DEVELOPMENT OF OPAQUE FRITS IN THE SPINEL SYSTEM

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ABSTRACT

Glazes are fundamental materials that provide ceramic bodies with physical advantages and aesthetic appearance. The frit, which is prepared by melting raw materials and rapidly quenching in water, is one of the main components of the glaze recipes. It can be also varied according to the desired surface property (transparent, opaque, gloss, matt).

High opacity plays an important role in the decoration of ceramic tiles. Zircon is a widely used raw material in both glaze and frit compositions to achieve desired levels of opacity. Due to the recent surge in the price of zircon, many studies have been carried out on alternative materials or new frits that crystallize to a glass-ceramic system that yields higher opacity. Phases in the spinel crystal structure (n=1.76-1.86) are the closest phases to the zircon (n=1.95) with their high refractive index. They can be also crystallized easily from a glass structure. If high spinel crystallization is obtained from a frit, the costs of opacifying the glazes can be reduced.

Another important property of the crystals in the spinel system are their high hardness (15-16 GPa). In addition, crystals in this system are formed in small crystal size. If high crystallization can be achieved in the glassy matrix, high abrasion resistant opaque glazes can be developed. Thus, tiles with high abrasion resistance can be used in heavy pedestrian traffic areas.

This study aims to obtain opaque frits without using zircon in the spinel system which crystallize to $Mg_{1-x}Zn_xAl_2O_4$. The frits applied were fired in a porcelain firing schedule and characterized by XRD and SEM together with opacity, glossiness and hardness.

1. INTRODUCTION

Opaque white frits are often formulated with zircon in order to obtain high opacification and whiteness. The upward fluctuations of the prices have driven the interest to focus on frit compositions without using zircon. Apart from the traditional frit compositions, glass-ceramic research allows possibilities for acquiring a wide range of functional frits [1-2].

The general objective of the present study is to develop a frit composition that can form spinel crystals for the purpose of achieving desired opacity and whiteness without using zircon.

2. EXPERIMENTAL AND RESULTS

Quartz, alumina, magnesite, sodium and potassium feldspar, zinc oxide and boric acid were used as raw materials. The chemical compositions are shown in Table 1. Three compositions were formulated with different MgO/ZnO mole ratios. ZM1, ZM3 and ZM7 were the compositions that had 1, 3 and 7 MgO/ZnO mole ratio, respectively. The mole percentage of the compositions are indicated in Table 1. The frits were prepared by melting the required amount of batch in an alumina crucible at 1600°C with a 10°C/min heating rate and 1 hour soaking time in an electrically heated furnace. The frits were mixed and milled with 5% kaolin. The mixture was then applied on a porcelain body and fired in an industrial kiln cycle.

Chemical Compositions (% Mole)							
	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	ZnO	B_2O_3
ZM1	50-55	20-25	9	1,5-2,0	1,5-2,0	9	3-5
ZM3	50-55	20-25	15	1,5-2,0	1,5-2,0	5	3-5
ZM7	50-55	20-25	18	1,5-2,0	1,5-2,0	2,5	3-5

Table 1. *Chemical Composition of frits.*

	ZM1	ZM3	ZM7
L	90,15	89,47	87,55
a	-0,23	-0,60	-0,57
b	-1,75	-1,37	-1,49
G(60º)	7,9	4,7	6,1

Table 2. *Color and gloss values of samples.*

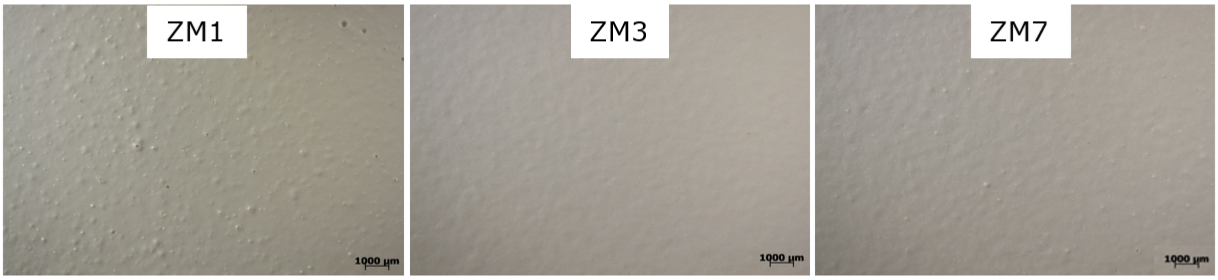

Figure 1. *Stereo microscope images of the sample surface (1000µm).*

The whiteness of the frits decreased on increasing the MgO against ZnO (Table 1). Mullite (m) and spinel (s) were the common phases for the three compositions. Indialite (i) also formed in the magnesium-rich compositions (ZM3 and ZM7, Figure 2). ZM3 had better surface quality than ZM1 and ZM7 (Figure 1). The spinel crystals and acicular mullite can be easily identified by the SEM image in ZM1 (Figure 3).

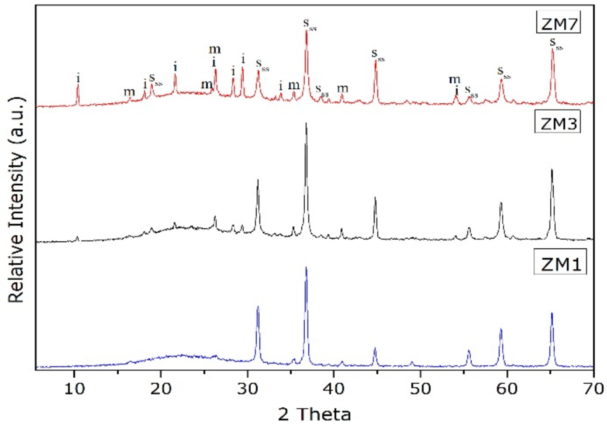

Figure 2. *XRD results of the samples.*

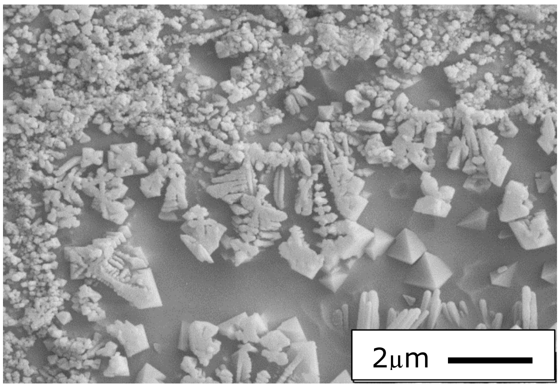

Figure 3. *Secondary electron image of the ZM1 sample.*

3. CONCLUSIONS

Spinel crystallization in the SiO_2-Al_2O_3-MgO-ZnO-Na_2O-K_2O-B_2O_3 system depends on ZnO concentration in the composition so that increased ZnO promotes spinel crystallization. The increase in MgO content encourages indialite and mullite crystallization in the system.

4. REFERENCES

[1] Encarna Bou et al, 2007, Journal of the European Ceramic Society, 27, 1791-1796

[2] M. Romero et al, 2002, Journal of the European Ceramic Society 22, 883-890