

# Thermal analysis of plasma sprayed oxide coatings sealed with aluminium phosphate

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## Abstract

Thermal analysis by thermogravimetry and differential scanning calorimetry was carried out for plasma-sprayed alumina and chromia coatings to study their stability after plasma spraying and for aluminum phosphate sealant to study phosphate reactions during the sealing heat treatment. Thermogravimetric analysis for alumina coating did not show any change in the coating due to the heat treatment, though the phase structure had changed from metastable  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In the chromia coating thermogravimetric analysis showed 1.7 wt.% weight increase due to the oxidation of the sprayed coating. During plasma-spray process the chromia coating had gained some under-stoichiometry or some of the chromia had decomposed into metallic chromium or other oxides. Thermal analysis for aluminum phosphate sealant showed weight loss of about 27 wt.%. This corresponds well to the formation of metaphosphates via dehydration of aluminum phosphate solution during the sealing heat treatment. Thermal analysis for the mixture of sealant and alumina coating showed slightly different behaviour than plain sealant. The sealant reacted with the alumina coating forming a crystalline phase, berlinite-type orthophosphate AlPO<sub>4</sub>. Thermal analysis for the mixture of sealant and chromia coating showed nearly similar behaviour than plain sealant and no indications of the chemical reactions were detected. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Aluminium phosphate; Al<sub>2</sub>O<sub>3</sub>; Cr<sub>2</sub>O<sub>3</sub>; Thermal properties; X-ray methods

## 1. Introduction

According to our earlier studies<sup>1–4</sup> aluminum phosphate sealing is a very effective sealing method for plasma-sprayed alumina and chromia coatings. Aluminum phosphate sealing improves dry abrasion wear resistance, erosion wear resistance as well as corrosion resistance of the porous alumina and chromia coatings. Lately we have carried out detailed microstructural studies for aluminum phosphate sealed coatings in order to understand the strengthening and sealing mechanism of aluminum phosphate sealant in the plasma-sprayed oxide coatings.<sup>5–7</sup> According to these studies two possible mechanisms for the phosphate bonding procedure in the coatings has been proposed: chemical bonding due to chemical reactions between the sealant and the coating and adhesive binding due to attractive forces between

the sealant and the coating. In the alumina coatings main mechanism is chemical bonding whereas in the chromia coatings sealing takes place by the adhesive binding.<sup>6–7</sup>

Thermal analysis methods are techniques in which a property of a sample is monitored against temperature. Thermogravimetric (TG) analysis is the study of weight changes of a specimen as a function of temperature. The technique is used for studying transformations involving absorption or evolution of gases from specimen consisting of a condensed phase. In differential thermal analysis, the temperature difference between a sample and a reference is determined as a function of time. The technique provides useful information about the temperatures, thermodynamics and kinetics of reactions. Differential scanning calorimetry (DSC) has a similar output but the sample energy change during the transformation is measured.<sup>8,9</sup> TG and DSC methods were used for studying the stability of as-sprayed coatings and aluminum phosphate reactions both in plain aluminum phosphate and in a mixture of aluminum phosphate and coating.

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As-sprayed alumina and chromia coatings were studied in order to check their stability after plasma spraying. It can be assumed that alumina coating is very stable in heating but there should be a phase change towards more stable phase structure.<sup>10–13</sup> In the chromia coatings the phase structure is very stable but there might be slight weight change in the coating due to under-stoichiometry or decomposed forms of chromia arising from plasma-spray process.<sup>14–18</sup>

Plain aluminum phosphate sealant was studied in order to find out what kind of reactions are involved in the sealant during the heat treatment. By knowing these reactions it is easier to interpret the behaviour of the sealant with alumina and chromia coatings. The studies<sup>19–32</sup> about the aluminum phosphates binders used in refractory industry and also about their reactions during heat treatment differ from each other in most cases and also the exact composition of used phosphate solution varies in all cases. However monoaluminum phosphate and amorphous aluminum phosphate phases seem to be pre-products for all phosphate binder reactions were the P/Al ratio is close to 3 and depending on the final temperature and reaction environment the final reaction products were either metaphosphates or orthophosphates.<sup>19–32</sup>

Mixtures of sealant and crushed alumina and chromia coatings were studied in order to determine the reactions occurring during the heat treatment and the interaction mechanisms between the sealant and the coatings. From our earlier studies it is known that in the case of alumina coatings sealant reacts with coating forming a crystalline phosphate phase whereas in the case of chromia coatings there are no reactions.<sup>6–7</sup>

## 2. Experimental procedures

Alumina and chromia coatings were produced with Sulzer Metco A3000 S plasma spray equipment (Sulzer Metco AG, Switzerland). The spray powders were Amperit Al<sub>2</sub>O<sub>3</sub> 740.1 and Cr<sub>2</sub>O<sub>3</sub> 704.1 from H.C. Starck GmbH (Germany) with particle size ranging from 22.5 to 45 µm. Coatings were sprayed with the optimized parameters, shown in Table 1, to the thicknesses of 800 µm for

Table 1  
Plasma spray parameters for alumina and chromia coatings

Parameter (unit)	Al <sub>2</sub> O <sub>3</sub> powder (740.1)	Cr <sub>2</sub> O <sub>3</sub> powder (704.1)
Current (A)	610	630
Voltage (V)	72	70
Gas flow for Ar (slpm)	41	65
Gas flow for H <sub>2</sub> (slpm)	14	13
Spray distance (mm)	120	110
Powder feed rate (g/min)	34	43
Carrier gas flow (slpm)	3.6	2.6
Electrode Ø (mm)	6	6

alumina and 500 µm for chromia. For thermal analysis the plasma sprayed coatings were crushed into powder with the particle size ranging from 2 to 200 µm in order to have as much surface reaction area as possible.

Aluminum phosphate sealant was prepared from the solution of aluminum hydroxide (Al(OH)<sub>3</sub>) and orthophosphoric acid (85% H<sub>3</sub>PO<sub>4</sub>) diluted with about 20 wt.% of deionized water. The Al(OH)<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub> ratio was 1:4.2 by weight giving the molar ratio of P/Al of about 3. The solution was initiated at a slightly elevated temperature (about 50–70 °C) on a magnetic stirrer to complete the exothermic reaction forming a clear and rather viscous solution.

Thermal analysis was performed using a simultaneous thermal analyzer (Netzsch STA 409, Germany). The stability of as-sprayed alumina and chromia coatings was studied in the temperature range of 20–1200 °C using the heating rate of 5 °C/min. For comparison, the spray powders were also analyzed with a similar procedure. The sample weights were 60–80 mg. Reactions in aluminum phosphate sealant were studied with the procedure planned to simulate the actual sealing heat treatment used for coatings. First a temperature scan from 20 to 400 °C with a heating rate of 2 °C/min, then an isotherm at 400 °C for 2 h and finally a controlled cooling to 20 °C with a cooling rate of 5 °C/min. The used sample weights were 20–40 mg. At this point it should be noted that in our earlier publications<sup>1–7</sup> we have used the three-step heat treatment (2 h 100 °C, 2 h 200 °C and finally 2 h 400 °C) but we have recently found out that the final reaction product is largely independent of the heating procedure prior to the 2 h annealing at 400 °C. For this reason we chose a more simple heating procedure for thermal analysis. Reactions between the aluminum phosphate sealant and plasma sprayed coatings were studied with the same procedure, used for simulating the actual sealing heat treatment, described above. Samples were prepared by mixing the crushed coating powder with aluminum phosphate sealant in the weight ratio of 1:1. The used sample weights were 50–100 mg.

The phase determination after thermal analysis was carried out using X-ray diffractometer (XRD), (Siemens Model D500, Germany), using copper K<sub>α</sub> radiation and a scan step of 2θ 0.02 with a step time of 1.2 s.

## 3. Results and discussion

### 3.1. As-sprayed alumina and chromia coatings

Stability and structural changes of as-sprayed alumina and chromia coatings were studied with thermal analysis procedure up to 1200 °C. The crystallographic structure of alumina is known to change during plasma spraying from the stable α-Al<sub>2</sub>O<sub>3</sub> into metastable γ-

$\text{Al}_2\text{O}_3$  and only some residual  $\alpha\text{-Al}_2\text{O}_3$  is left.<sup>10–13</sup> The reason for the formation of metastable  $\gamma\text{-Al}_2\text{O}_3$  is the high cooling rate of the molten particles and the easier nucleation of  $\gamma\text{-Al}_2\text{O}_3$  from the melt than  $\alpha\text{-Al}_2\text{O}_3$ . Presence of  $\alpha\text{-Al}_2\text{O}_3$  in the coating is because of some unmelted or partially melted alumina powder particles. In the TG-curves for alumina spray powder and as-

sprayed alumina coating, shown in Fig. 1, there were no changes in weight exceeding the experimental accuracy, indicating that the alumina is stable in its oxygen content. However, the XRD spectra for alumina coating before and after TG analysis, shown in Fig. 2, showed that a total phase change back to the stable  $\alpha\text{-Al}_2\text{O}_3$  has occurred due to heat treatment at high temperature.

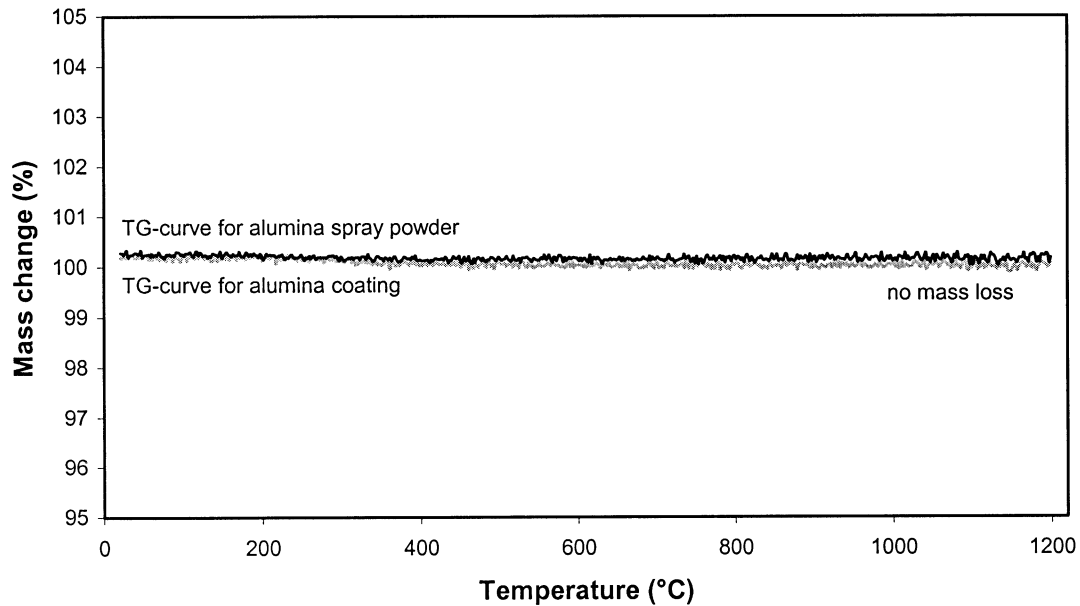


Fig. 1. TG curves for alumina spray powder and alumina coating. No detectable mass changes due to the heat treatment.

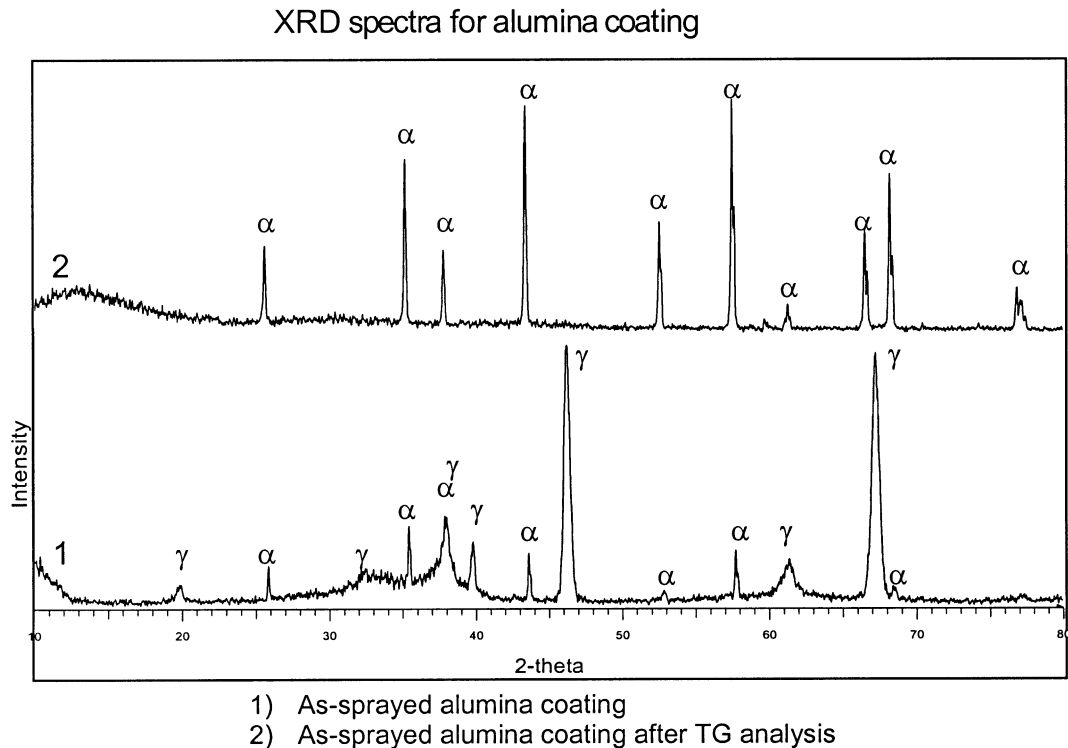


Fig. 2. XRD spectra for alumina coating before and after TG analysis. Alumina phases are indicated with  $\alpha$  and  $\gamma$ .

In the case of chromia no phase changes occur during the spraying process. Thus the phase structure of chromia coating remains as eskolaite type  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>. However, with typical spraying parameters chromia coating always becomes under-stoichiometric to some extent.<sup>14–18</sup> Chromia can also decompose during plasma spraying to metallic Cr, or to other lower oxygen content chromium oxides such as Cr<sub>3</sub>O<sub>4</sub>, CrO or CrO<sub>2</sub>.<sup>14–18</sup> The TG analysis for chromia spray powder and as-sprayed chromia coating, shown in Fig. 3, proves this. TG-curve for chromia spray powder shows no changes in weight due to the heat treatment but TG-curve for as-sprayed chromia coating shows a weight increase of 1.7%. The increase in weight can be assumed to be due to the oxidation of

sample. With this assumption evaluations about the coating structure can be made. In the following two different explanations for the structure of as-sprayed chromia coating are proposed.

#### Explanation 1:

- All of the weight loss is assumed to be due to the reduction of Cr<sub>2</sub>O<sub>3</sub>.
- 1 mol of Cr<sub>2</sub>O<sub>3</sub> spray powder gives 152 g of Cr<sub>2</sub>O<sub>3</sub> and a weight ratio of O/Cr is 0.46.
- Weight loss during plasma spray process is 1.7% and gives 2.58 g of oxygen loss.

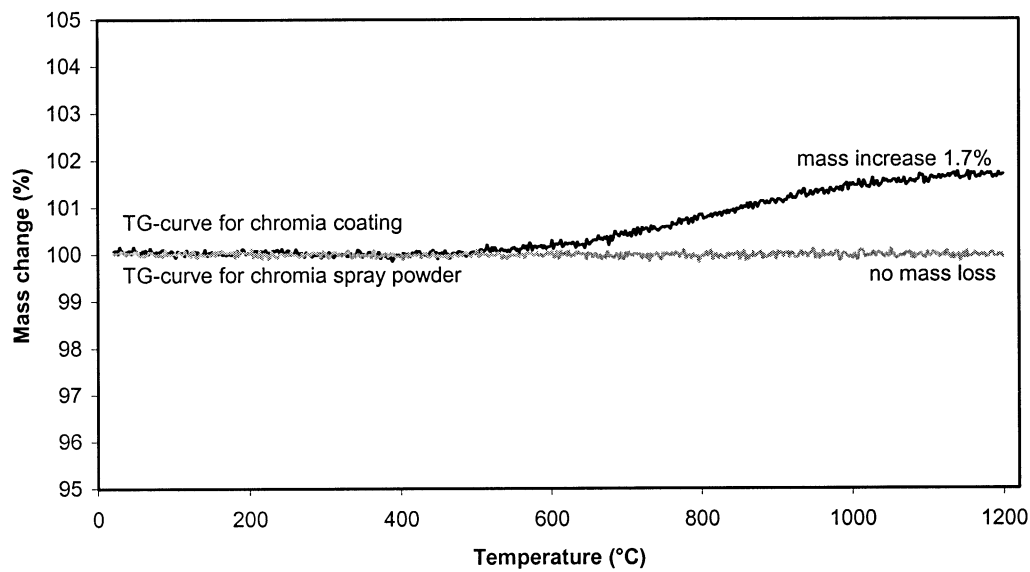


Fig. 3. TG curves for chromia spray powder and chromia coating. Spray powder has no mass change whereas chromia coating has a mass increase of 1.7%.

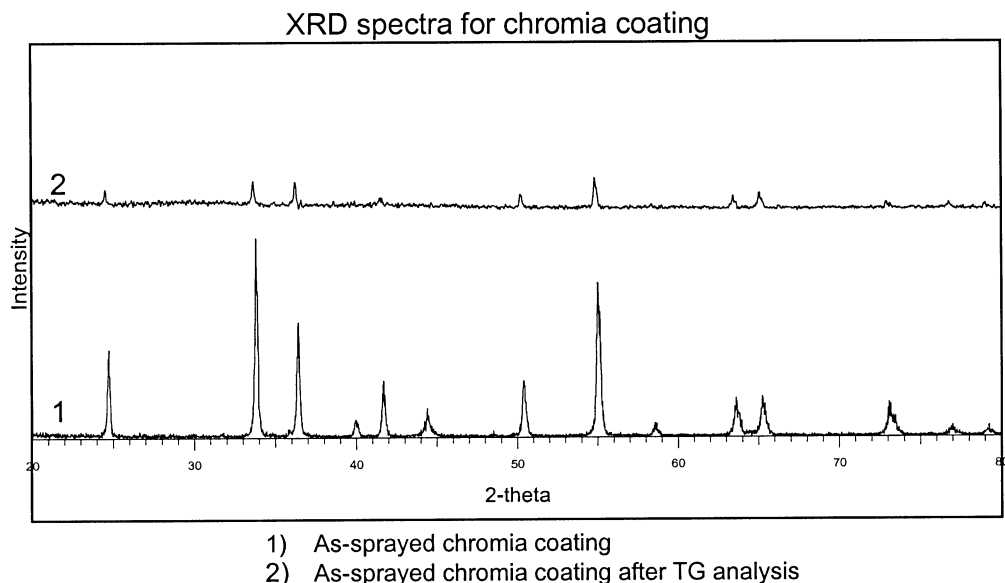


Fig. 4. XRD spectra for chromia coating before and after TG analysis. All the peaks correspond to eskolaite type  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>.

- Altogether 1 mol (152 g) of  $\text{Cr}_2\text{O}_3$  should have 48 g of oxygen but it has only 45.42 g of oxygen. ( $45.42/16 = 2.84$ ).
- The structure of  $\text{Cr}_2\text{O}_3$  coating is then  $\text{Cr}_2\text{O}_{2.84}$  and a weight ratio of O/Cr is 0.44.

#### Explanation 2:

- All of the weight loss is assumed to be due to the decomposition of  $\text{Cr}_2\text{O}_3$  to pure metallic Cr.
- 152 g (1 mol) of  $\text{Cr}_2\text{O}_3$  spray powder has lost 2.58 g of oxygen during plasma spray process.

- Due to the oxygen loss (O/Cr=0.46) 5.61 g of pure Cr has formed.
- The structure of coating is then 3.75 wt.% of Cr and 96.25 wt.% of  $\text{Cr}_2\text{O}_3$ .

In addition to these two explanations there are also other possibilities for the coating structure after plasma spraying.  $\text{Cr}_2\text{O}_3$  can decompose also into other oxides such as  $\text{Cr}_3\text{O}_4$ , CrO and  $\text{CrO}_2$ . Most probably coating structure is a mixture of many decomposed phases. XRD-curves, shown in Fig. 4, taken before and after the TG run revealed no new phases in the coating. The

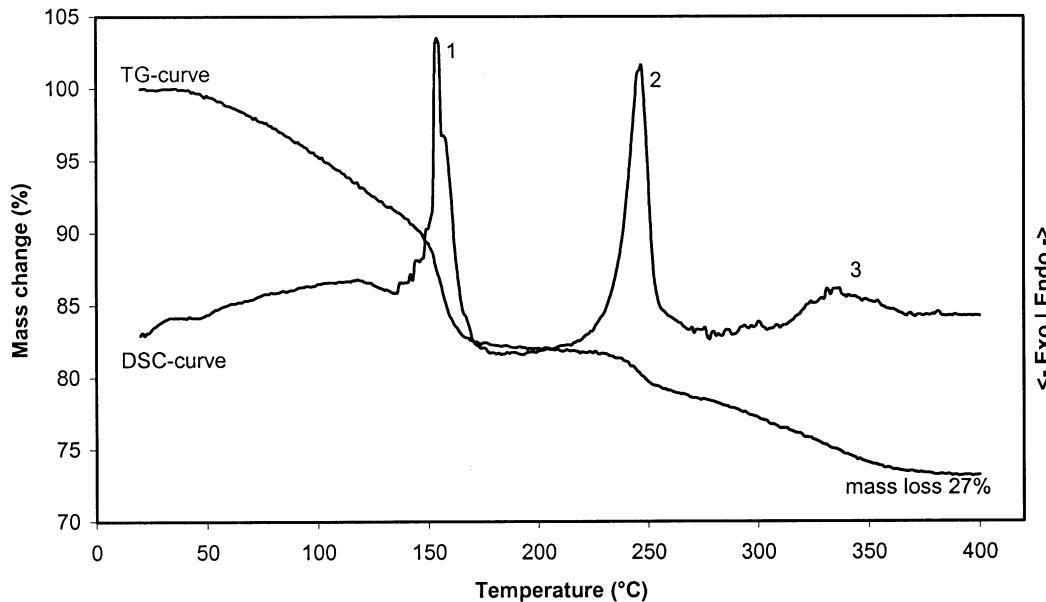


Fig. 5. TG/DSC-curves for aluminum phosphate sealant. Total mass loss for sealant is 27% and DSC curve has three endothermic peaks (indicated with 1–3).

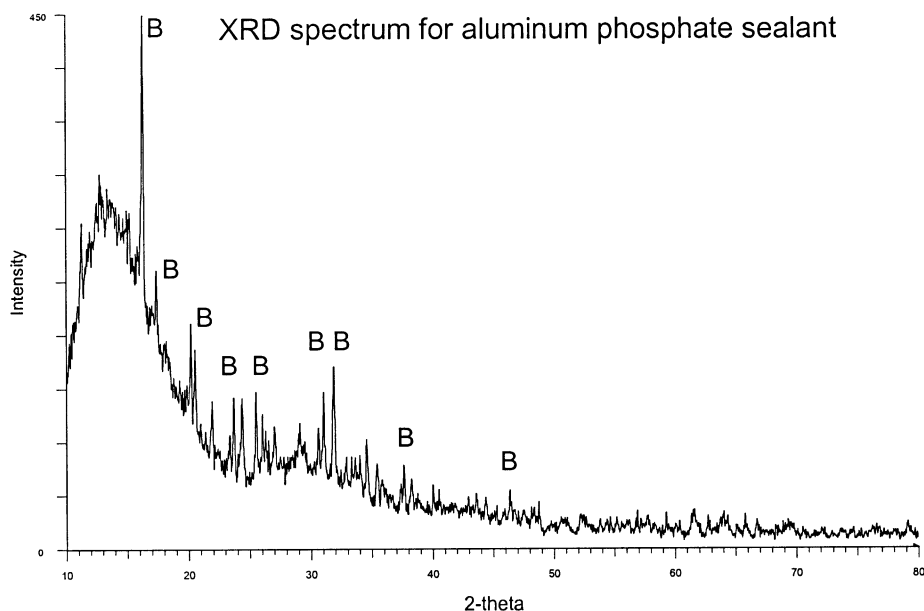


Fig. 6. XRD spectrum for TG sample of aluminum phosphate sealant. Main peaks correspond to B-type metaphosphate  $\text{Al}(\text{PO}_3)_3$ , marked with B.

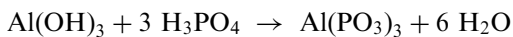
reason for not detecting any of those possible decomposed phases using XRD is due to low amounts of these phases in the coating being less than the reliable detection limit of used instrument.

### 3.2. Aluminum phosphate sealant

Aluminum phosphate sealant was studied with the procedure planned to simulate the actual sealing heat treatment. Aluminum phosphate sealant was heated to 400 °C, then held 2 h at 400 °C and finally cooled down to 20 °C. In addition to mass change also DSC signal was measured. Aluminum phosphate reactions at heating are known to be mostly dehydration reactions where structural water evaporates and new less water containing phases are formed.<sup>19–32</sup> The thermal analysis curves for aluminum phosphate sealant, shown in Fig. 5, indicate that the total weight loss during the heat treatment was about 27 wt.% and the three peaks in the DSC-curve indicate the reactions to be endothermic, which refers to loss of water and dehydration of the composition.<sup>8,9</sup>

The XRD spectrum for TG-sample of aluminum phosphate sealant, in Fig. 6, reported a similar kind of aluminum metaphosphate phase mixture than earlier taken for aluminum phosphate sealant.<sup>5–7</sup> This indicates that the reaction products are always same despite of the path how the final curing temperature of 400 °C for 2-h is reached for aluminum phosphate sealing.

Based on the phosphate binder studies<sup>21–32</sup> it can be concluded that the main reaction for the aluminum phosphate solution of having P/Al molar ratio of 3 would be the formation of metaphosphate  $\text{Al}(\text{PO}_3)_3$  via the dehydration of aluminum phosphate solution. The total weight loss (27 wt.%) is in good agreement with the theoretical reaction from the solution of aluminum hydroxide  $\text{Al}(\text{OH})_3$  and orthophosphoric acid  $\text{H}_3\text{PO}_4$  to aluminum metaphosphate  $\text{Al}(\text{PO}_3)_3$ , as shown in following:



$$78 \text{ g (21\%)} + 3 \times 98 \text{ g (79\%)} \rightarrow$$

$$264 \text{ g (71\%)} + 6 \times 18 \text{ g (29\%)}$$

However, it should be noted that as seen in the TG/DSC-curves, Fig. 5, the reaction from the aluminum phosphate solution to metaphosphate  $\text{Al}(\text{PO}_3)_3$  is more complicated one having several sub-reactions. Also prior to the actual sealing heat treatment the mixture of aluminum hydroxide  $\text{Al}(\text{OH})_3$  and orthophosphoric acid  $\text{H}_3\text{PO}_4$  was pre-heated and allowed to react and some deionised water was added to solution in order to maintain the constant solution volume. From this we can assume that the starting point for aluminum phosphate sealant reactions is an already reacted aluminum phosphate solution with some water. Depending on the final temperature and reaction environment final reac-

tion products are either hydrated aluminum phosphates, metaphosphates or orthophosphates.<sup>19–32</sup> For this reason we also need to discuss about the phase structure of aluminum phosphate sealant after heat treatment at 400 °C. Aluminum phosphate sealant is known to have a complicated phase structure after heat treatment; however, good fit to the X-ray peaks have been achieved with a mixture of aluminum metaphosphates  $\text{Al}(\text{PO}_3)_3$ <sup>5–7</sup> with the main phase of being B-type metaphosphate. Literature<sup>21–32</sup> gives many possible transformation paths from aluminum phosphate solution to aluminum metaphosphates: transformation occurs mainly via monoaluminum phosphate and amorphous phase, but also some amounts of  $\text{H}_2\text{AlP}_3\text{O}_{10} \cdot 2 \text{H}_2\text{O}$  and  $\text{H}_2\text{AlP}_3\text{O}_{10}$  or other hydrated aluminum phosphates may form during the dehydration. In many studies<sup>21–22,25,27,29–30</sup> the temperatures for the total dehydration of aluminum phosphate solution were higher than the 400 °C that we used. According to these notices it needs to be con-

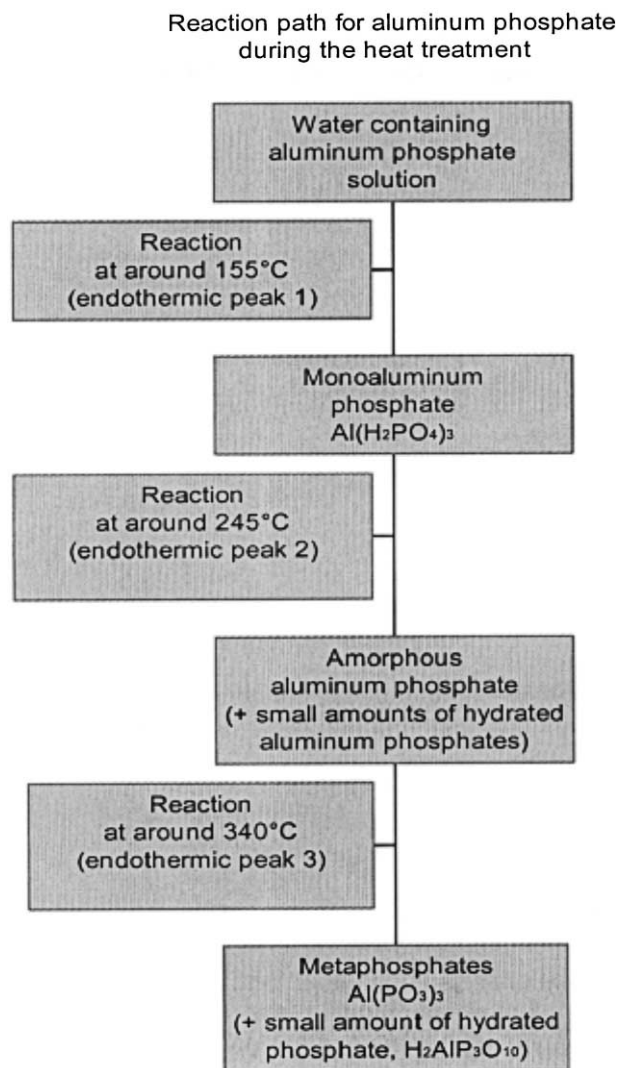


Fig. 7. The reaction path for aluminum phosphate sealant during the heat treatment.

sidered that there still could be some amount of hydrated aluminum phosphate in the sealant due to the uncompleted dehydration during the sealing heat treatment at 400 °C. According to Refs. 21,26,28,32  $H_2AlP_3O_{10}$  is one the most probable hydrated phosphate phase still left in the mixture after the heat treatment. XRD peaks for this phase overlap with aluminum metaphosphate peaks and therefore it is not possible to distinguish it from the sealant mixture. For this reason it has not been considered as a possible phase in the sealant mixture in our previous publications.<sup>5–7</sup>

Taking into consideration the above mentioned the TG/DSC-curve can be interpreted in more detail. The starting point for aluminum phosphate reactions would then be water containing aluminum phosphate solution. Until around 100–150 °C, where monoaluminum phosphate is known<sup>20–24,26,28</sup> to form due to dehydration, the weight loss is only due to evaporation of water from the solution. The formation of monoaluminum phosphate by dehydration together with its continuous dehydration due to temperature increase is seen clearly in the measured TG/DSC-curve at around 155 °C, where the weight loss rate increases and endothermic peak (marked with 1) is seen on the DSC-curve. At around 250 °C monoaluminum phosphate undergoes transformation to amorphous phase<sup>20–24,26,28</sup> and also small amounts of some hydrated aluminum phosphates, such as  $H_2AlP_3O_{10} \cdot 2H_2O$  and  $H_2AlP_3O_{10}$ , can be formed<sup>20–22,26,28,32</sup>. This was also seen in the measured TG/DSC-curve at around 245 °C by increased weight loss rate and endothermic peak (marked with 2) in the DSC-curve. Dehydration of amorphous phase to form metaphosphates is known<sup>20–24,26,28,32</sup> to occur at the

temperature range of 316–399 °C, which corresponds to the measured weight loss in TG-curve at around 340 °C and small endotherm (marked with 3) in the DSC-curve at the same temperature. From this it can be concluded that the dehydration of aluminum phosphate solution to form metaphosphate takes place in three steps during the heating as also shown in Fig. 7. As discussed earlier some amount of hydrated aluminum phosphates might still exist in the phase mixture after the heat treatment due to uncompleted dehydration.

### 3.3. Aluminum phosphate sealed alumina and chromia coatings

Aluminum phosphate sealed alumina and chromia coatings (mixture of crushed coating and aluminum phosphate sealant) were studied with a similar procedure to the plain sealant above. It should be noted that the situation is not quite the same with the mixture of sealant and crushed coatings than with coating impregnated with the aluminum phosphate. However, we wanted to have as much interaction area between the sealant and the coatings as possible. Both the TG- and DSC-curves were measured. Figs. 8 and 9 show thermal analysis curves for both sealant-coating mixtures. In both cases total weight loss was quite similar, about 14 wt.%. This value is, as expected, a half of the weight loss of aluminum phosphate solution. The overall form of the curve corresponds to that of the aluminum phosphate solution. In the case of alumina coating there were only two detectable peaks in the DSC-curve. This is probably due to a different reaction path within the interaction of sealant with the alumina coating forming

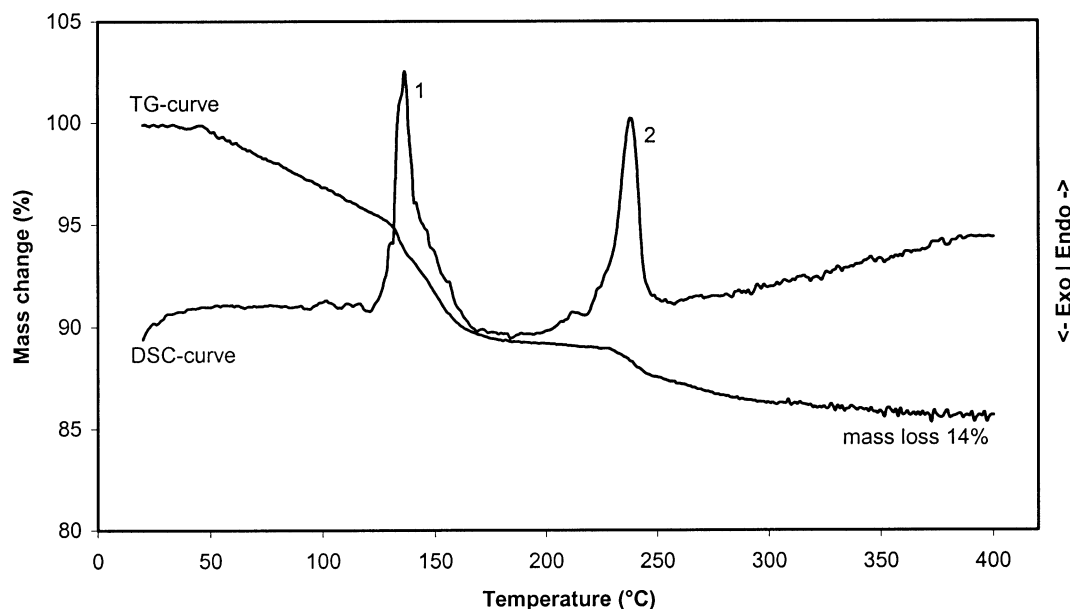


Fig. 8. TG/DSC curves for aluminum phosphate sealant and crushed alumina coating mixture. Total mass loss is 14% and DSC curve has two endothermic peaks (indicated with 1 and 2).

a new phase. In the literature<sup>20,22,26–27,29–31</sup> orthophosphates  $\text{AlPO}_4$  are referred to form when the aluminum content is high enough, meaning that the molar ratio of P/Al is close to 1, which is the case on the surface of alumina particles. However, the formation temperature for berlinite-type orthophosphate, which was detected

in the mixture, occurs at around 150 °C.<sup>20,22,26,29</sup> When comparing this temperature to the thermal analysis curve of aluminum phosphate sealant it can be noticed that the formation of monoaluminum phosphate by dehydration occurs at the same temperature range. Due to this it is impossible to interpret the orthophosphate

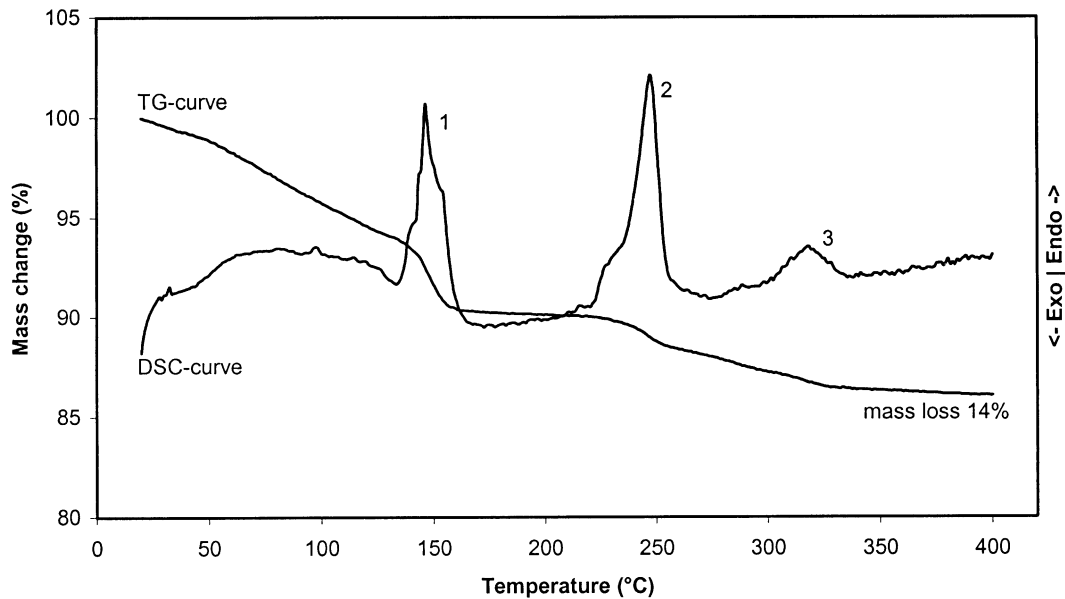


Fig. 9. TG/DSC curves for aluminum phosphate sealant and crushed chromia coating mixture. Total mass loss is 14% and DSC curve has three endothermic peaks (indicated with 1–3).

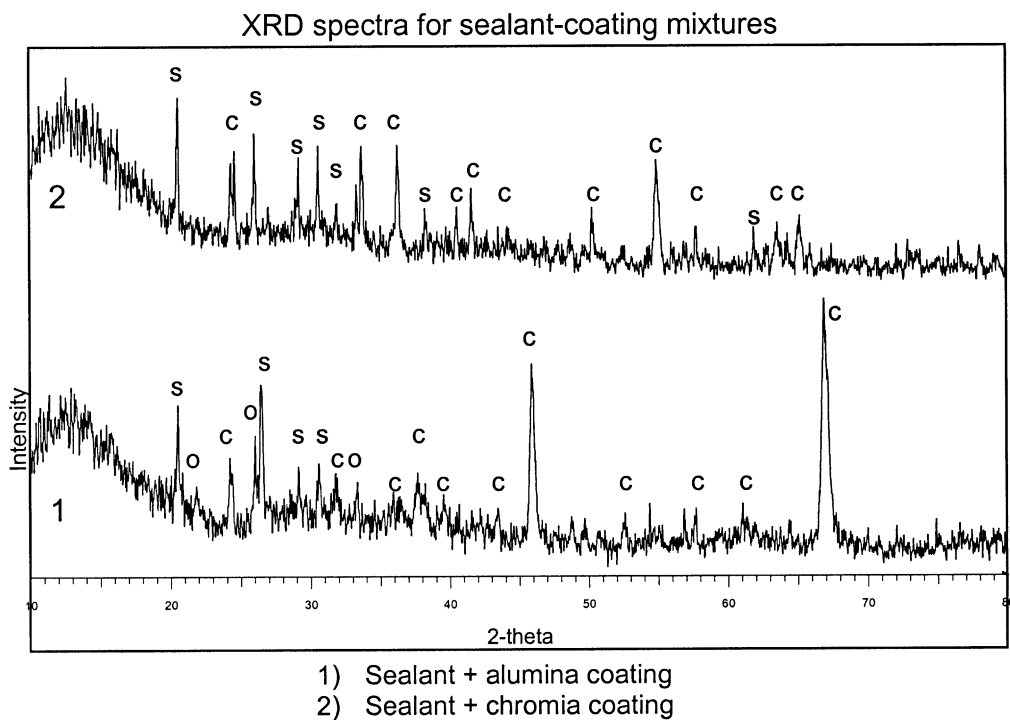


Fig. 10. XRD spectra for sealant-coating mixtures after thermal analysis. Peaks corresponding to the phases of the coating are indicated with c, peaks for aluminum phosphate sealant phases are indicated with s and peaks for aluminum orthophosphate phase from the reaction between the sealant and alumina coating are indicated with o.



reaction from thermal analysis curve of sealant-alumina coating mixture. Because of orthophosphate reaction more aluminum phosphate solution reacts earlier along the heating and due to this the amount of amorphous aluminum phosphate, which forms metaphosphate by dehydration, is much less. Thus the third endothermic peak around 340 °C is absent. In the case of chromia coating the thermal analysis curve corresponded well to that of plain aluminum phosphate indicating that there are no other reactions than phosphate dehydration reactions involved in the mixture sealant and crushed chromia coating. Thus there are no reactions between the sealant and the chromia coating.

The XRD spectra for TG-sample of aluminum phosphate sealant and coating mixtures, shown in Fig. 10, show a quite similar phase structure than earlier taken for aluminum phosphate sealed coatings.<sup>6,7</sup> In the case of alumina coating there is a new crystalline aluminum phosphate phase, berlinite-type aluminum orthophosphate  $\text{AlPO}_4$ . When comparing the XRD spectra of TG-samples to the XRD-spectra of sealed coatings the following conclusion can be made. There are much more crystalline aluminum phosphate in the TG-sample than in the sealed coating. This is due to fact that the aluminum phosphate in the coatings is still mostly in the amorphous form.<sup>6,7</sup> The reason for this difference is that in the coatings the complete hydration of amorphous aluminum phosphate is hindered due to slow diffusion of water from the pores to the coating surface. In our earlier studies<sup>6,7</sup> we have learned that the amount of crystalline phosphate phase increases towards the coating surface where the evaporation of water is higher.

#### 4. Conclusions

As-sprayed alumina coating proved to be stable under thermogravimetric analysis, only the phase structure transformed back to stable  $\alpha\text{-Al}_2\text{O}_3$  from. As-sprayed chromia coating gained some 1.7% weight during the thermogravimetric analysis due to the oxidation. The oxidation of chromia coating is due to under-stoichiometry or decomposition of  $\text{Cr}_2\text{O}_3$  into metallic Cr or other chromium oxides during plasma spray process.

Thermal analysis for aluminum phosphate sealant showed that the formation of metaphosphates  $\text{Al}(\text{PO}_3)_3$  from the aluminum phosphate solution occurs via transformation of monoaluminum phosphate  $\text{Al}(\text{H}_2\text{PO}_4)_3$  to amorphous phase, which crystallizes to metaphosphate by dehydration. Small amounts of hydrated aluminum phosphate phases might be left in the sealant after heat treatment due to the uncomplete dehydration.

Thermal analysis for aluminum phosphate sealant and crushed alumina coating mixture showed some minor differences when compared to the analysis of plain aluminum phosphate. More aluminum phosphate

solution reacted earlier during the heating and the amount of amorphous aluminum phosphate forming metaphosphates was much less. The phase analysis for sealant-alumina coating mixture indicated formation of crystalline orthophosphate  $\text{AlPO}_4$  phase during the heat treatment. The phase is formed in the reaction between the aluminum phosphate and alumina coating. Thermal analysis for aluminum phosphate sealant and crushed chromia coating mixture showed no particular differences when compared to the analysis of plain aluminum phosphate sealant. No indications of the reactions between the sealant and chromia coating were detected. Thus the main mechanism of the phosphate bonding in the alumina coating is chemical bonding whereas in the chromia coatings it is the adhesive binding.

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