic pressing (HIP) can be used to densify the whole coating-substrate system, but it requires expensive equipment. Sealing can be done also with the deposition of a dense layer by another method onto the porous coating surface. More often sealing of the porous coating is done by sealant impregnation. Numerous sealants are available for plasma-sprayed coatings, including inorganic sealants, organic sealants, and molten metals.^[7]

In our earlier studies,^[8-11] aluminum phosphate sealing

proved to be an effective treatment for the porous oxide coatings. Aluminum phosphate-sealed oxide coatings such as alumina and chromia had significantly improved abrasive and erosive wear resistance as well as corrosion resistance over the as-sprayed coatings.^[8-10] Our study^[11] about the residual stresses in sealed oxide coatings indicated that the aluminum phosphate sealing changes the stress state of the sealed coatings toward compression. The compressive stresses can be explained in two ways: Because of the bonds between the sealant and the coating, the coating system cannot relax to the original stress state during the cooling; or during the heat treatment, there may occur some volume expansion, which induces compressive stresses to the coating.

Aluminum phosphates, or more generally just phosphates, are traditionally used as binders in refractories and the reaction in the phosphate binder yields in the formation of crystalline or amorphous phosphates.^[12-14] The reaction products can be different depending on the composition of binder, the reaction time, and temperature.^[13] The phosphate bonding can be accomplished by two different methods: by using oxides with orthophosphoric acid, resulting in the formation of acidic phosphates; or by direct addition of acidic phosphates.^[12] The phosphate bond in the coating may form in two ways, by chemical reaction between the sealant and the coating or by adhesion resulting from attractive forces between the sealant and the coating.^[12-14] A few other studies have been conducted on phosphate-based sealing treatments for coatings.^[6,15-18] For example, Borisova and Tkachenko^[15] studied the sealing of porous oxide coatings with phosphate binders. They densified flame-sprayed aluminum, zirconium, chromium, and titanium oxides both with an aluminum-chromium phosphate binder and an 85% solution of orthophosphoric acid (H_3PO_4). Infiltrated coatings were heat treated in air at 500 °C. Main results in the study were that the infiltration and heat treatment decreased the open porosity of

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coatings by a factor of two to three, and decreased their gas permeability by three to four orders. In addition, the coefficients of friction and the abrasive action of the coatings on threads were reduced by two orders.^[15]

The microstructure of plasma-sprayed chromium oxide coatings has been studied rather rarely,^[1,2,5,19,20] although chromium oxide coatings are frequently used in industry. An even less studied field is the microstructure of aluminum phosphate-sealed, plasma-sprayed chromium oxide coatings. Therefore, the microstructures of the aluminum phosphate-sealed chromium oxide coating and the aluminum phosphate sealant were characterized to examine the sealing and strengthening mechanisms of aluminum phosphate.

2. Experimental Procedure

2.1 Production of the Coating

The chromium oxide coating was produced with Plasma-Technik A3000S plasma spray equipment (Sulzer Metco AG, Wohlen, Switzerland). The spray powder was the Amperit powder Cr₂O₃ 704.1 (H.C. Starck GmbH, Goslar, Germany), and the particle size ranged from 22.5–45 μm. The coating was sprayed with the optimized parameters, shown in Table 1, to a thickness of about 500 μm.

2.2. Sealing of the Coating

The plasma-sprayed chromium oxide coating was sealed with aluminum hydroxide [Al(OH)₃] and orthophosphoric acid (85% H₃PO₄) solution diluted with 20 wt.% of deionized water. The Al(OH)₃/H₃PO₄ ratio was 1:4.2 by weight, corresponding to the molar ratio P/Al of about 3. The solution, which was permitted to react at the temperature range of about 40 to 70 °C until becoming clear, was spread onto a porous coating and impregnated into the coating at room temperature under normal pressure for 12 h. The impregnated coating was then heat treated with the following continuous procedure: 2 h at 100 °C, followed by 2 h at 200 °C, and then 2 h at 400 °C. This three-step heat treatment procedure was derived from the known aluminum phosphate reactions, and the purpose is to confirm the complete dehydration of aluminum phosphate solution.

2.3. Coating Characterization

The main reason for the study was to find microstructural features, which might explain the strengthening mechanisms of aluminum phosphate sealant in the coating. The aluminum phosphate-sealed chromium oxide coating was characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), and analytical transmission electron microscope (AEM). XRD measurements were also made for as-sprayed coating and for aluminum phosphate sealant to determine the basis of the sealing treatment. XRD studies were carried out with the Cu-Kα radiation using the scan step for 2θ at 0.02° with the step time of 1.2 s. Microstructural studies for the sealed chromium oxide coating were performed with an SEM equipped with an energy dispersive spectrometer (EDS), and with an analytical transmission electron microscope (AEM) equipped with an EDS. The TEMs were operated at 200 kV. Cross-sectional AEM samples were

Table 1 Optimized Spraying Parameters for Plasma Sprayed Chromium Oxide Coating

Parameter	Value	Unit
Current	630	A
Voltage	70	V
Gas flow for Ar	65	slpm
Gas flow for H ₂	13	slpm
Spray distance	110	mm
Powder feed rate	43	g/min
Carrier gas rate	2.6	slpm
Anode bore	6	mm

prepared by embedding and gluing the coating cross sections into the Ti-grids and then by thinning and polishing them, first by hand and then by dimpling. The final thinning of the sample was performed by ion milling.

3. Results

3.1 XRD Measurements

XRD measurements for as-sprayed coating and for aluminum phosphate sealant were carried out to find out the basis for the sealing treatment. XRD measurements of aluminum phosphate-sealed chromium oxide coating were carried out for phase characterization. Spray powder for chromium oxide coatings has a phase structure of eskolaite type α-Cr₂O₃ having the hexagonal unit cell with $a = b = 0.495$ nm and $c = 1.359$ nm,^[21] as shown in Fig. 1(a), in which the α-Cr₂O₃ phase is indicated with the symbol α in the spectrum. There are no phase changes during the plasma spraying of chromium oxide powder. Thus, the as-sprayed chromium oxide coating also has a phase structure of α-Cr₂O₃ with the hexagonal unit cell.

During the heat treatment, nonimpregnated aluminum phosphate sealant forms a layer of crystallized powder onto the coating surface. According to our earlier studies,^[22] the major phase in the crystallized sealant is aluminum cyclohexaphosphate Al₂P₆O₁₈ with the monoclinic unit cell. Cyclohexaphosphate corresponds to the B-type polymorph of metaphosphates Al(PO₃)₃.^[23,24] The other dominant phases are other polymorphs of metaphosphates. Figure 1(b) shows the XRD spectrum for the crystallized sealant on the surface of coating in which the peaks for cyclohexaphosphate are marked with C.

Figure 1(c,d) shows XRD spectra for sealed chromium oxide coating. The XRD analysis was made both on the polished surface and on ground surface where a 50 μm layer from the coating was removed. The eskolaite type α-Cr₂O₃ phase is indicated with the symbol α in the spectra. Few small extra peaks, marked with P, in the spectrum of the polished surface indicate the presence of metaphosphate phases Al(PO₃)₃. No such peaks of the crystalline phosphates can be found from the spectrum of the ground surface, indicating that aluminum phosphate sealant is amorphous or the amount of crystallized sealant is very low in the coating.

3.2. SEM Studies

SEM studies were carried out to characterize the coating structure of sealed chromium oxide coating from the cross-

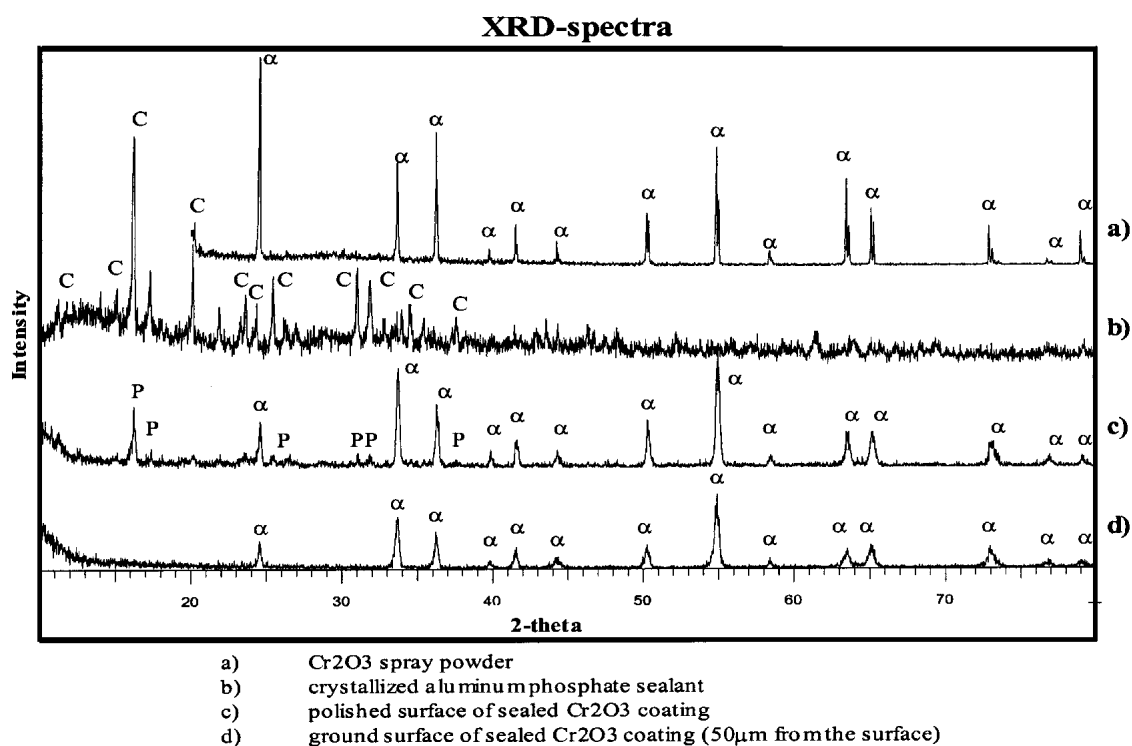


Fig. 1 XRD spectra for (a) the spray powder of chromium oxide coating, (b) the crystallized aluminum phosphate sealant, (c) the polished surface of the sealed chromium oxide coating, and (d) the ground surface of the sealed chromium oxide coating after grinding off a 50 μm layer. α = α -Cr₂O₃ phase, P = aluminum phosphate in the coating, and C = cyclohexaphosphate in the sealant

sectional samples, from both the fracture and the polished surface. Figure 2 shows the structure of the fracture surface of the sealed coating cross section. The coating has lamellar structure consisting of columnar grains extending parallel to lamella thickness, and there are still some pores and gaps between the lamellae even in the sealed coating. Figure 3 shows a polished cross section of the sealed chromium oxide coating studied with elemental x-ray mapping at the depth of 50 μm from the surface. Phosphorus-rich areas in the coating can be seen in between the lamellae and in the pores. The penetration of the sealant was determined with the EDS point analysis from the coating cross section. EDS point analysis near the surface indicated 0.5 at.% of aluminum and 1.1 at.% of phosphorus. Additional EDS analysis points indicated the average of 0.3 at.% of aluminum and 0.5 at.% of phosphorus throughout the coating thickness of about 500 μm.

3.3. AEM Studies

AEM studies were carried out to characterize the crystal structure of sealed chromium oxide coating. Figure 4 shows a cross section of the sealed coating, indicating that the coating lamellae consist of columnar grains extending through the lamella thickness as was also shown in the SEM studies. The aluminum phosphate sealant, which has filled the gap between the lamellae, is marked with an arrow. Figure 5 shows the aluminum phosphate sealant in between the lamellae at higher magnification. Figure 6(a) presents the [121] electron diffraction pattern from the columnar α -Cr₂O₃ grain. Figure 6(b) presents the elec-

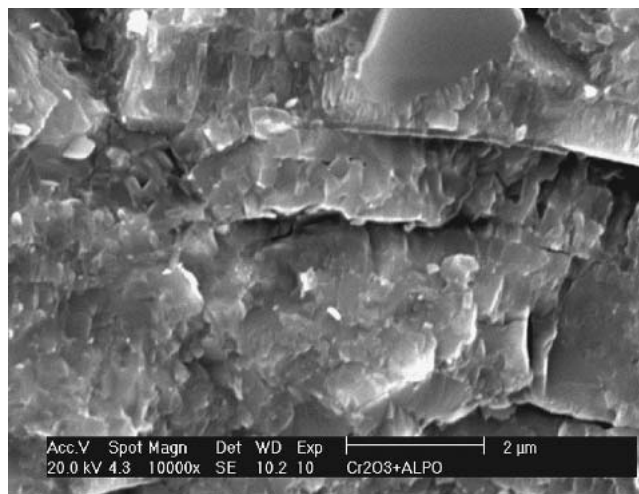
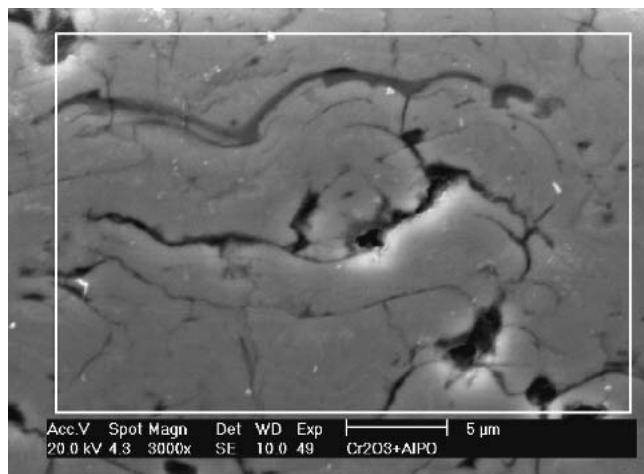
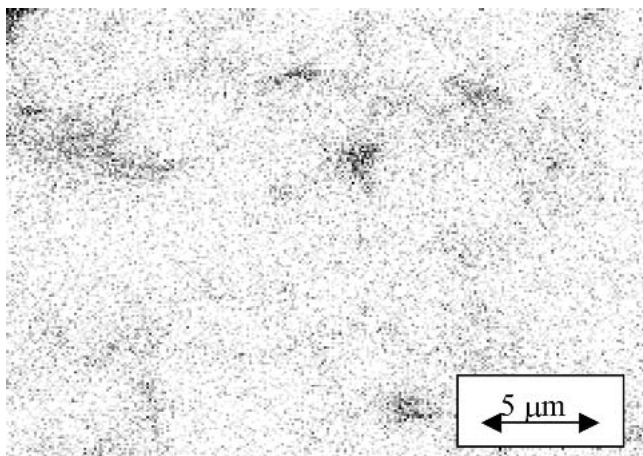


Fig. 2 Structure of the fractured cross section of the coating. The coating has lamellar structure with the columnar grains and structural defects such as pores and gaps between the lamellae.

tron diffraction pattern from the aluminum phosphate sealant area indicated by the ring in Fig. 5. The ring pattern indicates the amorphous or nanocrystalline structure of the sealant. According to the EDS point analysis, the relative composition for the sealant in the coating is 25 at.% aluminum and 75 at.% phosphorus, giving the molar ratio P/Al of 3.



(a)



(b)

Fig. 3 (a) Polished cross section of the sealed coating studied with elemental x-ray mapping, and (b) phosphorus map for the coating area

4. Discussion

4.1 Chromium Oxide Coating

Chromium oxide is available in the form of stoichiometric green oxide Cr_2O_3 and under-stoichiometric black oxide $\text{Cr}_2\text{O}_{3-x}$. With typical spraying parameters, chromium oxide coating is always black, referring to under-stoichiometric black oxide,^[25] as it was also in our coatings. According to literature,^[1,19,26,27] Cr_2O_3 decomposes during plasma spraying at some extent to metallic Cr, or to other chromium oxides such as Cr_3O_4 , CrO, or CrO_2 . Hermansson et al.^[19] showed that the minor distortions within two peaks (at the d -values of 0.204 nm and 0.118 nm) in the XRD spectra of α - Cr_2O_3 were due to metallic chromium. Similar minor distortions, as described in Ref. 19, could also be detected in the XRD spectrum for the sprayed chromium oxide coatings, indicating that there might be a minor amount of decomposed metallic chromium in the coating structure. The decomposition of Cr_2O_3 was more closely studied with SEM using back-scattering electrons (BSE) and EDS. Figure 7(a) represents a BSE image from the cross section of sealed chromium oxide coating. There are few

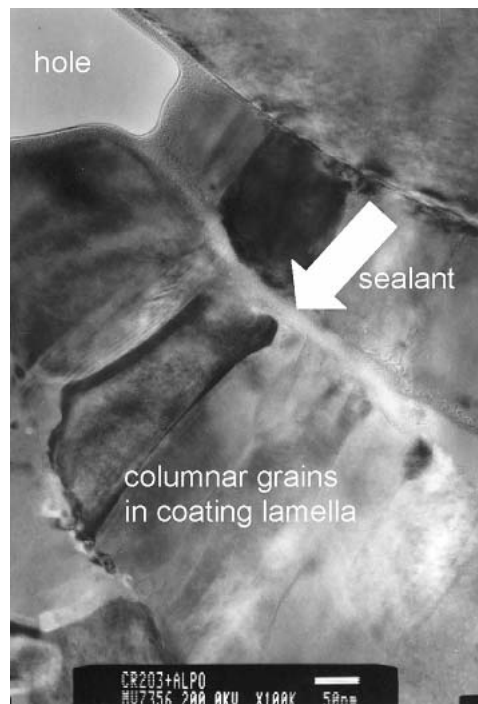


Fig. 4 AEM image from the cross section of the sealed coating. Coating lamellae consist of columnar α - Cr_2O_3 grains extending through the lamella thickness and aluminum phosphate sealant, marked with an arrow, has filled the gap between the lamellae.



Fig. 5 AEM image from the aluminum phosphate sealant in between the lamellae. The ring in the sealant indicates the selected area for electron diffraction.

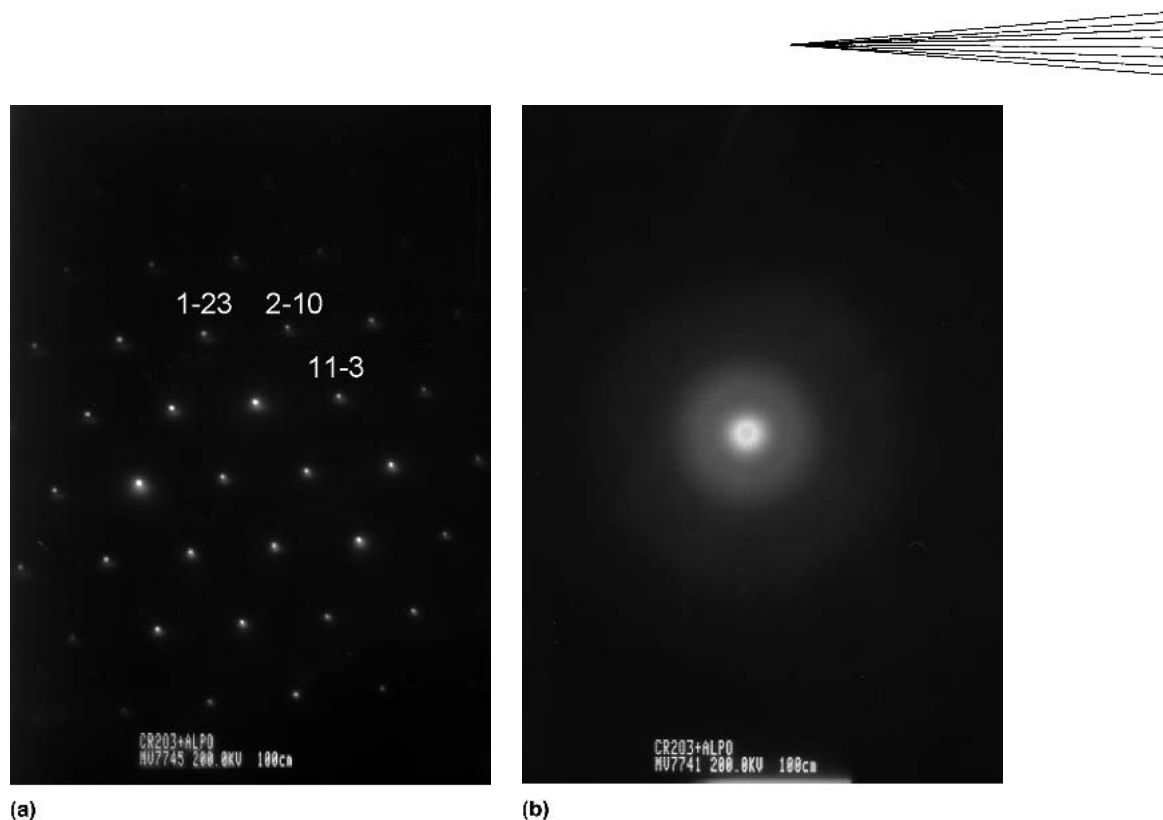


Fig. 6 Electron diffraction (ED) patterns from the sealed coating: **(a)** [121] selected area electron diffraction (SAED) pattern from the columnar α - Cr_2O_3 grain, and **(b)** SAED pattern from the aluminum phosphate sealant area indicated with the ring in Fig. 5

very bright areas in the lamellar structure with higher molar mass. Figure 7(b) shows the closer image of one of those bright areas and the white line over it indicates the path along which the EDS analysis was taken. Figure 7(c) shows the average amount of chromium and oxygen along the line. According to the EDS analysis, these bright areas contain much more chromium than Cr_2O_3 , because of the decomposition of Cr_2O_3 during plasma spraying. For example Pawlowski^[27] indicated similar areas in the plasma-sprayed chromium oxide coatings.

4.2. Aluminum Phosphate Sealing

In our studies of the sealant,^[22] the major phase in the sealant was determined to be aluminum cyclohexaphosphate, $\text{Al}_2\text{P}_6\text{O}_{18}$, with the monoclinic unit cell. Cyclohexaphosphate corresponds to the B-type polymorph of metaphosphates $\text{Al}(\text{PO}_3)_3$.^[23,24] The other phases in the sealant were other polymorphs of metaphosphates. These results correspond well to literature^[28] where the reaction for alumina or aluminum hydroxide with orthophosphoric acid is known to proceed in the following way: the solution transforms to either acidic mono-aluminum phosphate $\text{Al}(\text{H}_2\text{PO}_4)_3$ or an amorphous phase. Heating dehydrates the solution and metaphosphates $\text{Al}(\text{PO}_3)_3$ are formed. The availability and the further reaction with alumina can produce phosphates with a lower P/Al molar ratio, such as aluminum orthophosphates AlPO_4 .^[28]

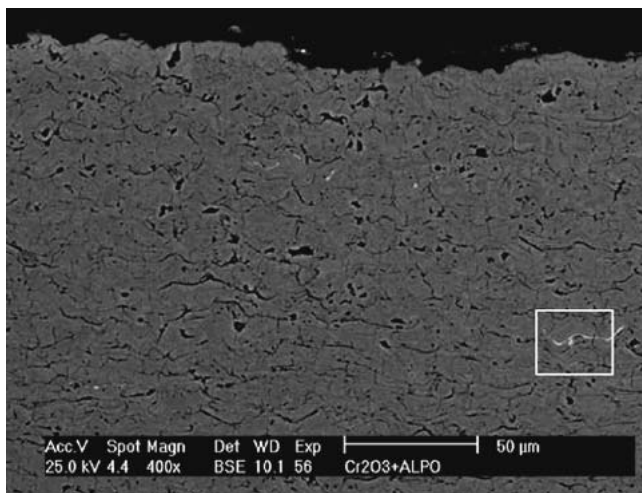
4.3. Aluminum Phosphate-Sealed Chromium Oxide Coating

According to the microstructural studies of the aluminum phosphate-sealed chromium oxide coating, the following conclusions about the sealing can be made.

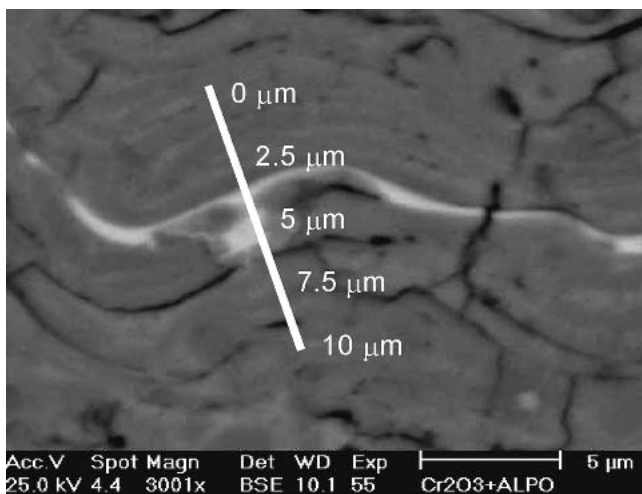
- Aluminum phosphate sealant penetrates effectively through the chromium oxide coating. The sealant does not seal the coating completely; there are still some pores and gaps between the lamellae of the sealed coating.
- The sealant seems to be in the amorphous form or the amount of crystallized sealant is very low in the coating, because there are no indications about crystalline phosphates inside the coating, according to XRD analysis in Fig. 1(d).

Nevertheless, it should be noted that it is difficult to interpret small amounts of phases reliably on the basis of XRD spectra because of the small number of the corresponding peaks and the poor peak-to-background ratio. The AEM studies also indicate the presence of an amorphous form of the sealant. The molar ratio of P/Al for the aluminum phosphate sealant in the coating is 3, which is same as in the aluminum phosphate solution. The molar ratio of 3 corresponds also to metaphosphates $\text{Al}(\text{PO}_3)_3$, which are characteristic for the sealant. This indicates that the sealing mechanism of the aluminum phosphate in the chromium oxide coating is based only on adhesive bonding of condensed aluminum phosphates, which have appropriate adhesive properties to the chromium oxide coating, and there are no chemical reactions involved.

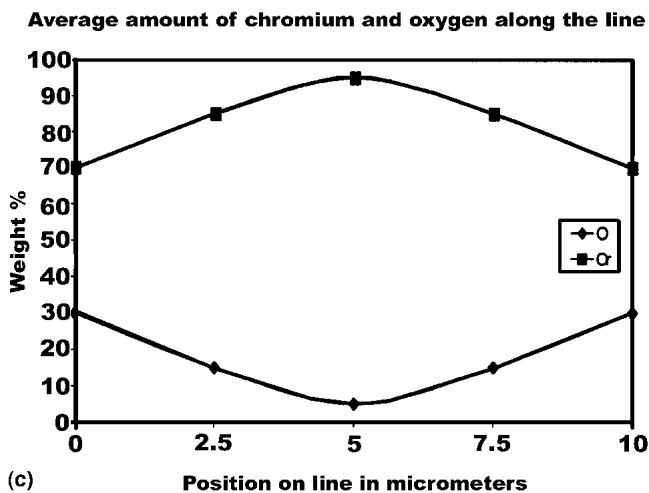
In addition, there could have been some chromium phosphate phases in the coating resulting from the reaction between the sealant and the chromium oxide coating.^[12,14,15] The chromium phosphates preferentially form in the reaction with orthophosphoric acid, not in the reaction with already reacted aluminum phosphate compound.^[12,14] It should also be noted that in the chromium oxide coatings the main phase is the stable α - Cr_2O_3 , whereas in the alumina coatings the phase structure consist



(a)



(b)



(c)

Fig. 7 (a) BSE image from the polished cross section of the sealed coating; the white box indicates the area that is analyzed more closely. (b) BSE image from the bright area with the higher molar mass; the white line indicates the path along which EDS analysis was taken. (c) Average amount of chromium and oxygen along the line indicated in item (b)

mainly of the metastable γ - Al_2O_3 with some residues of the stable α - Al_2O_3 . Therefore, the basis for the reaction between the aluminum phosphate sealant and the chromium oxide coating is not as advantageous as in the alumina coatings. XRD and EDS studies showed no indication about the reaction products from such reactions. However, it should be noted that the reaction products might be in amorphous form when they are rather undetectable in the XRD spectrum. In addition, the EDS analysis is very difficult to focus to such a small area such as the interface between the sealant and the coating, where the reaction products most probable are located.

As discussed, the phosphate bond in the coating may form in two ways: by adhesive binding as a result of attractive forces between the sealant and the coating, and by chemical bonding as a result of the chemical reaction between the sealant and the coating, as shown in Fig. 8. The chemical bonding as a result of the reaction between the sealant and the coating seems not to take place in chromium oxide coatings, as is the case with alumina coatings.^[29] In the microstructural study of alumina coatings with similar sealing treatment,^[29] the aluminum phosphate sealing mechanism was determined to be based both on chemical bonding resulting from the chemical reaction and on adhesive binding resulting from attractive forces between the sealant and the coating. The sealant penetration reached only a depth of about 300 μm in the alumina coating. The difference between the penetration depths could be based on surface properties of the different coatings and on binding mechanisms of the sealant. In the alumina coatings, the chemical bonding between the sealant and the coating can have a retarding effect on the sealant penetration.

Some minor changes (such as decomposition of chromium oxide to metallic chromium or to other chromium oxides) in the phase structure of chromium oxide can take place during the plasma spraying because of the high-temperature process. There is also a slight possibility of the formation of aluminum or chromium phosphates because of the chemical reaction between the sealant and the coating during the sealing treatment. However, these two phenomena are rather difficult to verify and for drawing the final conclusions about the phase structure of aluminum phosphate-sealed chromium oxide coating and the sealing mechanisms of aluminum phosphate sealant, more detailed studies should be carried out (by thermal analysis and AEM, for example).

5. Conclusions

Microstructural studies of the sealed coating showed that the coating structure is lamellar with the columnar α - Cr_2O_3 grains extending through the lamella thickness.

During the heat treatment, the excess aluminum phosphate sealant dehydrates and forms a mixture of metaphosphates $\text{Al}(\text{PO}_3)_3$ onto the surface of the coating. The major phase in this mixture is cyclohexaphosphate $\text{Al}_2\text{P}_6\text{O}_{18}$, which corresponds to the B-type polymorph of $\text{Al}(\text{PO}_3)_3$.

In the coating, amorphous aluminum phosphate penetrated through the chromium oxide coating following the structural defects such as pores, cracks, and gaps between the lamellae.

The molar ratio of P/Al for the aluminum phosphate sealant

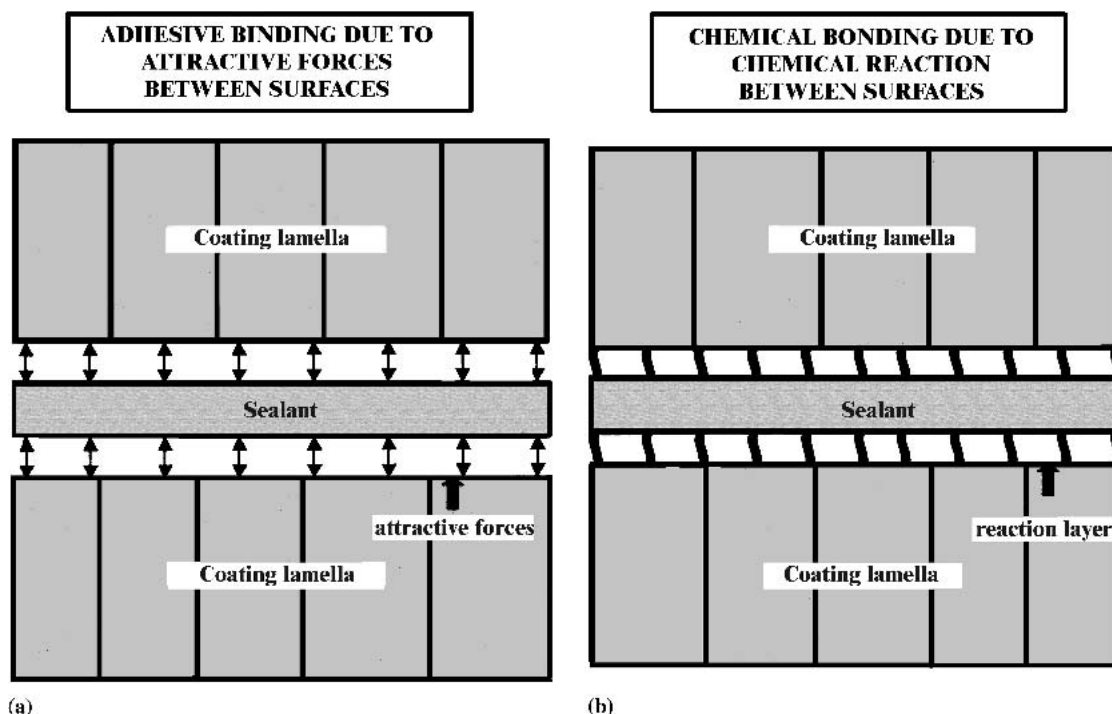


Fig. 8 Representation of phosphate bonding mechanisms in the aluminum phosphate-sealed oxide coatings: (a) adhesive binding resulting from the attractive forces between the sealant and the coating, and (b) chemical bonding resulting from the chemical reaction between the sealant and the coating

in the coating is about 3, which is same as in the sealant mixture and which also refers to metaphosphates $\text{Al}(\text{PO}_3)_3$. No indication about the phosphate phases resulting from the chemical reaction between the sealant and the coating was detected. It can be concluded that the aluminum phosphate sealing in the chromium oxide coatings seems to be based on adhesive binding of the condensed phosphates and not on chemical bonding, as in alumina coatings.

Acknowledgment

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