Laser treatment of nanoparticulated metal thin films for ceramic tile decoration

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Copper metallization, e-beam evaporation, oblique angle deposition, GLAD, Ceramic tiles, Laser irradiation, surface plasmon resonance, laser melting.

Abstract

This paper presents a new production method of metal-like decorative layers on glazed ceramic tiles. It consists of the laser treatment of copper thin films prepared by electron beam evaporation at glancing angles. A thin film of discontinuous copper nanoparticles was electron beam evaporated in an oblique angle configuration onto ceramic tiles and an ample palette of colors obtained by their laser treatment both in air and in vacuum. Scanning electron microscopy (SEM and FESEM) along with UV-vis-NIR spectroscopy and time of flight secondary ion mass spectrometry (TOF-SIMS) analysis were used to characterize the differently colored layers. Based on these analyses, color development has been accounted for by a simple model considering surface melting phenomena and different microstructural and chemical transformations of the outmost surface layers of samples.

Introduction

Materials processing by means of lasers has experienced a considerable burst during the last years thanks to the incorporation of both new laser tools (e.g., femtosecond lasers) and the development of hybrid technologies, where the action of laser beams is complemented with the incorporation of additional processes^{1, 2, 3}. The synergies achieved with these combinations have given rise to highly innovative procedures that are being progressively incorporated in the industry^{4, 5}. Unlike conventional annealing (e.g., using furnaces) where thermodynamic equilibrium phases are always obtained, clear advantages of laser mediated procedures stem from their temporal and spatial selectivity and the possibility of kinetically controlling the formation of metastable states⁶. As a consequence, the use of lasers to treat ceramic compounds has been increasing during the last years with outstanding examples aiming at the fabrication of ceramic powders⁷, machining of structural ceramics^{8, 9} or the improvement of mechanical properties¹⁰. More recent applications such as laser cladding of glass-ceramic sealants¹¹, the synthesis of glass microspheres with piezo electric properties or the synthesis of transparent ceramics^{12, 13} can be also highlighted.

Colored ceramics are important in the ceramic tile industry for the production of decorative products of high commercial demand. Color changes in metal-decorated ceramic tiles have been attributed to solid state reactions leading to chemical changes in the metal phase¹⁴ and to the generation of surface plasmon resonance effects¹⁵ associated to the reshaping of metal nanoparticles. In this work, we present a new methodology combining the evaporation of metals onto ceramic surfaces and their posterior treatment with a near IR laser to induce a new color state. The reported approach has not been previously used, either in industry or in research laboratories, because near IR laser processing of continuous metal thin films is hampered by light reflection at their mirror-like surfaces. To circumvent this impediment, in the present work we apply the oblique angle deposition (OAD) geometry for the preparation of the thin films^{16, 17, 18}. By this method, the metal flux arrives at an oblique angle with respect to the substrate surface, a geometrical arrangement leading to the formation of low reflective films formed by independent nanoparticles^{19, 20}. Besides describing the

principles of the method, we show that white ceramic tiles can be transformed into differently colored surfaces by adjusting the laser pulse width and scanning conditions and by controlling the environment (vacuum, air) during the irradiation. The possibilities offered by this method for color control and its advantages to decrease the environmental negative effects of conventional ceramic processing are discussed.

Experimental

Deposition of metallic copper was carried out by vacuum (i.e., 10^{-6} Torr) evaporation of pellets of metallic copper (Goodfellow) in an electron beam evaporator setup where the substrates were situated at 50 cm from the sublimation source. Depositions were carried out onto commercial tile substrates with a glaze composition based on ZrSiO_4 that were provided by TORRECID Group, S. L. The substrates were kept at room temperature with the perpendicular to their surface forming a zenithal angle of 80° with respect to the evaporation source of copper. Due to the shadowing effects that control the deposition process, the use of this oblique angle deposition (OAD) configuration leads to the formation of not-associated nanoparticle films^{16, 21}. In the course of the present investigation, it was realised that only samples with low reflectivity prepared at the highest deposition angles (i.e., 80° , 85°) were suitable for laser processing. The amount of deposited copper was controlled with a quartz crystal monitor (QCM) situated at normal geometry with respect to the evaporation source. Copper was deposited at a rate of $1 \text{ \AA s}^{-1}$ up to a nominal copper thickness of 30 nm, as determined with the QCM.

The copper-covered ceramic tiles were laser treated at wavelengths within the near IR (1064 nm) with a diode pumped solid-state nanosecond Nd:YVO₄ laser (Powerline E20, Rofin) for high vacuum conditions, another diode pumped solid-state nanosecond Nd:YAG laser (Powerline E20, Rofin) and a diode pumped Yb:YAG fiber laser device emitting at 1050 nm (Easy Mark 20, Jeanologia). The two last ones were employed for treatments in air. Despite the slight differences in the wavelengths of the laser beam, no significant differences were found when using either of these three laser sources. The laser head were fitted into a galvanometer beam steering system and coupled to a flat-field lens of 160 mm focal distance, giving a spot size of ca. 30 microns. A matrix of different laser parameters was configured by software in order to obtain sample areas

(30x4 mm) irradiated with different laser conditions. Lasers were operated in the pulsed mode, with repetition rates ranging from 20 to 500 kHz, output power values from 0.1 to 20 W and pulse widths from 50 to 220 ns. These conditions resulted in irradiance values comprised between 0.5 and 100 MW/cm². Scanning parameters were also employed with rates from 500 to 3000 mm/s yielding different overlapping values. This variation in overlapping showed no significant effects except for slow variations in the intensity of the colors obtained. After the optimization of the process in air, treatments were also performed in a high vacuum chamber (5 10⁻⁷ mbar), to study the effect of the external atmosphere on the laser induced solid state reactions leading to color changes.

UV-Vis-NIR Spectra, recorded in reflexion mode in the 200 to 1500 nm range, were taken with a Pelkin-Elmer Lambda 750 S spectrometer and used to characterize the optical behavior of ceramic tile samples covered by the Cu nanoparticle films before and after laser irradiation. For this analysis, the samples were placed in the front window of the integration sphere of the spectrometer. Reference samples, deposited on quartz substrates, were examined in transmission mode.

The sizes and shapes of copper particles evaporated either on the silicon wafer or on the ceramic support were examined by field emission scanning electron microscopy (FESEM) in a Hitachi S4800 microscope.

Depth profiles of the differently treated tile samples were obtained in a Time Of Flight Secondary Ions Mass Spectrometer (TOF-SIMS) using an instrument from Ion-ToF GmbH, Germany. The samples were bombarded with a pulsed bismuth ion beam. The generated secondary ions were extracted with a 10 kV voltage and their time of flight, from sample to detector, measured with a reflection mass spectrometer. Typical analysis conditions were 25 keV pulsed Bi⁺ ion beam energy, a 45° incidence and a rastering area of 500x500 mm². An electron flood gun for charge compensation was used during the measurements. The peak intensities were normalized to the total ion intensity.

Structural characterization of the treated tiles was carried out by X-ray diffraction (XRD) in a Siemens D5000 diffractometer working in the Bragg-Brentano configuration.

X-ray photoelectron spectra were recorded in the pass energy mode (PE=35 eV) in a Phoibos 100 DLD (SPECS) and Mg K α line as excitation source. The energy scale of the spectra was referred to the C1s line at 284.5 eV for the adventitious carbon contaminating the surface of the samples.

Results and discussion

Characterization of the copper nanoparticle films

To characterize the copper nanoparticles, reference samples were prepared on flat Si (100) wafers and quartz plates under similar evaporation conditions than on the tile substrates. The UV-vis-NIR transmission spectrum reported in Figure 1 for the “as deposited” films depicts a rather constant 55% transmission background and a broad absorption feature at low wavelengths. This spectrum is typical of absorption of an inhomogeneous and discontinuous distribution of copper nanoparticles¹⁵ and gives rise to a greenish color. This is effectively confirmed by the observation of the morphology of this layer, characterized by copper grains of different sizes (average size ca. 50 nm) close to percolation (Figure 1 inset). A similar morphology has been reported for nanoparticle films of silver prepared by OAD¹⁹.

[figure 1 here]

IR-Laser treatment of metal films

In general, laser energy absorbed by a substrate transforms into heat within a nanosecond spam time, while direct melting occurs more rapidly, typically for pulse widths over 10 ps. This means that copper modified tile substrates irradiated with near-IR laser with hundreds nanosecond long pulses will experience an intense raise in surface temperature leading likely to the melting of copper. This and other surface processes will take place provided that the metal film does not reflect light due to a mirror-like behavior²². Effectively, in previous works we found that, depending on incident angle of the laser incidence and surface morphology, infrared laser light reflection by metallic mirror-like films varies from 97 to 100 %²³, meaning that only a minute part of the incident light can be absorbed and transformed into local heat under such conditions. In agreement with this, no color changes were observed during the present investigation when using continuous copper films that, even if deposited at relatively low angles (0°, 60° and 70°), were characterized by a high reflection and reddish mirror-like aspect (data not shown). Unlike this behavior, laser coloring effects could be induced on the tile samples when copper was deposited at 80-90° evaporation angles. Similarly to the reference sample in Figure 1, the copper layers on the tile substrates prepared at 80° presented a microstructure formed by separated nanoparticles which rendered a greenish color. The new colors obtained by treatment of the ceramic tiles are summarized in Table 1, where optimized laser parameters and irradiation

conditions are also included. Si/Cu XPS atomic ratios have been also reported in this table to account for the uppermost layer compositions. These ratios suggest a certain agglomeration of copper and/or its partial coverage by melted material of the substrate, this latter due to the detection of Si and Zr in the analysis. In all these experiments, we conclude from the study of the binding energies and spectral shapes that silicon appears as Si⁴⁺ fully oxidized species, while copper oxidation state was either Cu²⁺, Cu⁺ or Cu⁰ depending on the sample (we will come back to this point below)²⁴. These compositional and morphological changes are attributed to heat induced processes affecting both the metal film and the substrate and, as discussed later, include mechanisms such as dewetting, melting, diffusion, agglomeration and, under certain conditions, ablation.

Table 1. Summary of colors and XPS Si/Cu ratios obtained as a function of laser conditions and substrates.

Condition	Substrate	Environmental conditions	Frequency (kHz)	Fluence (J/cm ⁻²)	Pulse Width (ns)	Irradiance (MW/cm ⁻²)	Color	Si/Cu ratio
M1	Ceramic	Air	100	15	200	75	Green	2.1
M2	Ceramic	Air	150	30	80	300	Yellow	0
M3	Ceramic	Vacuum	50	13.92	220	63	Cyan	2.6
M4	Ceramic	Vacuum	150	4.53	220	21	Brownish/Reddish	1.0

Coloring by laser treatment in air

A summary of some basic characteristics of samples M1-M2 is reported in Figures 2 and 3. According to Figure 2, the UV-vis-NIR spectrum of sample M1 obtained at lower irradiances (Table 1) was characterized by a high reflectance in the NIR region and a narrow absorption band at 595 nm. This feature can be attributed to an absorption

band due to surface plasmon resonances (SPR) of Cu⁰ nanoparticles²⁵ likely covered by an oxide outer layer¹⁵. This absorption behavior gives rise to a dark green color. In agreement with this assessment, SEM micrograph of this sample reveals Cu nanoparticles with a high dispersion of sizes and a bimodal distribution of well-defined 100-200 nm big particles together with much smaller nanoparticles of less than 50 nm (Figure 2 b) down-left). In addition, the TOF-SIMS analysis of this sample shows that these copper nanoparticles must be distributed beneath the surface, being covered by material of the substrate (a rough estimate of the thickness of this layer yields a value of approximately 200 nm). This assumption agrees with the TOF-SIMS observation that the initial part of the Si and Zr depth profiles are characterized by narrow rising peaks at the upmost layers of the samples and a sharp decrease followed by a smooth increasing variation until reaching the bulk state of the glaze. Meanwhile, the Cu signal decreases smoothly along the whole layer thickness examined during the profile analysis. This in-depth distribution agrees with the presence of Si at the surface, with a Si/Cu XPS ratio of 2.1 for this sample (c.f. Table 1). XPS also provided information about the chemical state of copper. The Cu2p photoemission and Cu LMM Auger spectra of sample M1 (c.f. Figure 3) reveals the presence of Cu⁰, Cu⁺ and Cu²⁺ species at the surface. These species are characterized by Auger parameter values of 1851.43, 1849.42 and 1850.36 eV, respectively²⁴ (for a more detailed discussion of the Auger parameter concept and its calculation see reference²⁴ and the supporting information S1). The spectral shape and the resulting attribution of species would agree with the existence of partially oxidized copper nanoparticles at the surface of the glaze²⁶.

[figure 2 here]

The UV-vis-NIR spectrum of sample M2 in Figure 2 a) is characterized by a high and constant visible and NIR reflectance edging at around 705 nm (1.75 eV). We attribute this spectrum and the resulting yellow color of this sample to the convolution of the absorption of copper oxide (I) Cu₂O (with a band gap at 2.17 eV) and copper oxide (II) CuO (band gap at 1.7 eV)¹⁴. The TOF-SIMS in-depth distributions of Cu, Si, and Zr elements in sample M2 reported in Figure 2c) is characterized by a relatively narrow distribution of Cu at the surface, followed by a rather constant in-depth distribution of Si and Zr species. These profiles agree with an atop and homogeneous distribution of

copper at the surface of the ceramic tile similar to that encountered in the evaporated sample. This view is also confirmed by the SEM micrograph of sample M2 in Figure 2 b) down-right), and its XPS analysis showing no hints of Si2p or Zr2p peaks (Table 1 and Figure 3). XPS also showed that copper is in the form of Cu_2O^{24} , as evidenced by the shape of the Cu2p and Cu LMM spectra in Figure 3 and the corresponding value of the Auger parameter (1849.37 eV, see supporting information S1). In agreement with this attribution, the XRD of this sample reveals the appearance of some small peaks due to Cu_2O superimposed on the typical diagram of ZrSiO_4 (see supporting information S2)

[figure 3 here]

The generation of the different surface topographies, chemical composition and final color of samples M1 and M2 can be accounted for by in the following terms. Light penetration depth in copper, taken as the inverse of the absorption coefficient with a value of $8,35 \cdot 10^6 \text{ cm}^{-1}$ at 1064 nm^{23} , can be estimated in 12 nm in the initial copper layer deposited by evaporation at oblique angles. This value is much smaller than the average thickness of 30 nm of this Cu layer, which implies its complete melting if enough energy is provided during irradiation. Since melting of laser irradiated copper already occurs at fluences over 11.3 J/cm^2 ²², the much higher values of this parameter used to manufacture samples M1 and M2 (c.f. Table 1) should suffice not only to partially melt the copper but also to soften and mobilize the substrate. In agreement with previous results on glass^{27, 28, 29}, we assume that a spinodal dewetting and agglomeration of the copper layer yields the big copper particles found in sample M1 and their partial embedment under a thin layer of the substrate material slightly soften during the irradiation process. This situation is schematically depicted in Figure 4. Meanwhile, the higher irradiance values utilized to synthesize sample M2 must produce a considerable increase in temperature of the upper sample layers and the effective melting of both metal and substrate. The exposure of the melted layer of copper to air would then produce its effective oxidation and recrystallization leading to the formation of an oxidized copper oxide layer on the ceramic substrate. The scheme in Figure 4 represents the final state of sample M2, where the high intensity laser irradiation in air must produce the dewetting and oxidation of copper and the formation of a homogeneous oxide layer covering the surface.

[figure 4 here]

Coloring by laser treatment in vacuum

Laser treatments under vacuum were carried to study the influence of the environment on coloration. Samples M3 and M4 were obtained upon laser irradiation in vacuum under the conditions reported in Table 1). Due to the easy formation of plasma plumes of ablated material under vacuum^{30, 31} and in order to keep the ablation process to a manageable limit laser irradiances were much smaller in the experiments under vacuum than in air., In fact, plasma plumes were easily observed with the naked eyes (conveniently protected with UV filters) during vacuum treatment, while they were not observed during treatment in air. For example, the lower irradiance used for sample M3 (63 MW/cm²) was already enough to produce a minimum but observable intensity for the plasma plume. This sample (Figure 5 a) had a cyan color resulting from a highly reflective surface and a well-defined absorption band at 618 nm, that can be attributed to a SPR of copper nanoparticles covered by a thin oxide shell¹⁵. An intense plume of ablated particles was observed during this laser treatment under vacuum, suggesting some removal of copper and the topmost surface layers of the tile substrates. The ablated material may be ejected and spread out from the laser impingement point and be re-deposited on areas previously treated since the surface is scanned during the laser treatment^{4, 5}. An effective surface ablation was indeed supported by the SEM observation of a homogeneous and flat surface with bright spots attributed to small copper nanoparticles buried beneath the surface (Figure 5 b-left). TOF-SIMS analysis confirmed that copper, though still enriched at the topmost surface layers, is distributed in a thicker zone within this sample, (e.g., Si appears in great amount at the surface yielding a Si/Cu XPS ratio of 2.6 in this case). We attribute this distribution to the effect of the mechanical shock waves that, produced during irradiation, are well-known for inducing the effective diffusion of metal species inside glaze matrixes³². The XPS analysis of the surface of this sample confirmed that most of the copper is in the form of Cu⁺ species (Auger parameter 1847.11 eV, see supporting information S1), with a minor amount of Cu²⁺ (Auger peak at 339 eV), a feature that we attribute to the effective oxidation of the metal by reaction with species of the ceramic glaze. According to the scheme in Figure 4, the higher irradiance used with sample M3 seems to be very effective not only to induce the ablation and redeposition of surface species,

but also to induce some agglomeration of copper and its effective diffusion to the interior of the film in the form of medium size metal particles.

Sample M4, obtained at high laser irradiances, was characterized by a constant absorption (50-55% reflectance) extending through the vis and NIR spectral regions, and a small absorption band around 700 nm that rendered a brownish-reddish color. Direct observation of this sample with an optical microscope showed the formation of grain outcrops on its surface that, enriched in copper, could be responsible for the observed color (see sporting information S3). This agrees with previous results reporting a similar aspect for an inhomogeneous distribution of copper nanoparticles surrounded by a copper oxide shell¹⁵. The SEM image presented in Figure 5 b-right showing big features of around 100 - 300 nm agrees with the dewetting of the Cu layer and a certain melting of the surface. The TOF-SIMS of this sample (Figure 5 c) shows a continuously decreasing Cu profile extending up to ca. 80 seconds of sputtering time, a fact that agrees with the formation of big copper agglomerates at the surface. Simultaneously, the Si⁺ and Zr⁺ profiles increase along this depth profile zone. The XPS analysis of this sample (Table 1) yields a Si/Cu ratio of 1.0, suggesting that either these copper agglomerates leave free a large area of the substrate or they are partially mixed with it. On the other hand, Cu⁺ is the majority oxidation state of the copper at the surface of these agglomerates as deduced from the Cu2p and Cu LMM spectra and the value of 1849.64 eV determined for the Auger parameter (see Figure 3). The presence of a small contribution of Cu²⁺ evidenced by a shoulder at 339 eV in the Auger peak must be also noticed. Although at first sight surface oxidation of copper nanoparticles seems contradictory with the vacuum conditions of the experiment, it can be accounted for by the interaction of copper with the excited oxygen species from the substrate that would be incorporated in the plasma plume upon irradiation³¹. Therefore, the microstructure of sample M4 schematically reported in Figure 4 would result from the interaction of copper with an expanded plasma plume of ablated species of the substrate, ending up in copper oxide agglomerates partially mixed or covered by the substrate material.

[figure 5 here]

Conclusions

In this work we have developed a new method of coloring commercial ceramic tiles consisting of the oblique angle vacuum deposition of particulate layers of copper and their near-IR laser treatment under different conditions. It is found that adjusting the laser irradiance and the environment around the samples (i.e. air or vacuum) provides an effective control over the heating, melting and/or ablation processes that, occurring at the upper surface layers of samples, induces the diffusion melting/solidification and oxidation of the metal and tile substrate materials leading to the appearance of specific colors. Thus, the obtained green, yellow, and brownish/reddish colors have been attributed to, respectively the formation of a $\text{Cu}_2\text{O}/\text{CuO}$ surface layer, agglomerates of non-stoichiometric copper oxide and copper nanoparticles depicting plasmon activity. The use of state of the art near-IR laser technology in combination with the developed oblique angle deposition technique for the surface coloring of ceramic tiles present some advantages if compared with traditional methods. First of all it avoids third fire decoration treatments what means an important reduction in energy consumption, and secondly it reduces substantially the amount of material needed for traditional ceramic coloring applications (usually up to 500 microns). Moreover, an outstanding novelty of the process is its unique feature to generate different colors from the same original layer composition just varying laser parameters. This possibility is not achievable with traditional methods requiring a specific formulation of precursor layer for the generation of each color.

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Figure 1. a) UV-vis-NIR transmittance spectra of the reference sample deposited on quartz. The inset presents a SEM micrograph of the same reference sample deposited on silicon.
112x78mm (150 x 150 DPI)

Figure 2. a) UV-vis-NIR total reflectance spectra of the ceramic tile and samples M1 and M2. The insets show the color images of the treated tiles. b) SEM images of the as-deposited (top) and air laser treated (bottom) samples M1 (down-left) and M2 (down-right). c) TOF-SIMS analysis of the time-evolution of Si+, Cu+ and Zr+ signals in the as-deposited and M1 and M2 samples.
115x241mm (150 x 150 DPI)

Figure 3. a) XPS Cu_{2p} peaks of the different samples analyzed in this work and b) Cu LMM Auger peaks of the same samples. The red dot-slash lines are included to guide the eyes indicating the position of features associated to each chemical species.

244x170mm (150 x 150 DPI)

Figure 4. Schemes describing the microstructure of samples obtained upon laser irradiation of copper coated tiles. Samples "as deposited" (a), M1 (b), M2 (c), M3 (d) and M4 (e). The green color represents the copper oxide, the red one the metallic copper, the blue color represents the ceramic glaze.
93x147mm (150 x 150 DPI)

Figure 5. a) UV-vis-NIR total reflectance spectra of the ceramic tile and samples M3 and M4. The insets show the color images of the treated tiles. b) SEM images of the laser treated samples in vacuum M3 (left) and M4 (right). c) TOF-SIMS analysis of the time-evolution of Si⁺, Cu⁺ and Zr⁺ signals in samples M3 and M4.

129x235mm (150 x 150 DPI)