Microstructure and elastic properties of plasma-sprayed alumina

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On deposition, plasma-sprayed ceramics are typically far from thermodynamic equilibrium, i.e., they contain metastable phases and also exhibit an extremely high density of lattice and other defects at many microstructural levels. Exposure to high temperatures is known to result in a consolidation of the material and can lead to both subtle and radical changes in the meso and microstructure. The effective elastic properties must be governed by the variety of structural defects and must also change as the defect structure changes during annealing. In the present study the microstructural development in plasma-sprayed alumina (Al₂O₃), as a function of annealing temperature is investigated using techniques of electron microscopy, X-ray diffraction and porosimetry. In addition, the effective elastic properties of this material have been studied using an ultrasonic spectroscopy technique which is especially suited for porous, highly attenuating materials. The results show that annealing even at moderate homologous temperatures already has a noticeable effect on the elastic properties. Upon annealing at higher temperatures, very strong elastic constant changes are observed: increases of about 300% as compared with the as-sprayed material. The underlying microstructural changes are discussed in detail. It is found that the elastic properties of plasma sprayed alumina must be largely governed by the aspect ratio and arrangement of internal defects and porosity.

1. Introduction

Plasma-spraying technology is gaining increasing acceptance in industry for the application of high performance coatings and even for the production of free standing bulk components with up to several millimetres wall thickness [1–3]. The technique is very versatile and almost any material can be plasma-sprayed. For ceramic materials the technique is of particular interest because it allows their application as thermal barrier and wear resistant coatings on all kinds of standard load-carrying substrates or as highly thermoshock resistant, free-standing parts [4, 5]. The properties of plasma-sprayed ceramics, which are largely governed by their defect-rich microstructures, can, however, be very different from those of corresponding conventionally sintered ceramics. This can be both advantageous and disadvantageous.

Plasma-spraying involves feeding a material powder mixed with a carrier gas/liquid into a high voltage electric arc. The gas forms an expanding plasma, which both melts the powder particles and accelerates them towards a substrate. The molten droplets are deposited at high temperature and velocity on a cooler substrate and are rapidly cooled at rates of about 10⁶ to 10⁷ K s⁻¹ [6]. Layer thickness is built up by moving the spraying apparatus (Plasma-gun) transversely across the substrate so successive splats can be deposited and cooled. After deposition, the plasma-sprayed layer can be separated from the substrate to leave a free-standing ceramic part.

In consequence of the impact and rapid cooling on deposition, a highly aligned, anisotropic microstructure with a high defect density forms, giving rise to peculiar mechanical properties. In particular, the strength and elastic stiffness of a plasma sprayed ceramics are typically an order of magnitude lower than those of the same ceramic when densely sintered [4, 7–9], whereas the fracture toughness can easily be comparable [10]. The unique combination of very low stiffness and decent toughness is responsible for the excellent thermoshock properties of these materials [11].

Post deposition exposure to high temperatures has been observed to lead to significant changes in the phase composition and microstructure of plasma-sprayed ceramics and it has been postulated that these changes must affect the effective elastic stiffness of the material as well as other properties [12]. Several studies on various plasma-sprayed oxide ceramics [3, 13–15], have shown that annealing at elevated temperatures can, indeed, lead to significant residual changes in effective elastic properties: both a decrease and an increase in elastic stiffness has been observed according to the material and annealing schedule. As yet, however, the two features of microstructural and elastic property development have seldom been the subject of a combined comprehensive study on a specific material.
In the present study, we focus on a commercially produced plasma-sprayed aluminium oxide. This material is characterised in as-sprayed state as well as in different heat-treated conditions using X-ray diffraction, electron microscopy and porosimetry. The results of these structural and morphological investigations are correlated with the evolution of the elastic constants of the material, determined by ultrasonic wave velocity measurements.

2. Experimental
2.1. Material and microstructure
The alumina material used in this investigation was atmospheric plasma-sprayed (APS), from an α-Al₂O₃ (99.5%) powder agglomerate, using a water stabilised arc plasma gun, by LWK Plasmakeramik, Gummersbach, Germany. A cylindrical alumina tube was produced with wall thickness of about 80 mm and the substrate was subsequently removed. All samples were cut from the bulk to avoid substrate influence, e.g., substrate/deposit cooling effects. As shown schematically in Fig. 1a and b, the principal material directions are the axial, tangential, and radial directions of the cylinder. In the following, these directions are referred to with the symbols a, t, and r, respectively. The orientation of the splats relative to these directions is shown schematically in Fig 1b. The as-sprayed material contained a mix of about 65% γ and γ-near transition phases and 35% α-Al₂O₃ [10].

Samples were heat-treated in air at 5 °C/min with hold times of 12 h at 900 °C, 1050 °C, 1180 °C and 1550 °C, and then furnace cooled to room temperature. These temperatures were chosen on the basis of the known transformation temperatures for the various metastable alumina [16]. The last heat treatment is just below a common sintering temperature for alumina materials [17], and is similar to treatments applied in industry to consolidate and make thermally stable sprayed products.

X-ray phase analysis was conducted using bulk samples and CuKα radiation in a Siemens D-500 diffractometer. Thin-foil transmission electron microscopy samples were observed and selected area electron diffraction (SAED) studies conducted in a Jeol 2000FX transmission electron microscope (TEM) operating at 200 kV. Scanning electron microscopy (SEM) was conducted on gold sputtered samples in a Leica Cambridge Stereoscan 360. Archimedean porosimetry was used to quantitatively follow the effects of heat treatment and phase change on porosity.

2.2. Characterisation of the elastic stiffness
2.2.1. Ultrasonic measurements
In order to characterize the elastic stiffness, the velocities of elastic waves propagating in the directions of the principal material axes were measured using an ultrasonic spectroscopy technique. For these experiments, cube-shaped samples with nominal dimensions 9 × 9 × 9 mm³ and edges parallel to the principal material axes a, r, and t were machined from the bulk by cutting and grinding.

Ultrasonic wave velocity measurements were carried out by attaching a pair of identical broadband ultrasonic transducers on opposite sides of the specimen using double sided sticky tape. One transducer was used to transmit a continuous, harmonic elastic wave into the specimen, the other one to receive the signal transmitted through the specimen. While sweeping the frequency f of the signal from 100 kHz upwards, the phase shift Δφ between the incident and transmitted waves was measured continuously. It is important to note that there always exists an upper frequency limit above which the attenuation due to scattering and absorption in the specimen is beyond the dynamic range of the measurement system. In the most extreme case of the present study, this upper frequency limit was as low as 2.8 MHz. It is the great advantage of this continuous-wave phase spectroscopy technique over ultrasonic pulse propagation methods that it allows for accurate wave velocity measurements on relatively small samples despite this constraint to relatively low frequencies. A detailed description of the technique and the experimental set-up has been reported elsewhere [18].

The wave velocity, v, is readily determined from the slope of the resulting Δφ(f) function (“phase spectrum”) according to the equation [18, 19].

\[
\nu = -2\pi f L \left( \frac{d\Delta \phi}{df} \right)^{-1}, \tag{1}
\]

Figure 1 Schematics showing (a) the geometry of the sprayed cylinder and (b) the orientation of the splats with respect to the principal material directions (for simplicity only some splats are outlined, in reality splats impinge on one another)