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Influence of bias voltage and oxygen flow rate on morphology and crystallographic properties of gas flow sputtered zirconia coatings

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ABSTRACT

The aim of this work is to gain a fundamental understanding of the influence of bias voltage and oxygen flow rate on the resulting microstructure and crystallographic properties of gas flow sputtered (GFS) yttria stabilized zirconia coatings.

At given substrate temperature of 500 °C fully yttria stabilized zirconia (FYSZ) coatings (10–30 μm) were deposited on a FeCrAl-alloy. The oxygen flow rate and the substrate bias voltage were varied over a wide range.

The resulting microstructures were columnar, but varied widely in porosity and column diameter. While increased oxygen flow rate generally results in coarser microstructures with higher porosity, bias voltage seems to increase the effective surface temperature due to ion bombardment at low voltage, but has a destructive effect at higher voltages leading to randomized grain orientations and small grain sizes.

Thermal cycling experiments were conducted between 100 °C and 1050 °C. Although no large scale spallation was observed, the former columnar coating degraded due to sintering, resulting in sinter necks between former single columns and diminished intra-columnar porosity. However, high oxygen flow rate and moderate bias increase the resistance to sintering due to coarser morphologies.

1. Introduction

Ceramic thermal barrier coating (TBC) layers enable higher surface operation temperatures of combustor walls and high-pressure turbine blades around 100–300 °C, allowing for higher combustion temperatures and/or reduced consumption of cooling air [1–3]. Both effects promise higher turbine efficiency and lower fuel consumption [4]. Most of these ceramic TBCs are based on yttria stabilized zirconia (YSZ) [3,5,6] due to its low thermal conductivity, high temperature capability, and chemical and thermo-mechanical compatibility with the underlying bond coat layer (usually MCrAlY or PtAl) which usually forms the hot gas corrosion protection and improves the TBC adherence [7]. While fully yttria stabilized zirconia films (FYSZ, ≥8 mol% yttria) show lower thermal conductivities and enhanced high temperature phase stabilities compared to partially yttria stabilized zirconia (PYSZ, <8 mol% yttria) films, the latter are preferred in service under cyclic thermal load due to their improved lifetimes and erosion resistance [7–9]. Among many deposition techniques, plasma spraying and electron beam physical vapor deposition (EB-PVD) are most widely used [10]. Each technique has merits depending on performance requirements, strain tolerance, thermal conductivity and cost.

1.1. Conventionally processed TBC

Plasma-spray techniques produce layered YSZ microstructures which consist of splats separated by fine inter-lamellar pores. These microstructures exhibit advantages in term of thermal insulation and process speed. Thermal conductivities lower than 1.0 W/m·K have been reported [11]. These coatings exhibit risks of delamination due to weak "mechanical" bonding between layer and substrate and due to the lack of in-plane compliance.

Another widely used process is EB-PVD. The characteristic inter-columnar gaps which are present in EB-PVD coatings lead to excellent strain tolerance and thermo-shock resistance under thermal cyclic conditions. Intra-columnar features such as voids between feather-arms can significantly reduce the thermal conductivity. The relation between thermal conductivity and the process-related micro- and nanostructure in EB-PVD YSZ coatings has been thoroughly investigated [12]. However, due to technical limitations, only a few parameters are accessible to alter the resulting microstructure, especially coating temperature and the direction of particle flux (tilting, rotation of the substrate) [12–16].

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Recently, important developments have been made in the technology gap between conventional PVD technologies and thermal spray processes by the extension of the low pressure plasma spraying (LPPS) technology towards lower pressures and higher plasma densities. The new processes have been described as plasma spray-thin film (PS-TF) processes, very low pressure plasma spray (VLPPS), or plasma spray-PVD [17–19].

1.2. Gas flow sputtered TBC

Sputtering, especially reactive sputtering under high process pressures, provides important additional process parameters to influence the texture and microstructure of YSZ TBCs. One example is the ion impingement on the growing surface, which can be controlled by an external bias voltage. The impinging ions are ionized argon atoms; the ionization of sputtered species is unlikely due to the typical plasma power densities achieved by DC sputtering. Other examples are the variation of the metal–oxygen ratio or a variation of the particle mean free path (process pressure). Pre-process ion etching of the substrate can promote the chemical bonding between layer and substrate. However, common low-pressure sputter techniques (e.g., magnetron sputtering) are not desirable for the fabrication of thick films >10 μm due to the comparatively low coating rates and due to the inherently dense microstructures leading to compressive film stress. In low pressure sputtering, the origin of this stress is usually ascribed to the energy flux to the substrate per deposited atom, which comes from the arriving film atoms and the reflected neutrals [20]. The reactive gas flow sputter process (GFS), which utilizes an intensive hollow cathode glow discharge and a gas-flow-based material transport at higher pressures, overcomes these drawbacks [21,22].

It is worth to be noted that for real service applications Ni-base superalloys are used and specific heat treatments, typically between 800 °C and 1300 °C, are mandatory to optimize their microstructure and mechanical properties [23]. Thus, low deposition temperatures (like 500 °C) as utilized here (in contrast to for example EB-PVD) would be an added advantage, as they do neither interfere with the recommended heat treatment parameters nor do they alter the superalloy microstructure.

This article shows the relation between process parameters that are easily accessible in the reactive gas flow sputter technique and layer structural properties. Hence, the focus is set on bias voltage and oxygen partial pressure. FSYZ has been used as coating material to benefit from the low thermal conductivity and phase stability. To evaluate the behavior of these coatings under service conditions, the influence of thermal cycling is presented.

2. Experimental details

2.1. Sample preparation

All experiments have been carried out in a vacuum chamber equipped with a linear type gas flow sputter source with two plane parallel water-cooled metallic targets. For a detailed description of the sputter source and the sputtering facility, see for example [24]. The targets are arranged face-to-face so that a hollow cathode is formed and a hollow cathode glow discharge can be achieved. The targets have a length of 250 mm and a spacing of 30 mm. Alloyed metallic sputter targets with a composition of 85.2 at.% Zr and 14.8 at.% Y were used which after reactive sputtering gives rise to fully yttria stabilized zirconia (FYSZ) containing 8 mol% yttria. The oxygen gas was added separately into the plasma torch. The argon gas is led through the source to prevent target poisoning and to effect convectional material transport. The process gases, argon and oxygen, are supplied by MKS mass flow controllers. A working pressure of 50 Pa, which is desirable for a hollow cathode glow discharge, is maintained using a Roots blower unit and a vacuum rotary pump with a total pumping capacity of 1000 m^3/h. A customized heatable sample holder covers the following functions: (i) motion drive to ensure the required layer thickness uniformity, (ii) heatable up to 500 °C with thermocouple temperature control, (iii) ability for substrate bias. Plasma excitation is realized by an Advanced Energy DC power supply and substrate biasing is implemented by an ENI RPG50 mid-frequency (MF) pulsed-DC power supply.

The coating was deposited on a grinded ferritic iron–chromium–aluminum alloy *Kanthal AF* provided by *Sandvik AB*, Sweden. Prior to the sputtering of FYSZ, the specimen was heated to the deposition temperature and its surface was ion etched.

To vary the microstructure as well as the crystallographic texture, the applied oxygen flow rate and bias voltage at a given temperature are of major importance. It is well known, that a bias voltage applied at the substrate can influence the adatom mobility during sputter growth and therefore influence the microstructure and texture of growing films [25,26]. Effective ion bombardment by biasing the substrate is accessible in the gas flow sputtering process since it utilizes a hollow cathode glow discharge which ensures a low energy distribution but high plasma density near the growing film [27,28].

YSZ samples were grown under variation of the nominal bias voltage (VB) between 0 and −100 V and of the oxygen flow rate between 18 and 120 sccm. However, coatings were dark gray and spallation occurred below 28 sccm, so that further analysis was limited to flow rates of 28 sccm and higher (compare Table 1). Note that the nominal bias voltage is essentially a mean value averaged during the pulse period. The remaining process parameters were held constant, i.e., sputter discharge power (5000 W), argon flow (5000 sccm), time of deposition (5250 s), substrate temperature (500 °C), bias frequency and reverse time (200 kHz and 1 μs, respectively).

2.2. Thermal cycling

Rectangular (10 × 14 mm^2) specimens were cut out of samples a–g and thermal cycling experiments based on ISO 13573 were conducted between 100 °C and 1050 °C for seven (83 cycles) and 17 (224 cycles) days, respectively. One cycle consists of a heating phase, followed by a hot dwell time of 60 min starting at 97% of the hot cycling temperature in Kelvin and an air fan assisted cooling phase down to 100 °C. The temperature was measured by a thermocouple which was in contact to the bottom of one specimen.

2.3. Characterization

Polished cross-sections, top views and cryogenic fracture surfaces coated with a thin gold layer have been examined before and after thermal cycling by scanning electron microscopy (SEM; Zeiss DSM982 Gemini) and optical light microscope. Although samples have not been polished, sufficiently large undisturbed areas exist, allowing evaluation of layer properties (compare middle row in Fig. 1). Layer thickness has been measured and averaged at 15 positions in polished cross sections in the optical light microscope.

Coating composition was determined by Cameca SX100 Electron Probe Micro Analyzer consisting of 5 WDS spectrometers each equipped with several diffracting crystals. The composition was determined on polished sample cross sections. Excitation energy was 10 keV. Five spots per sample were measured, and the resulting fractions were averaged.

For phase determination X-ray diffraction measurements were carried out in Bragg–Brentano geometry using a Philips X'Pert Pro MRD diffractometer with a Cu K_α source. The average grain size was estimated by applying the simple Scherrer equation [29] to every peak. The mean value was weighted with the peak intensity.

In most cases thin films are transversely isotropic, i.e., they do not have any distinguished orientation other than perpendicular to the film surface, therefore it is usually sufficient to measure the texture or preferred orientation of the crystal structure by evaluating the relative