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Thermal behaviour of clays for traditional ceramics with soda–lime–silica waste glass admixture

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Abstract

The thermal behaviour of clay body mixtures with soda–lime–silica waste glass for the production of traditional ceramics was assessed. The effect of calcite content in the body mixture, of the particle size distribution of glass and of the firing temperature was investigated. In the case of calcite-rich mixtures with glass, increased expansion may take place during firing, at temperatures slightly higher than 700 °C. This effect is attributed to the entrapment of released gases, mainly CO_2. Sintering starts at lower temperatures for the samples with glass, whereas, a second shrinkage zone was observed for temperatures approaching 1000 °C. The content of calcite is one of the main factors determining the mineralogy of the sintered body and the extent of glass devitrification. Devitrite, cristobalite and wollastonite are the products of devitrification within the glass grains, whereas, sodium aluminum silicate, most probably nepheline, has been formed at the inter-granular rim, between glass and ceramic matrix. Increase in the firing temperature and/or decrease in the particle size distribution of glass promotes the densification of the body.

Keywords: Glass; Traditional ceramics; Sintering; Recycling

1. Introduction

Soda–lime–silica (sls) waste glass, a significant proportion of the urban wastes, is a non-hazardous material produced in increasing quantities in Europe. Its reuse is still limited[1] by several factors dealing with societal and technological parameters. An overview of available processes for secondary recycling of sls waste glass is presented elsewhere.[2,3] Use of sls waste glass in the heavy clay industry may be a potential solution to the problem.

In 1957, Everhart[4] suggests that the addition of pulverized glass at a percentage higher than 2.5% results in improved values of fired strength and water absorption. As objectionable features, the author underlines a slight tendency of glass to develop a vitreous surface scum and the abrupt over-firing at 1100–1150 °C approximately. In 1972, Tyrrell and Goode[5] report improved technological characteristics for the body formulations with glass and a significant energy conservation. Tyrell et al.[6] also published on the fabrication and cost evaluation of building bricks made of waste glass, deriving from municipal incinerators. The authors conclude that glass-clay brick can be produced commercially without difficulty. In 1972, Shutt et al.,[7] developed wall panels and bricks with a varying glass content up to 94%, 6% clay and crushed brick. Compression and rupture tests of the bricks classified them stronger than concrete, whereas, water absorption values were similar or lower than concrete. In 1991, Gleditzsch et al.[8] reported that for increasing clay content in the glass-containing clay mixture, the sintering range shifts towards higher temperatures and the maxima of density and flexural strength, as a function of firing temperature, are less salient. Quartz, cristobalite and nepheline were identified as the main crystalline phases in the sintered bodies. In 1994, the glass industry trade association in the UK, British Glass,[9] reported that up to 10% addition of finely ground sls glass in commonly used brick clays can provide comparable strength to the bricks as if the temperature were 50 °C higher. In a more applicable and technology orientated level, the Clean Washington Center[10] has performed research on recycling of sls glass as a raw material for ceramics. A series of “best practices” guidelines has been also issued for the dissemination of results. In 2002, Ranogajec et al.[11] suggested that sls glass addition in a mixture for ceramic tiles activated the thermal decomposition of calcite and dolomite enabling the enrichment of alumino-silicate phases in CaO and MgO. The pores’ size distribution of the sintered ceramics was

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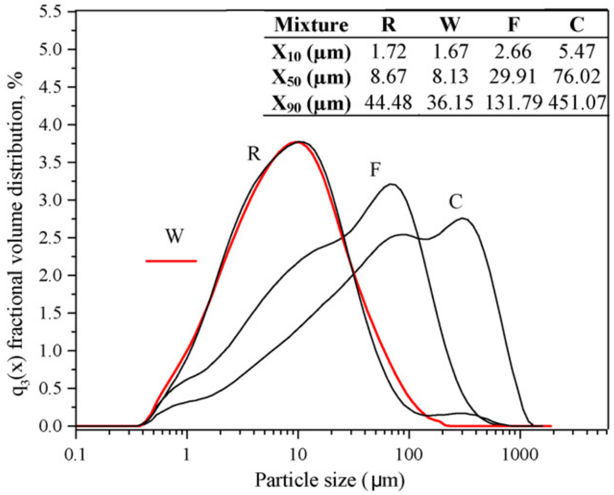
modified and the water absorption reduced. The glass used had a chemical composition considerably different from typical sls glass. Finally, Pontikes et al.[12] in 2005, report that 30 wt.% sls glass, in substitution of roofing tile body mixtures, led to fired products with improved characteristics in terms of water absorption and bending strength. Particle size distribution of glass and firing temperature both influenced the physical and mechanical characteristics of the fired bodies, whereas, had a minor effect on the mineralogy.

It becomes apparent from the above that use of glass in the production of traditional ceramics can be beneficial. Other factors, such as the solidification/stabilization effect minimising leaching phenomena, due to the promoted formation of glassy phase, or the reduced gas emissions on firing, further advance its use. Nonetheless, only a portion of the above studies deals with addition of sls glass to a clay body mixture, suitable for production of ceramics. Moreover, issues such as the behaviour during firing, the microstructure of the sintered bodies and the role of calcite content of the body mixture, still remain partially unaddressed. To establish a fundamental understanding of the governing mechanisms and thus enable a more efficient design of the raw blends and control of the sintering, the thermal behaviour of clay body mixtures, containing sls waste glass, was studied. The influence of the calcite content, the particle size distribution of glass and the firing temperature were the process parameters examined.

2. Experimental

Two clay body mixtures, industrially used for the production of bricks and roofing tiles, were used. Both mixtures consist of quartz, calcite, (Mg, Fe)-chlorite, muscovite and albite, their main difference being in the calcite and quartz content. Traces of mixed smectitic interlayer minerals, kaolinite and K-Feldspar are also likely to be present, whereas, illite was identified in the calcite-rich formulation as a minor constituent. The calcite-poor body gives fired bodies of orange–red colour, whereas, the calcite-rich gives white-cream; the body mixtures are thus denoted by letters R, for red, and W, for white. The sls glass was a typical waste glass used in two different particle size distributions, fine (F) and coarse (C), obtained by milling the cullet in a planetary mill. The particle size distribution is reported in Fig. 1. For each clay body mixture, three different series of samples were prepared: the reference one and one with coarse and fine sls glass, respectively, replacing the clay body mixture at a fixed percentage of 30 wt.%. The samples with fine glass are named RF and WF, whereas, the samples with coarse glass RC and WC, the first letter denoting clay body mixture and the second particle size distribution of glass. In Table 1, the chemical composition of the samples is presented.



Mixture	R	W	F	C
X_{10} (μm)	1.72	1.67	2.66	5.47
X_{50} (μm)	8.67	8.13	29.91	76.02
X_{90} (μm)	44.48	36.15	131.79	451.07

Fig. 1. Particle size distribution of clay body mixtures W and R, and of fine, F, and coarse, C, glass.

The thermal behaviour was studied by simultaneous differential thermal analysis and thermogravimetry, DTA-TG, (STA 409, Netzsch, Germany) and dilatometry (402ES, Netzsch, Germany). For DTA-TG analysis, samples were pulverized to a particle size less than 125 μm and tested in static air with a heating rate of 10 °C/min. Dilatometry was performed on rods, 25 mm in length and 5 mm in diameter, in static air, with a heating and cooling rate of 3 °C/min. The samples for dilatometry have been taken from extruded rods, after green machining and polishing with abrasive papers. The mineralogical composition of the fired samples was determined by powder X-ray diffraction analysis (PW1830, Philips, The Netherlands). The operating parameters were Cu Kα radiation, 30 mA and 40 kV, for a 2θ range from 10° to 70°. Analysis was performed on samples fired in a laboratory muffle furnace at three maximum temperatures 900, 950 and 1000 °C. The heating rate from room temperature to 600 °C was approximately 60 °C/h, holding time at 600 °C was 2 h, from 600 °C to maximum firing temperature heating rate was 40 °C/h and 4 h soaking time. Samples were left to cool inside the furnace until room temperature.

The microstructure of the fired samples was evaluated by means of optical (Metalloplan, Leitz, Germany) and scanning electron microscope, SEM, (JSM-6300, Jeol, Japan) equipped with an energy dispersive X-ray spectrometer, EDS, (Oxford, UK). Optical microscopy was performed on thin sections of the sintered samples, prepared according to the standard techniques, whereas, electron microscopy was used to observe both

Table 1
Chemical composition, in wt.%, of clay body mixtures W and R and soda–lime–silica (sls) glass

Material	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	L.O.I.	$CaCO_3$
R	61.43	12.31	8.40	5.45	1.98	1.77	0.52	7.41	13.8
W	50.34	9.11	13.19	4.91	2.04	1.98	1.66	16.02	22.7
sls Glass	72.60	0.97	10.33	0.28	1.84	0.25	13.00	–	–

fractured and polished surfaces. The preparation of the polished samples involved cold-resin mounting and polishing by means of an abrasive polishing device (Knuth-Rotor 2, Struers, Denmark) using SiC papers, up to 2400 grid. For SEM observation all specimens were Au-coated. For EDS analysis, the default standards of LINK ISIS have been used and the results are not normalized.

3. Results and discussion

The glass transition point was determined with DTA[13] and was found to be 540 °C. The DTA-TG curve for R and R with 30 wt.% sls glass is presented in Fig. 2. Endothermic peaks appearing at 124–126 °C and 484–489 °C are attributed to the dehydration of clay minerals, whereas, the peak at 571 °C corresponds to quartz inversion. The calcite dissociation initiates at 650–655 °C and has been concluded by 750 °C for R with glass and 770 °C for R. For higher temperatures, no reactions were identified. Both samples demonstrate a constant weight loss that is practically completed after the dissociation of calcite. For higher temperatures the weight loss continues but is only minimal, approximately 1%. The results from DTA-TG analysis for W and W with 30 wt.% sls glass present similar behaviour.

The dilatometry curves of the W group of samples are depicted in Fig. 3. For temperature in the range of 720 °C, WF undergoes an additional expansion. This is attributed to the entrapment of CO_2 resulting from the dissociation of calcite. It is more evident for W mixtures and fine glass, in view of the higher calcite content and the higher specific surface of glass which reduces the path ways for gas escape at a greater extent. Sintering starts at 733 and 744 °C for WF and WC, respectively; for W sintering starts at 770 °C approximately. At higher temperatures all mixtures undergo the typical expansion due to the presence of Ca-rich crystalline phases.[14] In the glass containing mixtures, a further shrinkage occurs before 1000 °C. This effect is attributed to the development of low viscosity liquid phase and can lead to dimensional deformation of the samples.[12] The firing shrinkage is higher for the mixtures with glass; WF presents the highest value. In the case of R group of samples, no expansion hump is recorded in the dilatometric curves due to the moderate calcite content.

In the XRD spectra, for coarse glass (C) fired at 900, 950 and 1000 °C, devitrite and wollastonite are present as the main devitrification products. The main difference is observed for firing at 1000 °C, where the peaks of wollastonite have relatively higher intensities. The XRD patterns for R and RC mixtures fired at 900, 950 and 1000 °C are reported in Fig. 4(a) and (b), respectively. The patterns for RF are similar to the ones for RC, at all tested temperatures. In the reference body R and firing at 900 °C,

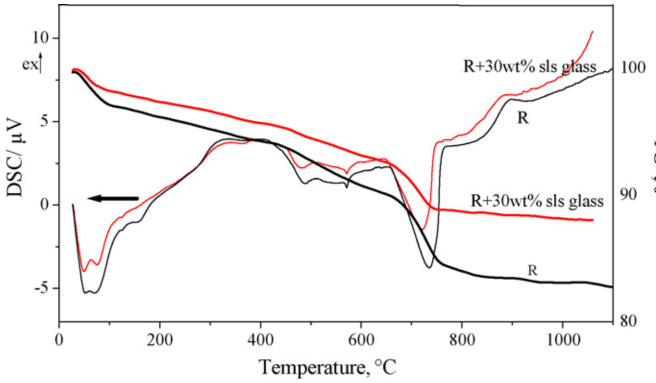


Fig. 2. DTA-TG curves of clay body mixture R and of R with 30 wt.% sls glass.

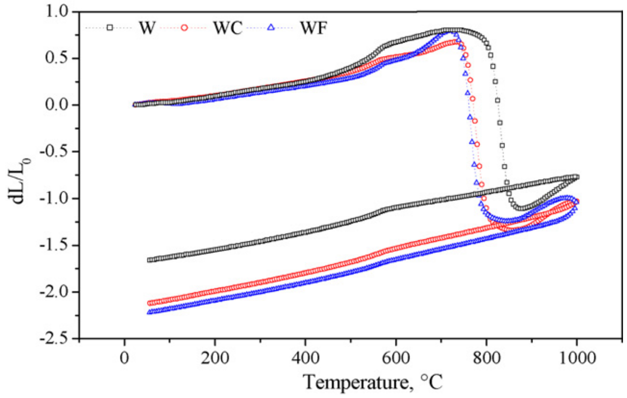


Fig. 3. Dilatometry curves of clay body mixture W and of W with coarse and fine glass, WC and WF, respectively.

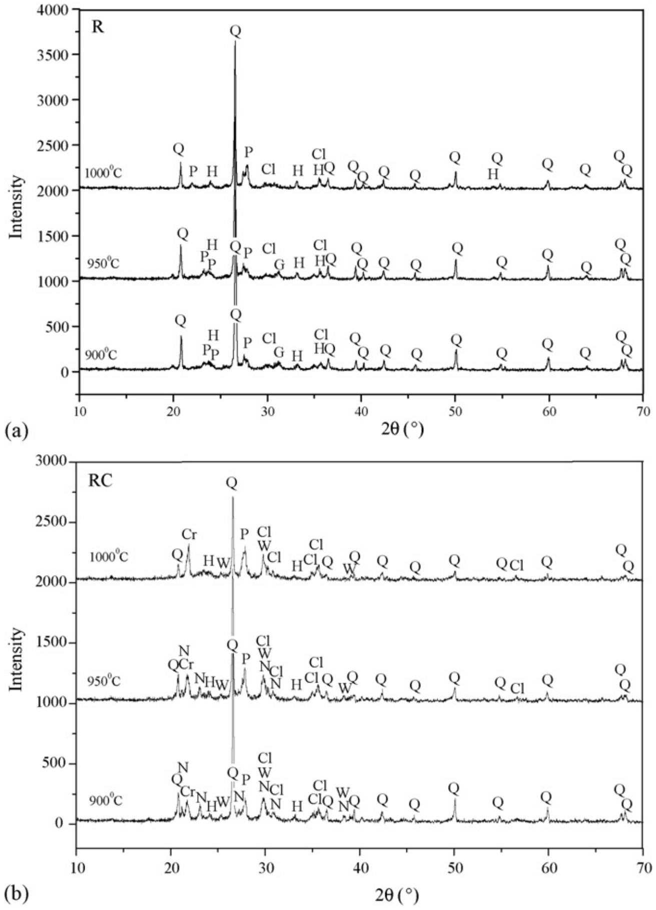


Fig. 4. X-ray diffraction patterns of (a) clay body mixture R and (b) R with coarse glass, RC, at the three sintering temperatures. Q: Quartz, Cl: Clinopyroxenes, H: Hematite, W: Wollastonite, G: Gehlenite, P: Plagioclase, Cr: Cristobalite, N: Nepheline.

the identified phases were quartz, plagioclase, clinopyroxenes, gehlenite and hematite. At a higher temperature, gehlenite gradually decreases, whereas, for firing at 1000 °C, the characteristic peak of anorthite at 21.97° (4.04 Å) becomes visible. In the RC and RF samples, the mineralogy is considerably different with respect to R. For firing at 900 °C, the identified phases were quartz, plagioclase, hematite, clinopyroxenes, and cristobalite, wollastonite and sodium aluminum silicate, most probably nepheline, as new phases. Nepheline has been identified by other authors as well, for a similar system of sls glass and clay.[5,8] Gehlenite, present in R for the same firing temperature, was not identified. This is attributed to the reduced availability of calcium rich microsites, linked with gehlenite formation,[15,16] due to the diffusion of Ca^{+2} in the glass grains. Sodium aluminum silicate was not present, whereas, the presence of devitrite was not confirmed due to peak overlapping. However, results from optical microscopy did verify its existence. At a higher temperature, the peaks of nepheline gradually decrease and at 1000 °C was not identified. The peaks of cristobalite and plagioclase present higher intensity peaks relatively to quartz.

The XRD patterns for W and WC mixtures fired at 900, 950 and 1000 °C are presented in Fig. 5(a) and (b), respectively. Also in this case, the XRD patterns for WF are similar to the ones for WC. In W fired at 900 °C, the identified phases were quartz, clinopyroxenes, gehlenite and plagioclase. For an increasing firing temperature the peaks of gehlenite gradually decrease, whereas, the clinopyroxenes to quartz intensity ratio of peaks increases. As in the case of R body, gehlenite is not present for firing at 1000 °C. For WC and WF fired at 900 °C, quartz, clinopyroxenes, and gehlenite were identified, in addition to wollastonite, sodium aluminum silicate and cristobalite resulting from the presence of glass. Plagioclase is also likely. For the samples fired at 950 °C, an increase of the wollastonite to quartz intensity ratio of peaks is observed, whereas, gehlenite has peaks of relatively lower intensity. At 1000 °C, gehlenite is not present, whereas, the intensity of the peak corresponding to wollastonite and clinopyroxenes (30.0°) is greatly increased. Nepheline and devitrite are both likely to be present as a minor constituent.

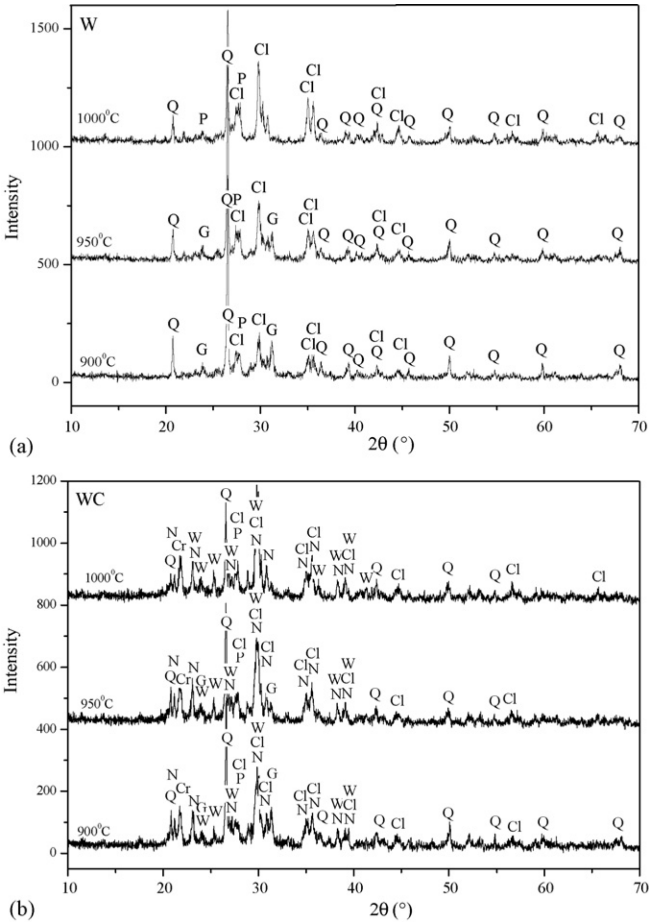


Fig. 5. X-ray diffraction patterns of (a) clay body mixture W and (b) W with coarse glass, WC, at the three sintering temperatures. Q: Quartz, Cl: Clinopyroxenes, G: Gehlenite, P: Plagioclase, W: Wollastonite, Cr: Cristobalite, N: Nepheline.

The influence of the glass-particles' size distribution on the mineralogy of the fired products was not established due to the large number of crystalline phases present. Nevertheless, it seems that the crystalline phases identified are independent of the glass-particles' size distribution. Changes in the relative intensities of the devitrification products, observed in the XRD patterns, can be linked to the fact that smaller glass-particles sinter faster, whereas, the volume of the coarse ones enables crystallization phenomena to take place more readily. SEM and thin sections images have provided evidence that wollastonite crystals were greater in size in coarse-grained glass.

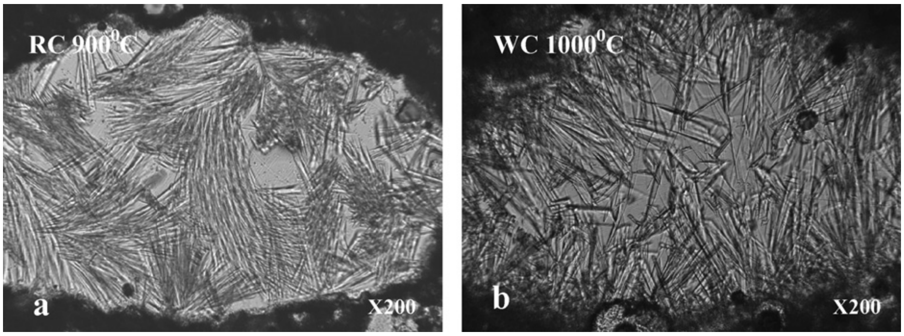


Fig. 6. (a) Thin section of clay body mixture R with coarse glass, RC, fired at 900 °C, 200×. Brush-like crystals of devitrite are mainly present. Lath-shaped crystals of wollastonite and spherulites, most probably cristobalite, are also visible, (b) Thin section of body mixture W with coarse glass, WC, fired at 1000 °C, 200×. Lath-shaped crystals of wollastonite are clearly present.

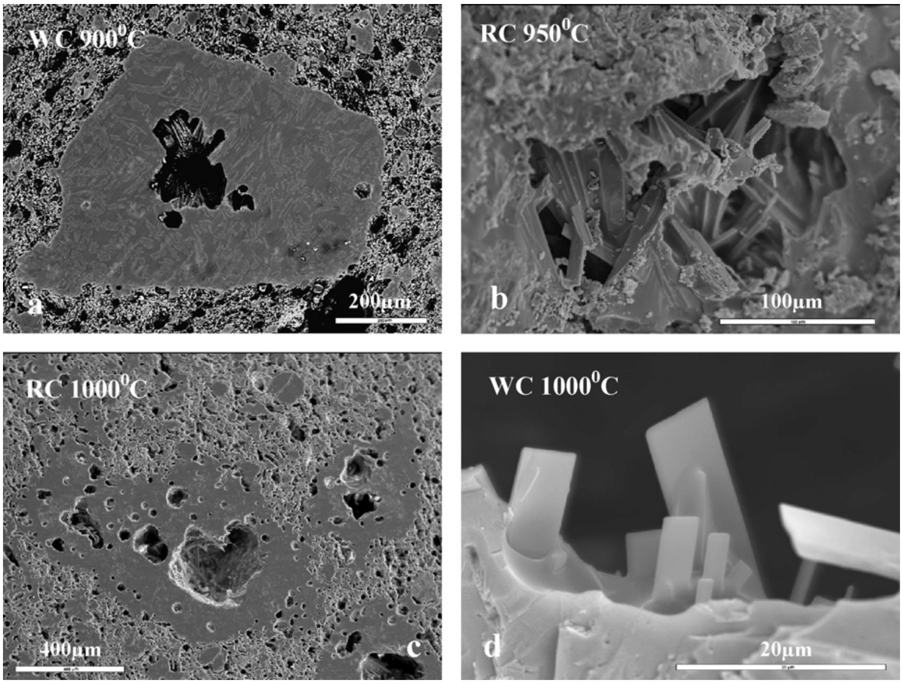


Fig. 7. (a) Backscattered electrons image of polished surface of clay body mixture W with coarse glass, WC, fired at 900 °C. Wollastonite crystals are widespread in the surface. Crystal growth is more pronounced in the centre where a closed pore has been formed, (b) fracture surface of clay body mixture R with coarse glass, RC, fired at 950 °C. The centre of a glass grain is depicted where a number of elongated and angular crystals have been formed, (c) polished surface of RC fired at 1000 °C. Extended crystallization, resulting in large closed pores is visible. (d) The wall of a pore in a glass grain from WC fired at 1000 °C. Lath-shaped wollastonite crystals having formed a meniscus with the glassy phase are visible.

Optical microscopy on thin sections of fired glass, revealed two main crystal formations present. Brush-like crystals were identified as devitrite ($Na_2O{\cdot}3CaO{\cdot}6SiO_2$).[17] Lath-shaped crystals were identified as wollastonite.[17–19] At 1000 °C devitrite crystals were not so extensively formed probably due to dissolution. For RC and WC, Fig. 6(a) and (b), devitrite and wollastonite crystals were present again within the glass grains. Spherulites and fern-leaf shaped crystals were also present and identified as cristobalite.[17] Wollastonite crystals were both greater in size for WC and for increasing firing temperature.

Microstructural observation on polished sections by SEM, revealed that glass grains present good adhesion with the surrounding matrix for all mixtures. For RC fired at 900 °C the presence of widespread elongated crystals in the bulk of the glass grain was evident. For WC, fired at the same temperature, the crystallization within the glass grain was more pronounced. A closed pore is usually observed in the centre of the glass grains, Fig. 7(a), inside of which newly formed crystals, elongated-angular in shape, are present. The formation of closed pores was more extended for higher firing temperatures and was sys-

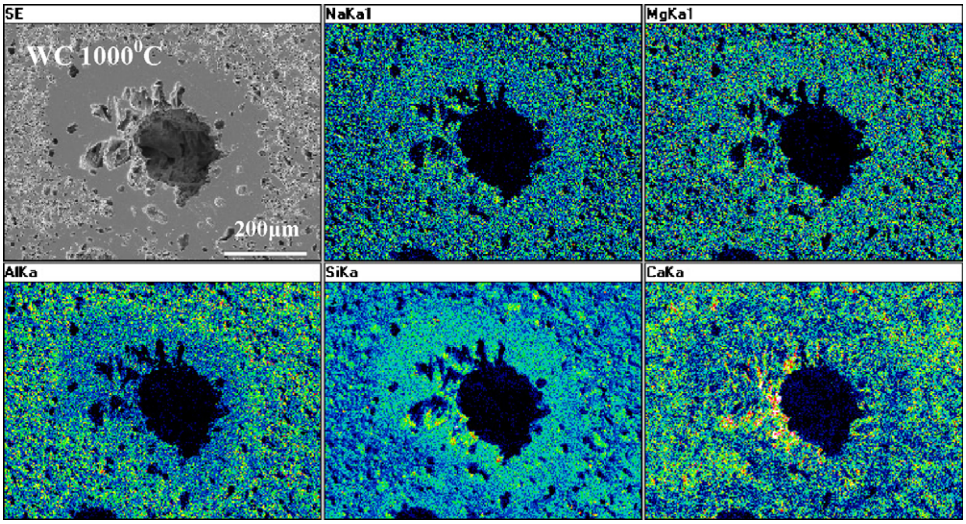


Fig. 8. Topographic elemental analysis over a polished section of a glass grain in clay body mixture W with coarse glass, WC, fired at 1000 °C. Wollastonite crystals exist in the high Ca^{+2} regions and pores. Al^{+3} is likely to form a diffusion rim.

tematically more intense for W mixtures. The main contributing mechanism is the precipitation of the crystals of wollastonite. The effect is intensified in view of the mass flux from the glass grain to the ceramic matrix, under the exerted capillary forces. Pore formation has been possibly assisted by the formation of gas-bubbles. As devitrification proceeds, the amount of glassy phase decreases and the concentration of dissolved gases in the glassy phase increases. If the solubility limits are overcame bubbles of gas can nucleate at the interface between crystal and glass.[20] For firing at 950 °C, the morphology of the glass grains is altered. The crystallization growth is enhanced and for both WC and RC closed pores are present. The shape of the crystals is also altered, towards better-formed lath-shaped crystals, although in the case of RC the prevailing crystal habit is still elongated-angular, Fig. 7(b). For firing at 1000 °C, the crystallization has been further enhanced, Fig. 7(c) and (d). The crystals are greater in dimensions compared to lower firing temperatures and in the case of WC well-defined lath-shaped crystals are formed, Fig. 7(d). Unlike firing at 900 °C, where wollastonite crystals were widespread in the bulk of the glass grain, there seems to be a concentric zone of crystals surrounding the closed pore and absence towards the interface. This behaviour is attributed to the unavailability of the crystalline particles to undergo viscous flow. EDS analysis on these crystals indicate an average composition of (mol%) SiO_2: 59%, CaO: 39%, close to wollastonite composition. Minor constituents were Fe_2O_3, MgO, Na_2O and K_2O, all typically accounting for <1 mol%. In Fig. 8, topographic elemental analysis with EDS revealed areas richer in Al at the inter-granular rim between glass and ceramic matrix, a possible indication of crystalline phases development.

4. Conclusions

Glass addition in clay body mixtures influenced the formation of gehlenite and increased the number of crystalline phases present in the sintered bodies. Cristobalite, devitrite and wollastonite result from the devitrification of glass and sodium aluminium silicate, most probably nepheline, appears to crystallise in the inter-granular rim between glass and ceramic matrix.

For temperatures higher than the glass transition temperature at 540 °C, glass contributes to the reduction of open porosity. In the case of calcite-rich body mixture with glass, increased expansion may occur at temperatures slightly higher than 700 °C due to the entrapment of released gases, mainly CO_2. Sintering starts at lower temperatures for the samples with glass and increase in the firing temperature promotes the densification of the body. A second shrinkage zone may appear for temperatures approaching 1000 °C and potentially lead to dimensional deformation. For higher firing temperatures the growth of wollastonite is enhanced, whereas, at 1000 °C, sodium aluminium silicate is not identified in the calcite-poor mixture with glass and partial dissolution of devitrite takes place.

The content of calcite in the body mixtures with glass is one of the main factors determining the mineralogy of the sintered body and the extent of glass devitrification. In the calcite-poor mixture with glass, elongated-angular crystals of wollastonite are present within the glass grains. In the calcite-rich mixture with glass, the crystal growth of wollastonite within the glass grains is enhanced, as a result of the higher availability of CaO, whereas, the morphology is lath-shaped, plate-like.

The influence of the particle size distribution of glass on the mineralogy of the fired products appears to be marginal however the crystal growth of wollastonite is enhanced in coarse-grained glass. A finer particle size distribution of glass enhances the densification of the body.

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