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PREPARATION AND STUDY OF RED-COLORED COPPER-CONTAINING CERAMIC GLAZE FIRED IN AN OXIDIZING ENVIRONMENT

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ABSTRACT

Red copper glazes, also known as Chinese red glazes, owe their coloration to the dispersion of colloid copper particles in the glaze and firing in a highly reducing atmosphere. The addition of some substances can be used for the reduction of copper oxide to metal nanoparticles and the glazed ceramics can be fired in an oxidation atmosphere. The colloidal copper red colouring of ceramic glazes was applied in this study. It was investigated the influence of copper oxide type (CuO or Cu_2O) added as colouring agent to a ceramic glaze and the firing temperature of the glazed for obtaining red colouring of the glaze. The samples were fired in an oxidizing atmosphere and SiC and SnO_2 were added as reductants. A structural and phase characterization of the obtained samples was done by using the XRD, DTA, FT-IR and SEM analyses. The reduction with silicon carbide when fired in an oxidizing atmosphere is more complete and the red glaze coloration is more intensive when copper is introduced as Cu_2O rather than CuO into the glaze. The best red coloration has been obtained for the composition containing 0.5 mass % Cu_2O + 1 mass % SiC added to the glaze and fired at 1200^{o}C.

Keywords: *red copper glaze, copper oxide, oxidizing atmosphere, reduction, colloid copper.*

INTRODUCTION

Depending on their nature, ceramic glazes are thin vitreous coatings that provide functional and decorative properties to products. The main charm of the modern ceramics is the colour and ceramicists of all times have been engaged in chemical research, trying to achieve the desired shades of glaze, to repeat in their works the beauty of the surrounding world. For thousands of years, the production of glazes for ceramic products has been continuously improved and diversified. A wide range of glaze colours can be obtained by small changes in the glaze composition, variation and quantity of colouring pigment, the valence of the colouring elements, firing conditions - temperature, duration and atmosphere etc. [1]. Colouring of ceramic glazes can be done with metal oxides, salts and pigments. Copper oxide has a good colouring effect in small quantities, and it is volatile at a temperature above 1050^{o}C. Cu_2O is preferred in glazes fired at a higher temperature and depending on the composition of the glaze it leads to the appearance of grass-green, blue-green, red or yellow colour. Simultaneously with the colouring, the copper oxide improves the gloss of the glaze [2 - 4]. Copper oxide was used to colour glazes in ancient Egypt, and later as the main colorant in Islamic ceramics. For the first time during ancient Egypt's 18th dynasty copper was used to colour the glass in red in 1500 BCE [5, 6]. Although the colloidal copper red technology comes from Egypt and the Middle East, it was used on Chinese porcelain very precise since the 8th-9th century and bright red coloured glazes are known as Chinese red. In Chinese glazes, copper is second in importance after iron as a colorant [7]. Many early Chinese glazes, coloured with copper, have been analysed and it was found they contain small amounts of tin oxide in addition to copper. The earliest known example of a successful firing of a copper red glaze is an object whose surface is decorated with both copper green and copper red [4].

The mechanism of copper colouring in copper-red glazes is not yet well studied. The red colour is due to the dispersion of colloidal particles of copper oxide in the glaze and firing in a highly reducing atmosphere. There is not enough research related to the preparation of copper-red glazes fired in oxidizing environments. Various studies have shown that SiC, CeO_2, SnO_2, graphite or ground charcoal can be used as a reducing agent for the reduction of metal oxide. When SiC is added into the glaze it is necessary to establish the temperature range and firing time to create a reducing environment in a copper red glaze. If the firing time is long, the SiC can be oxidized, and the glaze returns to green blue colour. Also, the quantity of SiC is important for the obtaining a good red glaze surface. If using a big amount of SiC or having an inappropriate firing temperature, glaze surface defects may occur. It due to the large amount of CO_2 produced which cannot be released from the glaze layers. [8]. The addition of tin oxide favourably affects the red coloration, and the addition of ferric oxide gives a violet coloration. Boron-alkali glazes are most suitable for copper red colouring. Copper-red glazes can also be obtained when a layer of copper oxide is applied directly to a ceramic mass, and on it a glaze rich in sodium oxide containing and a small amount of boron oxide. The content of MgO, Al_2O_3 and BaO should be low, and CaO - high. Firing must be carried out in a reducing atmosphere. A composition for a blood-red glaze was proposed by Lehnhauser based on a porcelain glaze with copper oxide and tin oxide and firing in a variable kiln atmosphere - alternating oxidizing and reducing environments [9]. SnO_2 is also studied as a reducing agent for stabilizing Cu nanoparticles in ceramic glazes or glasses [10 - 14]. Achieving a bright red uniform coating is quite a complex process due to the many conditions. Uneven colour often occurs. Also, the structure of the copper and its content in the glaze layer are considered to influence the colour of the glaze. Some authors assume that cuprite Cu_2O is the main colorant of the red copper glazes. They suppose, the native red colour of crystalline cuprite leads to the appearance of very opaque red glasses [15]. The red colour of Cu_2O is due to its semi-conducting properties and the optical gap of 2.1 eV [16]. The metallic Cu nanoparticles can be seen in many red colours as copper ruby red and opaque red instead of bright red colour of the cuprite. The red colour arises from light scattering (also known as "Mie scattering") by the metallic copper colloidal particles [17].

The aim of this paper is the obtaining and studying of red coloured copper-containing ceramic glazes fired in oxidizing environment.

EXPERIMENTAL

For the experimental studies, a ready-made glaze of the company Keramit OOD - GTR 07 was used, which is a high-quality transparent glaze created for a wide temperature range from 1020 to 1170°C. The glaze is aluminosilicate and lead-free. The glaze is characterized by a density of 1.55 kg m^{-3}. It can be used alone or as a base for coloured glazes. As red colouring oxides for the transparent glaze CuO and Cu_2O were used. SnO_2 and SiC were introduced in the glaze as reducing agents. The compositions of the obtained three series of glazes are presented in the Table 1. The starting components used are: transparent glaze GTR 07, CuO, Cu_2O, SnO_2, SiC. The quantity of transparent glaze in all compositions was 100 g. The first series of glazes (samples 0 - 2) contains CuO (0), 0.5 g CuO + 0.5 g SiC (1) and 0.5 g CuO + 1 g SiC (2). In the second series (samples 3 - 5), Cu_2O was added into the glazes, instead of CuO. In the third series (samples 6 - 8) of glazes, the two types of reducing agents - tin oxide and silicon carbide are included in

Table 1. Studied composition of the glaze samples.

Sample	Composition
0	100 g glaze + 0.5 g CuO
1	100 g glaze + 0.5 g CuO + 0.5 g SiC
2	100 g glaze + 0.5 g CuO + 1 g SiC
3	100 g glaze + 0.5 g Cu_2O
4	100 g glaze + 0.5 g Cu_2O + 0.5 g SiC
5	100 g glaze + 0.5 g Cu_2O + 1 g SiC
6	100 g glaze + 0.5 g CuO + 0.5 гр. SnO_2
7	100 g glaze + 0,5 g CuO + 0.5 g SnO_2 + 0.5 g SiC
8	100 g glaze + 0,5 g CuO + 0.5 g SnO2 + 1 g SiC

the glaze composition. After adding of colouring and reducing agents to the glaze, it was homogenized in a high-speed ball mill for 10 minutes. The coloured glazes were applied by dipping onto square pieces of raw non-fired pressed ceramic tiles. Glazed ceramic tiles were dried in a electric dryer at 100°C and then they were fired in an electric furnace at temperatures of 1150°C and 1200°C. A structural and phase characterization of the obtained glazed samples was done by using the XRD (Bruker D8 Advance apparatus and Cu K_{α} radiation with a Sol X detector), DTA (LINSEIS Messgeräte GmbH apparatus, speed 5°C min^{-1}), FT-IR (FT-IR spectrometer, model Varian 660 FT-IR spectrometer from Agilent Technology, with a range of 4000 - 400 cm^{-1}) and SEM (Carl Zeiss GmbH scanning electron microscope, model EVO 10, ZEISS brand) analyses.

RESULTS AND DISCUSSION

Fig. 1 shows the glazed tiles with glazes composition from 0 to 8 fired at a temperature of 1150°C with a holding time of 2 h at the maximum temperature. The figure shows that when there is not SiC in the glaze, the colour is green and in glazes with CuO and Cu_2O (compositions 0 and 3). When SnO_2 is added to a glaze with Cu_2O or CuO, decolouration of the glaze occurs (composition 6 - 8). When SiC is present in the composition, a red-violet coloration is observed in the glazes with Cu_2O. From the figure we observe that the reduction of silicon carbide is incomplete and small green dots are visible on the image on Fig. 1 (composition 5), indicating the presence of unreduced copper oxide.

Glazed tiles with compositions 4 and 5 containing Cu_2O and SiC fired at a higher temperature 1200°C show that when copper is added as Cu_2O and the firing temperature is higher, the reduction with silicon carbide when fired in an oxidizing atmosphere is more complete and the red colour of the glaze is more intensive (Fig. 2).

Fig. 3 shows the result from XRD analysis of the glaze with composition 5 fired at 1200°C in an

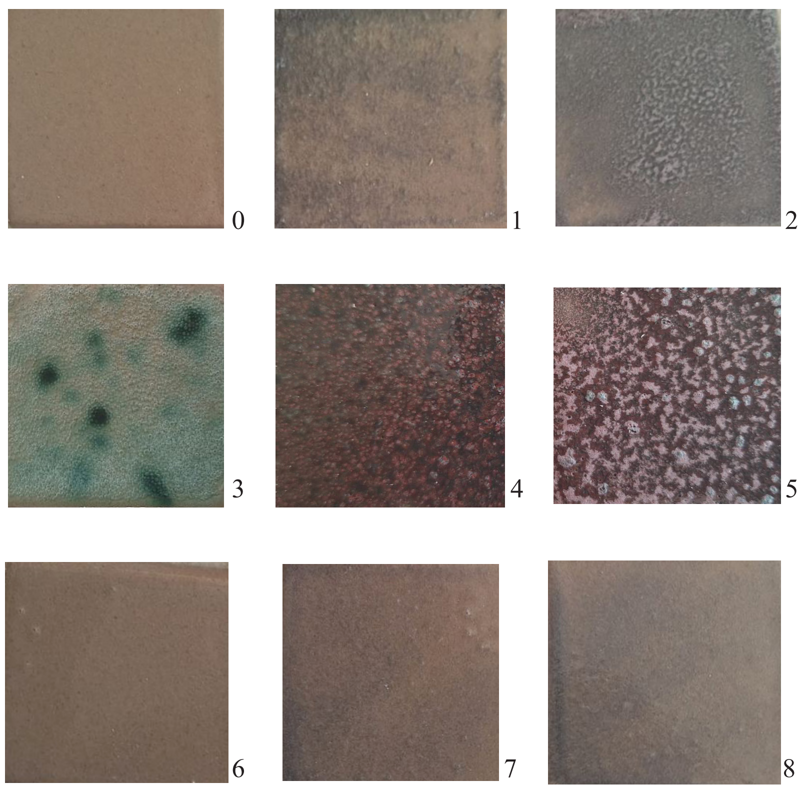
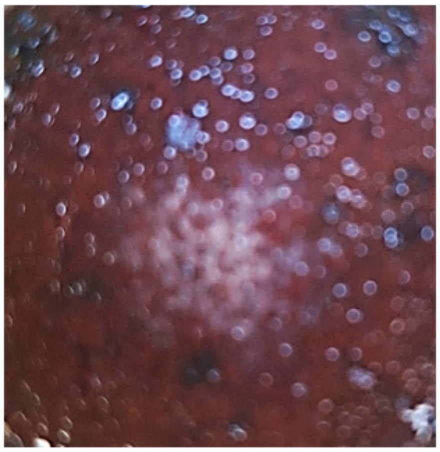


Fig. 1. Glazed ceramic tiles with compositions from 0 to 8 fired at a temperature of 1150°C with a hold of 2 h at the maximum temperature.



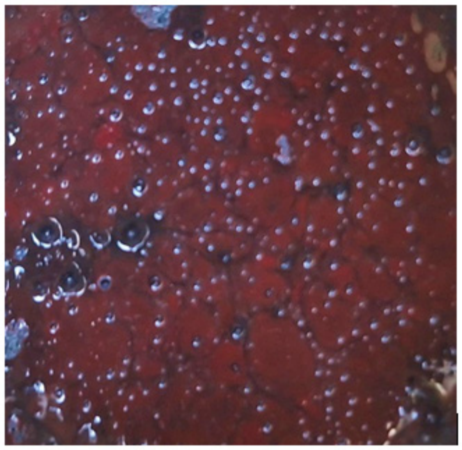


Fig. 2. Fired glazes with compositions 4 (left) and 5 (right) at a temperature of 1200°C in an oxidizing environment.

oxidizing environment, showing an amorphous halo and quartz contained in the sample. Most probably copper has dissolve in the glass because no peaks of copper or copper oxide are observed. This explains the red colour of glaze with composition 5 fired at 1200°C in an oxidizing environment.

The glass transition and crystallization temperatures of glaze with composition 5 were determined form DTA analysis and are presented in Fig. 4. Glass transition temperature Tg is 470°C and crystallization temperature Tc is 870°C.

The glaze with composition 5 was examined by FT-IR analysis also. The results are presented in Fig. 5.

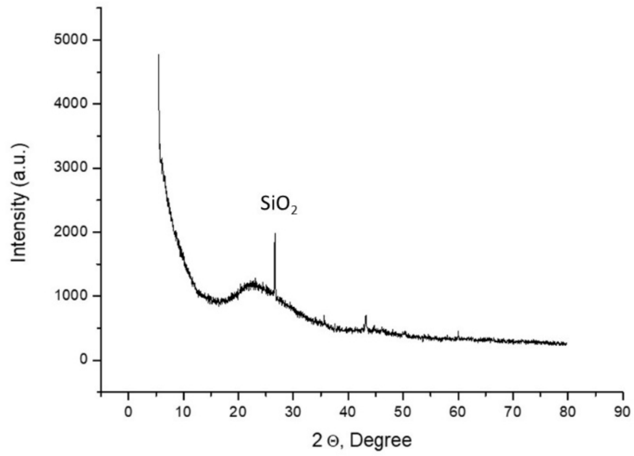


Fig. 3. X-ray diffraction of fired glaze with composition 5 (0.5 g Cu_2O + 1 g SiC) fired at 1200°C in an oxidizing environment.

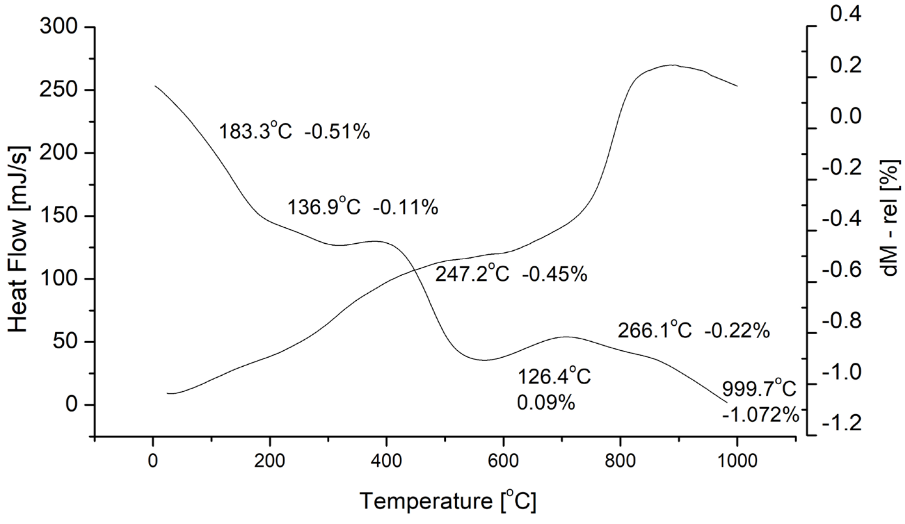


Fig. 4. DTA and TG curves of the glaze with composition 5.

The bands at 3418 cm^{-1} correspond to the stretching of the O-H group. The absorption band in the range 1050 - 1070 cm^{-1} is associated with the asymmetric vibrations of the Si-O bonds, and that at 453 cm^{-1} with the symmetric vibrations of the O-Si-O bonds. Vibrations are observed at the position at 791 cm^{-1}, which are probably Si-C bonds, which indicates that complete reduction has not occurred and unreacted SiC is detected in the sample. The band at 693 cm^{-1} in the spectrum corresponds to the Si-O bond.

Fig. 6 shows a SEM image of the boundary between the fired glaze and the fired ceramic body. The different morphology of the two materials is clearly visible. There are closed pores of different sizes in the glaze.

In addition to the microscopic images, EDX were performed at a point on the glaze surface (Fig. 7). EDX of the glaze with composition 5 confirms the presence of Cu in the glaze, as and the other elements of which the glaze is composed (Fig. 7).

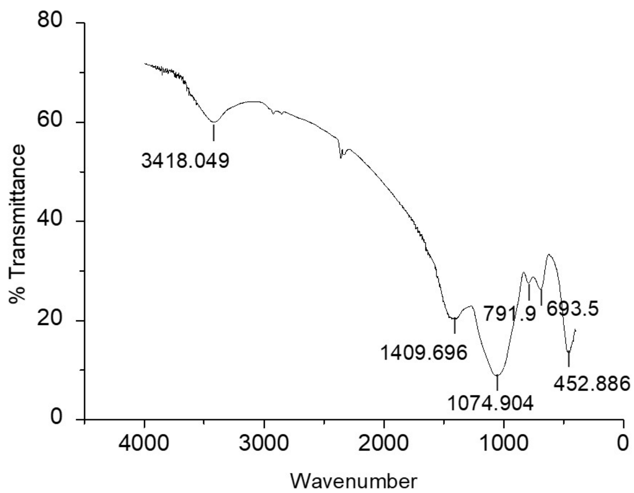


Fig. 5. FT-IR of fired glaze with composition 5.

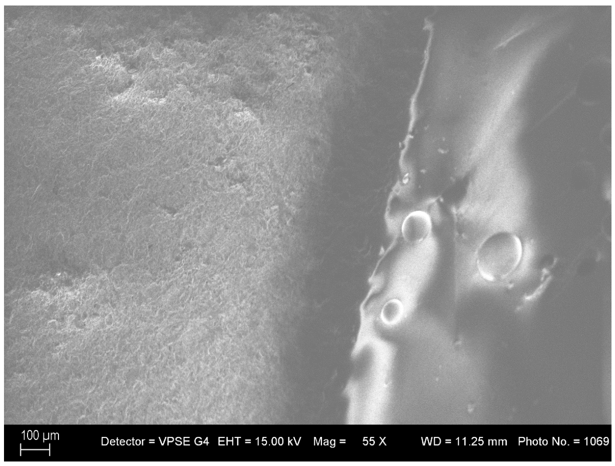
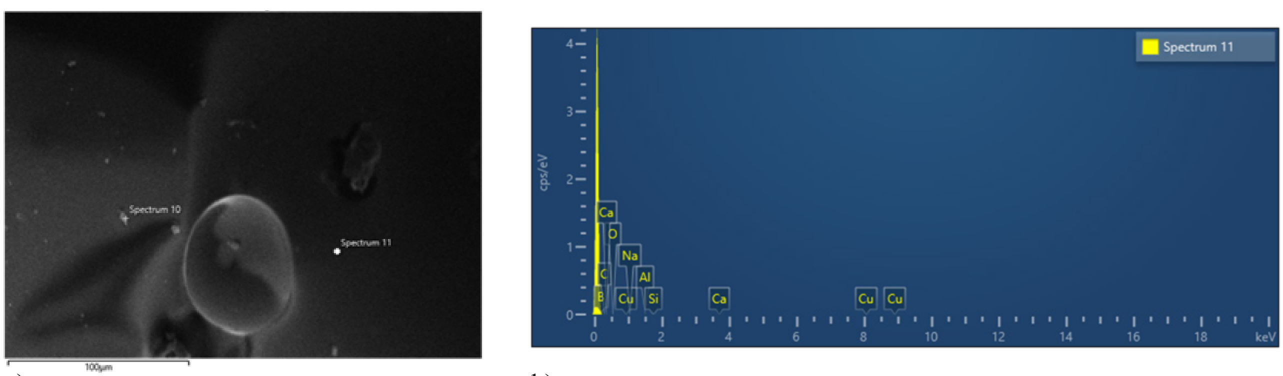


Fig. 6. SEM image of the ceramic body (left) and the glaze (right).



a) b)

Fig. 7. SEM image and EDX analysis of the glaze with composition 5.

CONCLUSIONS

The addition of copper oxides (CuO and Cu_2O) into aluminosilicate transparent glaze gives green colour when fired in an oxidizing atmosphere. When SiC is added to a glaze containing Cu_2O, a red glaze colour is observed at a firing temperature of 1200°C. Silicon carbide acts as a copper oxide reducer in the ceramic glaze. It has been found that the temperature mode of firing the glazes is essential for the final colour of the glaze. At a lower temperature (1150°C), a rose-red coloration is obtained. The reduction by silicon carbide when firing in an oxidizing atmosphere is more complete and the red colour of the glaze is more intensive when copper is introduced as Cu_2O (rather than CuO) into the glaze. The best red colour was obtained for composition containing 0.5 mass % Cu_2O + 1 mass % SiC.

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