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Preparation of innovative metallic composite glazes for porcelainized stoneware tiles

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Abstract

Innovative metallic glazes for porcelain stoneware tiles, containing stainless steel and a special Ni-based alloy (NiCoCrAlY, commonly used as bond coating material in thermal barrier coating systems on Turbogas superalloy components), have been studied. These new products, called "metallic composite glazes" (MCGs), showed different aesthetic properties than usual lustres or metallic glazes. After heating, the surfaces of these innovative glazes did not display any interesting behaviour, but, after polishing, a particular metallic aesthetic effect has been found. These new glazes can be described as composite materials made of a glass matrix reinforced with metal particulates. A deep characterisation of metallic powders and MCGs was performed by using several techniques. The glazes containing the NiCoCrAlY powders manifested the best aesthetic, microstructural, thermal and chemical properties.

Keywords: A. Solid state reaction; B. Composites; C. Chemical properties; D. Traditional ceramics

1. Introduction

Metallic glazes are a new particular type of ceramic decoration able to provide surface aesthetic properties (metallic shine) as *lustres* usually do. Lustres are the ancestor of these new materials: they were manufactured using metals as copper, iron, tungsten, silver and sometimes gold, added to the composition of the frits. In literature works, they have been defined as thin, nanostructured surfaces used as decoration for ceramic glazes [1]. Lustres have been studied for a long time as they come from the ancient Arabic pottery: the ancient procedure to create lustres involved adding the metals in the form of salts or oxides, on the surfaces of the glaze, and consolidating them using a sort of "third firing" process with a reducing atmosphere [2]. In order to create a reducing atmosphere, some studies related to lustres suggested the use of carbon black as part of the glaze as reducing element [3]. In some other reported researches, the formation process of lustres consisted of ion-exchange of alkalis (Na and K) by Cu and Ag, diffusion of the metal ions into the glaze and reduction of the metal ions to metallic nanoparticles [4]. Nowadays, the procedure to create lustres is adding metals as raw material into the frit composition in order to seal them into the glass matrix. Frits are then melted at high temperature and quickly cooled. This process causes a thermal shock to the glass, which consequently breaks up into little particles. At the end of the procedure, a frit is therefore obtained, which contains embedded metals or metal oxide particles that provide particular optical and decorative properties [5].

In some cases, the frit is then added to a mixture of other raw materials, taking part to the composition of the glaze. Unlike *lustres*, metallic glazes follow a different preparation procedure and they usually show the optical and aesthetic characteristics of the added metals. Specifically, metal powders are added to the glaze composition and not to the frit composition any more.

The present manuscript reports the production and characterisation of new metallic glazes, where the selected metal powders added to the glaze composition are stainless steel and a Ni-based superalloy belonging to the NiCoCrAlY alloys family. The main aim of the work is to design and create a new

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material for ceramic decoration using new types of metallic powders, selecting the most suitable kind of metals able to be added into new materials for ceramic decoration (metallic glazes). The stainless steel powders are already employed in the industry for the production of metallic composite glazes, while NiCoCrAlY powders, which have never been previously used, could provide better resistance against corrosion and degradation during high temperature firing (> 1200 °C).

The characterisation has been carried out on the metallic powders and on the final glazes. The characterisation was performed by using X-Ray fluorescence (XRF), Differential Thermal Analysis (DTA) and thermogravimetry, laser size distribution analysis, X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersion Spectroscopy (EDS). The chemical properties of the glaze surface were also tested.

2. Experimental procedure

The metallic powders used in this research were steel powders (AISI316L, Cogne Acciai Speciali S.p.A., Italy) and NiCoCrAlY powders, which are commonly used as raw material in the deposition process of thermal barrier coating systems as bond coating material (Turbocoating S.p.A., Italy) [6,7]. The chemical composition of the NiCoCrAlY metallic powders was investigated by X-Ray Fluorescence (XRF: Advant'X, ThermoFisher Scientific, Waltham, MA, USA). The thermal behaviour was studied by Differential Thermal Analysis (DTA) and Thermo-gravimetric (TG) Analysis (STA429, Netzsch, Selb, Germany). The mineralogical characterisation of powders was performed by X-ray Diffraction (XRD: PANAlytical, PW 3710 diffractometer) and surface microstructure was investigated by Scanning Electron Microscopy (SEM: Philips XL 40) with Energy Dispersion Spectroscopy (INCA: Oxford Instrument Analytical, High Wycombe, UK). Their particle size distribution was assessed by laser diffraction technique (Mastersizer 2000, Malvern Instruments, Malvern, UK) using the wet dispersion method (Hydro-S wet dispersion unit). The glazes were prepared at the laboratory scale simulating the industrial tile manufacturing process. The first step consisted in mixing and wet grinding the raw materials (Tables 1 and 2) in porcelain jars with dense alumina grinding media for 20 min in a planetary mill. The glazes were applied onto black-pigmented-engobed green single-fired wall tiles ($300 \times 300 \times 5$ mm^3) using a silk-screen printing technique. The thickness of the final layer glaze was about 25 μm. The engobe was applied on the green tile by disc application [8,9]. After glazing, the resulting tiles were dried at 120 °C for 2 h and fired in an industrial gas kiln in an oxidising atmosphere (10 vol% of oxygen) at the maximum temperature of 1200 °C, in a cold to cold cycle of 45 min. Subsequently, the glazed tiles were polished starting from a 400 mesh SiC abrasive paper and finished with 1800 mesh one. The glazes containing steel powders and NiCoCrAlY powders were labelled as T1 and T2, respectively. The characterisation of the glazes was performed using multiple techniques. X-ray diffraction (XRD, PANAlytical, X'Pert PRO diffractometer, using Cu-Kα radiation and an X'Celerator detector on the diffracted beam path) was performed on glaze specimens to detect and identify the crystalline phases formed during the heat treatments. Patterns were collected in the 10–80° 2θ range with step size of 0.02° and 3 s time/step, which are the same experimental parameters used for the XRD analysis of the powders. A scanning electron microscope (SEM, FEI XL-30) was used to observe the microstructure of the polished surfaces and cross-sections of the glazed tiles. A qualitative chemical analysis was obtained by means of an energy dispersive X-ray spectrometer coupled to the SEM. The chemical durability in HCl was tested according to the ISO 10545-13:1995 standard related to glazed tiles. The tile is hold in such a manner that image of a lamp is reflected on the untreated surface. The angle of incidence of the light upon the surface shall be approximately 45° and the distance between the tile and the light source shall be (350 ± 100) mm. The criterion of judgement shall be the sharpness of the reflection and not the brightness of the surface. The tile must be positioned so that the image falls simultaneously on both treated and untreated parts and determine whether it is any less clear on the treated part. The visual inspection allows ranking the glazes in different classes: class A corresponds to no visible effect, class B to definite change in appearance, and class C to partial or complete loss of the original surface. Finally, the aesthetic properties of the coatings was examined measuring the colour Hunter parameters, L* a*, b* (X-Rite, ColorEye XTH), before and after the chemical durability test. The total colour difference and ΔE* was also be calculated. The ΔE* is a single value which takes into account the differences between L*, a*, and b* of the tested sample and the standard, i.e. the sample before the chemical durability test. The more the measured value of ΔE* between the tested sample and the “standard” reference exceeds the numerical range 0.5–1, the more the aesthetic properties of the untested sample can be altered by a chemical attack, losing the initial aesthetic characteristics [10].

Table 1
Raw materials composition used to prepare metallic glaze composite.

Metallic composite	Glaze composition (wt%)
Metallic powders	45.7
Copper alloy	2.4
Transparent Glaze	48.0
Bentonite	3.9

Table 2
Transparent glaze composition used to prepare metallic glaze composite.

Transparent glaze	wt%
Glass-ceramic frit	31.8
Transparent frit	16.0
Caolin	4.4
Dolomite	2.5
Corundum	5.3
Nepheline	40.0