DEVELOPMENT AND CHARACTERIZATION OF NEW ART AND DECORATIVE ENAMELS

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ABSTRACT

The application of enamels on metals has many advantages as improving chemical, corrosion, antibacterial resistance and artistic and aesthetic value. The enamel and the substrate must have good adhesion and close coefficients of thermal expansion. In this study, new enamels based on glasses with a melting temperature of up to 1150°C for jewelry brass-coated steel and copper plates were developed. The theoretical properties as the coefficient of thermal expansion, firing temperature, density, compressive strength, tensile strength of the obtained enamels was calculated with the help of the additive constants of Winkelmann & Schott and Mayer & Havas. A good adhesion of the vitreous enamels to the metal substrates of brass-coated steel and to the copper plates was found. After firing at 800 - 820°C for 5 min at maximum temperature the resulting enamels are transparent (compositions 2, 4, 5, 6, 7 and 8), semi-transparent (composition 4) and opaque white (composition 1). Coloured enamels in yellow (with 1 mass % Fe_2O_3), turquoise blue (with 1 mass % CuO) and dark brown (with 1 mass % NiO) have been obtained. The new developed enamels can be used for the decoration of metals and for jewelry.

Keywords: *glass, enamels, metals, art, colour, adhesion, coating, frit.*

INTRODUCTION

Enamelling is a technological process of melting a glass powder in a certain low temperature interval on the surface of metal substrates. As a result of firing the glass powder spills over the metal surface creating a smooth, durable and decorative coating. Enamelling of metals has existed since the time of the occurring of glassmaking in ancient Egypt and then it has been spread to the shores of the Mediterranean Sea. In ancient times, only the objects made of precious metals as gold, silver or their alloys has been coated with the enamels. These were the so-called jewelry items decorated with enamels, since such metals do not need protection against corrosion. By the found enamel objects of Greek and Etruscan origin, it can be considered that enamelling in these countries has reached considerable perfection [1 - 4].

The application of an enamel on metals has many advantages related to improving chemical, corrosion and antibacterial resistance and artistic and aesthetic value. The enamel and the metal substrate must have a good adhesion and close coefficients of thermal expansion. Another important condition in the development of glass compositions is the firing temperature of the glass enamels. It must be significantly lower than the melting temperature of the metal substrate. The enamels can be applied to jewelry, artwork, architectural metalwork, household items and more to protect the metals against oxidation and for decoration. Enamelling is one of the oldest techniques for protecting metal products against the corrosion phenomena and for the improving their aesthetic appearance. This type of coating is still relevant due to its durability, the possibility of creating various aesthetic and artistic effects and the eco-sustainability of the production process. Therefore, the enamel coatings have a great potential in the field of product design [5 - 8]. Over the years, enamel compositions have been developed and changed. Lead used to always be a component of enamel because leaded enamels are more brilliant, with low firing temperature and a wider colour palette can be achieved until more recent decades, in which concerns for toxicity and environmental impact saw the replacement with unleaded versions. The enamels can be glossy or matte, transparent or opaque, white or coloured. Currently, the enamels are widely used for artistic purposes. The amorphous enamel coating on different metallic materials increases their corrosion resistance in various environments [9 - 11]. The color retention is an essential feature for many products, and in this regard, enamelling gives a lasting and time-resistant colour compared to many other coatings [7 - 9]. Special colouring oxides and pigments can be added to the enamel to obtain different color variations [7]. The main difficulty in the enamelling process is development of the composition of glass for enamel to match the metal base. The metal is usually gold, silver, copper, bronze, iron or their alloys [8 - 15]. To avoid distortion and deformation of the product during enamelling, the melting temperature of the metal must be significantly higher than the firing temperature of the enamel. Since the materials tend to expand and contract during the heat treatment process, the enamel should have a close but lower temperature coefficient of expansion than the metal.

The purpose of this paper is the development and characterization of new artistic glass enamels for to copper substrates and metal bases for jewelry.

EXPERIMENTAL

Materials and enamelling technology

New enamels on the base of multi-component glasses compositions with melting temperature of the glass batch up to 1150°C were developed (Table 1). The glasses for enamels contain silicon oxide, boron oxide, sodium oxide, potassium oxide, barium oxide, tin oxide, zinc oxide, aluminium oxide, etc. Chemical compositions of the potassium feldspar (Kaltun Minnig, Turkey), determined by X-ray fluorescence spectroscopy (XRF), is given in Table 2. The rest of the raw materials are pure for analysis with over 99.99 % purity. Batches containing the raw materials are weighed, mixed and homogenized. Then glasses were melted in corundum crucibles at the temperatures of up to 1150°C depending on the starting composition with a hold at the maximum temperature for 2 h and quenching the melt in water to obtain frits. The glass frits were dry ground for 1 h in a high-energy planetary ball mill with agate jars (0.250 L) and agate balls (with diameter from 1 to 2.5 cm and powder balls ratio 1:5) to obtain a powder with a particle size less than 40 µm. Glass powders are applied to the following types of metals - copper plates and metal supports for jewelry. The metal substrates were covered with the obtained glass powders and fired at 800 - 820°C for 5 min to achieve the enamel coating.

Methods

The obtained enamels and metal substrates were structurally and phase characterized by using the following methods and equipment: Chemical analysis

Table 1. Composition of the prepared enamels in mass %.

No.	SiO_2	B_2O_3	Na_2O	K_2O	SnO_2	ZnO	Al_2O_3	BaO	Fe_2O_3	CuO	NiO
1	35.0	15.0	16.0	7.0	25.0		2.0				
2	47.0	17.0	16.0	1.5		17.0	1,5				
3	55.0	12.0	23.0	8.0			2.0				
4	39.0	17.0	16.0	2.5	6.0	11	4.0	4.5			
5	39.0	17.0	16.0	2.5		14	4.0	7.5			
6	39.0	17.0	16.0	2.5		14	4.0	7.5	1.0		
7	39.0	17.0	16.0	2.5		14	4.0	7.5		1.0	
8	39.0	17.0	16.0	2.5		14	4.0	7.5			1.0

(ICP-OES); Powder X-ray diffraction (Bruker D8 Advance device) using Cu Kα - radiation with SolX detector; DTA (LINSEIS Messgeräte GmbH) with heating rates 5°C min^{-1}; UV spectroscopy - a two-beam UV-Vis spectrophotometer device with a spectral range 190-900 nm (VARIAN, Cary-100) and SEM-EDS (Carl Zeiss GmbH, EVO 10). The theoretical properties (coefficient of thermal expansion, tempering temperature, theoretical density, theoretical compressive strength, theoretical tensile strength) of the obtained enamels were calculated by using the additive constants of Winkelmann-Schott and Meier-Hawas [16 - 18].

RESULTS AND DISCUSSION

The metal jewelry substrates were examined with ICP-OES and SEM with EDS. The chemical composition of the metal jewelry backing is given in the Table 3. It can be seen that it mainly contains iron. The same was further examined by SEM with EDS and it was found that there is a brass coating on the surface of the iron base (Fig. 1). The art enamels were also applied to the copper plates from pure copper, supplied by Aurubis Bulgaria AD.

The glass frit with composition 1 is opaque and white, while the frits 2, 3, and 5 are transparent. The frit 4 is

Table 2. Chemical composition of the potassium feldspar.

Oxides, mass %	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	LOI
Potassium feldspar	68.62	16.96	0.145	0.037	0.37	0.05	2.26	11.11	0.11	0.33

Table 3. Chemical composition of the metal jewelry substrate.

Element	Fe	Mn	Cu	Zn	Pb
mass %	92.44	0.28	6.24	0.33	0.11

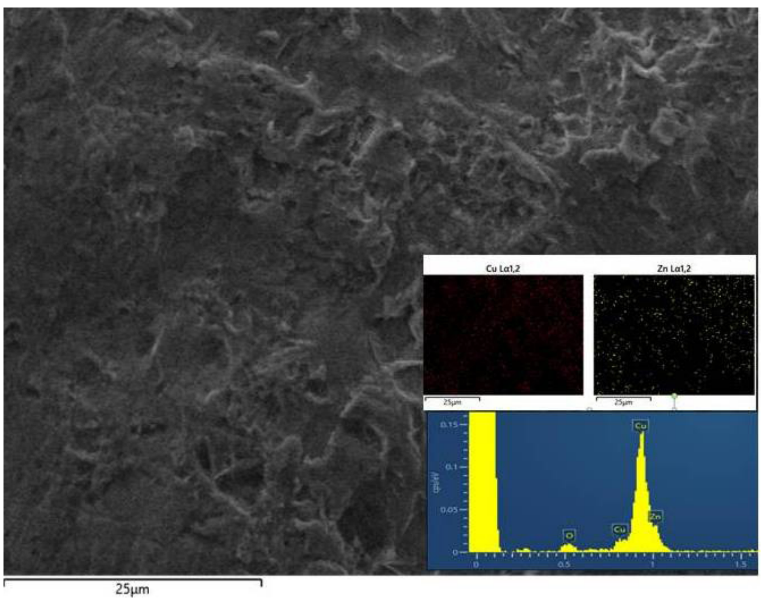

Fig. 1. SEM and EDS analysis of the metal jewelry substrates.

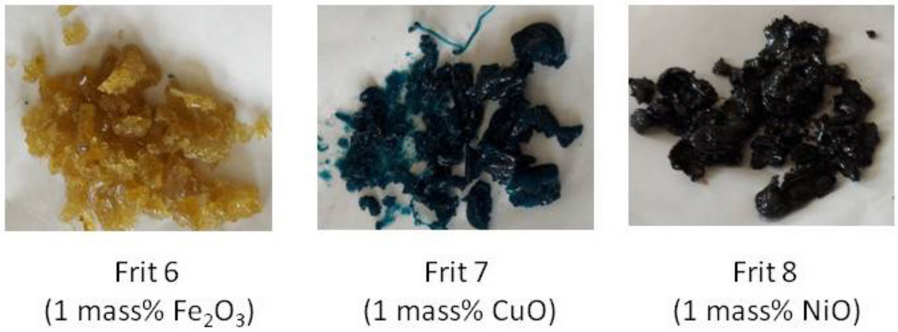

Fig. 2. Coloured frits with composition 6, 7 and 8.

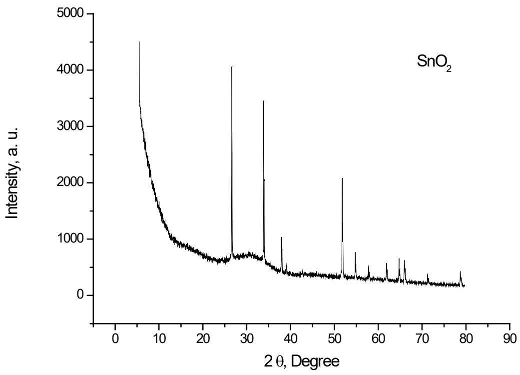

Fig. 3. X-ray diffraction patterns of frit with composition 1.

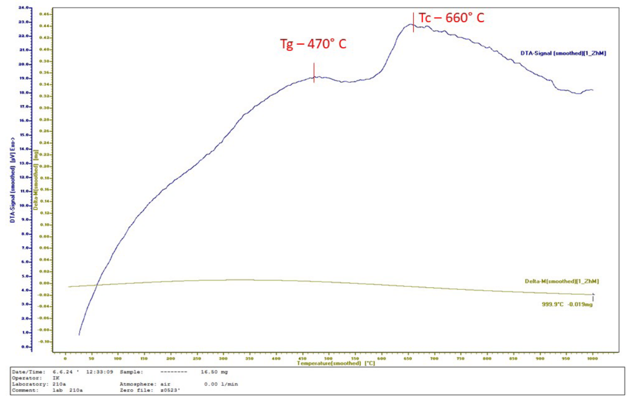

Fig. 4. DTA curves of frit with composition 1.

semi-transparent and the frits 6, 7 and 8 are coloured. The increasing amount of zinc oxide in some frits gives lower viscosity and better fluidity. Fig. 2 shows the frits coloured by 1 mass % F_2O_3 (Composition 6), 1 mass % CuO (Composition 7) and 1 mass % NiO (Composition 8).

The X-ray diffraction pattern of the powdered milled frit with the composition 1 is shown in Fig. 3. It is seen that the sample contains amorphous hallo and crystallization peaks related to SnO_2 (Cassiterite, PDF #41-1445). Fig. 4 presents the DTA curves of the frit with composition 1. The white glass-crystalline frit with composition 1 has a glass-transition temperature T_g at 470°C and temperature of crystallization T_c at 660°C. The diffractograms of frits with compositions 2, 3, 5, 6, 7 and 8 show that they all are amorphous. The diffractogram of glass with composition 2 is presented in Fig. 5. SEM images and EDS results of elemental composition of the enamel with composition 1 (Fig. 6) confirms the result of the XRD analysis. Fig. 7 shows the SEM image of the cross section of the contact between the metal substrate and the enamel. A good adhesion

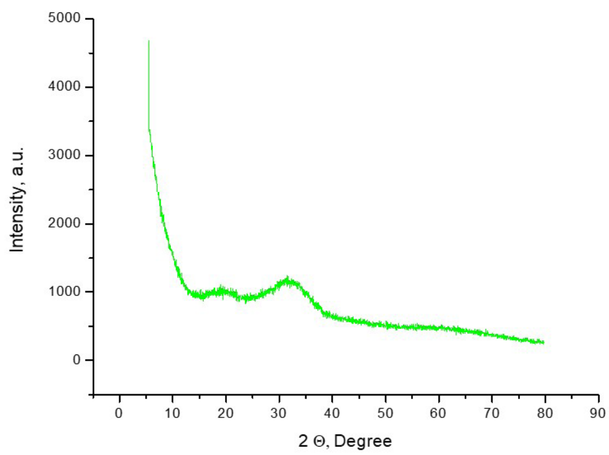

Fig. 5. X-ray diffraction patterns of glass with the composition 2.

between the two materials and the presence of pores in the enamel are observed.

UV-Vis spectrometry has been used to examine the colored enamels obtained from compositions 6, 7 and 8 with colouring oxides Fe_2O_3, CuO, NiO respectively in the amount of 1 mass %. Fig. 8 shows the UV-Vis transmission spectra of the enamels. The wavelengths

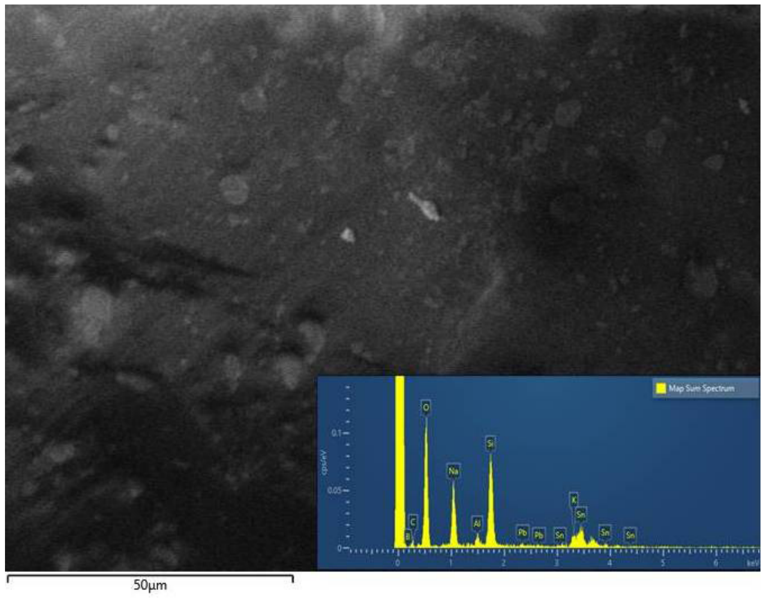

Fig. 6. SEM and EDS analysis of enamel with composition 1.

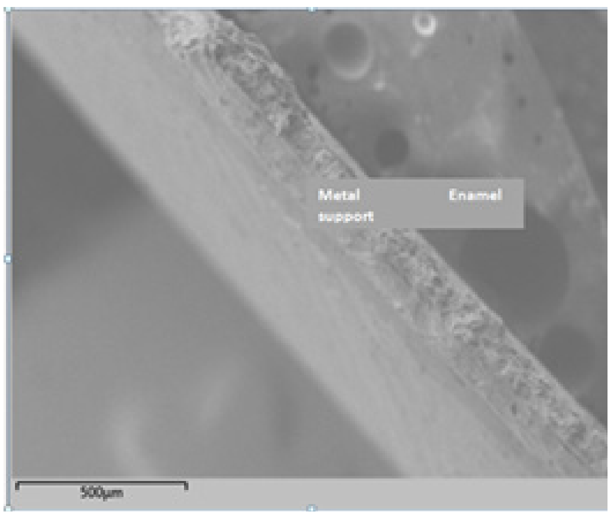

Fig. 7. SEM image of contact between the metal substrate and the enamel.

corresponding to the transmission bands match the colours of the enamel's samples.

The theoretical properties as coefficient of thermal expansion, melting temperature, density, compressive strength, tensile strength of the obtained enamels was calculated by using the additive constants of Winkelmann & Schott and Mayer & Havas [16 - 18]. The results are given in the Table 4. The calculated CTE values show that the enamels have a lower but close to steel, brass and copper CTE. The calculated tensile and compressive strength values also show that the enamels have good mechanical properties.

The developed transparent enamel with composition 2, the coloured enamels with compositions 6, 7 and 8 and the enamels with compositions 1, 3 and 4 coloured with different pigments were applied to metal jewelry substrates and to copper plates. The same are shown in Figs. 9 and 10.

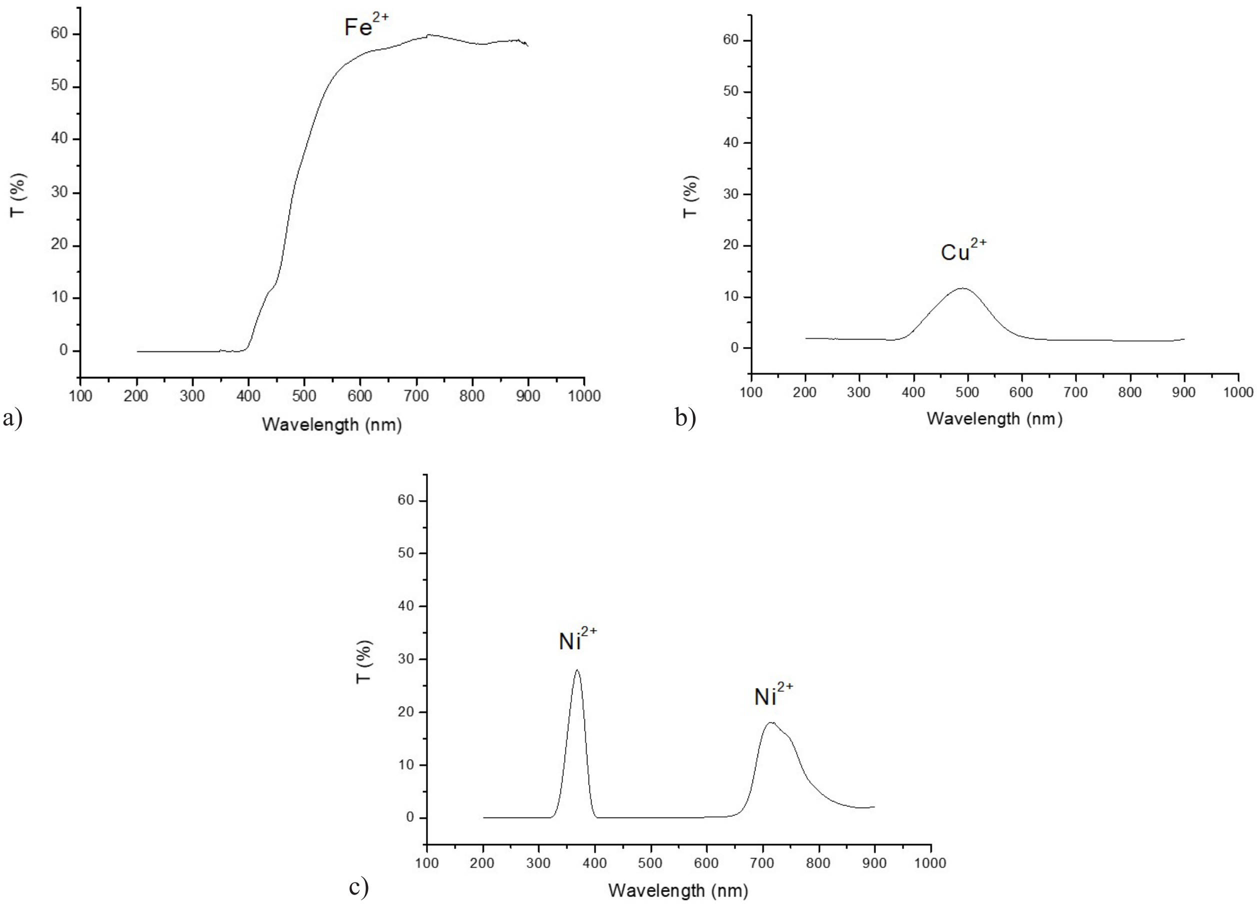

Fig. 8. UV-Vis spectra of the enamels with: (a) composition 6 (1 mass % Fe_2O_3), (b) 7 (1 mass % CuO) and (c) 8 (1 mass % NiO).

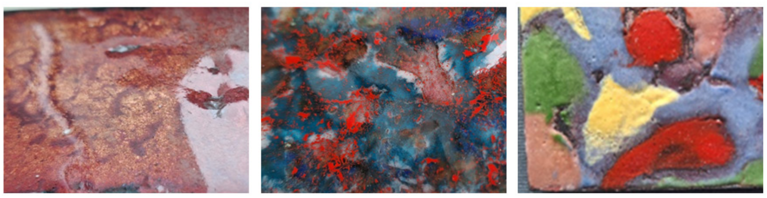

Fig. 9. White enamel (composition 1) (a) colored with different color pigments and (b) enamels (compositions 6, 7 and 8) applied on metals substrates for jewelry.

a) b)

Fig. 10. Decorative enamels on copper plates with transparent enamel (composition 2) and white enamel (composition 1) coloured with different colour pigments.

Table 4. Theoretical calculated properties of the enamels.

Compositions of enamels	Theoretical CTE, $\alpha.10^{-6}\,^{o}C^{-1}$	Theoretical density, g cm^{-3}	Theoretical tensile strength, MPa	Theoretical compressive strength, MPa	Firing temperature of enamel, ^{o}C
1	$10.5.10^{-6}$	2.70	70	921	810
2	10.10^{-6}	2.59	81	926	800
3	$11.5.10^{-6}$	2.55	65	928	820
4	$9.5.10^{-6}$	2.71	61	875	810
5	10.10^{-6}	2.42	66	900	800

CONCLUSIONS

New glass enamels suitable for steel, brass and copper metals have been developed. The enamels are based on the multi-component glasses with a melting temperature up to 1150°C. After applying the powdered glass frits on the metal substrates and firing at temperatures of 800-820°C with a hold at the maximum temperature of 5 min a durable enamel coating has been obtained. The approximate firing temperature of the enamels on the metal substrate was calculated by using additive constants. The composition of the metal substrates for jewelry used for the enamelling was established as a steel with a brass coating by chemical analysis with ICP-OES and SEM/EDS analysis. Pure copper plates from Aurubis Bulgaria AD were also used for enamelling base. A good adhesion of the vitreous enamels to the metal substrates of brass-coated steel and to the copper substrates was found. The resulting enamels are transparent (compositions 2, 3 and 5), semi-transparent (4) and opaque (composition 1). Opaque enamel is white, glass-crystalline with a low softening temperature of about 470°C and a crystallization temperature of about 660°C. Tin oxide is the crystalline phase in it. The enamels coloured in yellow, blue and dark brown have been prepared. New enamels with an art purpose for the decoration of metals and for jewelry have been obtained.

Authors' contribution: *The authors contributed equally to the study.*

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