Ceramics with decorative aspect

Cezara Voica
National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania
E-mail: cezara.voica@itim-cj.ro; cezara_voica@yahoo.com

Abstract. The last decades brought the development of bone china techniques used for producing the decorative articles. These products can be glazed with a transparent and thin glaze layer, even with more special (decorative) ones which gives new aesthetic aspect. The present article presents the results obtained after the studies performed for matte glazes for decorative bone china. As microcrystallization agent were used zinc oxide; the content of this oxide bring some changes of the basic glaze thus the chemical composition must be adjusted as the fluxes would present the desired properties after the heating process.

1. Introduction
The ceramic glazes are thin coatings covering the ceramic products. From structural point of view they are glass, non-crystalline masses, which confer gloss, smoothness, water resistance, as well as mechanical, aesthetic and hygienic properties to the product [1-3]. The diversity of glazes for fine ceramics is an actual goal that contributes to promotion of products on internal and external market. Special effects glazes are highly solicited in present days, for their special aesthetic aspect and for their superior thermal characteristics as well [4, 5].

The purpose of this research is to get certain microcrystalline glazes with a content of zinc excess, obtained through the current technology used in obtaining ceramic glazes to be deposited on the surface of bone china. Thus, the results of the research can be applied fast, and the firing process of the “effect” glazes does not need any changes, either in the diagram in the functioning of the kiln.

This study was reasearch informations regarding the fusibility range, the aspect of glazes after firing, the nature of formed components for the recipes of glazes with a variable content of zinc oxide as crystalizing agents.

Zinc oxide is an effective fluxing agent for glazes with a medium to high melting temperature, but only with other fluxing agents added in small amounts, it improves the gloss; used in larger amounts, however, it leads to opacification and matting of the glazes [6, 7]. The saturation of a glaze with zinc oxide is a method frequently used for obtaining a crystalline texture [8]. Zinc orthosilicate (Zn$_2$SiO$_4$) plays an important role in the fabrication of mat and crystalline glazes and sodium silicofluoride (Na$_2$SiF$_6$) promotes opacification of them [9].

2. Experimental
In order to study the glaze from the structure point of view and also the factors which influence the process of micro-crystallizing, it was started from a glaze’ preparation destined to the bone china as a vitreous matrix, of a borosilicate type, partial fritted, made according to the clasic technology of glazes (batching, mixing, grinding, sitting, firing). Base glaze was made of raw materials currently used in
industry: quartz, clay, feldspar, dolomite. The experiments have been done by using the basic glazes into which it has put compounds of zinc in different quantities, thus enabling the basic glaze to be devitrified [10].

Three sets of experiments were performed. First, was introduced zinc oxide in high proportions, up to 30%. The effect has been amplified by making some compositions with sodium hexafluorosilicate (Na$_2$SiF$_6$) and willemite (Zn$_2$SiO$_4$) – as admixtures, in different proportions, going up to 25% (the second and the third sets) [11]. The operating conditions – technological flux – are those of the materials (the density, the degree of dispersion, the thickness of the layer of the glaze) have been carefully controlled in order to assure the reproducible data. Table 1 presents the oxidic compositions of experimental masses.

**Table 1. Oxidic compositions of experimental masses.**

| Experimental samples          | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | ZnO  | Fe$_2$O$_3$ | CaO  | MgO  | Na$_2$O  | K$_2$O | B$_2$O$_3$ | PC  |
|------------------------------|---------|---------|-------------|------|-------------|------|------|----------|-------|-----------|-----|
| Basic glaze                  | 56.31   | 0.16    | 9.18        | 9.07 | 0.24        | 7.28 | 1.50 | 3.00     | 1.80  | 2.96      | 8.50|
| 10% ZnO                      | 50.14   | 0.15    | 8.17        | 19.07| 0.21        | 6.48 | 1.33 | 2.68     | 1.60  | 2.67      | 7.57|
| 20% ZnO                      | 49.50   | 0.14    | 8.07        | 20.07| 0.21        | 6.40 | 1.32 | 2.63     | 1.59  | 2.60      | 7.47|
| 25% ZnO                      | 40.83   | 0.12    | 6.66        | 34.07| 0.17        | 5.28 | 1.08 | 2.18     | 1.30  | 2.14      | 6.17|
| 30% ZnO                      | 37.73   | 0.11    | 6.15        | 39.07| 0.16        | 4.88 | 1.00 | 2.01     | 1.20  | 1.99      | 5.70|
| 25% ZnO + 2%, 4% Na$_2$SiF$_6$| 39.73   | 0.12    | 6.31        | 34.44| 0.21        | 5.66 | 1.01 | 1.88     | 1.23  | 2.90      | 6.50|
| 30% ZnO + 2%, 4% Na$_2$SiF$_6$| 36.71   | 0.11    | 5.83        | 39.44| 0.19        | 5.22 | 0.94 | 1.74     | 1.14  | 2.67      | 6.01|
| 33% ZnO + 2%, 4% Na$_2$SiF$_6$| 34.89   | 0.1    | 5.54        | 42.44| 0.18        | 4.96 | 0.89 | 1.65     | 1.08  | 2.54      | 5.73|
| 15% ZnO + 15% Zn$_2$SiO$_4$  | 58.94   | 0.025   | 1.39        | 35.39| 0.046       | 1.24 | 0.22 | 0.41     | 0.27  | 0.63      | 1.43|
| 20% ZnO + 20% Zn$_2$SiO$_4$  | 60.29   | 0.018   | 1.38        | 44.03| 0.023       | 1.12 | 0.14 | 0.20     | 0.18  | 0.40      | 0.93|
| 25% ZnO + 25% Zn$_2$SiO$_4$  | 61.64   | 0.012   | 0.91        | 52.68| 0.018       | 0.91 | 0.09 | 0.19     | 0.12  | 0.20      | 0.45|
| 25% Zn$_2$SiO$_4$            | 61.45   | 0.047   | 2.61        | 27.68| 0.08        | 2.33 | 0.42 | 0.77     | 0.50  | 1.19      | 2.69|

3. Results and discussion

The research has intended to determine the characteristic and correlation which is established with the ceramic support. Thus, the following has been observed: the thermic behaviour by observing the change of the aspect at the thermic microscope; establishing the optimum melting temperature; the thermal expansion and the compatibility with the ceramic mass; the aspect of the fired glazes and their phase composition.

To establish the technological firing conditions, the thermal analysis of glazes as performed, with a thermal analyzer type MOM Q 1500. The most samples have an almost similar thermal behaviour and results (table 2).

**Table 2. Thermal processes of experimental glazes.**

| Process                     | Type of process | Temperature (°C) |
|-----------------------------|-----------------|-----------------|
| Loss of water               | endothermal     | 210             |
| Polymorphous modifications of silica | endothermal     | 530             |
| Decomposition of CaCO$_3$    | endothermal     | 855             |

The melting process of the glazes has been observed at the thermal microscope for high temperatures Leitz, emphasizing the optimum melting temperature, the melting interval, the softening interval and the viscosity in the melting phase of the melted mixture (table 3). In experimental glazes containing sodium hexafluorosilicate has been observed that: the softening range increases with the melting range, keep constant the content of sodium hexafluorosilicate and modify the content of zinc oxide; the softening range increases with decreasing melting range, keep constant the content of zinc oxide.
oxide and modify the content of sodium hexafluorosilicate; the softening decreases with decreasing melting range, with the increasing content of ZnO and wilhemite.

The X-ray diffraction (XRD), performed by a DRON diffractometer with Cu Kα radiation has put in evidence the phase composition of the glazes treated thermically in the industrial kiln: zinc orthosilicate as majority, together with quartz and sometimes zinc oxide excess.

Table 3. The thermic behaviour of experimental glazes.

| Experimental masses | Beginning of softening [°C] | Beginning of melting [°C] | Beginning of flowing [°C] | Softening range [°C] | Melting range [°C] |
|---------------------|-----------------------------|---------------------------|--------------------------|---------------------|-------------------|
| Basic glaze         | 1010                        | 1060                      | 1160                     | 50                  | 100               |
| 10% ZnO             | 1010                        | 1060                      | 1160                     | 50                  | 150               |
| 25% ZnO             | 1010                        | 1040                      | 1160                     | 30                  | 150               |
| 25% ZnO + 2% Na₂SiF₆| 1035                        | 1060                      | 1100                     | 25                  | 65                |
| 25% ZnO + 4% Na₂SiF₆| 1030                        | 1055                      | 1090                     | 25                  | 60                |
| 30% ZnO + 2% Na₂SiF₆| 1050                        | 1080                      | 1145                     | 30                  | 95                |
| 30% ZnO + 4% Na₂SiF₆| 1040                        | 1090                      | 1110                     | 50                  | 70                |
| 33% ZnO + 4% Na₂SiF₆| 1060                        | 1110                      | 1140                     | 50                  | 80                |
| 15% ZnO + 15% Zn₂SiO₄|                           |                           |                           |                     |                   |
| 20% ZnO + 20% Zn₂SiO₄|                           |                           |                           |                     |                   |
| 25% ZnO + 25% Zn₂SiO₄|                           |                           |                           |                     |                   |
| 25% 2ZnO·SiO₂        | 1020                        | 1050                      | 1100                     | 30                  | 80                |

The most important thermal property of a glaze is its coefficient of linear thermal expansion, the value of which is usually determined experimentally. The measurements of thermal expansion in this study show a correct compatibility between glazes and the mass of bone china; the coefficients of thermal expansion of studied glazes are lower than the bone china (α×10⁻⁶[°C⁻¹]=7.62) (table 4).

Table 4. Thermal expansion of studied glazes.

| Experimental glazes | Thermal expansion α×10⁻⁶[°C⁻¹] |
|---------------------|--------------------------------|
| 10% ZnO             | 6.51                           |
| 20% ZnO             | 6.58                           |
| 25% ZnO             | 6.43                           |
| 30% ZnO             | 6.27                           |
| 15% ZnO + 15% Zn₂SiO₄| 5.62                           |
| 20% ZnO + 20% Zn₂SiO₄| 5.56                           |
| 25% Zn₂SiO₄         | 5.65                           |
| 25% ZnO + 4% Na₂SiF₆| 5.96                           |
| 30% ZnO + 2% Na₂SiF₆| 5.87                           |

Table 5 shows the aspect of experimental fired masses. Glaze base has a high capacity to dissolve the zinc oxide. Among to the approximately 10% of zinc oxide from frit base, the addition of 20-25% in raw glaze does not cause crystallization diagram on current firing bone china. The glaze with the best mattness was the one with the addition of 25% wilhemite. Glaze base has a high capacity to dissolve the zinc oxide. Among to the approximately 10% of zinc oxide from frit base, the addition of 20-25% in raw glaze does not cause crystallization diagram on current firing bone china.
Table 5. Aspect of experimental masses.

| Samples | Aspect                              |
|---------|-------------------------------------|
| 10% ZnO | transparent, glossy                 |
| 20% ZnO | transparent, glossy                 |
| 25% ZnO | transparent, glossy                 |
| 30% ZnO | transparent, glossy                 |
| 20% ZnO + 2% Na$_2$SiF$_6$ | satined                             |
| 25% ZnO + 2% Na$_2$SiF$_6$ | satined                             |
| 25% ZnO + 4% Na$_2$SiF$_6$ | satined, lightly crystallized       |
| 30% ZnO + 2% Na$_2$SiF$_6$ | crystals in relief, lightly satined |
| 30% ZnO + 4% Na$_2$SiF$_6$ | crystals in relief, lightly satined |
| 33% ZnO + 2% Na$_2$SiF$_6$ | crystals in relief, satined background |
| 33% ZnO + 4% Na$_2$SiF$_6$ | rude crystallization, pronounced relief |
| 15% ZnO + 15% Zn$_2$SiO$_4$ | sugar-like                          |
| 20% ZnO + 20% Zn$_2$SiO$_4$ | sugar-like                          |
| 25% ZnO + 25% Zn$_2$SiO$_4$ | sugar-like                          |
| 25% Zn$_2$SiO$_4$ | mat                                 |

4. Conclusion

This study presents experimental works for obtaining ceramic glazes with a quality higher than those applied until now and a complex study of their properties for producing bone china articles. The study followed obtaining a rich scale of effect glazes, matte, satined, through introduction of raw materials that cause special aesthetic effects in vitreous mass: micro crystallizations.

The influence of ZnO on the aspect, phase composition and thermal behaviour in bone china glaze have been investigated, with aim at obtaining glazes with high aesthetic effect. The sodium hexafluorosilicate addition strengthens the micro-crystallization decorative of ZnO in the studied glazes. The measurements of thermal expansion show a correct compatibility between glazes and the mass of bone china. The glaze with the best mattness was the one with 25% of wilhemite. The glazes are capable of being used under the current flux technology.

These glazes are definitely expensive, but they can be used for certain products which require a more sophisticated aspect which justify their use.

References

[1] Teoreanu I 1995 Introduction in physical chemistry of solid phase, oxidic compounds vol I (Bucureşti: Editura Didactică şi Pedagogică)
[2] Aliprandi G 1974 Ceramurgia & Tecnologia Ceramica (Genova-Corso Europa: Editioni Culturali Internazionali) pp 881-908
[3] Shaw K 1971 Ceramic glazes (Amsterdam, London: Elsevier)
[4] Escardino A, Amoros J L, Orts M J, Mestre S, Belda J, Marco J and Salas J J 2000 Proc. World Congress on Ceramic Tile Quality vol 1 93-109
[5] Dakkai S, Orlova L A and Miklailenko N 1999 Glass and Ceramics 5-6 177-80
[6] Moreno A, Bon E, Bordes M C, Navarro M C, Deraedt J and Lerusse A 2000 Qualicer VI Proc. World Congress on Ceramic Tile, Quality vol 1 27-40
[7] Karosu B, Caki M and Turan S 2000 J. Eur. Ceram. Soc. 20 2225-31
[8] Stefanov S and Batscharov S 1988 Ceramic glazes (Wiesbaden: Bauverlag)
[9] Parmelee W C 1951 Ceramic glazes (Chicago Illinois: Industrial Publications Inc.)
[10] Rahaman M and Lakkwani S 1999 Adv. Sci. Technol. 14 33-40
[11] Voica C, Gagea L and Literat L 2006 Proc. Nat. Simp. Chem. Eng. (Cluj-Napoca: Accent) p 78.