Journal of Ceramic Processing Research. Vol. 12, No. 2, pp. 135~139 (2011)

J O U R N A L O F
Ceramic Processing Research

Characterization of diopside-based glass-ceramic porcelain tile glazes containing borax solid wastes

G. Kaya[a,*], B. Karasu[b] and A. Cakir[b]
[a]*Dumlupinar University, Faculty of Engineering, Department of Ceramic Engineering, Merkez Campus, Kutahya, Turkey*
[b]*Anadolu University, Faculty of Engineering and Architecture, Department of Materials Science and Engineering, Iki Eylul Campus, 26555 Eskisehir, Turkey*

In recent years glass-ceramic systems became industrially important for their high softening point, good coating capability for relevant substrates and high chemical and abrasion resistance. The ZrO_2-CaO-MgO-SiO_2 (ZrCMS) glass-ceramic system exhibits a high resistance to abrasion and surface scratches thanks to the diopside crystals formed during firing. In this current study, certain amounts of wastes of the Eti Maden Kırka Boron Company of Turkey possessing the world biggest borax deposit were evaluated in the production of ZrCMS system frits as being suitable for porcelain tile glazes. Newly-produced frit based glass-ceramic glazes were applied on porcelain tile bodies then, fast fired under both laboratory and industrial working conditions. The final products were characterized in terms of microstructural changes and phase formation, hardness, colour parameters and glossiness of glazed surfaces.

Key words: The ZrO_2-CaO-MgO-SiO_2 system, Glass-ceramic, Glaze, Diopside, Characterization.

Introduction

Porcelain tiles are glass-bonded materials with excellent technical performance for ceramic tiles, such as mechanical, wear, frost and chemical resistance that make their use possible in many different places where heavy human traffic flows [1]. In the last decade, the growth rate of the global production of porcelain tiles increased more than other ceramic products; in fact, the technical properties of porcelain tile, coupled with even more improved aesthetic appearance, gave it a prominent role in the tile market [2]. The main standard requirement for a porcelain tile is very low water absorption (it should be < 0.5% according to ISO 13006) that is largely fulfilled, being < 0.1% in most products. However, a residual closed porosity is always present-ranging usually from 2 to 8% significantly affecting the product performance, especially in terms of mechanical properties and resistance of polished tiles to stains [3].

Glass ceramics are polycrystalline solids containing a residual glassy phase [4]. They are produced from a base glass by controlled crystallization [5]. The concepts of controlled crystallization of a glass designate the separation of a crystalline phase from the parent glass in the form of tiny crystals. Their growth rate and thus also their final size are controlled by a suitable heat treatment [6].

Glass-ceramic glaze systems have excellent coating capability with a higher softening point, higher chemical and abrasion resistance when compared to traditional glazes. Furthermore, when evenly dispersed tiny crystalline phases in a coating layer are developed, the coating aspects turn from transparent to opaque, from glossy to satin or matte, from smooth to patterned or textured, enabling a wide range of aesthetic effects to be achieved [4].

The development of new glass ceramic glazes is limited by some constraints, mainly derived from the sort of support and heating conditions such as final firing temperature and heating rate. Nowadays, most research aim to improve the quality of glazes by the development of new glaze products with smoother surfaces and desirable mechanical and chemical properties under similar firing conditions [7]. These new glazes may be made by using a glass ceramic production route. By considering the requirements of compatibility with the body properties and resultant outstanding properties, formulations that are based on the LiO_2-Al_2O_3-SiO_2, MgO-Al_2O_3-SiO_2, CaO-MgO-SiO_2 and ZrO_2-CaO-MgO-SiO_2 glass ceramic systems have found practical applications as tile glazes [8].

The ZrO_2-CaO-MgO-SiO_2 (ZrCMS) glass-ceramic system is one of these and exhibits high resistance to abrasion and surface scratches thanks to the diopside ($CaMgSi_2O_6$) crystals occurring during firing [9].

Boric acid is currently used in frit-based ceramic glazes since borate compounds are soluble and cannot be used in a wet process without undesirable effects appearing. In addition, it is the second most important network-former after silica [10]. Compared with silica, the introduction of boric oxide into a glaze increases the elasticity and decreases tensile strength. When added up to certain amounts, it lowers the thermal expansion coefficient [11]. As the boron level

*Corresponding author:
Tel : +90-274-2652031 ext. 4310
Fax: +90-274-2652066
E-mail: gkaya@dumlupinar.edu.tr

in a glaze increases, the mechanical strength and scratch resistance are enhanced [10].

The present studies was undertaken to make diopside-based glass-ceramic glazes produced by evaluating the concentrator (CW) and derivative (DW) borax solid wastes. The first part of the investigation was conducted to determine a standard frit composition suitable to end up with a diopside-based glass ceramic glaze. Secondly, consequent glazes were produced and characterized.

Experimental

The study was carried out in five steps; frit preparation, frit melting, glaze preparation, firing of glazed tiles and characterization of the final products. The raw materials used for frit preparation were quartz, calcite, magnesite, boric acid, zirconia, kaolin, concentrator and derivative borax wastes. Oxide compositions of the wastes taken from Eti Maden Kırka Boron Company are indicated in Table 1.

Frit preparation and melting

The composition range of the frits studied are listed in Table 2. As a result of compositional changes based on previous experiments [9], a standard frit composition was chosen. 34 frit batches were prepared and melted.

The most suitable and satisfactory frit, in terms of hardness, colouring parameters, brightness values and wear resistance, was coded as D4.

The boric oxide content supplied from the boric acid in the D4 frit recipe was then replaced by the boric oxide coming from CW and DW in the mol ratios of 0.02, 0.04, 0.06, 0.08 and 0.1 without changing the main oxide contents in the D4 chemical composition. The new frits were coded CG2-CG10, where the boric oxide requirement was fulfilled from CW as 0.02 and 0.1 (in mol) and labelled as DG2-DG10, where the boric oxide requirement was supplied from DW as 0.02 and 0.1 (in mol).

Starting raw materials and borax wastes were precisely weighed and homogeneously mixed. Then, the batches were put into high alumina containing crucibles of 400 g capacity.

Melting operations were performed in a Protherm brand electrically heated furnace at 1500 °C for 1 h under laboratory conditions. The frits were obtained by quenching the melt into water at ambient temperature.

Table 1. Chemical composition of the borax wastes (in wt. %)

Oxides	Type of Waste	
	CW	DW
SiO_2	19.97	17.31
Al_2O_3	2.44	0.34
TiO_2	0.05	-
Fe_2O_3	0.5	0.33
CaO	11.37	17.55
MgO	13.75	17.97
Na_2O	7.5	2.86
K_2O	2.34	5.05
SrO	1.06	1.3
B_2O_3	14.3	5.87
*L.I	26.73	31.42

*L.I.: Losses on ignition.

Table 2. The compositional range of frits studied

Oxides	Molar Range
K_2O	0-0.05
CaO	0.40-0.50
MgO	0.50-0.60
ZrO_2	0.02-0.08
B_2O_3	0.08-0,15
SiO_2	1.50-1.90

Glaze preparation

Glaze preparation was based upon the recipe given in Table 3. Weighed raw materials were wet milled in porcelain jet-mills containing alumina balls for 60 minute. The prepared glazes were sieved to 90 μm to remove the coarse grains and applied onto porcelain tiles by spraying. The glazed porcelain tiles were dried in an oven at 105 °C for 2 h.

Firing of glazed tiles

Having been dried, glazed porcelain tiles were fired in a fast firing furnace in Eskisehir Toprak Ceramic Co. at 1197 °C for a total time of 55 minute.

Characterization of final products

Glossiness and colouring parameters of the final products were determined using a Multi-Gloss 268 model gloss meter and a CR-300 model chromometer. Hardness values were measured by means of a Emcotest M1C 010 model under 5 a kg load. Microstructural changes and phase formations of the glazes after firing were inspected with a Zeiss Supra TM 50 VP series scanning electron microscope (SEM) and a Rigaku Rint 2000 series diffractometer (XRD). An ultra thin window energy dispersive X-ray spectrometer (EDX-LINK ISIS 300) attached to SEM was also used for chemical analysis.

Results and Discussion

Table 3. The glaze recipe studied (in wt. %)

Frit	85
Na-feldspar	10
Kaolin	5
*CMC	0.15
**STTP	0.25

*CMC: Carboxyl methyl cellulose
**STTP: Sodium tripolyphosphate

Although the CG2 and CG4 frit-based glazes with CW experienced a maturation problem, the rest were produced without any problem or defects at the end of fast firing.

The brightness of the glazes can be followed from Tables 4 and 5. According to the test results of glazes, using CW in the frit recipes had a positive effect on the mattness. However, due to the insufficient maturation the CG2 and CG4 with a lower brightness could not be valuated. The CG10 glaze has the highest mattness amongst the others. As clearly seen if the amount of CW and DW is increased in the frit recipes, the mattness generally rises except in the case of the CG6 and DG6 glazes.

Colouring parameters of the glazes studied are given in Tables 6 and 7. It is quite obvious that the whiteness values fall in the range of 89.06 and 94.46 as a result of CW additions. However, the whiteness of the glazes containing DW did not change particularly.

Microhardness values are presented in Tables 8 and 9. The PEI wear resistance test (according to TS EN ISO 10545-7) was only conducted on the D4 glaze, indicating a high wear resistance, ease of cleaning and classified as a PEI-V class. The glazes shown in Tables 8 and 9 were fast single fired under industrial working conditions. Amongst the others, the CG10 and DG10 glazes have the desired surface quality and at the same time possess a higher microhardness when compared to those of the D4 glaze and could be thought of as PEI-V class. Furthermore, the relevant test on them will also be made to satisfy such an expectation.

Table 4. Brightness test results of the glazes with CW

Glazes	Brightness	
	20°	60°
D4	2.0	7.7
CG2	1.3	3.6
CG4	1.8	8.1
CG6	3.0	17.4
CG8	1.7	8.8
CG10	1.6	6.7

Table 5. Brightness test results of the glazes with DW

Glazes	Brightness	
	20°	60°
D4	2.0	7.7
DG2	1.6	19.1
DG4	2.4	18.5
DG6	2.8	15.6
DG8	2.0	9.6
DG10	2.0	9.2

Table 6. Colouring parameters of the glazes with CW

Glazes	L*	a*	b*
D4	94.15	-0.65	1.79
CG2	92.73	-0.85	1.96
CG4	94.46	-1.04	2.58
CG6	89.06	-0.29	0.84
CG8	90.05	-0.43	1.40
CG10	94.27	-1.01	3.33

Table 7. Colouring parameters of the glazes with DW

Glazes	L*	a*	b*
D4	94.15	-0.65	1.79
DG2	94.72	-1.06	2.68
DG4	94.46	-0.90	2.02
DG6	94.41	-0.91	3.10
DG8	94.58	-0.79	2.86
DG10	94.45	-0.75	3.33

Table 8. Micro-hardness test results of the glazes prepared with the use of CW

Glazes	(GPa)
D4	7.00
CG2	10.58
CG4	9.46
CG6	7.97
CG8	7.87
CG10	7.55

Table 9. Micro-hardness test results of the glazes produced with the use of DW

Glazes	(GPa)
D4	7.00
DG2	7.49
DG4	7.84
DG6	7.59
DG8	7.69
DG10	7.38

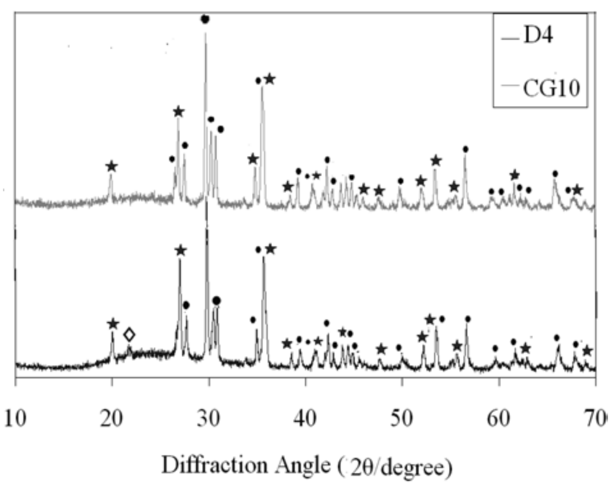

Fig. 1. X-ray diffraction patterns of the D4 and CG10 glazes (★ : Zircon, ◇ : Cristobalite, ● : Diopside).

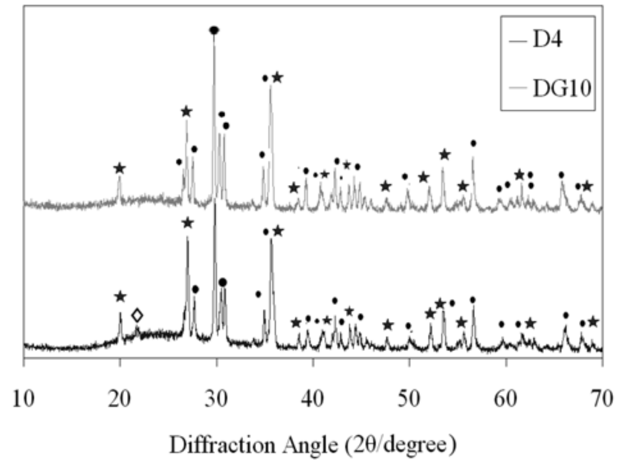

Fig. 2. X-ray diffraction patterns of the D4 and DG10 glazes (★ : Zircon, ◇ : Cristobalite, ● : Diopside).

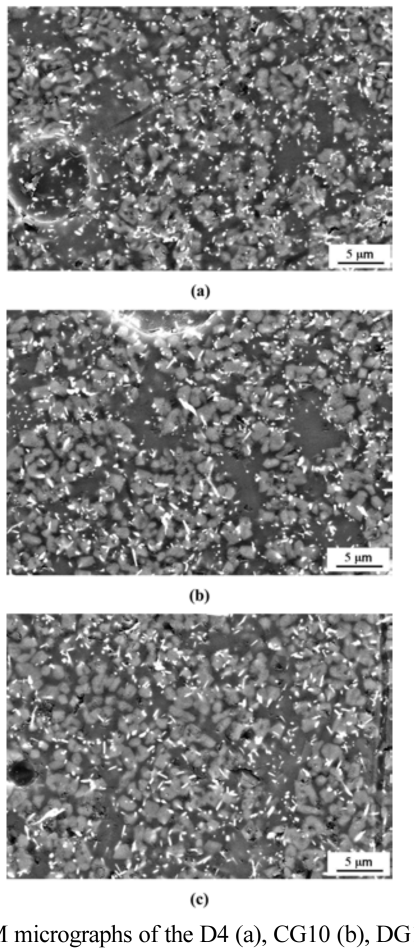

Fig. 3. SEM micrographs of the D4 (a), CG10 (b), DG10 (c) frit-based glazes.

The crystalline phases formed during firing were detected by means of XRD analyses and represented in Figs. 1 and 2. While the D4 glaze contains diopside, cristobalite and zircon, the CG10 and DG10 glazes with CW and DW incorporations have only diopside and zircon without a trace of cristobalite.

SEM micrographs of the D4, CG10 and DG10 glazes

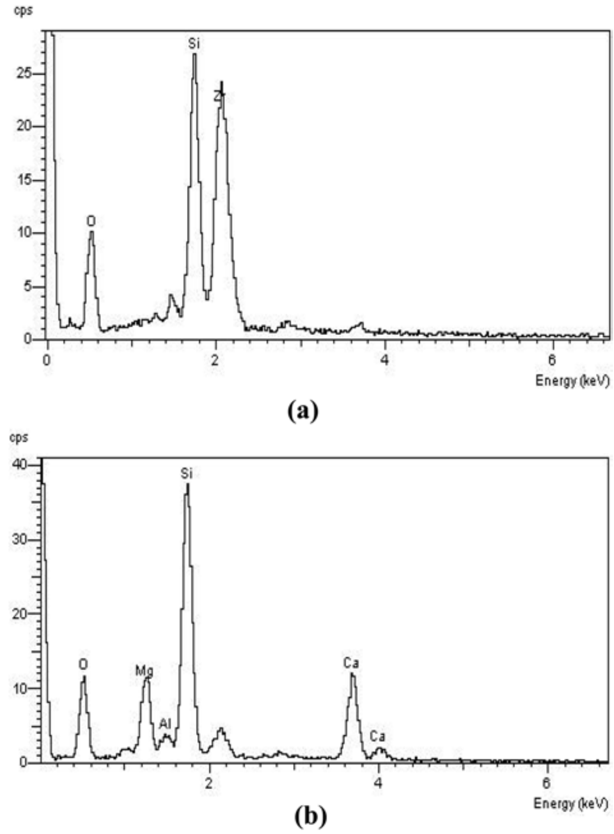

Fig. 4. EDX analyses taken from grey (diopside) (a) and white-coloured (zircon) (b) crystals.

are presented in Fig. 3 exhibiting that incorporating the wastes in frit recipes causes nearly no change in the overall glaze microstructure. Moreover, it was observed that glazes produced by employing borax wastes were fired without remaining porosity and such an evaluation of wastes accelerates the formation of two major crystalline phases in glazes noticed as grey and white-coloured regions (Fig. 3).

EDX analyses in Fig. 4 confirmed that the grey particles belong to diopside, white ones to zircon, agreeing with the XRD patterns showing diopside and zircon crystallization.

Conclusions

In this study, diopside-based glass-ceramic porcelain tile glazes with high mattness were developed via utilizing borax wastes in frit compositions. The CG10 and DG10 frit-based glazes were determined as the most satisfactory ones in terms of crystallization, surface texture, mattness and microhardness compared to the others.

Acknowledgement

The authors would like to thank to TUBITAK (Science, Technology and Research Association of Turkey), Supporting Programme of 1001 Scientific and Technological Research Projects for the financial support to the project numbered 105M351.

We also very much appreciate the permission given by Eskisehir Toprak Ceramic Co. to use their facilities.

References

1. A.P. Luz and S. Riberio, Ceram. Int. 33 (2000) 761-765.
2. M. Dondi, M. Raimondo and C. Zanelli, in Proceedings of the 8th World Congress on Ceramic Tile Quality, (2004) pp. 247-259.
3. V. Biasini, M. Dondi, M. Raimondo., E. Generali and D. Settembre Blundo, Key Eng. Mater. 206-213 (2002) 1799-1802.
4. T. Manfredini, in the Proceeding of the 7th Conference Exhibition of the European Ceramic Society, Edited by E. Armanios (Trans. Tech. Publication, 2002) pp. 2031-2034.
5. W. Holland and G. Beall, in Glass Ceramic Technology (The American Ceramic Society Press, 2002) pp. 372-374.
6. Z. Strnad, in Glass-Ceramic Materials: Liquid Phase Separation, Nucleation and Crystallization in Glasses (Elsevier Press, 1996) pp. 200-203.
7. L. Barbieri, C. Leonelli and T. Manfredini, Ceram. Eng. Sci. Proc., 17 (1996) 11-22.
8. F.J. Torres and J. Alarcon, J. Euro. Ceram. Soc., 23 (2003) 817-826.
9. B. Karasu, G. Kaya and M. Taykurt, in the Abstract Book of the 9th International Ceramic Processing Science Symposium, (2006) p. 25.
10. J.R. Taylor and A.C. Bull, in "Ceramics Glaze Technology (Pergamon Press, 1986) pp. 300-301.
11. W.C. Parmelee, in Ceramic Glazes (Industrial Publications, 1951) pp. 77-79.