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Porosity investigation of yttria-stabilized zirconia topcoats using NMR cryoporometry

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ABSTRACT

Axial suspension plasma spraying (ASPS) is a new, innovative plasma spray technique using a feedstock consisting of fine powder particles suspended in a liquid. With ASPS, thermal barrier coating (TBC) topcoats with columnar structures have been produced that are built up by fine powder particles. The microstructure consists of micro-, meso-, and macro-pores. Due to the wide pore size range including nano-porosity it is challenging to measure porosity and pore size distribution in TBC topcoats. However, it is important to characterize the porous structure as it affects the thermal conductivity. Nuclear magnetic resonance (NMR) cryoporometry is a promising method for performing such measurements because of its capability of measuring pores down to nanometer size and providing information about the pore geometry. The aim of this paper is to introduce NMR cryoporometry as a new characterization technique for determining porosity, pore size distribution and pore geometry of TBC topcoats produced by ASPS. The study includes the comparison of two different yttria-stabilized zirconia topcoats and NMR cryoporometry is complemented by microstructural characterization using scanning electron microscopy.

1. Introduction

Thermal barrier coatings (TBCs) play an important role as protection of components in the hot section of gas turbines. TBC topcoats insulate from high temperature loads, thereby extending the lifetime of the turbine and enabling higher combustion temperatures which in turn enhance the engine efficiency and decrease emissions [1]. One of the important properties of the topcoats is therefore its thermal conductivity, i.e. how effectively the coating can insulate the underlying material from the hot combustion gases. Contributions from convective, conductive and radiative heat transfer have to be considered for the coatings in order to investigate their insulating properties. While convection may be important in the presence of substantial through-thickness cracks, radiative heat transfer can become significant at very high temperatures [2]. Generally, heat transfer occurs mainly via phonon conduction and depends to large extent on the existing scattering sites as they shorten the mean free path of the phonons [2]. Thus, thermal conductivity is highly influenced by the microstructure of the TBC topcoats and specifically by the grain boundaries, the in-built porosity and the pore size distribution. Therefore, topcoats should be produced with an optimal designed microstructure to achieve low thermal conductivity and strain tolerance.

1.1. Characteristics of suspension plasma sprayed coatings

Suspension plasma spraying (SPS) is one of the most recent and innovative plasma spray processes. It is similar to the atmospheric plasma spraying (APS) process, except that a liquid carrier is used when injecting the powder particles into the plasma jet. When using a liquid feedstock the injected powder particles can be finer [3,4]. The particles in the suspension used in SPS can be of sub-micron size, i.e. <1 μm [5], while particle sizes of 10–100 μm are common in APS [6]. The larger particle size in APS results in coatings with lamellar structure which are built up by flattened and solidified particles (splats) [7]. Due to the formation process, it is usually not possible to obtain very fine structured or even nanostructured coatings by APS.

The smaller particle sizes in SPS and the sensitivity of the particles to the velocity of the plasma are held responsible for the smaller grain size and the occurrence of the columnar structure typical for SPS [8]. Moreover, suspension plasma sprayed TBC topcoats with columnar structure have already shown equally or improved properties in terms of thermal properties and thermal shock resistance [9] compared with more

Abbreviations: APS, atmospheric plasma spraying; ASPS, axial suspension plasma spraying; CPMG, Carr-Purcell-Meiboom-Gill; MIP, mercury instrusion porosimetry; NMR, nuclear magnetic resonance; SEM, scanning electron microscopy; SPS, suspension plasma spraying; TBC, thermal barrier coating; USAXS, ultra small angle x-ray scattering; YSZ, yttria-stabilized zirconia.

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conventional counterparts with lamellar structure. When spraying with finer powder particles, coatings consisting of a wide range of pore sizes have been produced. Both nm- and μm-sized pores are present in the SPS coatings, and macro pores are found in-between the columnar structure. The macro pores can be parts of segmentation cracks (through thickness cracks) that are suggested to be beneficial due to their ability to improve the strain tolerance. Though, the segmentation cracks have a negative influence on the thermal conductivity, as they allow hot combustion gases to reach the substrate [2].

Yttria-stabilized zirconia (YSZ) is widely used as TBC topcoat material due to its heat insulating properties and its high coefficient of thermal expansion [1]. In YSZ, heat transfer takes place foremost by conduction, but at enhanced temperatures also radiation plays a role [2]. The thermal resistance is improved by phonon scattering at inhomogeneities, for example vacancies, grain boundaries and pores. By doping zirconia with yttria, the zirconium cation (Zr^{4+}) is replaced with yttrium (Y^{3+}) and thermal conductivity is decreased by the increasing amount of oxygen vacancies which scatter phonons [10]. Use of finer powder particles during the plasma spray process leads to the possibility of creating coatings with finer grain sizes and in turn an increased number of grain boundaries. Hence, thermal conduction is substantially reduced by phonon scattering especially if the grains are nano-sized [11,12]. The thermal insulation can be improved by incorporating porosity in the coatings. YSZ has a higher thermal conductivity than gas-filled pores and an increased porosity will therefore decrease the overall conductivity remarkably [2]. Furthermore, nano-sized pores are expected to decrease thermal conductivity as they increase the number of interfaces at which phonons (and electrons) are easily scattered [2]. Even pore geometry influences thermal conduction. If the pores are elongated, with the long axis perpendicular to the heat transfer direction, the insulating effect is higher due to a large amount of interfaces normal to the heat flow direction [2]. At evaluated temperature, as during operation of the gas turbine, the radiative component will significantly influence the thermal conductivity [2,12]. However, Klemens and Gell [12] stated that larger inhomogeneities (micron-sized) play an important role in the reduction of the radiative heat at operational temperatures while small defects have little influence. The authors also suggested that the optimal design for a TBC topcoat with desirable low thermal conductivity would be a matrix of nm-sized grains which scatters the phonons, and that contains large stable inclusions of ~500 nm (for example pores) which scatter the radiative heat.

The porosity is not only affecting the thermal conductivity, but also to what extent sintering occurs when TBC topcoats are exposed to extreme temperatures (≥1500 K) for extended times during operation of the engine [13]. To optimize the thermal properties and to maintain them during service of the components, it is important to have topcoats with an optimized porosity. Therefore, determination of porosity, pore size distribution, and pore geometry is an essential part of TBC design. It is thus necessary to have a suitable method at hand to investigate these properties in thermal spray coatings such as TBCs.

1.2. Techniques to measure porosity

Two common methods for determining porosity and pore size distribution in TBC topcoats are image analysis and mercury intrusion porosimetry. Image analysis is frequently used in industry because of its accessibility. Digital image processing (of e.g. binary or gray-level intensity images) is performed on cross-sectional images recorded by scanning electron microscopy (SEM). In order to detect and to obtain statistics on both small and large pore sizes, a large number of images are required at different magnifications. It is challenging to correctly measure the size of the smaller pores, and in general, it is difficult to obtain correct porosity measurements as information about connectivity and the 3D pore network cannot be directly observed. Furthermore, image analysis is a destructive method and the porosity might be affected during the sample preparation.

Mercury intrusion porosimetry (MIP) is a technique capable of measuring a broad pore size range, theoretically from a few nanometer up to a few hundred micrometer, and has been used to measure porosity and quantify pore size distributions in plasma sprayed coatings [14–16]. The technique relies on the fact that a non-wetting liquid (mercury) will only intrude the porous structure of a material when a pressure is applied. The volume of mercury intruded into the pores can therefore be measured as a function of applied pressure, and the pore size distribution can be calculated using the Washburn equation [17]. The major drawbacks with MIP are the use of mercury, the risk of material deformation, and the limitations in recording pore cavities connected by smaller pore bottlenecks. The hazardousness of mercury leads to a progressively restricted use of the technique.

In addition to MIP and image analysis, ultra-small angle X-ray scattering (USAXS) has been introduced for porosity measurements of SPS TBC topcoats. USAXS is a non-destructive characterization technique which can with high accuracy provide information on a wide range of pore sizes for materials with open, connected and closed porosity [8,18,19]. USAXS is suitable to measure nano-pores but is not able to detect the presence of large inhomogeneities, i.e. pores over a few micrometer in size [20]. An additional drawback with USAXS is the limited availability and access to synchrotron sources.

Nuclear magnetic resonance (NMR) cryoporometry is a technique which has been introduced during the last decades and has been used to determine porosity, pore size distribution and pore geometry in various porous materials like silica, cement, pharmaceutical coatings, and paper pulp [21–25]. However, to our knowledge the technique has not been used for investigating porosity in TBC topcoats. NMR cryoporometry is capable of measuring pore sizes in the range of nm up to μm [26]. The method relies on the Gibbs–Thomson effect, i.e. that confined solid matter is in phase transition equilibrium with its melt at a lower temperature than corresponding bulk material and thus a depression in the melting/freezing point occurs for material present in confined medium [23,27,28]. Experimentally, a porous material is saturated with a chosen liquid and cooled down to complete solidification. Thereafter, the temperature is slowly raised and liquid confined in smaller pores will melt at a lower temperature than liquid in larger pores. The liquid fraction is recorded in steps of temperature increase and recalculated to pore volume as a function of radius whereby the pore size distribution is attainable by the central difference formula [29].

The purpose with this paper is to introduce NMR cryoporometry as a suitable characterization technique for determining porosity and pore size distribution of TBC topcoats produced by suspension plasma spraying.

2. Theoretical background of NMR cryoporometry

The Gibbs–Thomson equation [30] describes the melting and freezing temperature depression, ΔT, of a confined liquid within pore radius, r, as

$$\Delta T \sim -1/r \tag{1}$$

The inverse radius proportionality refers to the dependence on the pore surface-to-volume ratio (freezing) and its derivative (melting). The full expression of Eq. (1) also includes parameter K, relating to bulk properties of the liquid. Moreover, using this wetting substance in the porous material, an omnipresent liquid-like layer exists between the substance in frozen state and the walls of the porous material [21]. A modified Gibbs–Thomson equation is therefore used to take into account the existence of this non-frozen layer of thickness τ, and the expressions for melting and freezing temperature depression, respectively, of a confined liquid can be written as

$$\Delta T_m = T_m - T_{bulk} = -(x-1)K/(r-\tau) \tag{2a}$$

$$\Delta T_f = T_f - T_{bulk} = -xK/(r-\tau) \tag{2b}$$