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Production and characterization of metastable Al_2O_3–TiO_2 ceramic materials

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Abstract Producing nanostructured materials through metastable phases is interesting in the field of ceramic materials. Metastable phases can be obtained by the Atmospheric Plasma Spray (APS) technique which, is a well-known technique to produce coatings. The initial powders are melted during the spraying obtaining a homogenized phase due to their solubility in the liquid state. Afterwards, the molten droplets are quenched in a cooled medium, producing the sought metastable phases. Finally, during material consolidation, the metastable structure evolves due to a dual structure. A suppression of the grain growth is produced as a consequence of the immiscibility of both phases in the solid state. Due to their small grain size and uniform structure, these nanostructured materials exhibit very interesting properties such as higher hardness and toughness. The aim of this research has been to produce nanostructured Al_2O_3–TiO_2 ceramic powders through APS + quenching route, starting from commercially available micron-sized powders. A complete characterization of the obtained structures using XRD, SEM, FESEM and EDS has been carried out in the Thermal Spray Center (CPT) of the University of Barcelona.

Introduction

The Al_2O_3–TiO_2 system is an interesting material for obtaining tough ceramics. This system becomes of interest to study new materials that can be advantageously used as catalytic supports [1], among many other potential applications [2, 3]. Moreover, Al_2O_3–TiO_2 coatings are widely known due to their excellent wear and corrosion behaviour [4]. Their enhanced properties are reported in many studies [5, 6]. Nanostructured ceramic materials show superior resistance to wear, erosion, cracking and spallation [7].

In order to obtain nanostructured materials, one way is to use nano-scaled powders. Another way is to obtain metastable structures using micro-sized powders as feedstock. The second way has two steps: formation of metastable ceramic powder by plasma-spraying and, afterwards, high-pressure sintering (HPS) of the metastable powder to obtain nanocrystalline ceramics.

Recent research [8] in the field of nanostructured ceramic materials has underscored the importance of using feedstock powders with metastable phases. Materials consisting of metastable phases have an interesting behaviour during consolidation processes. A suppression of the grain growth takes place due to the immiscibility of the two phases in the solid state. Due to their small grain size and uniform structure, these nanocomposites exhibit very interesting properties such as higher hardness and toughness [9].

Metastable structures can be produced using Atmospheric Plasma Spray (APS) technique [10, 11]. The molten droplets accelerated from the plasma jet are quenched in a liquid medium, such as water, or onto a chilled substrate forming metastable phases.

In this research the main target has been to obtain metastable phases from different commercial powders of

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Al_2O_3–TiO_2. Furthermore, nanostructured coatings have been obtained and characterized.

Experimental procedure

In order to analyze the effect of powders with different characteristics, two feedstock powders have been evaluated for the Al_2O_3-13 wt.%TiO_2 composition: an agglomerated and sintered powder with a particle size distribution between 22.5 μm and 45 μm (Flame Spray Technologies-Netherlands) and a fused and crushed powder with a particle size distribution between 5 μm and 25 μm (Saint Gobain-France). The agglomerated powder is composed of Al_2O_3-α and TiO_2-rutile phases, whereas the fused powder is composed of Al_2O_3-α and Al_2TiO_3-α phases. The different morphologies of the initial powders can be observed in the free surface images (Fig. 1) obtained by scanning electron microscopy (SEM-Jeol5100).

In order to obtain *metastable phases*, the powders have been sprayed using a F4 plasma torch and, immediately the melted or semi-melted particles are cooled. CPT group has run some tests to compare the results obtained with a water/ice cooling and with a cryogenic + splat cooling. In the first case, the device consisted of a simple powder collector filled with water/ice (Fig. 2a) where the powder was directly sprayed. The second one has tried to simulate a splat quenching onto a copper tube (Fig. 2b). This tube has been filled up with liquid nitrogen to increase the cooling rate and to keep a low temperature at the impact surface during spraying. In this case the melted or semi-melted particles were sprayed onto the tube and collected in the container.

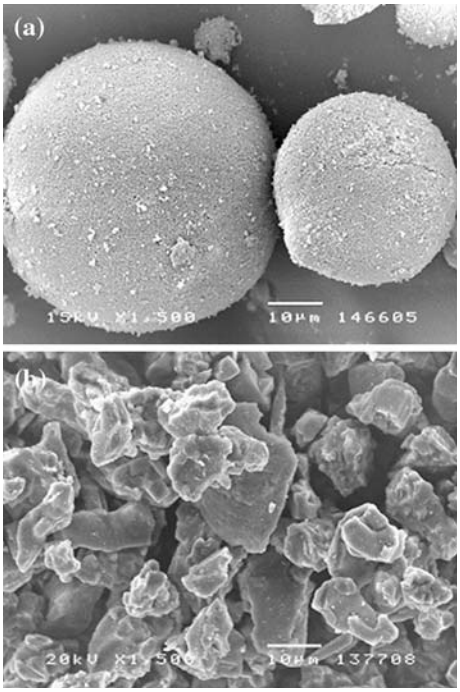


Fig. 1 SEM micrographs of the different initial powders: (**a**) agglomerated powder and (**b**) fused powder

Likewise, *metastable coatings* have been obtained from commercial Al_2O_3-13 wt.%TiO_2 powder. The powder has been sprayed over a copper substrates (100 × 200 × 5 mm.) which have been previously degreased with acetone and grit blasted with white corundum at 5.6 bar. In order to achieve the metastability the substrates have been cooled in liquid nitrogen.

Experimental conditions are registered in Table 1 where plasma spray and grid blasting conditions are specified.

As-obtained powders and coatings have been characterized by X-ray diffraction and scanning electron microscopy (JEOL JSM-5310).

Heat treatments at 800, 1,000 and 1,200 °C for 1 h have been carried out in order to simulate the consolidation process. The phase transformations and the nanostructure formation have been evaluated after these thermal treatments.

Results and discussion

Powder production

A multiphase powder has been obtained after metastable processing by direct spraying onto water in all cases (spraying both initial powders). Al_2O_3 (α-phase), TiO_2 (rutile) and Al_2O_3 (spinel-phase) appear when the quenching is directly carried out into water (Fig. 3). This means that a combination of metastable (Al_2O_3 pattern refs.: 77-0396 and 73-1199) and equilibrium (Al_2O_3-α and TiO_2-rutile, see equilibrium phase diagram in Fig. 4) phases has been obtained. However, the XRD of the water quenched results from fused powder shows a small amount

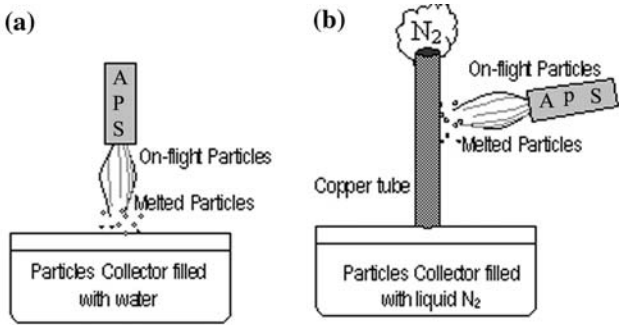


Fig. 2 Scheme of cooling systems, (**a**) consisting of a simple powder collector filled with water/ice where the melted particles are collected; (**b**) it incorporates a tube filled up with liquid nitrogen where the melted particles impact before to be recollected in the powder container

Table 1 Spraying and grit blasting conditions

Spraying conditions						
Current (A)	Voltage (V)	Air flow (NLPM)	H_2 flow (NLPM)	Powder rate (g/min)/Carrier gas	Spray distance (mm)	Gun speed (mm/s)
600	57	32–36	11–15	15/Ar	120	500/250
Grit blasting conditions						
Pressure (bar)		Abrasive		Final roughness (μm)		
5.6		Corundum (grade24)		>5		

of TiO_2-rutile and lower amount of α-Al_2O_3 (stable phases) indicating a reduction of the phases segregation

The presence of rutile TiO_2 and the high amount of Al_2O_3-α phase give an idea of low cooling rates and the phase separation which is not interesting for the metastability of the powder. The primary Al_2O_3-α will not decompose during subsequent processing after heat-treatment, since it is the stable form of alumina. Thus, the presence of Al_2O_3-α in the as-obtained powder is not advantageous for production of homogeneous nanostructured powder.

Nevertheless, the powder sprayed following a cryogenic + splat quenching (Fig. 2a), shows only the metastable Al_2O_3 phase, as it can be seen in Fig. 5. It is possible that in the water quench process, the cooling rate and the delay time were suitable for the formation of equilibrium phases (Al_2O_3-α and TiO_2-rutile phases, Figure 4) whereas in the splat quench process these equilibrium transformations have not taken place indicating a faster cooling out of the equilibrium state.

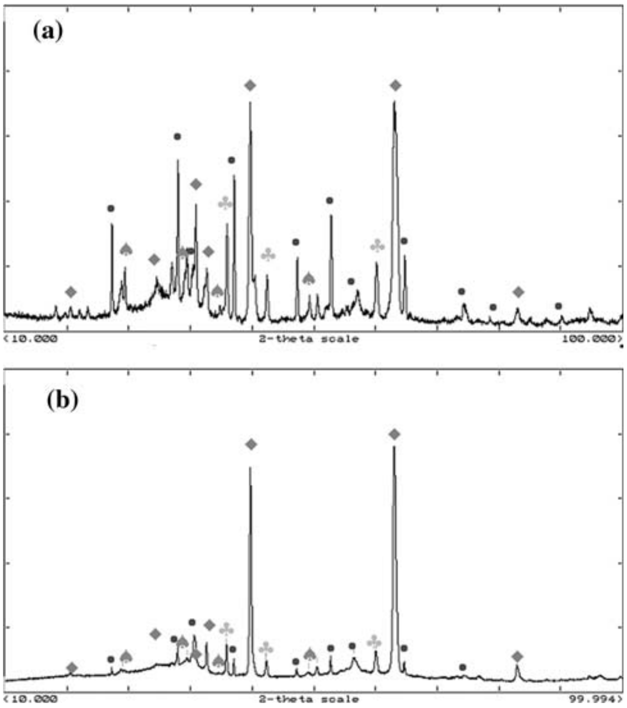


Fig. 3 XRD of the powders obtained through water quenching from agglomerated powder (**a**) and from fused powder (**b**). [• Al_2O_3-α (ref. 46–1212); ♠ TiO_2 rutile (ref. 21–1276); ♦ Al_2O_3-spinel (ref. 77–0396); ♣ Al_2O_3 oxide (ref. 73–1199)]

Moreover in this later case, non-essential differences have been observed when the results from different initial powders (agglomerated and fused) are compared. XRD patterns of the obtained powders show identical phases (Fig. 5) and SEM images show morphologies with identical characteristics. Also the final structure-obtained are exactly the same independently of initial powder and thus similar conclusions could be drawn.

Morphologically, the powder obtained by water quenching shows dendritic and/or cellular-dendritic microstructure, indicating that the expected segregation-solidification in water quenching took place. However, when a chilled splat quenching is used, the powders exhibit a featureless structure with less segregation (Fig. 6b).

These results are in good agreement with Kear et al. [10], who have described that the particles experiencing moderate cooling rates (~10^4 °C/s) display a well-defined dendritic/cellular-dendritic microstructure and exhibit some phase separation. However, particles experiencing exceptionally high cooling rates (~10^6 °C/s), as in splat quenching onto a chilled plate, showed a segregation-less solidification which is needed in order to obtain homogeneous nanocomposites.

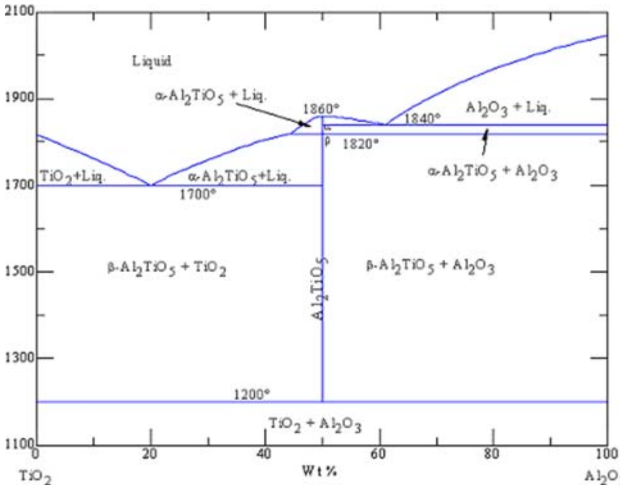


Fig. 4 Phase equilibrium diagram of Al_2O_3–TiO_2 system

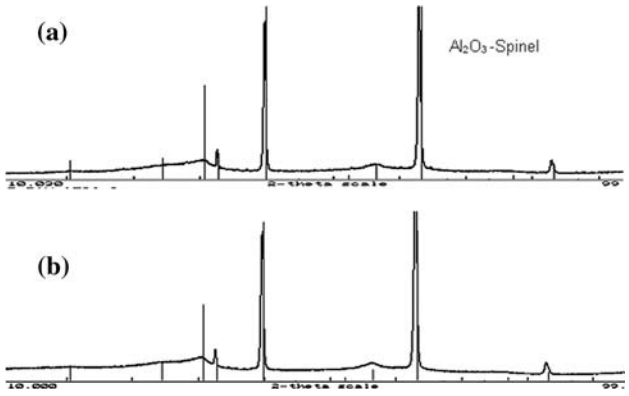


Fig. 5 XRD corresponding to the splat + quenching sprayed powder from (**a**) agglomerated & sintered powder and (**b**) fused & crushed powder [Al_2O_3-spinel (ref. 77–0396)]

Coating production

Preliminary results have demonstrated that metastable coatings can be produced by this process. The coatings obtained have been homogeneous and showed a good adhesion with the substrate (Fig. 7a).

As Fig. 7b shows, a completely metastable coating which is composed only from Al_2O_3-spinel, is achieved after 5 layers (25 μm approximately). Copper observed in the coating belong to the substrate because of the low thickness of the coating. However, stable phases such as Al_2O_3-α appear when 7 layers (35 μm approx.) are deposited. These results expose that an optimization of the cooling system is needed in order to increase the coating thickness for industrial applications.

Heat treatments

Thermal treatments have been carried out to verify phase transformations. The tested temperatures have been 800, 1,000 and 1,200 °C, which have allowed to evaluate the evolution of the metastable phase. When the splat-quenched powder was heated, thermal transformation of the original phase (Al_2O_3-spinel) took place since establishing

Fig. 6 SEM micrographs of powders obtained by water (**a**) and splat (**b**) quenching

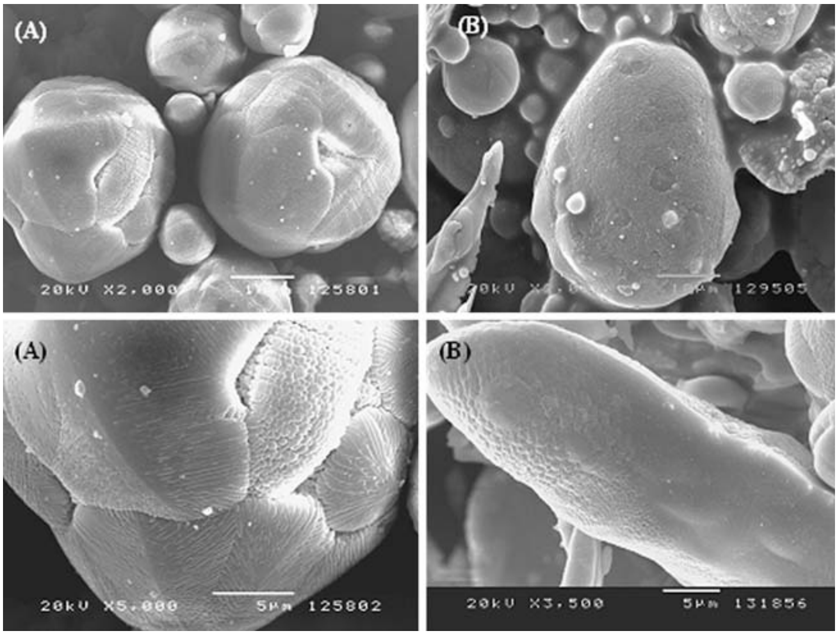
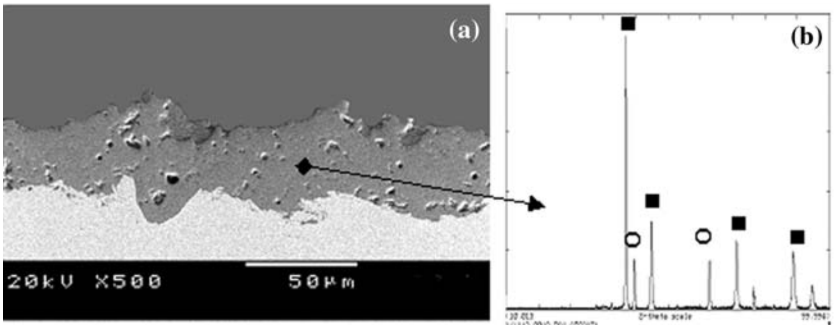


Fig. 7 Al_2O_3-13 wt.% TiO_2 coating sprayed onto a cooled substrate (**a**) SEM micrograph and (**b**) XRD pattern where ■ is copper and ○ Al_2O_3-spinel



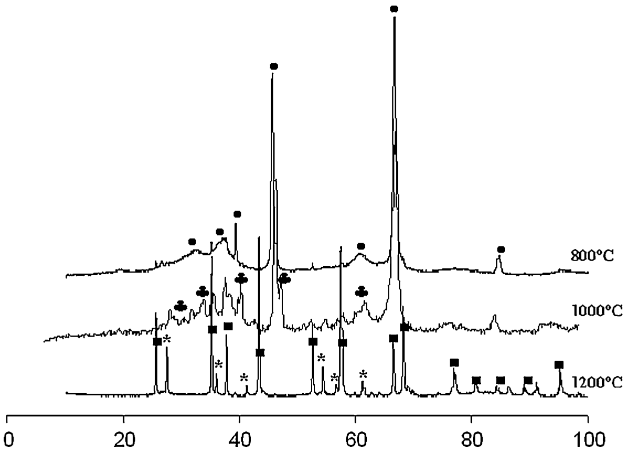


Fig. 8 XRD of powders treated at 800 and 1,200 °C [■ (Al_2O_3-α, • Al_2O_3-spinel, ♣ Al_2TiO_5, * TiO_2-rutile]

of the equilibrium two-phase structure [12]. Figure 8 shows the XRD patterns of heat-treated splats at different temperatures. At 800 °C, there was a strongly disordered structure in the diffraction pattern that indicated a non-equilibrium state. In this case, only the spinel phase was well-defined. At 1,000 °C, a multiphase powder is observed where the Al_2TiO_5 phase appears well-defined while this phase is not predicted by the phase equilibrium diagram at this temperature. At 1,200 °C it was clear that the structure evolved to a crystalline state where the main phases were Al_2O_3-α and TiO_2-rutile phase. It is expected that the consolidation of this material by standard techniques as HPS sintering will be possible at lower temperatures and pressures than from conventional powder.

SEM images of the splat heat-treated at 1,200 °C are shown in Fig. 9 where it can be seen that the TiO_2 grains kept their nanometric size after the heat treatments.

Conclusions

Producing nanostructured Al_2O_3–TiO_2 ceramic powders through APS + quenching route, starting from commercially available micron-sized powders has been demonstrated. Firstly, metastable powders have been obtained and characterized. Metastability grade has been evaluated on XRD patterns and only a completely metastable powder has been produced when a splat effect has simultaneously been produced during the spraying.

Totally metastable coating have been also obtained although after seven layers stable phases have started to emerge. Experiments will be underway to increase the coating thickness.

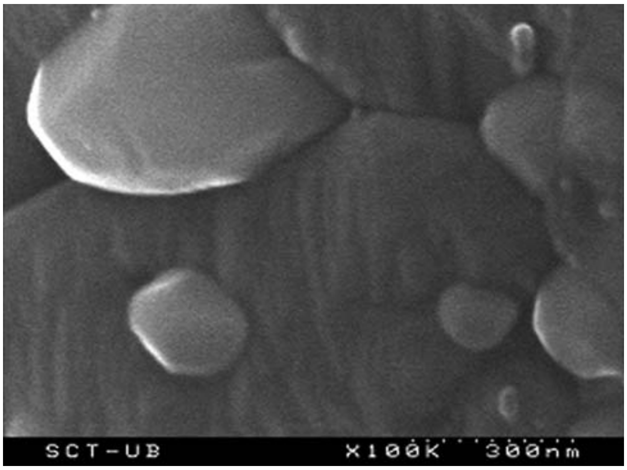


Fig. 9 SEM images of the annealed powder (Al_2O_3-13 wt.%TiO_2 obtained by splat quench process) at 1,200 °C

The phase evolution from metastable to crystalline phases has taken into place after a 1,200 °C heat-treatment, showing a final nanometric structure.

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