Surface & Coatings Technology 204 (2009) 149–156

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Influence of liquid nitrogen quenching on the evolution of metastable phases during plasma spraying of (ZrO_2–5 wt.% Y_2O_3)–20 wt.% Al_2O_3 coatings

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ARTICLE INFO

Article history:
Received 19 January 2009
Accepted in revised form 5 July 2009
Available online 13 July 2009

Keywords:
Plasma spraying
Ceramics
Metastable
Nanocrystalline microstructure
Aging
Quenching

ABSTRACT

The preparation of nanostructured (ZrO_2–5 wt.% Y_2O_3)–20 wt.% Al_2O_3 coatings by atmospheric plasma spraying of commercially available micron-scale powders is reported. Materials were prepared by means of a standard spraying technique and by using an improved technique that allows for the quenching of the material using liquid nitrogen-cooled substrates. Quenching leads to the controlled formation of metastable phases. The influence of liquid nitrogen cooling on the formation of the metastable phases was studied by X-ray diffraction under a grazing incidence angle of 1°. A significant increase in the amount of the metastable zirconia phase and a more homogeneous composition along the thickness were found compared to the regularly sprayed coatings. All materials were subjected to a thermal treatment for 1 h at 1400 °C to study the evolution of stable phases.

1. Introduction

Thermal spray technologies like plasma spraying are common techniques for the application of ceramic coatings. The ceramic coatings are formed by the piling-up of molten particles hitting a surface. The ceramic starting powder is molten in the plasma zone and accelerated onto the substrate. Upon contact with the metallic substrate, the droplets flatten and the heat is removed from the molten droplet during solidification. The contact area increases during the impact, which increases heat transfer along the interface due to the high velocity of the molten particles. Very high cooling rates of $>10^6$ K/s can be achieved [1–3]. These high cooling rates very often lead to the formation of metastable [4–6] or even amorphous phases [7–10] due to the limited time for diffusion. The formation of metastable phases may be promoted by ultrahigh cooling rates achieved during quenching on liquid nitrogen-cooled substrates [7,11–15].

Plasma-sprayed zirconia coatings find applications as thermal barrier coatings (TBCs) in gas turbines or aircraft engines and have been utilized as wear resistance coatings. The fracture toughness and wear resistance may further be enhanced by the addition of alumina [16,17] and improvements in corrosion resistance [18,19] and lowered thermal conductivity [20] of zirconia TBCs may be attained.

In the case of composite materials that are usually immiscible at room temperature, such as ZrO_2 and Al_2O_3, supersaturated phases can be formed. While yttrium ions easily form a solid solution with zirconia, alumina exhibits only limited solubility. Rapid quenching of molten zirconia–alumina particles leads to the formation of an Al^{3+}-supersaturated t-ZrO_2 phase [14,21]. This effect may be enhanced by incorporating an additional liquid nitrogen feeder to cool the substrate during deposition. The immiscible starting materials are molten during the short residence time in the plasma jet, intimately mixed, and homogenized due to the extended solubility in the liquid state. In this way entrapped aluminum ions are known to stabilize the tetragonal zirconia phase even in the absence of yttrium [22]. Tetragonal as well as cubic zirconia can be stabilized when aluminum as well as yttrium is present during solidification [23].

This paper describes the production of free standing nanocrystalline metastable materials with the composition of (ZrO_2–5 Y_2O_3)–20 Al_2O_3 (all compositions are given in weight %) by plasma spraying of commercial powders with and without using a liquid nitrogen-cooled substrate. Free standing materials with a thickness larger than 0.5 mm can be produced and are subjected to microstructural characterization. The structure of the as-prepared ceramics will be identified as well as that resulting after a thermal treatment for 1 h at 1400 °C. Thickness-sensitive structure analysis is performed to describe the influence of liquid nitrogen cooling on the formation of metastable phases.

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0257-8972/$ – see front matter
doi:10.1016/j.surfcoat.2009.07.005

2. Experimental

2.1. Material processing

Commercially available agglomerated and sintered micron-sized powders (Tosoh, Japan) with a mean particle size of 57 μm were used as feedstock for this study. The feedstock powder was sprayed using an Atmospheric Plasma Spray (APS) A-3000S system with an F4 plasma torch (Sulzer Metco, Germany). Table 1 shows the spraying parameters chosen for material production. The powder particles were fed into the plasma jet, where they were molten and accelerated onto a substrate. Two liquid nitrogen feeders (Air products, PA) were used to refrigerate the sprayed material (Fig. 1). The experimental setup is described in more detail in reference [15]. The substrates were flat steel plates (UNS G41350) of 50 mm × 20 mm × 5 mm in dimension. Free standing coatings with a thickness of 600–700 μm can be achieved easily by peeling off the material from the substrate. The preparation of free standing coatings is necessary to study the influence of the thermal treatment on the microstructure at high temperatures of 1400 °C.

2.2. Microstructural characterization

X-ray diffraction (XRD) was performed using a D5000 powder diffractometer (Siemens, Germany) with Ni-filtered Cu K_α radiation in reflection (θ–2θ geometry). The diffraction patterns were analyzed by Rietveld refinement with the TOPAS software (Bruker-AXS, Germany). The instrumental parameters were determined by means of a NIST LaB_6 standard. In order to characterize the phase composition as a function of depth, grazing incidence X-ray diffraction (GIXRD) was employed using an angle of 1°, corresponding to a penetration depth of the X-rays of approx. 1 μm. After each GIXRD measurement the sample was ground by approx. 100 μm. A mild grinding procedure was used to avoid phase transitions in the coating because of the applied stresses. The surface of the sample was slowly removed using a high speed diamond grinding wheel. The feed rate was 2 μm for each passage. This procedure was performed on two samples from the same coating from both sides to obtain the full information over the entire thickness. It is calculated that the X-ray penetration depth in θ–2θ geometry is about 20 μm.

The density of the materials was measured using helium pycnometry (Pycnomatic, Porotec GmbH, Hofheim, Germany) — averaging at least 20 density values. High-resolution SEM (XL 30 FEG, Philips, Eindhoven, The Netherlands) equipped with an EDX system (EDAX, Mahwah, NJ) was used to investigate the microstructure and chemical composition of ground and polished cross sections and fracture surfaces. Analysis of the recorded images was performed using the UTHSCSA ImageTool program (developed at the University of Texas Health Science Center at San Antonio, Texas. http://ddsdx.uthscsa.edu/dig/itdesc.html) to determine the degree of porosity.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction patterns of both the conventionally processed samples as well as the material obtained by liquid nitrogen quenching were recorded to gain better insight into the crystallographic structures formed during plasma spraying and after thermal treatment. In all cases the patterns were obtained from the interface side of the coating. The patterns are shown in Fig. 2. The starting powder consists of corundum (α-Al_2O_3) as well as of a mixture of monoclinic and tetragonal zirconia, whereas the tetragonal phase is the dominant

Table 1
Summary of plasma spray parameters.

Current	Voltage	Ar flow	H_2 flow	Spray distance	Feed rate	Torch traverse speed
600 A	67.5 V	35 nlpm	12 nlpm	120 mm	12 g/min	500 mm/s

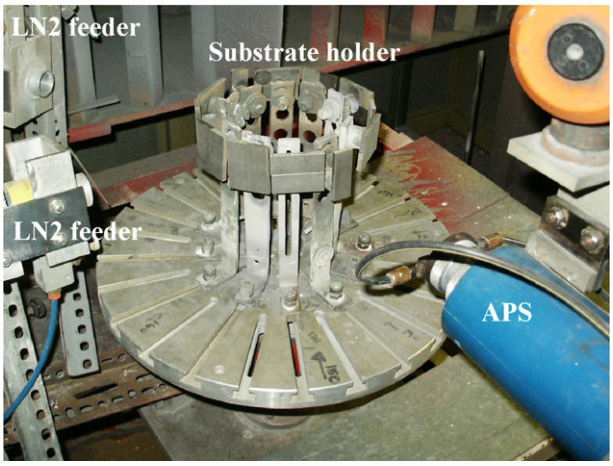

Fig. 1. Image of the experimental setup used for the spray deposition clearly showing the two liquid nitrogen (LN_2) feeder, the substrate holder, and the plasma torch.

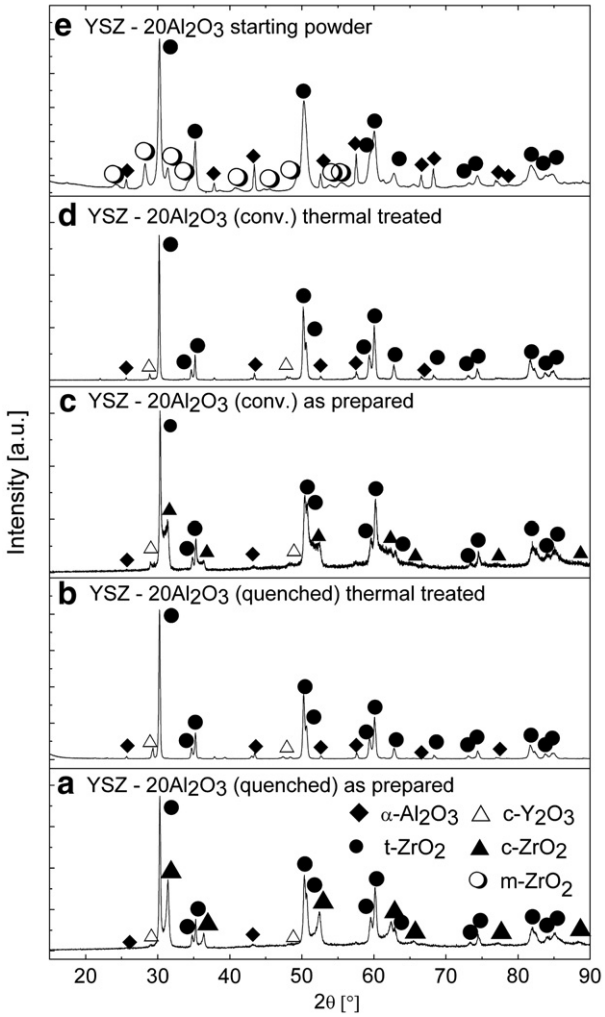

Fig. 2. X-ray diffraction patterns of plasma-sprayed YSZ–$20Al_2O_3$ composites: (a) splat-quenched as prepared, (b) splat-quenched after thermal treatment, (c) conventionally processed as prepared, and (d) after thermal treatment. The diffraction pattern of the starting powder is given in (e).