Mater. Res. Soc. Symp. Proc. Vol. 1765 © 2015 Materials Research Society
DOI: 10.1557/opl.2015.810

Influence of Glassy Additives on the Formation of Crystalline Phases in Sintered Red Ceramic Bodies

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ABSTRACT

The main objective of this research work was to study the influence of glassy additives on the formation of crystalline phases in sintered red ceramic bodies used for the fabrication of ceramic floor tiles, whose composition is a mixture of quartz (SiO_2), kaolinite [$Al_2Si_2O_5(OH)_4$], albite ($NaAlSi_3O_8$), muscovite [$KAl_2(Si_3Al)O_{10}(OH)_2$] and calcite ($CaCO_3$). The additives used were: fly ash, soda-lime glass, borosilicate glass, glass frit, $Na_2P_3O_{10}$ and cryolite (Na_3AlF_6). These were added in variable proportions to the nominal composition of the red ceramic bodies, either as single or as combined additions, aiming to accelerate the densification of the materials during their sintering process. For all the additive types used, the crystalline phases formed in the samples sintered using a peak temperature ranging from 950 to 1030 ºC were: quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), and hematite (Fe_2O_3). It is known that the presence of anorthite is particularly beneficial for the mechanical properties, chemical stability and densification of the sintered red ceramic bodies. However, some of the considered additions tended to be detrimental for the formation of this phase in the studied materials, especially at the lowest peak sintering temperature employed. This was verified by means of XRD and SEM analysis.

INTRODUCTION

The addition of glassy additives to the red ceramic bodies used for the fabrication of ceramic floor tiles can accelerate their densification during the sintering process [1-3]. However, the employment of these additives could affect the nature and microstructural characteristics of the crystalline phases that are formed in the sintered ceramic bodies, with a likely detrimental effect on their mechanical, physical and chemical properties. Crystallization of anorthite [$CaAl_2Si_2O_8$, calcium aluminosilicate belonging to the family of feldspars (plagioclase)] is particularly desired in the microstructure of the red ceramic bodies, since it significantly increases their mechanical properties, chemical stability and density. Thus, it is of practical importance to verify that the formation of this phase is not significantly affected by the addition of glassy fluxing agents to the initial mixture of raw materials employed for the production of the red ceramic bodies.

EXPERIMENTAL DETAILS

The nominal composition of the red ceramic bodies was (in wt.%): 50-60 % SiO_2, 17-19% Al_2O_3, 5-7% Fe_2O_3, 2-3% CaO and 2-3% K_2O. This was formulated from a mixture of stoichiometric proportions of quartz (SiO_2), kaolinite [$Al_2Si_2O_5(OH)_4$], albite ($NaAlSi_3O_8$), muscovite [$KAl_2(Si_3Al)O_{10}(OH)_2$] and calcite ($CaCO_3$). Table I shows the glassy additives used in variable proportions for the initial mixtures of raw materials. Only the results obtained for some selected addition levels of the additives are reported in this work.

Table I. Additives employed (all compositions are in wt.%).

Additive	Identification	Composition
Fly ash (byproduct of a Mexican state-owned coal-burning power generation plant)	FA	59% SiO_2, 2% CaO, 28.6% Al_2O_3, 5.6% Fe_2O_3, and 4.7% of other minor oxides
Soda-lime glass	MV	70.9% SiO_2, 14.3% Na_2O, 9.3% CaO, 3.5% MgO, and 2% of other minor oxides
Borosilicate glass	VE	39% SiO_2, 33% B_2O_3, and 27.9% Na_2O
Glass frit	Glass frit	56.9% SiO_2, 14.8% CaO, 9.6% ZnO, 9.3% Na_2O, 5% Al_2O_3, 1.4% K_2O, 1.4% MgO, and 1.6% of other minor oxides
$Na_2P_3O_{10}$	$Na_2P_3O_{10}$	Reagent-grade
Cryolite (Na_3AlF_6)	C	Reagent-grade

The initial mixture of raw materials (with or without the addition of the glassy additives) was milled in a planetary mill for 15 minutes in order to homogenize it. Then, 20g-charges of it were pressed at 30 MPa, obtaining cylinders with a diameter of 4 cm and a height of 1 cm (5 specimens for each additive). These samples were fired in a microwave furnace, according to the following thermal cycle: 1) heating from room-temperature up to 830 ºC at a rate of ~18 ºC/min; 2) heating from 830 ºC up to a peak temperature ranging from 950 to 1030 °C at a rate of 7.5 ºC/min, where they were held for 30 min, and 3) cooling down to room-temperature at a rate of ~4 ºC/min.

All samples were analyzed by X-Ray Diffraction (XRD) using a Philips X´Pert diffractometer and CuKα radiation, as well as by Scanning Electron Microscopy (SEM) employing a Philips XL 30 ESEM device. For the XRD analysis, the sintered samples were ground with an alumina mortar and pestle until a particle size of 25-75 μm was obtained. For the SEM analysis, the samples were mounted in bakelite and then ground using SiC papers with successive grit sizes from 80 grit to 1200 grit. The ground surface was then polished using diamond particles with successive sizes of 3 and 1 μm.

DISCUSSION

For reference purposes, Figure 1 shows the XRD patterns obtained for red ceramic bodies of nominal composition in their green as well as in their sintered states, without any glassy additives. As it can be seen, the crystalline phases formed in the ceramic bodies of nominal composition sintered using a peak temperature of 1000 °C were quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), and hematite (Fe_2O_3).

Figures 2 and 3 show the XRD patterns obtained for red ceramic bodies sintered using peak temperatures ranging from 950 to 1030 °C, in the first case with the addition of either 10% FA + 5% VE (Fig. 2a) or 10% MV + 5% VE (Fig. 2b), and in the second case with the addition of either 5% glass frit (Fig. 3a) or 5% FA + 1%C + 4%VE + 1% $Na_2P_3O_{10}$ (Fig. 3b). All additions are in wt.%. As it can be noticed, for all peak sintering temperatures considered in this work the crystalline phases formed in the ceramic bodies were again quartz, anorthite and hematite, independently either of the nature of the employed additives or of the amount of the latter materials added to the nominal composition of the ceramic bodies. However, it can also be noted that when a peak sintering temperature lower than 1000 °C was employed, the relative intensity of the XRD reflections corresponding to all crystalline phases formed under those conditions decreased considerably. This was more evident for the case of anorthite, in such a way that only a very small relative proportion of this phase could be detected in the samples sintered using a peak temperature of 950 °C. The relative proportion of anorthite increased in the ceramic bodies with increasing peak sintering temperature, which was more notorious for the case of the additions of the 10% FA + 5% VE mixture (Fig. 2a) and 5% of the glass frit (Fig. 3a).

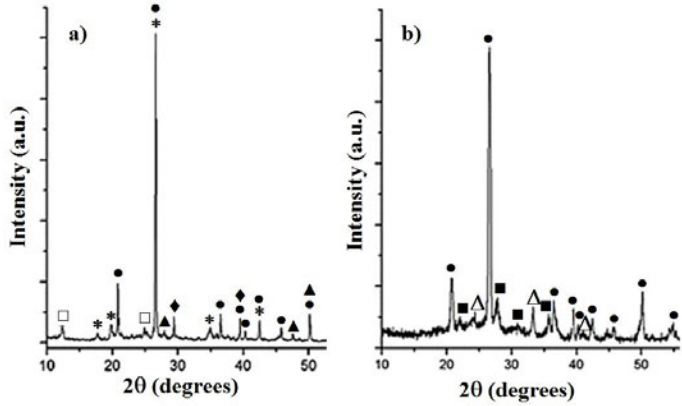

Figure 1. XRD patterns obtained for red ceramic bodies of nominal composition without glassy additives: a) green mixture, and b) mixture sintered at 1000 °C. Key: ● Quartz (SiO_2), □ Kaolinite [$Al_2Si_2O_5(OH)_4$], ▲ Albite ($NaAlSi_3O_8$), ✶ Muscovite [$KAl_2(Si_3Al)O_{10}(OH)_2$], ♦ Calcite ($CaCO_3$), ■ Anorthite ($CaAl_2Si_2O_8$), and △ Hematite ($Fe_2O_3$).

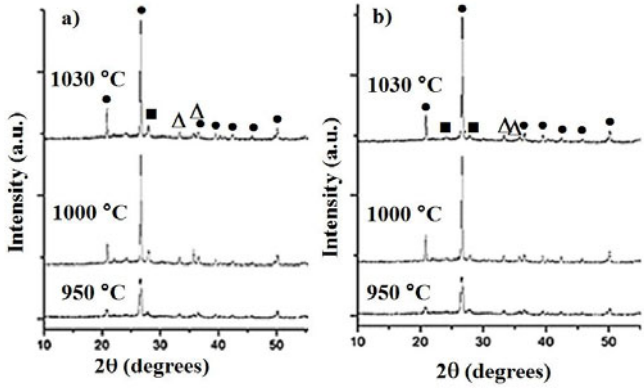

Figure 2. XRD patterns obtained for red ceramic bodies sintered using peak temperatures ranging from 950 to 1030 °C, with the addition of (in wt.%): a) 10% FA + 5% VE, and b) 10% MV + 5% VE. Key: ● Quartz (SiO_2), ■ Anorthite ($CaAl_2Si_2O_8$), and △ Hematite (Fe_2O_3).

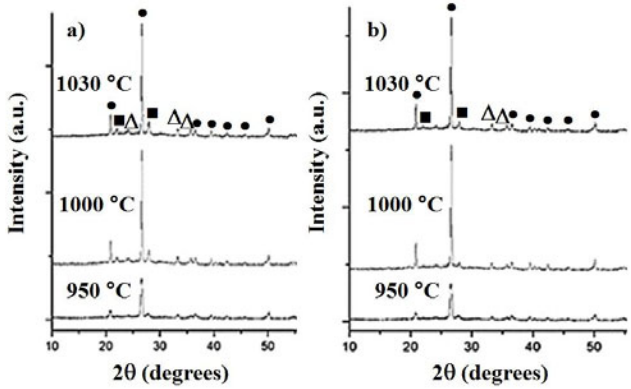

Figure 3. XRD patterns obtained for red ceramic bodies sintered using peak temperatures ranging from 950 to 1030 °C, with the addition of (in wt.%): a) 5% glass frit, and b) 5% FA + 1%C + 4%VE + 1% $Na_2P_3O_{10}$. Key: ● Quartz (SiO_2), ■ Anorthite ($CaAl_2Si_2O_8$), and △ Hematite (Fe_2O_3).

These results suggest that the addition of 10% MV + 5% VE (Fig. 2b) and 5% FA + 1%C + 4%VE + 1% $Na_2P_3O_{10}$ (Fig. 3b) mixtures tended to be detrimental for the formation of anorthite in the ceramic bodies sintered using a peak temperature of 950 °C, and that this effect could not be completely overcome by increasing the sintering temperature either up to 1000 °C or 1030 °C. This is likely related to a strong fluxing effect caused by both additions in the initial mixture of raw materials, which probably resulted in the generation of a large amount of transient liquid

during sintering at any of the peak temperatures considered in this work. The generation of a considerable amount of transient liquid at those temperatures could interfere with the reaction mechanism responsible for the formation of anorthite. It has been reported [4] that the formation of anorthite occurs according to the following reaction mechanism:

a) First, gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) intermediate phase is crystallized from metakaolin ($Al_2O_3{\cdot}2SiO_2$) and calcium oxide according to reaction 1; metakaolin and CaO are obtained from the calcination of kaolinite and calcite, respectively.

$$Al_2O_3{\cdot}2SiO_2 + (2 + n)\,CaO \rightarrow 2CaO{\cdot}Al_2O_3{\cdot}SiO_2 + nCaO{\cdot}SiO_2 \quad (1)$$

b) Then, anorthite is formed by reaction of gehlenite with alumina and silica from metakaolin, and with silica from the remaining fine quartz (reaction 2).

$$2CaO{\cdot}Al_2O_3{\cdot}SiO_2 + 3SiO_2 + Al_2O_3 \rightarrow 2(CaO{\cdot}Al_2O_3{\cdot}2SiO_2) \quad (2)$$

Lastly, when the microstructures of the sintered materials with additions of either 10% FA + 5% VE mixture (Fig. 4a) or 5% glass frit (Fig. 4b) were compared, it could be noticed that in the second case the material was denser and had a smaller mean particle size, which suggested that this material had the potential to show the best mechanical properties among both materials. Some of the largest pores found in the material of Fig. 4a had the characteristic spherical shape associated with the hollow glassy cenospheres contained in the FA, which indicates a lack of chemical interaction of the added FA with the rest of the components of the initial mixture of raw materials. This could be avoided by subjecting the precursor mixture to an additional milling step, prior to the sintering process.

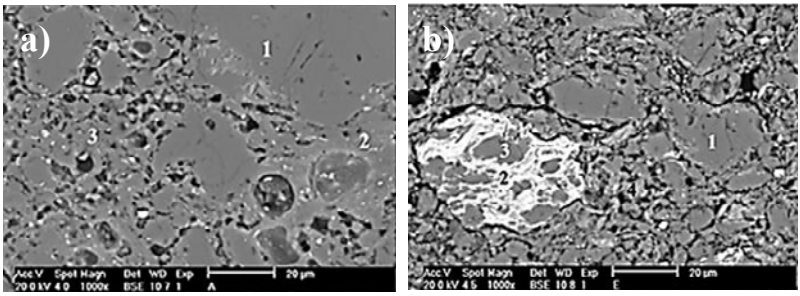

Figure 4. SEM micrographs obtained for a red ceramic body sintered using a peak temperature of 1000 °C, with the addition of: a) 10% FA + 5% VE (in wt. %); key: zone 1, quartz; zones 2 and 3, anorthite and hematite; b) 5 wt.% glass frit; key: zones 1 and 3, quartz; zones 2 and 4, anorthite and hematite.

CONCLUSIONS

For all the additive types used, the crystalline phases formed in the samples sintered using a peak sintering temperature ranging from 950 to 1030 ºC were: quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), and hematite (Fe_2O_3). However, the addition of the 10% MV + 5% VE and 5% FA + 1%C + 4%VE + 1% $Na_2P_3O_{10}$ mixtures tended to be detrimental for the formation of anorthite in the ceramic bodies, especially at the lowest peak sintering temperature employed, and this effect could not be completely overcome by increasing the peak sintering temperature either to 1000 or 1030 °C. Although the addition of both the 10% FA + 5% VE mixture and 5% glass frit promoted the formation of anorthite in the materials sintered at all peak temperatures employed in this work, the densest microstructure and the smallest mean particle size were obtained for the second additive.

ACKNOWLEDGMENTS

A.F.CH.V. thanks CONACYT for granting him a M.Sc. scholarship as well as to Cinvestav-Saltillo for the financial support provided to carry out this research work (project 880).

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