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# Effect of $TiO_2$ addition on the microstructure and nanomechanical properties of $Al_2O_3$ Suspension Plasma Sprayed coatings

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ABSTRACT

Alumina–titania coatings are widely used in industry for wear, abrasion or corrosion protection components. Such layers are commonly deposited by atmospheric plasma spraying (APS) using powder as feedstock. In this study, both $Al_2O_3$ and $Al_2O_3$–13 wt% $TiO_2$ coatings were deposited on austenitic stainless steel coupons by suspension plasma spraying (SPS). Two commercial suspensions of nanosized $Al_2O_3$ and $TiO_2$ particles were used as starting materials. The coatings microstructure and phase composition were fully characterised using FEG-SEM and XRD techniques. Nanoindentation technique was used to determine the coatings hardness and elastic modulus properties. Results have shown that the addition of titania to alumina SPS coatings causes different crystalline phases and a higher powder melting rate is reached. The higher melted material achieved, when titania is added leads to higher hardness and elastic modulus when the same spraying parameters are used.

## 1. Introduction

Nanostructured materials have been extensively studied in the past decades [1–3] showing that nanostructure significantly increases material performances [4–6]. In particular, nanostuctured coatings are expected to provide several industries with enhanced components leading to better properties and longer lifetime [7–9]. Atmospheric Plasma Spraying (APS) is one of the most widely used techniques in industry to deposit thick ceramic coatings. APS process consists in injecting a powder into a plasma plume. During the flight in the plasma, the feedstock is molten and accelerated towards a substrate where it impacts creating a coating [10].

The production of nanostructured coatings by APS requires agglomerating the nanoparticles into micrometer sized aggregates, which can be sprayed as easily as conventional powders [11–13]. The use of agglomerated powders is actually considered as a very efficient way to deposit a coating based on nanoparticles. However, the production of aggregated powders is a complex process with several steps [13,14] which affect the cost of powders and may restrict the possible industrial applications. Moreover, a big challenge is to carefully control the deposition process in order to keep the initial nanostructure in the final coating [15]. Some examples of nanostructured ceramic coatings obtained by APS from agglomerated powders include alumina [16,17], titania [18,19], alumina-titania [14,20], yttria-stabilised zirconia [21,22] or pyrochlore [23].

Another possible way to obtain nanostructured coating by thermal spraying consists of using a carrier liquid instead of a carrier gas to inject the nanoparticles inside the plasma plume [12]. This technique is known as Suspension Plasma Spraying (SPS) and differs significantly from conventional APS since the suspension is fragmented into droplets and the liquid phase vaporised before the solid feedstock is processed [24,25]. This novel technique has recently undergone an extensive development, leading to the deposition of nanostructured coatings with unique properties for solid oxide fuel cells (SOFC) functional layers [28,29], thermal barrier coatings [30,31], photocatalytic layers [32,33], wear resistant coatings [34] or bioactive layers [35].

Among the materials usually deposited by plasma spraying, alumina-based coatings show one of the most versatile fields of application [36]. Alumina is commonly used as an electrical insulator due to its high dielectric strength and its ability to manufacture hard and chemically stable coatings even at very high temperatures. Furthermore, $Al_2O_3$-based coatings are widely used for wear, corrosion or erosion protection components. In such coating alumina is mixed with other oxides to enhance its properties. It has been shown that the addition of $TiO_2$ improves the coating fracture

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toughness in conventional APS coatings [36], usually obtained from fusing and crushing powders, as well as in coatings from nanostructured feedstocks which are commonly obtained by simple mixture of the oxides [37]. Indeed $Al_2O_3$–$TiO_2$ coatings obtained by APS from both conventional feedstocks and agglomerated powders has been extensively studied [38–44]. However, the research on SPS $Al_2O_3$–$TiO_2$ is still incipient and very few authors have studied such layers [45]. Consequently, it is still necessary to study the effect of the addition of $TiO_2$ on the characteristics of alumina SPS coatings.

In the present work, both $Al_2O_3$ and $Al_2O_3$–13 wt% $TiO_2$ coatings have been deposited by Suspension Plasma Spraying using two commercial aqueous nano-suspensions as feedstock. Resulting microstructures were fully characterised by FEG-SEM observations and X-Ray diffraction analysis. Furthermore, the mechanical properties (hardness and elastic modulus) of the coatings were characterised using the nanoindentation technique.

## 2. Material and methods

### 2.1. Materials

Coatings were deposited from an $Al_2O_3$–13 wt% $TiO_2$ suspension prepared by mixing two commercial aqueous suspensions: a nano-$Al_2O_3$ suspension (AERODISP® VP630X, Evonik Degussa GmbH, Germany) and a nano-$TiO_2$ suspension (AERODISP® W740X, Evonik Degussa GmbH, Germany), following the methodology described elsewhere [26]. The main nanosuspensions properties are summarised in Table 1 as given by the manufacturer. Both suspensions have been fully characterised in previous works [26,27].

Stainless steel (AISI 304) disks have been used as substrates (25 mm diameter and 10 mm thickness). Before deposition, the substrates were grit blasted with corundum (Metcolite VF, Sulzer Metco, Switzerland) and cleaned with ethanol.

### 2.2. Coating deposition

Coatings were deposited with a F4-MB monocathode torch (Sulzer Metco, Switzerland) with a 6 mm internal diameter anode operated by a robot (IRB 1400, ABB, Switzerland). The substrates were preheated between 350 °C and 400 °C to enhance coating adhesion. In preliminary experiments it was found that if the substrate was not preheated above 350 °C, $Al_2O_3$–$TiO_2$ SPS coatings did not properly bond to the substrate.

The suspensions were injected using a SPS system developed by the Institute for Ceramic Technology (Instituto de Tecnología Cerámica, ITC). This system is formed by two pressurised containers which force the liquid to flow through the injector. A filter was used to remove agglomerates larger than 74 μm and possible contaminations. Main spraying parameters are given in Table 2.

### 2.3. Coating characterisation techniques

X-ray diffraction patterns were collected to identify crystalline phases in coating samples (Bruker, Theta-Theta D8 Advance, Germany).

The microstructure was analysed on polished cross-sections using a HITACHI S4800 Field Emission Microscope (FEG-SEM) under secondary (SE) and backscattered (BSE) electron mode. The BSE detector was configured symmetrically to ensure a good reflection of the backscattered electrons from all angles. Elemental analysis was performed in SEM using energy dispersive X-rays analysis (EDX). An optical reflection microscope Nikon LV-100 Eclipse under Nomarski illumination on the cross-section was used.

Hardness (*H*) and elastic modulus (*E*) of coatings were acquired by a G-200 nanoindenter from Agilent Technology (Santa Clara, USA). An array of 25 indentations was performed at 2000 nm constant depth for each analyzed sample. The Continuous Stiffness Measurement (CSM) method used it provides the stiffness profile in-depth and hence, the subsequent calculation of H and E. A Berkovich-geometry tip was used. The area function for this indenter was previously calibrated on silica as reference material.

## 3. Results

### 3.1. Crystalline phase composition

As reported elsewhere, commercial titania feed suspension is mainly formed by anatase with some rutile. In the case of the alumina starting suspension, it contains Alu-C nanoparticles (Degussa/Evonik, Germany) [14] which are formed by transition δ- and γ-$Al_2O_3$ [46]. Fig. 1 shows the X-ray diffraction patterns of both $Al_2O_3$ and $Al_2O_3$–$TiO_2$ projected coatings.

Pure alumina SPS coating was mostly formed by corundum (α-$Al_2O_3$) with δ-$Al_2O_3$. Traces of γ-alumina were also identified. This result indicates that powders have experimented a phase transformation during the deposition process which is usual in plasma spraying in both conventional and nanostructured alumina coatings [47,48]. The formation of α-$Al_2O_3$, which is the stable phase of the aluminium oxide, is of special interest due to its thermal stability and good mechanical properties.

When titanium oxide is added to the feed suspension, X-ray diffraction analysis revealed that the alumina found in the coating is mainly present as α-$Al_2O_3$ and γ-alumina phases. Low amounts of brookite-$TiO_2$ were also identified with traces of rutile. However most of the initial titania reacted with alumina during the deposition process, leading to the formation of aluminium titanate ($Al_2TiO_5$). This phenomenon has been previously reported for APS alumina-titania coatings with different $TiO_2$ content [38,40].

### 3.2. Microstructure

The microstructures of $Al_2O_3$ + 13 wt%$TiO_2$ and $Al_2O_3$ coatings are shown in Fig. 2a and b, respectively. In both cases, a bimodal microstructure formed by a mixture of fully melted grains and softer lakes of material was observed. Nevertheless, when $TiO_2$ was added to the feedstock, a higher ratio of melted material was observed. The softer microstructure was probably formed by partially melted material. However it was not possible to observe the original nanostructure at higher magnifications, indicating that certain sintering degree was achieved.

In order to investigate the solubility distribution achieved by $TiO_2$ in $Al_2O_3$ in these microstructures, BSE maps and EDX images of the $Al_2O_3$–$TiO_2$ coating were also recorded. The BSE image (Fig. 3a)

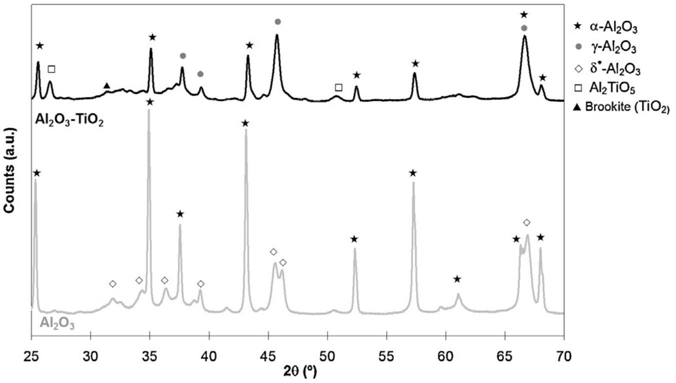

**Fig. 1.** X-ray diffraction pattern of suspension plasma sprayed $Al_2O_3$ (down) and $Al_2O_3$–13 wt%$TiO_2$ (up) coatings.