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Architecture and phases composition of suspension plasma sprayed alumina–titania sub-micrometer-sized coatings

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ABSTRACT

Sub-micrometer-sized Al2O3–TiO2 plasma-sprayed coatings exhibit superior performances compared to micrometer-sized ones. Two routes can be implemented to manufacture such finely structured coatings:i)spraying micrometer-sized agglomerates of nanometer-sized particles which results in a two-scale coating architecture and ii) spraying a suspension of sub-micrometer-sized particles (suspension plasma spraying, SPS). SPS was implemented in this study and Al_2O_3-base coatings with 13 and 60 wt.% of titania, respectively, were manufactured by spraying a suspension made of a mixture of Al_2O_3 and TiO_2 particles both of 300 nm, average diameter. Coating structural features and phase contents were studied. Results show that the coatings exhibit a very fine lamellar structure with a homogeneous repartition of Al and Ti. Complex phases, made of inter-mediate Al, Ti, and O oxides, have been also identified. Indeed, coatings formation results from rapid solid-ification rates and high transient thermal fluxes imparted by the plasma flow to the substrate due to the short spray distance encountered in SPS (in the order of 30 mm) requested by the small kinetics and ther-mal inertia of sub-micrometer-sized particles.

1. Introduction

Lot of works has established that such finely structured coatings were exhibiting superior performances than micrometer-sized coatings, in particular mechanical ones [1]. One explanation arises from the decrease in grain size. In thermal spray coatings, the presence of sub-micrometer-sized or nanometer-sized structures permit to limit the crack propagation [2] leading to higher wear resistance. Suspension plasma spraying (SPS) is an emerging process to manufacture finely structured coatings. Sub-micrometer-sized particles carried by a liquid phase (both, with the addition of a surfactant, constitute a suspension) are injected into the plasma plume where they are processed [3]. Because of the initial size of precursor, the structural characteristic dimension of the coatings is smaller than that in conventional spraying where micrometer-sized particles in the 10–50 μm range are usually processed. This process has demonstrated their capability in manufacturing Al_2O_3 coatings exhibiting higher mechanical and tribological performances in comparison to conventional ones [4]. In addition, it is possible to manufacture composite ceramic coatings [5]. Al_2O_3-based coatings are widely used for wear, corrosion or erosion protection components, in particular with the addition of TiO_2 [6,7] which further improves coating fracture toughness (in particular with a 13 wt.% content). The objective is to study Al_2O_3–TiO_2 composite suspension plasma sprayed coatings with two different mass fractions of TiO_2 in sprayed suspensions. The coatings structures were analyzed and Al_2O_3–TiO_2 transition phases identified.

2. Experimental protocols

2.1. Spray process and related operating parameters

Coatings were manufactured implementing a F4-MB plasma torch (Sulzer–Metco, Wohlen, Switzerland) equipped with a 6 mm anode nozzle diameter and operated with a plasma flow mass enthalpy of 14.5 MJ kg^{-1} with an arc current intensity of 600 A. Plasma forming gas was a mixture of Ar–He (40–20 SLPM). Cinematic parameters were a torch scan velocity of 1 m s^{-1}, a scanning step of 10 mm $pass^{-1}$ and a spray distance of 30 mm. Substrates were pre-heating at an average temperature of 250 °C. Suspension injection was performed through a sapphire-made calibrated diaphragm of 150 μm, average diameter. Polished substrates (Ra = 0.07 μm) were made of low carbon steel coupons 25 mm in diameter and 20 mm in thickness.

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Table 1
Suspension and coating characteristics.

Designation	AlTi13		AlTi60	
Particles	Al_2O_3	TiO_2	Al_2O_3	TiO_2
Al_2O_3 powder in the mixture	AKP30	K2300	AKP30	K2300
wt.% of each material (Al_2O_3/TiO_2)	87/13		40/60	
Liquid phase	Et–OH (99.5% purity)			
wt.% of powder in the suspension	10%			
wt.% of electrosteric dispersant in comparison to powder wt.	2%			

2.2. Feedstock and suspensions

Alpha-alumina powder, referenced AKP30, was supplied by Sumitomo Chemical Corp. (Tokyo, Japan). It exhibits an average particle size (d_{50}) of 300 nm (supplier data). Rutile-titania powder was referenced K2300 as supplied by Kronos (Leverkusen, Germany). It exhibited an average particle size (d_{50}) of 300 nm (supplier data). Ethanol-based suspensions of powders were prepared according to the compositions detailed in Table 1. Ethanol and the dispersant were first combined until complete dilution with ultrasonic and magnetic stirring. Then the powder is added according to a charge of 10% in weight always with ultrasonic and magnetic stirring to disperse the remaining agglomerates. This dispersant percentage deals with the lowest viscosity of 0.02 mPa s and a high stability during sedimentation tests higher than 3 days. The powder mass percentage value results from previous works on alumina suspensions [8] permitting to obtain the best coating cohesion.

2.3. Coatings characterization techniques

Coatings polished cross-sections were observed by scanning electron microscopy in secondary electron or backscattered modes (SE-SEM and BSE-SEM, respectively). A transmission electron microscope (200 kV TEM Jeol 2010 equipped with energy dispersive X-ray analytical system) was implemented to observe the substrate/coating interface. X-ray diffraction (XRD) was performed to address powders and coatings phases compositions (Siemens D5000 diffractometer equipped with a Cu anti-cathode, $\lambda = 1.54$ Å). The data acquisition parameters were as follows: 20°–80° 2θ angle range, 0.04° scanning step.

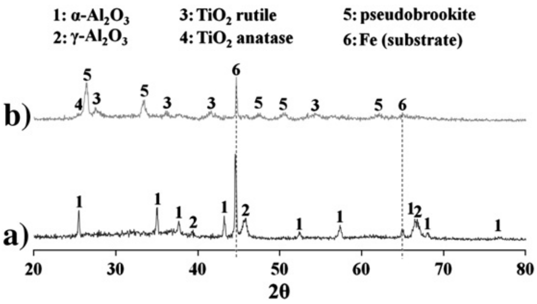

Fig. 2. X-ray diffraction patterns of a) AlTi13 and b) AlTi60 alumina titania coatings.

3. Results and discussions

3.1. Coatings microstructure

Fig. 1 displays BSE cross-section views of AlTi60 composite coating. Gray element is representative of an aluminum-rich phase and white element of a titanium-rich one. Of course, Ti element content in coatings is increasing with the TiO_2 content in initial suspension, as expected. Also, coatings structures exhibit a homogeneous distribution through the thickness with a fine alternation of thin (i.e., ~100 nm) Al- and Ti-rich lamellae. Transmission electron microscopy observation of AlTi60 coating is presented in Fig. 1. The view field is located at the substrate/coating interface and corresponds hence to the very first coating features resulting from the impact, spreading and solidification of impinging particles. The typical lamellar structure is well seen with lamellae typical thicknesses ranging from 50 to 200 nm. In addition, nanometer-sized voids can be observed in between some lamellae together with a poorly cohesive interlamellar area.

3.2. Coatings composition

Fig. 2 displays X-ray patterns of resulting coatings. On the one hand, AlTi13 coating is made of a majority α-Al_2O_3 phase at the expense γ phase. γ-Al_2O_3 results from the rapid quenching of lamellae upon solidification (cooling rate in the order of 10^6 K s^{-1}). Indeed,

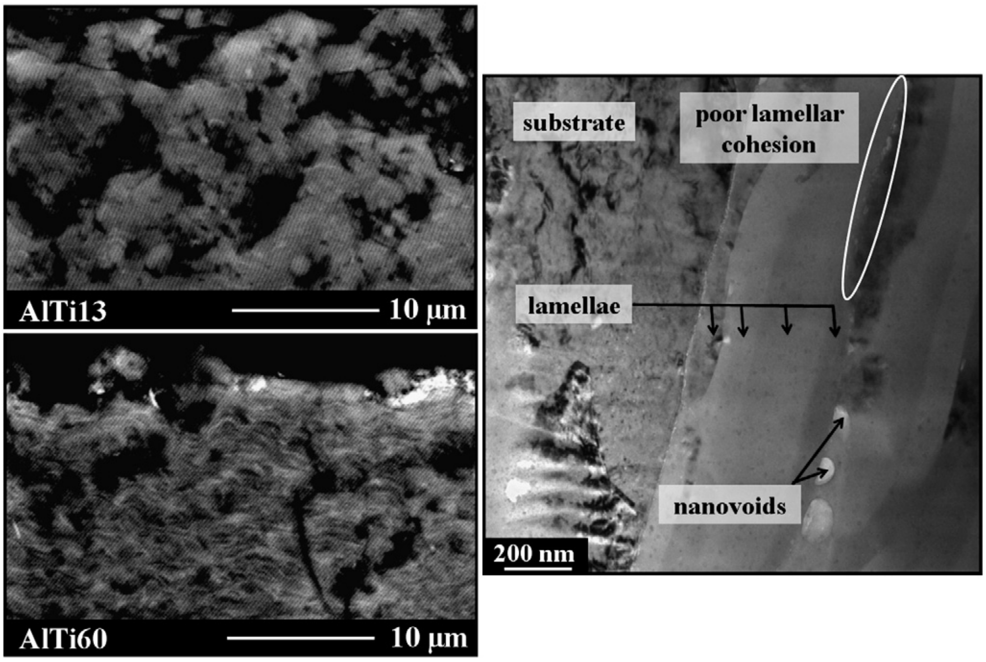

Fig. 1. Coating cross sections of AlTi13 and AlTi60 coatings (BSE-SEM) and TEM analysis of AlTi60 coating.

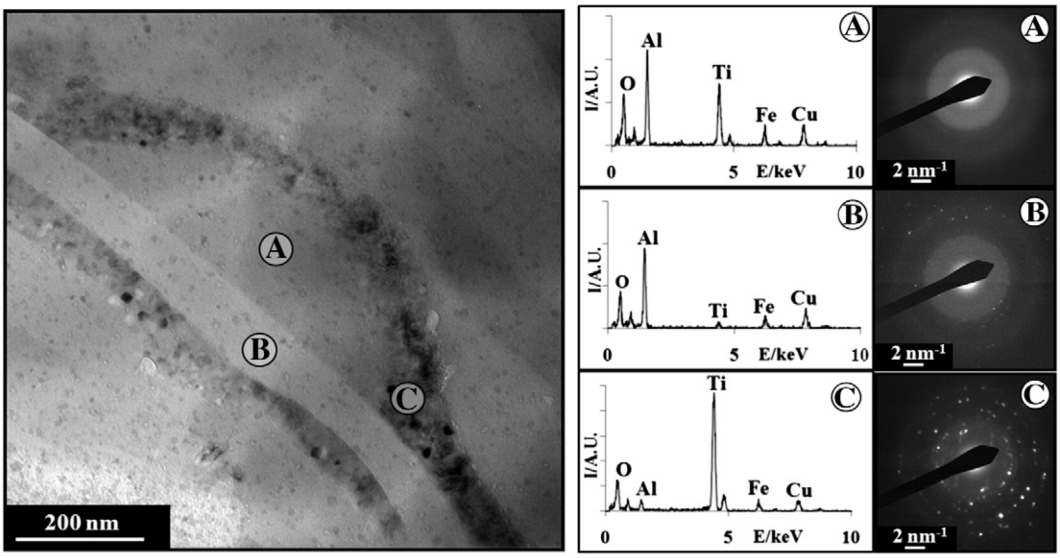

Fig. 3. EDS and diffraction patterns realized on three different types of lamella identified in AlTi60 coating.

α-alumina phase presence is probably not due to unmolten particles embedded in the coating as encountered in APS process with micrometer-sized feedstock particles because most of the structure exhibits lamellar features resulting from well molten and flattened particles. Charska et al. [9], among others, have demonstrated that by heating thermal spray alumina coatings mostly made of γ-alumina phase, the transformation into α-alumina phase via transition aluminas occurs at about 1000 °C. Etchard-Salas [10] has measured that the substrate temperature during coating manufacturing can reach transient temperatures much higher than 1000 °C during a few second (corresponding to the torch pass). Those transient temperatures lead to coating annealing and very likely to the transformation of metastable γ-alumina into stable α-alumina or can induce a delay in lamellae cooling impeding rapid quenching of alumina.

With TiO_2 content increasing, rutile and anatase TiO_2 phases are indentified in the coatings together with a pseudobrookite phase which even represents the predominant phase when considering the AlTi60 coating. Surprisingly, diffraction analysis reveals only a phase which would correspond, according to peak labeling, to $FeAlTiO_5$ (JCPDS: 01-076-1157) pseudobrookite phase (instead of the expected Al_2TiO_5 encountered most of the time). Al_2TiO_5 phase peaks (JCPDS: 00-041-0258) do not match nevertheless with X-ray diffraction pattern profile. $FeAlTiO_5$ phase appears not to be realistic because the presence of Fe would signify a reaction at the interface between coating and substrate very likely only at the first nanometers or tenths of nanometers of the coating and resulting peaks on X-ray pattern would hence not be so intense. Moreover, TEM observation reveals no interfacial reaction area, Fig. 1. For those reasons, it appears more relevant to consider this pseudobrookite phase as being of the tialite Al_xTiO_y type.

Fig. 3 presents energy dispersive spectrometry (EDS) analysis realized with TEM on AlTi60 coating. The analysis was performed on three different areas exhibiting different contrasts. In fact, contrast depends upon atomic number of materials: the higher the atomic number, the darker the material appearance. The brighter lamella (B) is composed mostly of Al and O elements: this lamella is typical of alumina phase (Fe and Cu peaks are induced by the TEM polar pieces). The presence of the Ti peak is due to the embedding of a neighboring Ti-rich lamella and the TEM spot size was not small enough to analyze only the targeted area. Beside, the darker lamella (C) is made mainly of Ti and a small amount of Al elements involving titania or brookite phases. For an intermediate contrast lamella (A), the EDS spectrum shows three elements: Al, Ti and O. This is representative of the tialite phase. In addition, it appears in others TEM pictures that there is very small amount of pure alumina lamellae in AlTi60 coating and that the main identified phases are the tialite phases and to a lesser extent titania or brookite phases. This corroborates AlTi60 X-ray diffraction pattern where alumina peaks are not identified. That means that most of the alumina phases have reacted with titania to form tialite phases as the accordance between TEM and X-ray analyses indicates. Selected area electron diffraction (SAED) patterns are displayed in Fig. 3. It clearly appears that lamellae composed of Ti and O (C) are rather crystallized. However, it has to be noticed that lamellae composed of a mixture of Al, Ti and O elements (A) and Al and O elements (B), can be considered as amorphous phase. Also, this phase can correspond to Al_2TiO_5 phase. Because of highly constraints due to high residual stresses developing in such coatings, those stresses could induce Al_2TiO_5 peaks shifts.

4. Conclusions

Suspension plasma spraying permits to manufacture composite ceramic layers with a good homogeneity in material alternation. With TiO_2 content increasing, Al_xTiO_y or Al_2TiO_5 compounds content increases. For the specific 60 wt.% of titania composition, alumina has almost reacted totally with TiO_2 to form a tialite phase. Moreover crystallization of these phase have been studied and it appears that only lamellae composed of Ti and O are rather crystallized, lamellae composed of a mixture of Al, Ti and O elements or Al and O elements being amorphous phase.

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