DIOPSIDE BASED WHITE PORCELAIN TILES

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INTRODUCTION

In this study, a porcelain tile body containing a substantial amount of alkaline earth elements was formulated to form diopside crystals (and/or wollastonite crystals if required) during firing. It is thought that less pure raw materials, especially clays containing iron oxide can be used without substantially degrading the whiteness of the tile since diopside can dissolve iron in its lattice by substituting for magnesium.

EXPERIMENTAL

The porcelain body was formulated by using a frit, Ukrainian clay, quartz, albite, calcite and altered magnesite. The compositional range of the body is given in Table 1. The frit was added in order to facilitate easy sintering during fast firing. Although any type of frit can be used, a diopside forming frit was developed in order to obtain maximum diopside formation during firing. The frit contained SiO_2, CaO, MgO and K_2O. Industrial melting of the frit was carried out in a rotary furnace at 1400°C.

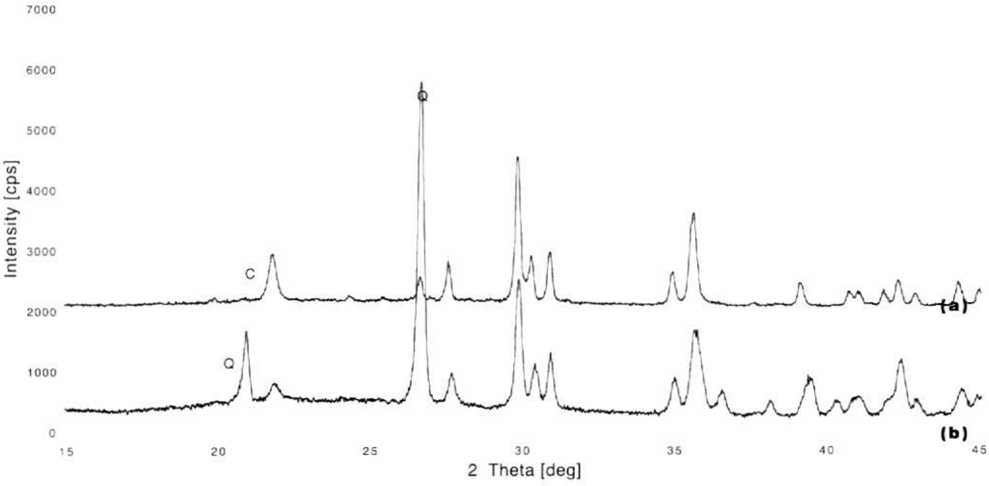
SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2
65-75	7-12	6-12	4-10	1-3	1-3	0.20-0.35	0.30-0.35

Table 1. Oxide composition range of the diopside forming body.

The crystalline phases that developed during firing of the body were characterised by X-ray diffraction (XRD) and shrinkage behaviour was followed by a dilatometer. The microstructure of the sintered porcelain tile was investigated using a scanning electron microscope. For industrial production trials, 30 tons of spray dried granules were prepared and 330x330 mm and 300x600 mm size tiles were pressed at 40 MPa. These tiles were sintered at a peak temperature of 1210°C in an industrial roller kiln for 55 min and 65 min for 330x330 mm and 300x600 mm size tiles, respectively.

RESULTS

The XRD spectrum of the frit after crystallisation at 1130°C in a fast firing furnace and that of the porcelain tile after sintering at 1210°C are given in Fig. 1. Frit crystallises mainly to diopside but some amount of cristobalite also occurs (Fig. 1a). The porcelain tile body contains diopside and quartz as main phases but a trace of cristobalite is also present (Fig. 1b).



C= cristobalite, Q= quartz, unmarked peaks represent diopside.

Figure 1. XRD spectra of (a) the diopside forming frit after crystallisation at 1150C (b) the porcelain tile after sintering at 1215 C.

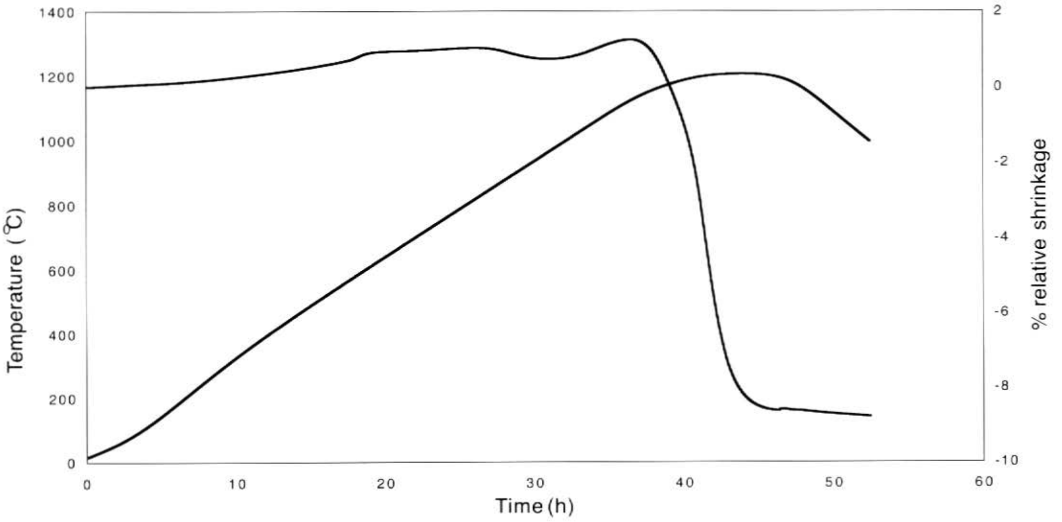


Figure 2. Shrinkage behaviour of the diopside porcelain.

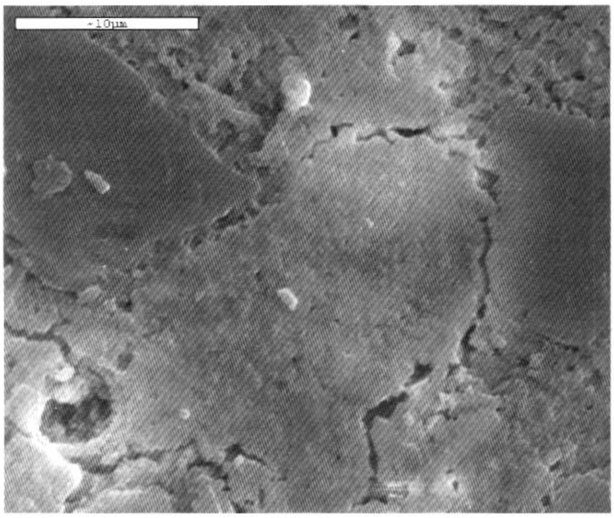


Fig. 2 shows the shrinkage behaviour of the body. There are two volume expansions: one is at 573°C and the other starts at about 1000°C and continues until the onset of shrinkage at 1120°C. The expansion seen at 573°C is due to the well known α-β quartz transformation whereas that starting at 1000°C is thought to result from the volume expansion due to the formation of diopside from the reaction of a mixture of quartz, magnesium and calcium oxides. The amount of volume expansion due to diopside formation is 0.5%. Before this volume expansion, 0.3% volume shrinkage is also evidenced at around 900°C in Fig. 2. This is attributed to diopside crystallisation from the frit. The diopside crystals forming from the frit act as seeds for further diopside formation from the reaction of quartz, magnesium and calcium oxides. Total linear shrinkage was observed to be 9.5%. The SEM micrograph of the sintered tile after light etching with HF is shown in Fig. 3. Diopside and quartz crystals are embedded in a glassy matrix. The size of the diopside crystals is less than 1μm. Some properties of the porcelain tile produced on an industrial scale are listed in Table 2.

Dry strength (kg/cm^2)	13
Fired strength (kg/cm^2) (ISO 10545-4)	625
Water absorption (%)(ISO 10545-3)	0.02
Thermal expansion coefficient (ISO 10545-8)	6,76x10-^{6}
Deep abrasion resistance (mm^3) (ISO 10545-6)	131
Chemical resistance (ISO 10545-13)	UHA
Colour	L=91.55, a=-0.56, b=5,47

Table 2. Properties of diopside based porcelain tiles.

The fired strength of the new tile is somewhat higher than that of commercial porcelain tiles, which lies between 500-550 kg/cm^2. This can be attributed to a large amount of diopside formation in the composition. Whiteness of the tile is also quite high. In order to observe the effectiveness of diopside crystals on whiteness, a diopside forming composition and a traditional porcelain tile composition were prepared with the same amount of Fe_2O_3 (0.33%) and TiO_2 (0.32%). The colour values of the diopside forming composition were L=89,63, a=-0.37, b=7,50, whereas those of the traditional porcelain tile composition were L=81,13, a=-1.21, b=7,96. This is believed to be due to the fact that iron ions are substituted for magnesium ions in the diopside lattice and thus they have the valency of +2. Iron ions with +2 valency do not cause colouring. Deep abrasion resistance is also better than that of commercial porcelain tiles, which varies between 139-147 mm^3. Similarly to the mechanical properties, a large amount of diopside crystals improves abrasion resistance.

CONCLUSIONS

A diopside based new porcelain tile has been developed. This new tile can be produced with high whiteness compared to conventional tiles when the same amount of impurities is present in the composition. Thus, relatively impure raw materials can be tolerated when producing tiles with high whiteness. The new tile is mechanically stronger with higher abrasion resistance. Depending on the CaO/MgO ratio in the starting composition, diopside, diopside-wollastonite and wollastonite containing tiles can be produced.