

DESIGN AND THERMAL CONDUCTIVITY CHARACTERIZATION OF A FUNCTIONALLY GRADIENT CERAMIC BASED ON $\text{CaZrO}_3 - \text{MgO}$ COMPOSITION

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ABSTRACT

Space exploration involves the use of state-of-the-art technologies such as satellite production, propulsion systems, avionics, aerodynamics, research and development of materials, etc. In the particular case of human spaceflight, the insulation system of the spacecraft is also required in order to ensure crew safety in re-entry of the atmosphere and, if possible, the spacecraft re-use. In the case, where the structure is exposed to high temperature gradients, among other systems a thermal barrier must be used for the structure in order to protect it from critical damage. Based on this concept, in this work it was developed and characterized a design of a functional gradient ceramic coating.

Recently, several studies have proposed the stoichiometric composition of calcium zirconate (CaZrO_3) as a viable alternative for harsh environments subjected to high temperatures, corrosion and wear, and the mechanical properties of this compound can be improved through a solid solution ion order to obtain a $\text{CaZrO}_3\text{-MgO}$ multiphase ceramic composites. In this work, a functional gradient material was produced with successive layers with variation in its molar composition (1:3, 1:1 and 2:3 of $\text{CaZrO}_3\text{:MgO}$) and its thermal conductivity characterized.

Keywords: Advanced ceramic, Thermal Barrier Coatings, Functionally Gradient Material, $\text{CaZrO}_3\text{:MgO}$.

INTRODUCTION

During the re-entry into the atmosphere, the spacecraft structure is exposed to high-temperature gradients and, among other systems, a thermal barrier must be used for the structure in order to protect it from critical damage. During this re-entry, spacecraft need to withstand a heating range from 377°C to 1400°C [1], which leads to a search for alternatives of current thermal barrier coatings (TBC). The most common TBC have a metallic bond coating of Ni, Co and/or Fe alloys, and a ceramic topcoat which is typically yttria-stabilized zirconia (YSZ). Typical damage in TBC are related to residual tension due to the coating process, a mismatch between the top and bond coats, bond coat oxidation, ceramic sintering, plastic deformation and crack resistance. With that, the choice for raw materials that will be part of the bulk TBC material is restricted for some basic requirements as a high melting point, low thermal conductivity, good adherence to the metallic substrate and low sintering rate of the porous microstructure [2].

Current TBCs have limited properties, so a need for an alternative is a must. Several studies presented alternative materials such as the rare earth oxide materials with pyrochlore or defect fluorite-type structure ($\text{A}_2\text{B}_2\text{O}_7$) which have the potential to improve thermal properties: e.g. $\text{Gd}_2\text{Zr}_2\text{O}_7$ with a k of 1.2-1.7 W/mK [3] and $\text{La}_2\text{Zr}_2\text{O}_7$ with a k of 1.56 W/mK [4].

Another alternative are the materials based in zirconate (ZrO_2) such $SrZrO_3$ with a k of 1,82 W/mK [5] or $CaZrO_3$ with a k of 2.0 W/mK [6]. $CaZrO_3$ can be considered as a good alternative as it is the most stable compound in the system ZrO_2 -CaO and presents good corrosion resistance, low thermal conductivity due to its perovskite type structure, high melting point (~ 2365 °C) beside the fact that is economic [6]. Several studies proposed $CaZrO_3$ -MgO composition as a good alternative to YSZ [7]. In this sense, the present work proposes a functional gradient material with successive layers with variation in its molar composition (1:3, 1:1 and 2:3) based on the composition $CaZrO_3$:MgO.

EXPERIMENTAL

Commercially available calcium-zirconate ($CaZrO_3$, CZ) powder (*Alfa Aeser*) with a purity of 99.2 % and magnesia (MgO, M) powder (*Alfa Aeser*) with a purity of 96 % were used as starting materials. Were prepared 3 types of mixes with different molar composition: 1:3, 1:1 and 2:3 $CaZrO_3$:MgO (1:3 CZ; 1:1 CZ and 2:3 CZ).

The powders were attrition milled during 3 h with zirconia balls and using isopropyl alcohol as media and their particle size optimised. The milled powders were dried at 60 °C during 24 h. Samples with individual composition (1:3 CZ; 1:1 CZ and 2:3 CZ) and successive layers are uniaxially pressed at 20 MPa into discs and sintered at 1450 °C during 2 h. The sample surfaces to be subjected to heating during the thermal conductivity tests were polished (*Struers DAP-V*) to minimize thermal contact resistance.

To this test, some assumptions were taken: steady operating conditions since the surfaces temperature remain constant at the specified values; heat transfer could be approximated as being one-dimensional; no heat generation; thermal conductivity constant; no heat loss through cylinders and samples surfaces; heat transfer by radiation were negligible. Heat transfer test by conduction was performed by measuring the electromotive force in specific points of thermocouples, and, from the heat source, water volume related to the cooling during 480 s.

Since it is possible to know the thermal conductivity by knowing the heat transferred by conduction and the fluid thermal power loss, then with an energy balance to the cylinder it is possible said that the energy through the cylinder is equal to the energy rate that is transferred to cooling fluid. With this, it is possible to calculate the thermal conductivity of the samples, k [W/mK], according the equation 1 (*Fourier Law and Rate of Heat Transfer*).

$$k = \frac{q}{A_c \cdot (\Delta T / \Delta x)} \quad (1)$$

Where “ q ” is the rate of heat transfer in [W], ΔT is the temperature difference between surfaces, Δx is the height [m] of the sample, and A_c [m^2] is the sample/cylinder section area. The characterization of the material is ongoing, but for this methodology the result obtained at room temperature was coherent with literature. The results of the thermal conductivity of the ceramic samples are in the order of magnitude of 1 W/mK. Based on the literature and these preliminary results the material proposed in this work is a suitable candidate for TBC top coat.

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