Emergence and impact of $\text{Al}_2\text{TiO}_5$ in $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ APS coatings

A Richter$^{1,*}$, L-M Berger$^2$, S Conze$^2$, Y J Sohn$^1$ and R Vaßen$^1$

$^1$ Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), 52425 Jülich, Germany
$^2$ Fraunhofer Institute for Ceramic Technologies and Systems, Fraunhofer IKTS, Winterbergstr. 28, 01277 Dresden, Germany

* e-mail: ale.richter@fz-juelich.de

Abstract. Despite numerous studies and decades of industrial application, there is still a lack of understanding about the formation and the impact of aluminum titanate ($\text{Al}_2\text{TiO}_5$) in $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ thermal spray coatings. Especially the influence of the feedstock powder characteristics on the phase composition has only crudely been investigated so far. Therefore, in this work we have characterized commercial fused and crushed $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ feedstock powders: three of them containing 13 wt.% TiO$_2$ and three containing 40 wt.% TiO$_2$. The effect of the varying phase compositions of the powders and their relevance on the deposition efficiency, the phase compositions, the porosity, and the hardness of the respective APS coatings is described in detail. While detrimental to the mechanical properties of 40 wt.% TiO$_2$ coatings, we have found an enhancement of the hardness for 13 wt.% TiO$_2$ coatings with a high Al$_2$TiO$_5$/Al$_6$Ti$_2$O$_13$ content in the feedstock powder. Furthermore, it was found that Al$_2$TiO$_5$ may reform during APS when sprayed from an Al$_2$TiO$_5$-free powder.

1. Introduction

Thermal spraying is a group of technologies that is very versatile regarding the coating material (predominantly oxides, metals and hardmetals) to produce coatings with a typical thickness in the range of 100-500 µm with a high deposition rate. Atmospheric plasma spraying (APS) is the most common thermal spray process for ceramic materials using Ar, H$_2$, and/or N$_2$ as plasma forming gases. In the case of oxides, as the most important ceramic material group, melting of the feedstock material during the spray process is common [1–3]. The coatings are then built up by individual splats of rapidly solidified spray powder particles. Changes of the chemical and/or the phase composition of the coating as compared to the feedstock occur due to chemical reactions with plasma-forming gases, burning products (in the case of flame spraying) or with the environment. When spraying $\text{Al}_2\text{O}_3$ coatings, for example, the thermodynamically stable $\alpha$-$\text{Al}_2\text{O}_3$ commonly solidifies in its metastable $\gamma$-$\text{Al}_2\text{O}_3$ modification, which has a significant impact on the properties of the coating [4,5]. Furthermore, titanium oxide feedstock may be reduced during thermal spray [6,7] producing coatings with non-ordered and ordered (Magnéli-phases) suboxides, which would affect the melting point of the particles [6,8] and the electrical [6,7] as well as the thermal conductivity [9] of the sprayed coating.

Several commercially available feedstock powder compositions of the $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ system ($\text{Al}_2\text{O}_3$ with 3, 13, and 40 wt.% TiO$_2$) are commonly processed to coatings. However, in the $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ system a compound, aluminum titanate ($\text{Al}_2\text{TiO}_5$), exists at about 44 wt.% TiO$_2$. It is thermodynamically stable in a temperature range of about 1280 °C up to its melting point at 1860 °C [10], but may also exist in a metastable state as long as the rates of diffusion are sufficiently low.
(typically up to about 800 °C). This compound is proposed to have a significant impact on the properties of materials of the Al$_2$O$_3$-TiO$_2$ system as its properties strongly deviate from the properties of both single oxides. For example its hardness and elastic modulus are much lower than that of α-Al$_2$O$_3$. It does show some promising thermal properties, however, due to a pronounced isotropy in its thermal expansion coefficient, leading to an average thermal expansion coefficient close to zero in polycrystalline Al$_2$TiO$_5$ ceramics [11].

Furthermore, it has to be taken into account that the process of Al$_2$TiO$_5$ decomposition is strongly affected by the oxygen partial pressure [12] and the grain size of Al$_2$TiO$_5$ [13]. For the decomposition process a contraction of Al$_2$TiO$_5$ crystals in the $a$ direction of the lattice and a concurrent expansion in the other two directions, $b$ and $c$, at different rates was proven. However, the complex mechanism has not been fully understood yet. Depending on the oxygen partial pressure Al$_2$TiO$_5$ forms an Al-rich solid solution Al$_{2-x}$Ti$_{1+x}$O$_5$ of anosovite (Ti$_3$O$_5$) and Al$_2$TiO$_5$ [12,14,15,17] which oxidizes and decomposes to Al$_2$O$_3$ and TiO$_2$ as final products in air. Reformation of decomposed Al$_2$TiO$_5$ above 1280 °C has been described in air and in vacuum [16,18,19]. The formation of a solid solution has also been observed in the case of thermal spray coatings [20]. Depending on the spraying conditions, changes in the composition of the solid solution could be observed between the feedstock material and an APS coating. It has been found that the homogeneity of distribution of Al and Ti in the powder is a key issue for the formation of Al$_2$TiO$_5$ in feedstock powders and the corresponding coatings [20].

More recently, several authors described Al$_6$Ti$_2$O$_{13}$ as an additional phase in the Al$_2$O$_3$-TiO$_2$ system [21–24], which was proposed to exist in thermal spray coatings as well [25]. It can be assumed that the properties of this compound are closely related to the properties of Al$_2$TiO$_5$. All of the described phases are expected to affect the properties of the coatings and, therefore, need to be controlled during the spraying process.

APS Al$_2$O$_3$-TiO$_2$ coatings have found widespread use in industry for the functionalization of metallic substrates with a focus on mechanical and electrical properties. Furthermore, the machinability, wear resistance or conductivity of the coatings can be adjusted by changing the TiO$_2$ content. Current applications of Al$_2$O$_3$-TiO$_2$ coatings include alternator parts, heaters, valves, textile manufacturing tools, and wear parts [26,27]. Several studies have addressed the influence of feedstock powders of different composition on the properties of APS coatings in the past [25,28–36]. Most of these studies focus on the comparison between nanostructured powders and the clad powder Metco 130, which consists of coarse alumina particles cladded with sub-µm titania [28–32,36,37]. However, the most commonly used type of commercial Al$_2$O$_3$-TiO$_2$ feedstock, namely fused and crushed powders, which are often preferred due to their low production costs, are rarely investigated.

Despite the multitude of academic studies and a long history of application of APS coatings there are still issues with the reliability of the coating properties, which stem from insufficient attention to the feedstock powder properties. In this study we address this issue by taking a deeper look at the influence of the compounds from the Al$_2$O$_3$-TiO$_2$ system on the properties of the coatings with a special focus on the different commercially available fused and crushed feedstock powders. Controlling the phase contents in fused and crushed powders is not straightforward and strongly depends on the heating, mixing and the cooling conditions during fabrication. Therefore, we have selected six fused and crushed powders of two common compositions, characterized them in detail, and investigated the impact of their phase composition on the properties of APS Al$_2$O$_3$-TiO$_2$ coatings. Furthermore, we investigated the behavior of an experimental powder, obtained by heat treatment of a commercial powder with very high Al$_2$TiO$_5$ content, during the spray process.

2. Experimental and materials

2.1. Feedstock powders
A selection of six different commercially available Al$_2$O$_3$-TiO$_2$ feedstock powders (three with a nominal composition of 13 wt.% TiO$_2$ and three powders with 40 wt.% TiO$_2$) was used in this study. For both compositions one powder was produced by blending separately fused and crushed Al$_2$O$_3$ and
TiO$_x$ powders. These powders will be denoted as “blend13” and “blend40” in the following. The other two powders for each composition were produced by jointly fusing and crushing of the individual oxides by different manufacturers and under different processing conditions. They will be referred to as “jA13/jA40” and “jB13/jB40” in the following. The phase composition of powder jB40 was modified by a thermal treatment at 1150 °C with a heating rate of 5 K min$^{-1}$ and 4 h holding time in a Nabertherm LH30/14 chamber furnace under flowing air.

All feedstock powders were characterized in detail. This included a characterization of the cross-section of each powder by a FEI Phenom First Generation scanning electron microscope (SEM) in backscattered electron (BSE) mode. The particle size distribution was determined by laser diffraction (Horiba LA-950-V2) and the density of the powders characterized via a helium pycnometer (Quantachrome Instruments Ultrapycnometer 1000). A Bruker D4 Endeavor was employed to determine phase contents of each powder via X-ray diffraction (XRD). Each diffraction pattern was recorded in a range of 2$\theta$=10..130° with a step size of 0.02° and a measurement time of 2 s per step in a simultaneous measurement range of 4°. Phase quantification was then performed by Rietveld refinement using the TOPAS Software [38]. The mass changes of the feedstock powders were determined by gravimetric tests in alumina crucibles (triple determination of mass gain using 2 g of feedstock powder) at 1300 °C and for 6 h holding time under a continuous air flow.

2.2. Coatings
Atmospheric plasma spraying (APS) was used to produce coatings with thicknesses of 500 to 800 µm. In particular, an Oerlikon Metco F4 plasma torch with a nozzle diameter of 6 mm was used in an Oerlikon Metco Multicoat System. Each coating was sprayed with an Ar/H$_2$ gas mixture with flow rates of 40 and 10 slpm, respectively. The stand-off distance was set to 150 mm and the torch was operated at a constant current of 550 A, resulting in a torch power of about 40 kW. The surface speed of the torch was set to 500 mm/s in relation to a stationary substrate. Prior to spraying, each grit-blasted mild steel substrate (50x50x2 mm³) was preheated to about 120 °C. During spraying, the substrate was cooled by two air jets. The feed rate of each powder was determined at the beginning of the spraying experiments. This feed rate was then used to estimate the deposition efficiency (DE) after measuring the mass gain of the substrate. All powders were fed with a constant Ar flow rate of 3.5 slpm.

Following the coating deposition, each substrate was cut using an ATM Brillant 221 saw. XRD measurements were performed on as-sprayed coatings similarly to those for the powders, but with a reduced measurement range of 2$\theta$=10...80° and a measurement time of 0.75 s per step. Materialographically prepared cross-sections were firstly characterized by confocal laser microscopy (LaMi) to determine the porosity of each coating and the coating thickness. Ten LaMi images were recorded at a magnification of x500 and then analyzed via ImageJ [39]. Furthermore, BSE SEM images were recorded using a Hitachi TM3000. The Vickers hardness of the coatings was determined on the cross-sections by using a Leitz Miniload 2 with an applied force of 3 N (HV0.3) for 30 s. At least five indentations were made per coating.

3. Results and discussion
3.1. Feedstock powders and the respective coatings
A similar powder morphology of irregularly shaped particles was found for all powders. In combination with a high similarity between the size distributions of all powders as exemplified by the $d_{50}$ in Table 1, this allows for a direct comparison of their behavior in the spray process. However, differences were detected for the powder densities (Table 1). In fact, the densities were in agreement with the phase analysis results obtained via Rietveld refinement (Figure 1). In the following “TiO$_2$” implies the rutile structure. The powder blends exhibited a pycnometric density in between the crystallographic densities of α-Al$_2$O$_3$ (4.0 g cm$^{-3}$) and TiO$_2$ (4.3 g cm$^{-3}$). In contrast, powders with a significant content of Al$_2$TiO$_5$ (crystallographic density 3.7 g cm$^{-3}$) showed a lower density. Overall
the blend13 and blend40 powders consisted of α-Al2O3 and TiO2 or several TiOx phases. Although, a mass gain of blend40 powder of 0.4 % indicated a low O-deficiency. Contrary, the jointly fused and crushed powders jA and jB differed significantly in their oxidation behavior as well as in their phase compositions. The theoretic maximum Al2TiO5 content is about 30 and 90 wt.% for compositions with 13 wt.% TiO2 and 40 wt.% TiO2, respectively. While the jA powders contained an Al2-xTi1+xO5 solid solution [20], the jB powders contained significant amounts of Al2TiO5 and Al6Ti2O13 [21,23]. Due to the inhomogeneous distribution of the metallic constituents, the α-Al2O3 content in the jA powders is higher than for the theoretic compositions due to an incomplete reaction with TiO2. A significant mass increase for the jA powders by oxidation in air is connected to the reaction of Al2-xTi1+xO5 to Al2TiO5 and TiO2 [20]. The compositions of the jB powders corresponded well to the theoretic compositions according to the results of the phase analysis if Al6Ti2O13 is included.

### Table 1. Mean diameter \( d_{50} \) and density of the investigated Al2O3-TiO2 powders.

| powder   | 13 wt.% TiO2 | 40 wt.% TiO2 |
|----------|--------------|--------------|
|          | blend13      | jA13         | jB13         | blend40      | jA40         | jB40         |
| \( d_{50} \) (µm) | 35           | 37           | 32           | 34           | 34           | 30           |
| pycnometric density (g cm\(^{-3}\)) | 4.0          | 4.0          | 3.9          | 4.1          | 4.0          | 3.7          |
| average mass gain (%)  | 0.16         | 0.73         | 0.03         | 0.40         | 1.91         | 0.42         |

The cross-sections of the powders are presented in Figure 2 a-c and g-i) for the 13 and the 40 wt.% TiO2 powders, respectively. A clear distinction can be made between the individual bright TiO2/TiOx and the dark Al2O3 particles for the powder blends in Figure 2 a) and g). Surprisingly, a similar elemental contrast was observed for the jA powders in Figure 2 b) and h). Even though they were produced by joint fusion of Al2O3 and TiO2, they are characterized by an inhomogeneous distribution of the metallic constituents. Both jA powders also showed the highest mass gains in the oxidation experiments in their corresponding groups. Only few powder particles show a homogeneous intermediate grayscale. The analysis results for the jA40 powder are consistent with the results of the earlier study [20]. In contrast, a homogeneous elemental distribution was found in both jB powders (Figure c) and i)). This corresponds well to the results of the phase analysis. Apparently, an insufficient intermixing of the metallic elements impeded the formation of Al2TiO5 for the jA powders, while for the jB powders a homogeneous intermixing of the elements facilitated its formation. Despite the decomposition of Al2TiO5 below 1280 °C [10], this phase can appear in the feedstock powder due to rapid cooling [40,41]. The formation conditions of Al6Ti2O13 are still unclear. It is noteworthy that an inhomogeneous distribution of the metallic constituents in the jA powders correlates with a high deficiency of O relative to Al2TiO5, while for the jB powders the homogeneous distribution of Al and Ti and a low deficiency of O coincides with the co-existence of Al2TiO5 and Al6Ti2O13. It appears that the presence of Al2TiO5 and Al6Ti2O13 indicates a homogeneous distribution of the metallic elements and non-reducing conditions during the preparation of the powder.
Cross-sections of the APS coatings produced from the various powders are presented in Figure 2 d)-f) and j)-l). Similarly to the feedstock powders, mostly dark or bright splats were observed in the microstructures of the coatings produced from the blended powders (Figure 2 d) and j)). Accordingly, the XRD patterns in Figure 3 indicate the presence of γ-Al2O3, TiO2, and some α-Al2O3. The formation of γ-Al2O3 in thermal spray coatings from α-Al2O3 feedstock powders is well known [4,5]. However, no formation of Al2TiO5 or other compounds was detected in the coatings. In addition to γ-Al2O3, TiO2, and α-Al2O3, the coatings produced from powder jA exhibited some peaks that can be related to Al2-xTi1+xO5 (Figure 3), especially for jA40. With respect to the feedstock powders, the peaks related to this solid solution were slightly shifted to higher diffraction angles for the coatings, indicating an increased Ti content [20]. Similarly, the cross-sectional images in Figure 2 e) and k) show several splats with an intermediate gray scale between the Al2O3 and TiO2 splats. So, in contrast to the blend powders, some changes in the phase composition of the jA powders occurred during APS, although these changes were probably restricted to powder particles containing both metallic elements. Lastly, the images of the coatings produced from the jB powders (Figure f) and l)) exhibited a low contrast between the individual splats, indicating a homogeneous distribution of the elements, similarly to the feedstock powders. Furthermore, only peaks related to Al2TiO5 were observed in the XRD pattern of the coatings produced from the jB40 powder (Figure 3). However, a clear distinction between Al2TiO5 and Al6Ti2O13 is difficult from the XRD patterns of the coatings due to very broad peaks and a high similarity between the structures of these phases. Contrary to the jB40 coating, mostly γ-Al2O3 could be identified in the coatings sprayed from the jB13 powder with only minor peaks pointing at residual
Al$_2$TiO$_3$. At the same time, no peaks related to TiO$_2$ or TiO$_x$ could be identified. This may be due to Ti being incorporated in $\gamma$-Al$_2$O$_3$. This assumption is supported by a slight shift of the $\gamma$-Al$_2$O$_3$ peaks to lower diffraction angles (e.g. at 67°) which indicate an increase in its lattice constant. Transmission electron microscopy (TEM) investigations by Goberman et al. also indicated an incorporation of Ti in $\gamma$-Al$_2$O$_3$ for APS Al$_2$O$_3$-TiO$_2$ coatings [35,42]. Yang et al. have suggested the incorporation of Ti in an amorphous Al$_2$O$_3$ phase which is related to the amorphous “hump” at 2$\theta$=25..40° in the XRD diagrams of the coatings [29].

![XRD diagrams of APS coatings sprayed by using the 13 wt.% TiO$_2$ feedstock powders (left) and 40 wt.% TiO$_2$ powders (right).](image)

**Figure 3.** XRD diagrams of APS coatings sprayed by using the 13 wt.% TiO$_2$ feedstock powders (left) and 40 wt.% TiO$_2$ powders (right).

The $DE$, porosity and hardness of the APS coatings are presented in Figure 4. Low $DE$s were observed for the coatings sprayed from the blended powders. This can be related to the high melting point of Al$_2$O$_3$ at about 2050 °C which leads to insufficient melting of the pure Al$_2$O$_3$ particles in the plasma plume which will then bounce off the substrate/coating surface [3]. An improved intermixing of the metallic elements in each feedstock powder particle significantly decreases its melting temperature and thereby increases the $DE$. In the Al$_2$O$_3$-Al$_2$TiO$_3$ part of the phase diagram of the Al$_2$O$_3$-TiO$_2$ system this could lead to an up to 200 °C lower melting temperature. Accordingly, a higher $DE$ was observed with the jB powders as compared to jA or the blend powders for both compositions. Surprisingly, the coatings sprayed with jB13 exhibited a slightly higher $DE$ than the coatings sprayed with jB40. A possible explanation is the much lower thermal conductivity of Al$_2$TiO$_3$ (about 2 W (m K)$^{-1}$) [43,44]) phase in comparison to $\alpha$-Al$_2$O$_3$ (about 34 W (m K)$^{-1}$). Therefore, a lower melting degree is obtained due to impeded thermal transport through the particles despite a lower melting temperature.

The porosity of the coatings is also strongly affected by the degree of melting of the feedstock powder. This is especially evident for the 13 wt.% TiO$_2$ feedstock powders. Here, the coatings produced from blend13 and jA13 showed a significantly higher porosity than the coating from jB13 (Figure 4). With the 40 wt.% TiO$_2$ powders, however, a low and highly similar porosity was found for all coatings. Here, the phases with lower melting temperatures, namely TiO$_x$ and Al$_2$TiO$_5$, might have sufficiently promoted the densification of the coating.

The hardness of a coating is influenced by its porosity and phase composition. Therefore, the similar porosities of the coatings from the 40 wt.% TiO$_2$ powders allow for a comparison of the effect of the different phases. In particular, the occurrence of Al$_2$TiO$_3$ decreased the coating hardness distinctively (Figure 4). The highest hardness was measured for the coatings produced from blend40. Coatings prepared from feedstock powders with 13 wt.% TiO$_2$ showed hardness values higher than 1000 HV0.3 due to an increased amount of $\gamma$-Al$_2$O$_3$. Here, a slightly higher hardness was measured for the coating produced from the jB13 powder as compared to the other coatings. This might be related to the lower porosity of the coating, but could additionally stem from the distorted $\gamma$-Al$_2$O$_3$ phase as indicated by the XRD results in Figure 3. The latter assumption is also supported by spraying
experiments at an increased stand-off distance of 350 mm (not shown). Here, a similar hardness was reached for the jB13 coating despite an increase of the porosity to 9%.

Figure 4. Deposition efficiency $DE$, porosity, and hardness HV0.3 of the APS coatings sprayed by using different feedstock powders for two $\text{Al}_2\text{O}_3$-$\text{TiO}_2$ compositions.

3.2. (Re-)formation of $\text{Al}_2\text{TiO}_5$

After annealing at 1150 °C for 4 h, the powder jB40, initially consisting of $\text{Al}_2\text{TiO}_5/\text{Al}_6\text{Ti}_2\text{O}_{13}$, solely contained $\alpha$-$\text{Al}_2\text{O}_3$ and $\text{TiO}_2$. The XRD patterns of the two powders are directly compared in the lower part of Figure 5 a) and show a full decomposition of $\text{Al}_2\text{TiO}_5/\text{Al}_6\text{Ti}_2\text{O}_{13}$. At the same time the morphology of the powder was preserved according to SEM images (not shown). Both powders were then used in APS and the XRD patterns of the corresponding coatings are presented in the upper part of Figure 5 a). Surprisingly, highly similar phase compositions were obtained for both coatings, indicating a complete reformation of the $\text{Al}_2\text{TiO}_5/\text{Al}_6\text{Ti}_2\text{O}_{13}$ during the spraying process. Also, the $DE$, the porosity, and the hardness were similar for both coatings. The small difference in the $DE$ may be attributed to the lower thermal conductivity of $\text{Al}_2\text{TiO}_5$ in the jB40 powder. Here, the thermal properties of $\text{Al}_6\text{Ti}_2\text{O}_{13}$ are assumed to be similar to those of $\text{Al}_2\text{TiO}_5$. The higher porosity of the coating can be related to the development of a fine porosity within the feedstock powder due to the thermal decomposition. This porosity is then partially transferred to the coating. The reformation of $\text{Al}_{2-x}\text{Ti}_{1+x}\text{O}_5$ from an annealed powder (the original powder corresponded to jA40 in this work) has also recently been observed by Berger et al. for another APS process [20]. However, the $\text{Al}_{2-x}\text{Ti}_{1+x}\text{O}_5$ content of the feedstock powder and in the resulting coating were much lower in that case due to insufficient intermixing of the metallic constituents [20].
Figure 5. a) XRD diagrams of the powder jB (full), the same powder after thermal treatment (dotted), and the respective APS coatings. b) Deposition efficiency $DE$, porosity and Vickers hardness HV0.3 of the APS coatings produced from jB and the thermally treated powder.

4. Conclusions

In the current study we demonstrated the importance of controlling the phase composition in Al$_2$O$_3$-TiO$_2$ thermal spray coatings by a detailed characterization of the feedstock powder, especially with respect to the content of Al$_2$TiO$_5$ and Al$_6$Ti$_2$O$_13$. The presence of these phases in the jB powders indicates a homogeneous distribution of the metallic elements and non-reducing conditions during the preparation of the powder. Powders with a high content of these phases resulted in an improved sprayability, but severely decreased the hardness of Al$_2$O$_3$-40 wt.% TiO$_2$ APS coatings, while yielding a slight increase in hardness for Al$_2$O$_3$-13 wt.% TiO$_2$ coatings as compared to equivalent feedstock powders with inhomogeneous distributions of Al and Ti and low Al$_2$TiO$_5$/Al$_6$Ti$_2$O$_13$ contents.

Furthermore, we observed a full reformation of Al$_2$TiO$_5$/Al$_6$Ti$_2$O$_13$ during APS after a thermal treatment of the original Al$_2$O$_3$-40 wt.% TiO$_2$ feedstock powder, leading to a full decomposition of these compounds into Al$_2$O$_3$ and TiO$_2$. This illustrates that the formation of Al$_2$TiO$_5$ during spraying is possible if a sufficient intermixing of the single oxides is provided. Accordingly, it is paramount to be aware of the phase composition and phase distribution in any Al$_2$O$_3$-TiO$_2$ thermal spray feedstock powder and to control its manufacturing route to achieve full control of the phase composition and ultimately obtain reliable coating properties. Additional studies will focus on the localization of Ti in the 13 wt.% TiO$_2$ coatings and systematically determine the effect of varying Al$_2$TiO$_5$ contents on other coating properties, especially their thermal, electrical, tribological, and corrosion behavior. Furthermore, the deliberate stabilization of Al$_2$TiO$_5$ in the powders and coatings via additional oxides will be explored.

Acknowledgments

This work was funded via the AiF (IGF: 19.471B / DVS: 02.109) by the German Federal Ministry of Economics and Technology within the framework of the program for promotion of “Industrial Joint Research” (IGF) of the Research Association on Welding and Allied Processes of the German Welding Society (DVS). The authors acknowledge the following members of the project advisory board for providing the feedstock powders: Ceram Ingenieurkeramik GmbH (Albbruck-Birndorf, Germany), H.C. Starck GmbH (Laufenburg, Germany), and Saint Gobain (Cologne, Germany).

Furthermore, the authors would like to thank Frank Kurze and Sigrid Schwartz-Lückge for assistance with spraying the coatings and characterizing the feedstock powders.
References

[1] Fauchais P 2004 Understanding plasma spraying J. Phys. D. Appl. Phys. 37 R86–108
[2] Sampath S and Herman H 1996 Rapid solidification and microstructure development during plasma spray deposition J. Therm. Spray Technol. 5 445–56
[3] McPherson R 1981 The relationship between the mechanism of formation, microstructure and properties of plasma-sprayed coatings Thin Solid Films 83 297–310
[4] McPherson R 1980 On the formation of thermally sprayed alumina coatings J. Mater. Sci. 15 3141–9
[5] Stahr C C, Saaro S, Berger L M, Dubský J, Neufuss K and Herrmann M 2007 Dependence of the stabilization of α-Alumina on the spray process J. Therm. Spray Technol. 16 822–30
[6] Berger L-M 2004 Titanium oxide - new opportunities for an established coating material Thermal Spray 2004: Advances in Technology and Application: Proceedings of the International Thermal Spray Conference, 10-12 May, 2004, Osaka, Japan pp 934–45
[7] Sharma A, Gouldstone A, Sampath S and Gambino R J 2006 Anisotropic electrical conduction from heterogeneous oxidation states in plasma sprayed TiO2 coatings J. Appl. Phys. 100 114906
[8] Lewinsky Y 1997 O-Ti p-T-x Phase Diagrams
[9] Ok K M, Ohishi Y, Muta H, Kuroasaki K and Yamanaka S 2018 Effect of point and planar defects on thermal conductivity of TiO2-x J. Am. Ceram. Soc. 101 344–46
[10] Freudenberg B 1987 Etude de la Reaction a l’etat Solide Al2O3 + TiO2 -> Al2TiO5 Observation des Microstructures (EPFL)
[11] Thomas H A J and Stevens R 1989 Aluminium Titanate - A Literature Review - Part 1: Microcracking Phenomena Br. Ceram. Trans. J. 88 144–51
[12] Low I M, Oo Z and O’Connor B H 2006 Effect of atmospheres on the thermal stability of aluminium titanate Phys. B Condens. Matter 385–386 502–4
[13] Low I M and Oo Z 2010 Effect of Grain Size and Controlled Atmosphere on the Thermal Stability of Aluminium Titanate AIP Conference Proceedings vol 1202 pp 27–31
[14] Sperisen T and Mocellin A 1991 On structures of mixed titanium aluminium oxides J. Mater. Sci. Lett. 10 831–3
[15] Buscaglia V 1998 Decomposition of Al2TiO5 and Al2(1−x)MgxTi(1+x)O5 Ceramics J. Am. Ceram. Soc., 81 2645–53
[16] Low I M and Oo Z 2008 Reformation of phase composition in decomposed aluminium titanate Mater. Chem. Phys. 111 9–12
[17] Asbrink G and Magnéli A 1967 X-Ray Studies on Some Mixed Oxide Systems of Pseudobrookite Structure Acta Chem. Scand. B 21 1977
[18] Low I M and Pang W K 2013 In situ diffraction study of self-recovery in vacuum decomposed Al2TiO5 J. Aust. Ceram. Soc. 49 48–52
[19] Low I M and Oo Z 2008 In situ diffraction study of self-recovery in aluminum titanate J. Am. Ceram. Soc. 91 1027–9
[20] Berger L M, Sempf K, Sohn Y J and Vaßen R 2018 Influence of Feedstock Powder Modification by Heat Treatments on the Properties of APS-Sprayed Al2O3-40% TiO2 Coatings J. Therm. Spray Technol. 27 654–66
[21] Norberg S T, Hoffmann S, Yoshimura M and Ishizawa N 2005 Al6Ti2O13, a new phase in the Al2O3-TiO2 system Acta Crystallogr. Sect. C Crystal. Struct. Commun. C61 i35–8
[22] Hoffmann S, Norberg S T and Yoshimura M 2005 Structural models for intergrowth structures in the phase system Al2O3-TiO2 J. Solid State Chem. 178 2897–906
[23] Berger M H and Sayir A 2008 Directional solidification of Al2O3-Al2TiO5 system J. Eur. Ceram. Soc. 28 2411–9
[24] Göbbels M and Boström D 1997 Kristallzüchtung und Struktur von “Al6Ti2O13” Berichte der Dtsch. Mineral. Gesellschaft 91 128
[25] Vargas F, Ageorges H, Fournier P, Fauchais P and López M E 2010 Mechanical and tribological performance of Al₂O₃-TiO₂ coatings elaborated by flame and plasma spraying Surf. Coat. Technol. 205 1132–6

[26] Vuoristo P 2014 Thermal Spray Coating Processes Comprehensive Materials Processing vol 4, ed D Cameron pp 229–76

[27] Di Girolamo G, Brentari A, Blasi C and Serra E 2014 Microstructure and mechanical properties of plasma sprayed alumina-based coatings Ceram. Int. 40 12861–7

[28] Kear B H, Kalman Z, Sadangi R K, Skandan G, Colaizzi J and Mayo W E 2000 Plasma-sprayed nanostructured Al₂O₃/TiO₂ powders and coatings J. Therm. Spray Technol. 9 483–7

[29] Yang Y, Wang Y, Tian W, Yan D, Zhang J and Wang L 2015 Influence of composite powders’ microstructure on the microstructure and properties of Al₂O₃-TiO₂ coatings fabricated by plasma spraying Mater. Des. 65 814–22

[30] Vicent M, Bannier E, Benavente R, Salvador M D, Molina T, Moreno R and Sánchez E 2013 Influence of the feedstock characteristics on the microstructure and properties of Al₂O₃-TiO₂ plasma-sprayed coatings Surf. Coatings Technol. 220 74–9

[31] Wang Y, Tian W, Zhang T and Yang Y 2009 Microstructure, spallation and corrosion of plasma sprayed Al₂O₃-13%TiO₂ coatings Corros. Sci. 51 2924–31

[32] Lima R S, Moreau C and Marple B R 2007 HVOF-Sprayed coatings engineered from mixtures of nanostructured and submicron Al₂O₃-TiO₂ powders: An enhanced wear performance J. Therm. Spray Technol. 16 866–72

[33] Matikainen V, Niemi K, Koivuluoto H and Vuoristo P 2014 Abrasion, Erosion and Cavitation Erosion Wear Properties of Thermally Sprayed Alumina Based Coatings Coatings 4 18–36

[34] Wang M and Shaw L L 2007 Effects of the powder manufacturing method on microstructure and wear performance of plasma sprayed alumina-titania coatings Surf. Coatings Technol. 202 34–44

[35] Goberman D, Sohn Y H, Shaw L, Jordan E and Gell M 2002 Microstructure development of Al₂O₃-13wt.% TiO₂ plasma sprayed coatings derived from nanocrystalline powders Acta Mater. 50 1141–52

[36] Zois D, Lekatou A, Vardavoulias M, Panagiotopoulos I and Vazdirvanidis A 2008 A comparative microstructural investigation of nanostructured and conventional Al₂O₃ coatings deposited by plasma spraying J. Therm. Spray Technol. 17 887–94

[37] Jordan E H, Gell M, Sohn Y H, Goberman D, Shaw L and Jiang S 2002 Fabrication and evaluation of plasma sprayed nanostructured alumina–titania coatings with superior properties Mater. Sci. Eng. A 301 80–9

[38] Bruker AXS 2008 TOPAS V4: General Profile and Structure Analysis Software for Powder Diffraction Data

[39] Schneider C A, Rasband W S and Eliceiri K W 2012 NIH Image to ImageJ: 25 years of image analysis Nat. Methods 9 671

[40] Naghizadeh R, Rezaie H R and Golestanifard F 2009 The influence of composition, cooling rate and atmosphere on the synthesis and thermal stability of aluminum titanate Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 157 20–5

[41] Hoffmann S, Norberg S T and Yoshimura M 2006 Melt synthesis of Al₃TiO₅ containing composites and reinvestigation of the phase diagram Al₂O₃–TiO₂ by powder X-ray diffraction J. Electroceramics 16 327–30

[42] Gell M, Jordan E H, Sohn Y H, Goberman D, Shaw L and Xiao T D 2001 Development and implementation of plasma sprayed nanostructured ceramic coatings Surf. Coatings Technol. 146–147 48–54

[43] Papitha R, Suresh M, Das D and Johnson R 2013 Effect of micro-cracking on the thermal conductivity and thermal expansion of tialite (Al₂TiO₅) ceramics Process. Appl. Ceram. 7 143–6

[44] Freudenberg B 1991 Aluminum Titanate Concise Encyclopedia of Advanced Ceramic Materials pp 20–2