High temperature treatment effects on the microstructure and properties of a plasma sprayed 25 mol% Al$_2$O$_3$- 25 mol% Cr$_2$O$_3$- 50 mol% TiO$_2$ coating

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Abstract. In this study, the influence of heat treatments up to 1200°C in vacuum on coatings prepared by atmospheric plasma spraying (APS) from a blend of 25 mol% Al$_2$O$_3$, 25 mol% Cr$_2$O$_3$ and 50 mol% TiO$_2$ on microstructure, porosity, hardness and sliding wear resistance was investigated. The well-known transformation from α-Al$_2$O$_3$ to γ-Al$_2$O$_3$ occurred as a result of the spray process, as well as small amounts of titanium were found in Cr$_2$O$_3$ splats due to an interaction between the feedstock particles. No significant changes were found after a heat treatment at 400°C or 800°C. Heat treatment at 1200 °C led to complete coating delamination. Besides the retransformation of γ-Al$_2$O$_3$ to α-Al$_2$O$_3$, interactions between Cr$_2$O$_3$ and TiO$_2$ splats and the formation of CrTi$_2$O$_5$ was observed. The formation of Al$_2$Ti$_2$O$_5$ was observed in result of a reaction at the outer regions of the Al$_2$O$_3$ splats. At the same time, a reduction in porosity and healing of microcracks were observed as a result of sintering processes, which leads to an increase of the coating hardness to 1170 HV0.2.

1. Introduction

Coatings sprayed from the single oxides of the Al$_2$O$_3$-Cr$_2$O$_3$-TiO$_2$ system and some commercially available binary compositions show multifunctional properties and are widely used for many technical applications. Ternary compositions are promising for further improvement of their performance and the extension of the application range [1-3]. As shown in previous studies, such coatings can effectively be produced by atmospheric plasma spraying (APS) using ternary blends of the three oxides. When spraying these powder blends, the following main observations were made:

Due to the specific behavior of the components (differences in the difficulty of melting factor (DMF) [4] and the thermal diffusivity), the spraying process can act selectively [2]. Thus, considerable differences between the chemical composition of the feedstock powder and the coating can occur. However, this can be largely avoided by the spray parameter selection and a suitable process control [2]. The coating properties are influenced by both the elemental distribution and phase composition. Different interactions between the different particles were observed despite the very short process times. In all previous studies, small amounts of Ti were detected in Cr$_2$O$_3$ lamellae by energy dispersive X-ray spectroscopy (EDS) point measurements [1-3]. Results for Al$_2$O$_3$-based ternary coatings revealed that Cr and Ti atoms can be dissolved in γ-Al$_2$O$_3$ affecting the properties [3].
Ceramic coatings are often applied at high temperatures [5,6]. For this reason, the effects of high temperature treatments on the microstructure and the resulting properties of the coating are of interest. Since as-sprayed coatings are in a thermodynamic non-equilibrium state many different effects can be expected in result of a thermal post-treatment or in high temperature service conditions.

The disadvantageous phase transformation from α-Al2O3 in the feedstock material to γ-Al2O3 in the coating, occurring due to the high cooling rates and preferential formation of γ-Al2O3 nuclei above a certain degree of undercooling [7], is typical for thermal spraying. The reverse transformation is described to be complete at about 1180 °C (with sufficient heat-treatment time) [8-11]. Such phase transformations in plasma sprayed coatings have also been reported for (Al, Cr)2O3 solid solutions [12]. A study on Al2O3-based coatings produced by water-stabilized plasma spraying shows that typical additives such as TiO2 and Cr2O3 influence the transformation temperature of α-Al2O3 in the heat treatment [13]. The reverse transformation is associated with the formation of cracks in the coatings due to the density differences between γ-Al2O3 and α-Al2O3 [9-11].

In result of the spray process, oxygen-deficient TiOx feedstock powders can be partially oxidized to stoichiometric TiO2 in the coating [2]. It can be assumed that a heat treatment can have a further effect depending on the atmosphere. It is well known that in atmospheric conditions above 1000 °C Cr2O3 tends to oxidize to hazardous volatile Cr(VI)-oxide [14]. For plasma sprayed coatings of the binary system Cr2O3-TiO2, significant changes in the microstructure and the formation of the E-phase (Cr2Ti3O7) were observed as a result of high temperature sliding wear tests at 800 °C [15].

As a result of a heat treatment of plasma sprayed coatings, a densification of the coating due to sintering processes is often described [12,15].

In this study, APS coatings from a powder blend consisting of 50 mol-% titania and 25 mol-% each of alumina and chromia were prepared. Heat treatments of these coatings were carried out in order to investigate their effects on the microstructure, hardness and sliding wear resistance of the coatings.

2. Experimental and materials

The feedstock composition was obtained by blending fused and crushed Al2O3, Cr2O3 and TiO2 powders, which are described in Table 1 and were already characterized in previous studies [1,3]. The blend consisted of 50 mol% TiO2 and 25 mol% each of Al2O3 and Cr2O3, corresponding to 24.6 wt-% Al2O3, 36.7 wt-% Cr2O3, 38.6 wt-% TiO2 or 12.5 at-% each of Al, Cr, Ti and 62.5 at-% oxygen.

| Material | Supplier | Particle Size | Granulometric data in µm |
|----------|----------|---------------|-------------------------|
| Al2O3    | Saint Gobain Coating Solutions, Avignon France | -45 + 15 µm | d10  | d50  | d90  |
| Cr2O3    | GTV, Luckenbach, Germany | -45 + 15 µm | 19  | 34  | 54  |
| TiO2     | Ceram Ingenieurkeramik, Albruck-Birndorf, Germany | -45 + 20 µm | 22  | 39  | 61  |

The substrates made of low-carbon steel (S235JR, 1.0038) were grit blasted (3 bar, 20 mm distance, 70° angle) with alumina (EK-F 24) and cleaned in an ultrasonic ethanol bath before depositing the coating. The APS process was performed with an F6 torch (GTV, Luckenbach, Germany) mounted on a six-axis robot using a stationary fixture for the samples with parameters given in Table 2. The parameter set selected resulted to dense coatings with a thickness of ~100 µm and a chemical composition similar to that of the feedstock powder.
The heat treatment of the coated samples was carried out at 400, 800 and 1200 °C in a vacuum furnace at a pressure of 10⁻³ bar. Vacuum was selected to protect the substrate from oxidation and Cr₂O₃ from oxidation to volatile CrO₃. Low heating and cooling rates of 200 K/h were applied. The holding time at the treatment temperatures was 6 hours.

The preparation of coating cross sections was made according to the standard metallographic procedure. In order to investigate the local chemical composition of individual splats and the local compositions, the coatings were studied by scanning electron microscopy (SEM) (Leo 1455VP, Zeiss, Oberkochen, Germany) equipped with an EDS detector (GENESIS, EDAX, Mahwah, NJ, USA) using an accelerating voltage of 25 kV. To determine the porosity, five SEM images taken at a magnification of 500x, were evaluated for each coating using an image analysis method (Olympus, Shinjuku, Japan). By using the backscattered electron detector (BSD), the distribution and homogeneity of the elements were visualized by different gray levels. The local chemical composition of individual splats was studied for each coating by five EDS point measurements. The measuring points were located at positions where an influence of surrounding areas on the measuring process could be largely excluded.

In order to investigate the changes in microstructure that occur during the spray process and as a result of the heat treatment, the phase compositions of the powder blend, the as-sprayed coating and the coating heat-treated at 1200°C were studied by X-ray diffraction (XRD) (D8 Discover X-ray diffractometer, Bruker AXS, Billerica, MA, USA) using Co Kα radiation with a tube voltage of 40 kV and a tube current of 40 mA. The diffraction patterns were measured for a 2θ range from 10° to 130°, with a step size of 0.01° and a dwell time of 1.5 s/step.

The Vickers microhardness of the coatings was measured by 10 indentations with a test load of 2.94N on the cross sections using a Wilson Tukon 1102 device (Buehler, Uzwil, Switzerland). For measurement of the dry, unidirectional sliding wear resistance, coatings which were ground (Rₛ < 1 µm) and tested at room temperature with a ball-on-disk tribometer (Tetra, Ilmenau, Germany). For the as-sprayed coating and the coatings heat-treated at 400 °C and 800 °C, three runs were carried out on the rotating, coated sample according to the test parameters given in Table 3. The volume of the resulting wear tracks was determined using an optical 3D profilometer MikroCAS (LMI, Teltow, Germany).

### Table 2. Parameters of APS process.

| Plasma Gas Flow Rate | Current | Argon | Hydrogen | Spraying Distance | Traverse Speed | No. of Passes | Powder Feed Rate |
|----------------------|---------|-------|----------|-------------------|----------------|---------------|-----------------|
|                      | 600 A   | 41 l/min | 11 l/min | 110 mm           | 0.4 m/s        | 4             | 25 g/min         |

### Table 3. Sliding wear test parameters.

| Force | Radius | Speed | Cycles | Wear Distance | Counter Body |
|-------|--------|-------|--------|---------------|--------------|
| 10 N  | 5 mm   | 0.05 m/s | 3183   | 100           | Al₂O₃         |
|       |        |        |        |               | 6 mm          |

### 3. Results and discussion

Despite the low coating thickness and the low heating and cooling rates selected, at 1200 °C the coating delaminated from the substrate. However, the coating itself remained not damaged. Thus, the characterization was carried out with the exception of the sliding wear test.

Figure 1 displays the SEM images of the coatings. Some specific features of thermal spray coatings, such as the splat-wise build up, pores and some microcracks as well as some not or only partially melted particles can be observed. The three components of the coating are clearly identifiable in the images due to their different gray levels in the BSE contrast. The light gray areas correspond to Cr₂O₃, the dark gray areas belong to Al₂O₃ and the medium gray areas consist of TiO₂ or TiO₂. Due to the high DMF [2,4]
and low thermal diffusivity non-melted particles are mostly Al$_2$O$_3$. Non-melted Al$_2$O$_3$ particles as well as Al$_2$O$_3$ and Cr$_2$O$_3$ splats are predominantly in direct contact with titania splats (Fig. 1a). The as-sprayed coating and coatings heat-treated at 400°C and 800°C show very similar microstructures (Fig. 1a-c). The coating heat-treated at 1200°C shows a significantly lower amount of microcracks (Fig. 1d). Original porosity decreased due to sintering, but new porosity is formed in result of solid state diffusion processes. In the coating heat-treated at 1200°C, the contrast between Cr$_2$O$_3$ and TiO$_2$ splats is significantly lower. Overall, the proportion of light gray areas associated with Cr$_2$O$_3$ appears to decrease in favor of gray TiO$_x$ areas. In addition, the outer areas of Al$_2$O$_3$ splats started to react. The former interface of the Al$_2$O$_3$ lamellae with the surrounding material shows a different grayscale. These observations indicate that more intensive diffusion processes take place at 1200°C, significantly changing the microstructure and phase composition of the coating.

Figure 1. SEM image of (a) as-sprayed coating and coatings heat-treated at (b) 400°C, (c) 800°C and (d) 1200°C.

The local chemical composition determined by EDS point measurements of the different areas in the SEM images are shown in Figure 2. Neither Ti nor Cr were detected in the dark areas corresponding to Al$_2$O$_3$. As also shown in previous studies [1-3], low amounts of Ti (1-2 at.-%) can be reliably detected in the Cr$_2$O$_3$ splats as a result of the spray process. The heat treatment did not affect the composition of both Cr$_2$O$_3$ and Al$_2$O$_3$ areas, regardless of the annealing temperature. Interestingly, changes in the chemical composition of the medium gray TiO$_x$/TiO$_2$ areas were found. After heat treatment at 1200°C, 5-12 at.-% Cr and traces of Al were found in these areas. The diffusion directions during heat treatment seemed to be the opposite compared to the spray process. As a result of the heat treatment at 1200°C Cr$_2$O$_3$ lamellae disappear due to interaction with the surrounding TiO$_x$ areas.
Figure 2. Chemical composition of splats with different grayscale (Fig.1) determined by EDS point measurements.

The XRD patterns shown in Figure 3 clearly reveal a change of the phase composition of the coating compared to the feedstock powder. The powder blend consisted mainly of α-Al₂O₃, Cr₂O₃ and a variety of TiOₓ phases. Gravimetric measurements in another study have indicated that x in this TiOₓ powder is about 1.9 [16]. The XRD pattern of the as-sprayed coating indicates the expected occurrence of the typical phase transformation from α-Al₂O₃ to γ-Al₂O₃. This is connected with the appearance of new peaks at 2θ = 53.8° and 2θ = 79.6° associated with γ-Al₂O₃ and the decrease of the peak intensities of α-Al₂O₃. A further change in the phase composition is noticeable by analyzing the TiO₂ or TiOₓ peaks. In the as-sprayed coating, additional peaks associated with the rutile structure of TiO₂ at 2θ = 48.3° and 2θ = 64.0°, a considerable broadening of the left shoulder of Cr₂O₃ at 2θ = 42.2° as well as the simultaneous loss of TiOₓ peak intensities are observed. This shows that oxidation of the non-stoichiometric titanium oxide phases during the APS process leads to the formation of stoichiometric rutile. The evaluation of the XRD pattern of the coating heat-treated at 1200°C is challenging, as a result of the intensive interaction between the components. Due to the formation of solid solutions, some peaks are shifted compared to their standard position. In addition, the local composition is sometimes varying. However, it is noticeable that the intensity of the α-Al₂O₃-related peaks increases significantly. This indicates a retransformation of γ-Al₂O₃ into α-Al₂O₃ above 800 °C, as already described in other studies [5-8]. The decrease of the intensity of Cr₂O₃ and TiO₂ is connected with the formation of new phases. The additional peaks are identified as Al₂Ti₇O₁₅ and CrTi₂O₅ and described in the literature [17,18]. It is assumed that vacuum conditions during heat treatment, support the formation for these phases. Both phases contain Ti³⁺ and Ti⁴⁺ atoms. Accordingly, they are sensitive to oxidation at higher temperatures in atmospheric conditions. Taking into account the results of the EDS point measurements, it can be assumed that Cr₂O₃ lamellae react with the surrounding TiO₂<x> splats and form CrTi₂O₅. Furthermore, it is suspected that Al₂Ti₇O₁₅ is formed at the outer regions of the Al₂O₃ splats. Moreover, the transformation from α-Al₂O₃ to γ-Al₂O₃ can increase the reactivity in solid state reactions above 800 °C.
Figure 3. XRD patterns of the powder blend, the as-sprayed and the coating after heat-treatment at 1200 °C.

Figure 4. Ball-on-disc wear rate, porosity and hardness for the as-sprayed and heat-treated coatings.

Figure 4 shows the results of the porosity, hardness and sliding wear resistance measurements. No significant changes in the coating properties are found due to a heat treatment up to 800°C. This is in good agreement with the corresponding microstructures of the coatings. Indeed, slightly reduced porosities are measured, which also lead to a slight increase in hardness and can be presumably associated with sintering processes. Due to the increased number of microcracks which appear as a result of additional stresses caused by the heat treatment, decrease of porosity does not improve the sliding wear resistance. In summary, porosity, hardness as well as the coating wear rate K after heat treatment at 400°C and 800°C are at a similar level compared to the as-sprayed coating. These changes are less significant than...
found for plasma sprayed coatings of the binary system Cr$_2$O$_3$-TiO$_2$, as a result of high temperature sliding wear tests at 800 °C [15]. The delaminated coating heat-treated at 1200 °C has the lowest porosity of 0.99 ± 0.2 % probably due to healing of microcracks. Due to the extensive microstructural changes, this coating has a hardness of 1170 (±101) HV0.2, which is approximately 50% higher than for the as-sprayed coating. Further studies are required to determine the reason for the hardness increase. It has to be clarified, if this can be attributed entirely to the healing of microcracks and phase transformation from γ- to α-Al$_2$O$_3$ or is also influenced by the newly formed CrTi$_2$O$_5$ and Al$_2$Ti$_3$O$_7$ phases. The influence of the vacuum on phase formation has to be studied as well.

4. Conclusions
The effects of heat treatments up to 1200°C in vacuum on the microstructure and properties of APS coatings using a powder blend consisting of 50 mol-% TiO$_2$ and 25 mol-% each of Al$_2$O$_3$ and Cr$_2$O$_3$ were investigated. The following conclusions can be drawn:

- The microstructural analyses and investigations of hardness and sliding wear resistance reveal that significant changes occur after heat treatment at 1200°C.
- As already described in other studies, a reverse transformation of γ-Al$_2$O$_3$ to α-Al$_2$O$_3$ takes place between 800°C and 1200°C.
- As a result of the thermal spray process, small amounts of Ti were detected in Cr$_2$O$_3$ splats by EDS point measurements. After heat treatment at 1200°C, the amount of Ti in remaining Cr$_2$O$_3$ splats remains unchanged.
- SEM images, EDS point measurements and XRD patterns suggest that heat treatment of the coating at 1200°C causes Cr$_2$O$_3$ lamellae to dissolve by reacting with surrounding TiO$_2$ splats to form CrTi$_2$O$_5$ in vacuum.
- In addition, new peaks probably associated with Al$_2$Ti$_3$O$_7$ are also present in the XRD pattern of the coating heat-treated at 1200°C in vacuum. The evaluation of the SEM studies suggests that this phase is located at the outer areas of the Al$_2$O$_3$ splats.
- The reactions between the individual splats above 800 °C and the possible influence of the furnace atmosphere on the formation of new phases (Al$_2$Ti$_3$O$_7$, CrTi$_2$O$_5$) needs further investigation.
- Through sintering processes and the mentioned phase formation in the coating heat-treated at 1200 °C, the number of microcracks is considerably reduced and the porosity of the coating is decreased.
- These microstructural changes lead to a significant increase in the hardness of the coating, but also to coating delamination. For a successful heat treatment of the coating, the bonding of the coating must be improved by selection of a suitable substrate material and application of a bond coat.

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