I O U R N A L O F

Ceramic Processing Research

Preparation of glass-ceramics from vermiculite clay mineral

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In this study glass-ceramics were produced from vermiculite, a clay mineral found in abundance in the Northeast of Brazil. These materials were characterized by X-ray fluorescence, X-ray diffraction, the Vickers microhardness test and scanning electron microscopy. Chemical analysis revealed the material contains a wide variety of metal oxides which are potentiators of crystal formation in glass-ceramics. XRD patterns indicating sodium aluminosilicates as the main crystalline phase in all the samples treated at 750 °C. Scanning electron microscope (SEM) images show crystalline regions in all the samples.

Key words: Glass-ceramics, Clay mineral, Vermiculite, Melt-quenching.

Introduction

In recent years, glass production has attracted considerable interest from the research community and industry. Using these materials for glass ceramics (GC) production creates a series of attractive materials such as construction materials, kitchen tiles, bioceramics, optic materials and fuel cells, among other possibilities [1-4].

Obtaining glass ceramics from minerals is a powerful engineering tool to develop new products with several chemical and mechanical properties. The glass ceramic materials produced primarily exhibit mechanical properties and attractive visual aspects for use as coatings in civil construction and for industrial applications with high functional performance.

Glass ceramic technology is closely related to the control of the nucleation and crystallization processes of glasses. The nucleation process involves the formation of ordered regions in the midst of a phase with structural disorder. This generates intermediate states that are favored by the interface and activation energy of the environment. The process may be homogeneous when germ composition is the same as that of grown crystals, or heterogeneous when it is different. It can be induced by impurities, that is, growth in these crystals continues either until neighboring crystals conglomerate creating a highly crystalline body with a small amount of vitreous matrix or when the vitreous phase is also crystallized, forming a totally polycrystalline material.

The present study investigates the use of vermiculite

clay mineral for production of glass-ceramic. The addition of zinc and aluminum oxides in the synthesis process also was investigated. Vermiculite is a clay mineral abundant in Northeast Brazil, originating in igneous rocks, particularly those where feldspars are predominant. It can also be found on large leaves in pegmatite dikes, in various felsitic lavas and porphyries and in a number of shale and gneisses mainly associated to muscovite.

Experimental

Vermiculite clay mineral used in this work was collected in the region of Santa Maria in Paraíba State, Northeast Brazil. The raw vermiculite was ground and sifted in 48 mesh mixed with sodium tetraborate and doped with zinc oxide or aluminum oxide, as shown in Table 1. The initial glass was obtained through a conventional technique known as melt-quenching [5].

The reagents were stoichiometrically mixed, producing a total mass of five grams in the composition of each sample. Once completely homogenized, the mixture was

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	Raw materials (% weight)			
SAMPLES	Vermiculite	Sodium tetraborate	Aluminum oxide	Zinc oxide
Glass ceramic 1	60%	40%	-	_
GC1		х		
Glass ceramic 2 GC2	60%	35%	-	5%
Glass ceramic 3 GC3	60%	35%	5%	_

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placed into a platinum/gold crucible and placed in an EDG FC-2 resistive oven at 1200 °C for 30 minutes for fusion. The liquid was then poured into a copper mold in order to obtain the vitreous material. Following the quenching process, vitreous samples were thermally treated at 750 °C, 800 °C and 850 °C for 12 hours, in order to achieve the crystalline phase formation. Phases were identified by X-ray diffraction using Cu-Ka radiation and a scanning speed of 2 ° min-1 on a Rigaku Miniflex X-ray diffractometer. Chemical analysis of the vermiculite samples was done using the classic/instrumental method [5]. Morphological analysis was conducted using an model ESEM-XL30 PHILIPS electron, for determination of microhardness assays, samples were embedded in acrylic resins and polished with a polishing machine to level the sample surfaces for the respective measures. These measures were done on a SHIMADZU HMV -2 microdurometer, with the application of loads between 0.100 and 0.300 Kg and a loading time of 15s, in the glass ceramic reheated at 750 °C.

Results and Discussion

Chemical analysis of the undoped sample (Table 2) reveals high levels of silicon, magnesium and aluminum oxides in its composition. The three samples described in Table 1 do not exhibit macroscopic physical variations in relation to color when thermally treated at temperatures used in this study.

They also show strong opacity which may be related to the high content of iron present in vermiculite clay mineral. The oxidation state of iron is an important factor in the composition of glasses and glass ceramic materials. The presence of Fe^{2+} ions in silicate-based glasses absorbs light in the infrared region, whereas Fe^{3+} absorbs light in the ultraviolet area, with an absorption capacity 15 times lower in the visible region than Fe^{2+} . According to Berrocal *et al* (2006) [7], glasses containing Fe^{3+} are yellow, whereas those containing Fe^{2+} are brown. It is quite interesting to note that there was a change in oxidation state in all glass

Table 2. Chemical composition of raw vermiculite from Santa Maria, Brazil, treated at 750, 800 and 850 °C/12 h.

COMPOSITION	% (p/p)
SiO ₂	38.52
MgO	17.9
Al_2O_3	13.5
Fe_2O_3	7.81
CaO	0.25
K ₂ O	1.7
TiO_2	0.32
Na ₂ O	3.87
Organic material	16.13
Total	100

ceramics. This is because iron initially present in the vermiculite clay mineral has a +3 oxidation state from the iron oxide (Fe₂O₃) found in the raw vermiculite. This was reduced to +2, producing a brown GC material in all the samples (figure not shown). This variation in iron oxide state, from +3 to +2 and, consequent change in color is likely related to the thermal treatment applied to the samples as described by Lee (1991) [8]. X-ray fluorescence analysis enabled us to identify the semiquantitative composition of these materials to assist in the characterization of possible crystalline phases formed as well as identify traces or the presence of elements that may act as nucleant agents in the crystallization process. Glasses studied in this work were characterized using X-ray diffraction to confirm the amorphous state of samples and any crystalline phases in formation. Figure 1 illustrates the X-ray patterns obtained after the amorphous character of the studied materials. However, slight indications of crystalline phases are identified in peaks emerging at the 35 to 40 ° interval, showing the possibility of aluminosilicate crystal formation in this region.

X-ray patterns of sample GC1, were recorded at different crystallization temperatures for 12 hours, as shown in Figure 2. In all the figures are observed formation of solid solutions of NaAlSiO₄. In the GC3 DRX patterns were identified peaks attributed the Na₂OAl₂O₃SiO₄ and Mg₂SiO₄ solid solutions with the increase of temperature. The investigatation of phases is not simple, once there is formation of solution solid and can occur miscibility gap of two or more phases.



Fig. 1. X-ray patterns of the glasses obtained by fusion and rapid cooling at 1200 °C for 30 minutes. Glass 1; Glass 2 and Glass 3.



Fig. 2. X-ray patterns of GC1 as a function of temperature.

X-ray patterns were also obtained for GC2 samples submitted to different thermal treatments over 12 hours (Figure 2), this figure shows the increase in crystallinity at temperatures above 750 °C. The rise in crystalline phases in this material is related to the addition of zinc oxide in the matrix sample since the oxide may act as a nucleation agent in the original vitreous matrix structure (sample GC1). It should be pointed out that the highest peak undergoes a type of dismemberment, changing phase with the rise in temperature. The peak in sample GC2, treated at 750 °C was attributed to the presence of sodium aluminum silicate. This phase undergoes a slight variation when treated at 800 °C and 850 °C, forming a solid solution Mg₂SiO₄ + ZnFe₂O₄.

When obeserved the influence of thermal treatment temperature of sample GC3 for 12 h (Figure 4), the crystallinity of this material was observed to be a function of temperature. This is confirmed by an increase in the crystallization reflection with a rise in temperature. The intense peak is well defined at approximately 34.80° and does not undergo phase change, as occurred in GC2 (Figure 4). Instead, the Na₂O.Al₂O₃.SiO₂ crystalline phase remains as the primary phase. However, when treated at 850° C/12 appear and the displacement of these peaks occurs with the formation of forsterite mineral (Mg₂SiO₄).

Measures of microhardness provide values for sample surfaces and are influenced by the presence of crystalline phases, as well as by the type of phases. The



Fig. 3. X-ray patterns of GC2 as a function of temperature.



Fig. 4. X-ray patterns of GC3 as a function of temperature.

closer the crystals are to one another the greater the resistance offered to the glaze is when penetrated by a sharp object. Tables 3 and 4 show both the microhardness values obtained for initial glasses after the fusion/rapid

Table 3. Result of Vickers microhardness (HV) applied to starting glasses after the fusion and rapid cooling process.

Samples	Applied Load		
	0.1 kg (GPa)	0.3 kg (GPa)	
G1	3.28	3.11	
G2	4.51	6.07	
G3	4.71	5.11	

Table 4. Result of Vickers microhardness (HV) applied to GC test specimens obtained at 1200 $^{\circ}$ C/30 min and reheated at 750 $^{\circ}$ C/12 h.

Sampes	Applied Load		
	0.1 kg (GPa)	0.3 kg (GPa)	
G1	5.68	6.10	
G2	6.24	6.26	
G3	6.66	6.36	

cooling process, and those of the glass ceramics prepared at 1200 °C/30 min and reheated at 750 °C/30 min, respectively. Vitreous sample 1 (Table 3) displays a low Vickers microhardness value. This may be due to the amorphous nature of this material, as per the X-ray patterns in Figure 1. For the samples with zinc oxide and aluminum oxide, a significant increase in hardness occurs in this material when it is still in its amorphous state. This is related to the doping of these oxides as they tend to increase the crystalline phase fraction of vitreous material. Microhardness values of the three ceramics are different in all the samples when load indentation values increase from 0.1 to 0.3 kg. The

Hardness measures of the GC materials rise in initial glasses, varying from 5.68 to 6.66 GPa, when submitted to loads of 0.3 kg. This is related to the number of crystalline phases formed when reheating the parts [10]. Indeed, the literature reports that in glazes where several crystalline phases are devitrified, Vickers hardness rises owing to the increase in crystallinity of this material. Other GC materials composed of alkaline aluminosilicate phases generate similar values to those found in the glass ceramics produced in this study [11, 12]. The Vickers hardness of these GC materials exhibit similar properties to those of GC plates characteristic of materials traditionally used in the construction industry. These values are also characteristic of materials with biomedical applications, such as in bone and tooth replacement [13].

Morphological analysis of the starting glasses and glass ceramics was conducted using a SEM. Figures 5a and 5b show the surface of the initial glass (sample G1) after fusion and rapid cooling. Figures 5c and 5d exhibit micrographies of GC1 glass ceramics treated at 800 °C and 850 °C, respectively. Figures 5a and 5b depict a smooth surface with a high vitreous phase proportions and small concentrated regions of crystalline phases. These phases are denominated nuclei, which will later promote crystallization of the glass ceramic. These results are in accordance with the X-ray patterns of initial glasses (Figure 1) since they indicate the onset of a reflection at approximately 35 ° in relation to these



Fig. 5. SEM images of: a) starting glass G1, b) starting glass G1, c) GC1 treated at 750 °C/3 h and d) GC1 treated at 850 °C/12 h.



Fig. 6. SEM images of: a) starting glass, G2, b) starting glass, G2, c) GC2 treated at 750 °C/12 h and d) GC2 treated at 850 °C/12 h.



Fig. 7. Scanning electron microscopy images of: a) starting glass, G3, b) GC3 treated at 750 °C/12 hours, and c) GC3 treated at 850 °C/12 h.

nuclei. Figures 5c and 5d demonstrate thermal treatment efficiency in this sample when submitted to temperatures of 800 °C/12 h and 850 °C. A large concentration of crystals is observed, corroborating that observed in the X-ray patterns of this sample (Figure 2).

Microstructural analysis of sample GC2 containing 5% zinc oxide (Figure 6), shows an amorphous material without large concentrations of crystalline phases (Figure 6a and 6b) following fusion and rapid cooling. When thermally treated at 750 °C, a predominance of well-defined needle-shaped crystals is observed (Figure 6c), a phenomenon also observed in ZnO-CaO-SiO₂ glass ceramics system [14]. A higher concentration of these phases is recorded in samples thermally treated at 850 °C (Figure 6d). For this sample, accelerated devitrification occurs, compared to the sample treated at 750 °C. This can be explained by the presence of zinc oxide in the vitreous structure matrix as vermiculite, the clay material

used to produce this glass ceramic, does not contain zinc oxide. In this case, zinc oxide can be characterized as modifier of the vitreous structure.

Micrographs of sample GC2 indicate the presence of small pores. These are not characterized as surface defects, since they originate from the formation of new crystalline regions. Thermal treatment occurs from the surface to the nucleus of the vitreous sample and the formation of new crystals seems to emerge from the surface of the material. Figure 7a shows the micrograph of the GC3 system after the fusion/rapid cooling process. It does differ significantly from the other two studied glass ceramics, displaying a dark region characteristic of a totally amorphous material. When submitted to controlled thermal treatment at 750 °C/12 h and 850 °C/12 h (Figure 7b and 7c), it does not exhibit dense regions of formed crystals as in GC2 (Figure 6c and 6d). This effect may be related to the

low treatment temperature of this sample since the literature reports crystalline glass ceramics such as aluminum oxide at approximately $885 \text{ }^{\circ}\text{C/3} \text{ h}$ [14] and $925 \text{ }^{\circ}\text{C/30} \text{ min}$.

Conclusions

The production of glass ceramic materials from the vermiculite clay mineral provides economic feasibility since it adds value to a mineral resource abundant in Brazil and extracted at low cost. The glass ceramic materials were produced at a relatively low fusion temperature (1200 °C) compared to other commercial glass ceramics which have fusion temperatures between 1350 °C and 1550 °C for up to 9 hours of treatment. All samples exhibit more than one crystalline phase, possibly due to the use of vermiculite clay mineral. This is because it contains a significant variety of crystalline oxides as glass ceramics prepared with industrial inorganic residues [15], rich in an assortment of oxides and dolomite clays [16]. The investigated ceramics glasses contain phases with the same structure, but not the same composition. The prolonged thermal treatment process demonstrated that these GC materials have a strong predisposition to selective crystallization.

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