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# Influence of substrate temperature on morphology and behavior under cyclic thermal load of gas flow sputtered zirconia coatings

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ABSTRACT

The aim of this work is to gain an understanding of the influence of substrate temperature during deposition on the resulting microstructure and crystallographic properties of gas flow sputtered (GFS) partially yttria stabilized zirconia coatings (PSZ).

PSZ coatings were deposited on a FeCrAl-Alloy substrate, varying the substrate temperature between 500 °C and 800 °C. Regardless of the substrate temperature, all coatings were columnar, but varied in their morphology. Four different groups of sub-microstructures, each defined by a substrate temperature range, were identified based on morphology and X-ray diffraction (XRD) pattern.

The two low-temperature groups exhibit a novel microstructure characterized by three dense ridges at intervals of 120° converging at the column center. Supported by these ridges small stacked plates lead to a featherlike porosity. The XRD pattern revealed a monoclinic fraction, besides the tetragonal and/or cubic one, and a ⟨111⟩ growth direction. Higher temperatures diminish the monoclinic fraction until it vanishes at 800 °C accompanied by a change in growth direction to ⟨100⟩.

Thermal cycling experiments were conducted between 1050 °C and 100 °C. Macroscopic spallation occurred for one group while the other samples were intact after the end of the experiment at 1300 cycles. Microscopic delaminations were found between a pure alumina scale and a mixed oxide zone, consisting of zirconia particles embedded into an alumina matrix. A hypothesis was proposed explaining the observed failure mode.



## 1. Introduction

Ceramic thermal barrier coatings (TBC) are used in gas turbines or in aircraft engines protecting components and enabling higher operating temperatures [1,2,3]. This leads directly to higher operation efficiencies [4]. Zirconia is the state of the art material for these coatings [1,5,6], exhibiting a low thermal conductivity and a comparatively low mismatch to the thermal expansion coefficient of the subjacent bond coat (usually MCrAlY or PtAl). Since pure zirconia undergoes phase transformations under operating conditions accompanied by volume changes, it is stabilized by varying amounts of yttria. Lower thermal conductivities and enhanced high temperature phase stabilities can be achieved if the stabilizing content exceeds 8 mol% yttria (fully stabilized zirconia). Nonetheless, for service applications, partially stabilized zirconia (PSZ; ~4–4.5 mol% yttria) [2] is usually preferred featuring an improved erosion resistance and thermal cycling lifetime [7,8,9].

Widely used deposition techniques are electron beam physical vapor deposition (EB-PVD) and air plasma spraying, which lead to different coating morphologies and properties [10]. Characteristic for air plasma sprayed coatings is the lamellar splat structure separated by fine inter-lamellar pores. This morphology enables thermal conductivities lower than 1.0 W/m K [11]. The fast processing speed is accompanied by a relatively weak interlocked adhesion and no chemical bonding of the coating [2].

EB-PVD thermal barrier coatings consist of columns oriented perpendicular to the substrate allowing an excellent strain tolerance and thermo-shock resistance under thermo-cyclic load. Besides the intercolumnar porosity, feather arms and globular elongated pores further reduce the thermal conductivity. The morphology can be altered by process parameters (mainly substrate temperature, vapor incident angle and substrate rotation) [12,13,14,15,16].

Various approaches are pursued obtaining the superior columnar microstructure with newly developed deposition techniques at lower costs. Increasing the substrate temperature, highly vertically segmented air plasma sprayed coatings with increased thermal cyclic lifetime are reported [17]. Structures closer to EB-PVD coatings (feathery

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substructures) can be manufactured by suspension plasma spraying: Fine powder is dispersed in a suspension and directly fed into the plasma torch [18,10]. A further development of the low pressure plasma spray towards lower pressures and higher plasma densities is the plasma spray physical vapor deposition process. Powder feedstock material can be evaporated, and depending on the deposition rate columnar structures are possible [19,20,21,22].

Besides developments originating from thermal spray processes, sputter technologies are also considered. For thick layers, common sputter processes (e.g. magnetron sputtering) usually lead to undesired inherently dense coatings accompanied by compressive stresses. These stresses are related to bombarding energetic particles (arriving film atoms and reflected neutrals) leading to argon entrapment or atomic peening [23].

The reactive gas flow sputter process (GFS) overcomes these drawbacks. The GFS technique is characterized by a dense hollow cathode glow discharge with typical plasma densities as high as $10^{19}$ $m^{-3}$ and low electron temperatures of several 100 meV due to collisional energy loss. Material transport during this sputter process is supported by an argon gas-flow with flow velocities in the 10–30 m/s range at elevated pressures of 10–100 Pa. Depending on the discharge power and gas flow, gas temperatures well above 600 °C and up to 800 °C have been measured in a previous work [24]. For the target erosion, a pure metallic sputter mode within the source is observed even in the presence of oxygen in the coating chamber as the applied inert gas (Ar) flow through the hollow target prevents target poisoning. So, unlike other sputter processes, target erosion and reactive film growth can be treated as independent processes and the presence of oxygen in the vicinity of the substrate does not negatively affect the deposition rate. Various microstructures can be obtained (from totally dense to columnar feathery structures) by varying process parameters such as oxygen flow rate, argon ion impingement through applied bias voltage, particle mean free path through chamber pressure and substrate temperature [25,26,27,28,29,30]. Although the substrate temperature is a significant factor, its influence has yet to be studied in detail for the GFS process.

For thermal barrier applications, the control of the film microstructure is important, as key coating performance properties are dependent on the microstructure, i.e. thermal conductivity, erosion resistance, and behavior under thermal cyclic load. Additionally, a control of the crystallographic phases and texture during growth of the films may be advantageous to benefit from the anisotropy of mechanical properties, such as Young's modulus [31] or thermal expansion coefficient [32]. These properties have a large impact on mechanical stresses occurring under thermal cycling and are crucial for failure propagation.

Hence, this article shows the relationship between substrate temperature during growth and resulting microstructure of the partially stabilized zirconia coating with its resulting texture.

In addition, the GFS coating's performance under thermo-cyclic load will be a key factor determining the competitiveness of the GFS process itself and is therefore studied as well.

## 2. Experimental details

### 2.1. Sample preparation

The experiments have been conducted in a vacuum chamber (Fig. 1) using a tubular type gas flow sputter source with a water-cooled metallic target (composition: 92.4 at% Zr and 7.6 at% Y) exhibiting an inner diameter of 50 mm and a length of 150 mm. Plasma excitation was realized by an ENI DCG-200 DC power supply. Argon gas (3 slm) is fed through the source, enabling transport of the sputtered species and preventing target poisoning due to the oxygen inlet (100 sccm) behind the sputter source. After reactive sputtering, this composition gives rise to partially stabilized zirconia containing 4 mol% yttria. Both gases are regulated by MKS mass flow controllers. A roots vacuum pump (Leybold RUVAC WSU 2001) and a rotary vane pump (Leybold Sogevac SV300)

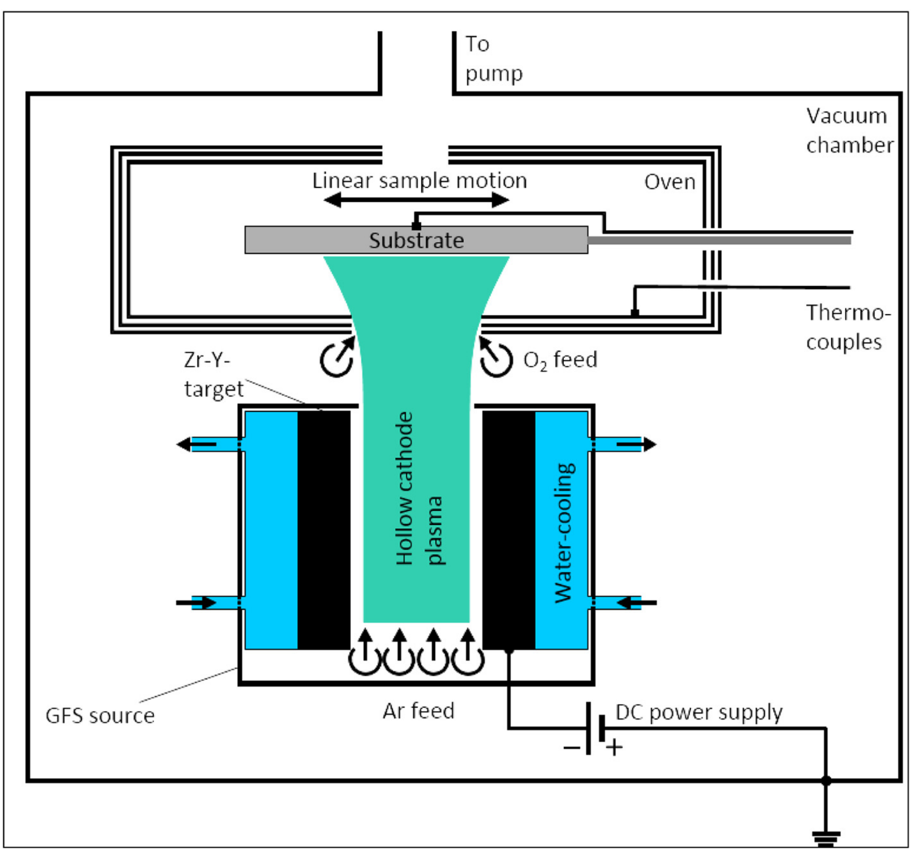


**Fig. 1.** Cross-section scheme of the GFS coating setup.