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Recycling in ceramic glazes of zirconia overspray from thermal barrier coatings manufacturing

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Abstract

Glazed ceramic tiles are the most common building material for floor and wall covering. Glazes are produced from frits. The aim of this work is to make a total or partial replacement of a raw material, zircon, widely used in ceramic tiles manufacturing, with a waste material, in order to prepare ceramic frits. The waste material used in this work, is the overspray zirconia, which is produced during the deposition process by atmospheric plasma spraying (APS) of thermal barrier coatings (TBC) on turbine blades. In particular, a replacement of 100 wt%, 1 wt% and 0.2 wt% of zirconium silicate with zirconia has been studied. Ceramic glazes prepared mixing frits and other raw materials are applied on a single-fired tile. The glazes obtained were characterized with different analytical techniques. This study has revealed that the substitution of zircon with waste zirconia is possible in small percentages due to the presence of small amount of chromophore ions in the overspray zirconia, which tend to colour the glaze.

Keywords: Zirconia; Thermal barriers; Tiles; Glazes

1. Introduction

Glazed ceramic tiles are the most common building material for floor and wall covering. Glazes are produced from frits. Frit is a ceramic composition that has been melted in a special melting oven, quenched to form a granulated glass. Frits form an important part of the batches used in enamels and ceramic glazes formulations.

Among the available commercial frits, those containing zircon ($ZrSiO_4$) and zirconia (ZrO_2) are of great interest. $ZrSiO_4$ gives rise to opaque frits, which are commonly called "zirconium whites". This type of frits, which is glossy and opaque, contains high amount of zircon because it improves the chemical properties and the degree of opacity. Zircon and zirconia can be added to the glaze as a mill addition or included as zirconia in the frit. Many studies have been performed on the effect of Zircon and zirconia on the final glaze properties.[1–3]

Unfortunately, the cost of pure zircon and zirconia, in the last few years has greatly increased. Therefore, finding alternatives or replacements to these raw materials may be very advantageous from an economic point of view.

In industrial gas turbines applications, the state of the art for the protection of the external surface of nickel superalloy components is the so called Thermal Barrier Coating (TBC) system, which has the double purpose to prevent oxidation of the substrate and to decrease the component surface temperature of more than 100 °C. Therefore, the TBC system is composed by an high temperature oxidation resistant metallic bond coat on the substrate, based on a MCrAlY alloy (M = Ni or CoNi or NiCo), and a ceramic top coat on the bond coat, made of a highly porous Yttria Stabilized Zirconia (YSZ), which is the layer that must induce the temperature drop (thermal barrier effect).[4,5] YSZ is by far the most widely studied and used material for the top coat, because it represents, at the present time, an excellent "compromise" thanks to its thermal, chemical and mechanical properties.[6] Among the deposition processes to apply ceramic

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coatings, Atmospheric Plasma Spraying has been widely employed to manufacture the top layer of TBCs, because the process produces a coating structure with inherent desirable qualities, such as strain tolerance and, in particular, low thermal conductivity.[7] Unfortunately, during the process, a high amount (up to 70–90%) of thermally sprayed zirconia does not stick to the growing coating, becoming "overspray", that is a waste material which can either stick, instead, to the walls of the deposition chamber, or, mainly, fall on the ground or be sucked in by the air filter. The mentioned low deposition efficiency is due to the high refractoriness of YSZ and to the requirement to obtain a very porous coating, with increased thermal strain tolerance and insulation. At the present time, a very common procedure is to collect this relevant amount of overspray from the booth filter or the ground floor and then send it to waste disposal. It is well known that, at the European level, waste disposal is the less virtuous of the possible solutions to deal with an industrial waste, while the recycling route is strongly suggested. This waste material may be a useful alternative to zircon, which is traditionally used in the production of ceramic frits.

For this reason, the present research investigates the recycling of YSZ overspray, produced in the TBCs manufacturing process by APS, as a secondary raw material for the replacement of zircon in frits and glazes formulation in the ceramic tiles manufacturing process.

Three frits with a replacement of 100%, 1% and 0.2% of zirconium silicate with overspray YSZ into an industrial frit named "FSA" were prepared. The choice of these concentrations is due mainly to two reasons: the replacement of 100% of zircon with YSZ has been made to study the influence of the latter on the properties of the glaze; the other low percentages have been studied, because the amount of overspray YSZ produced by a SME involved in the thermal spraying of industrial gas turbines components cannot satisfy the year amount of ZrO_2 required by a large Italian ceramic tiles industry for a complete replacement of zircon. Subsequently each frit was used to prepare glazes for single fired tiles. A thorough characterization of zirconia overspray, frits and glazes has been performed by using different analytical techniques. Finally, a glaze containing an industrial frit available on the market was also prepared, in order to compare the properties of the new products with the commercial one.

2. Materials and methods

2.1. Frits preparation

The industrial frit, Table 1a, (labelled FSA) was provided by Colorobbia Italia S.p.A., Fiorano Modenese, Italy, mixing industrial grade quartz, alumina, calcite, soda and zircon as raw materials. The studied frits were prepared replacing 100 wt% (labelled A), 1 wt% (labelled B) and 0.2 wt% (labelled C) of zircon with overspray YSZ, collected after the APS deposition process on gas turbines Ni-superalloy components in the industrial plants of Turbocoating S.p.A. (V. Mistrali 7, 43040 Rubbiano di Solignano, Parma). In the APS spraying booth, the only deposited coating material is YSZ, but different commercial YSZ powders are employed according to components to be coated. Therefore, the overspray employed in this research must be considered a mixing of three commercial feedstocks, whose main constituent is ZrO_2–7 wt% Y_2O_3 (nominally, >98%). It is important to highlight that spraying companies focused on TBCs manufacturing deposit MCrAlY bond coatings by Low Pressure Plasma Spraying (LPPS) or High Velocity Oxygen Fuel (HVOF) spraying in spraying booths completely separated from the ones where YSZ ceramic top coatings are manufactured by APS, preventing in this way all possible contaminations caused by the use of different powder feedstocks in the same booth. Subsequently, the batches were loaded into a mullite crucible and the melting process was carried out in an electrically-heated furnace (Lenton, mod. EHF 17/17), applying the following heating cycle: from room temperature to 1000 °C at a heating rate of 10 °C/min, with a soaking time of 1 h at 1000 °C to allow the decomposition of the carbonates, and from 1000 °C to 1500 °C at a rate of 10 °C/min, using 1 h of soaking time at 1500 °C. The melt was then quenched in water to obtain the frits.

Table 1
Chemical analysis of FSA frit (a) and overspray zirconia (b).

Oxides	Wt%
(a)	
Na_2O	6
CaO	25
Al_2O_3	12
ZrO_2	12
SiO_2	45
(b)	
Al_2O_3	1.01
MgO	0.03
Na_2O	0.52
K_2O	0.009
TiO_2	0.06
SO_3	0.09
ZrO_2	82.08
MnO	0.02
HfO_2	2.88
Y_2O_3	8.32
Cr_2O_3	0.96
NiO	2.39
Co_3O_4	0.58
Nb_2O_5	0.11
others	0.94

2.2. Glazes preparation

All frits (150 g) were poured into an alumina jar with 5% of kaolin, 40% of nepheline (60%SiO_2, 23%Al_2O_3, 10.4% Na_2O, others to 100%), 45% of frit and 150 g of water with alumina balls having different diameters for milling. The kaolin was added to improve the rheological behaviour of the slurry, while nepheline to decrease the melting point of glaze. This is a common procedure in ceramic tiles manufacturing to test new experimental frits. Milling was performed for about 15 min. After milling, the prepared glaze slips were wet sieved, taking, as usual for glaze applications, the fraction passing through a 45 μm sieve. Glazes were applied (35 g) onto a green