Preparation of glass-ceramic materials using kaolin and oil well drilling wastes

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\textbf{ABSTRACT}

The high production of drill cuttings during oil well drilling operations is one of the main causes of the huge amount of waste created by the oil industry. Meanwhile, large amount of kaolin waste is produced during the kaolin mining processes. These wastes are usually deposited in landfills with no specific use. Thus, recycling of solid wastes by their incorporation in ceramics has been considered an attractive way to obtain high added value technical solutions, enhancing the culture of reuse. Glass-ceramics have been receiving this same approach with the advantage of obtaining a high-performance product from recycled raw materials. The current study proposes the synthesis of glass-ceramics of the $\text{SiO}_2$-$\text{Al}_2\text{O}_3$-$\text{CaO}$-$\text{Na}_2\text{O}$-$\text{K}_2\text{O}$-$\text{MgO}$ system from a mixture of kaolin and oil well drilling wastes. A mixture of the recycled raw materials (wastes) and $\text{Na}_2\text{CO}_3$ (a commercial material used to adjust the glass composition) was melted at 1500°C for 1 h to obtain a glass-ceramic precursor material. The resulting vitreous powder was studied by thermal, chemical and structural characterization techniques, pressed into pellets and further sintered at 850°C. The microstructural analysis of the obtained glass-ceramics showed the attainment of dendritic-like crystals combined with an amorphous phase.

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1. Introduction

The uncontrolled generation and disposal of solid wastes in addition to the absence of regulatory guidelines for their management are among the most urgent modern problems [1]. The oil industry, for instance, is one of the main motivators of local and global economies. This specific industry generates several types of residues resulting from the exploration and production activities, where the two largest ones (in volume) are the water and the oil well drilling wastes, which can be liquids (drilling fluids or mud) or solids (rock debris) [2]. The amount of oil well drilling wastes can reach 1.2 times the volume of the drilled cylinder. In 2014, the northeastern region of Brazil alone produced around 100,000 m$^3$ of this kind of waste [3].

The mining industry also holds great importance in the world economy for providing raw materials for several industrial sectors. These activities generate sterile waste, a material with no economic value usually discarded after the mining
Table 1 – Chemical compositions of oil well drilling and kaolin wastes.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Oil well drilling waste (wt.%)</th>
<th>Kaolin waste (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>28.07</td>
<td>–</td>
</tr>
<tr>
<td>SiO₂</td>
<td>30.31</td>
<td>67.26</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.86</td>
<td>1.88</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.17</td>
<td>23.84</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.01</td>
<td>4.45</td>
</tr>
<tr>
<td>MgO</td>
<td>2.81</td>
<td>0.71</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.55</td>
<td>–</td>
</tr>
<tr>
<td>BaO</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>SrO</td>
<td>1.21</td>
<td>–</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>–</td>
<td>1.01</td>
</tr>
<tr>
<td>NbO₃</td>
<td>–</td>
<td>0.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Sm₂O₃</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MnO</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ZnO</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 1 – X-ray diffraction pattern of the oil well drilling waste.

Fig. 2 – X-ray diffraction pattern of the kaolin waste.

Fig. 3 – Dilatometric analysis of the CKN glass.

processes; and tailings, unusable materials discarded after the beneficiation stage. Among more than 80 non-energetic minerals that Brazil produces, kaolin is a white clay of vast industrial application with most of its production located in the north and northeast of the country. Although it is not possible to precisely indicate the exact volume of the kaolin waste produced during the kaolin mining process, it ranges 50–90% of the extracted/benefited kaolin [4–6].

The way in which waste has been treated has received differentiated attention in recent years, especially with the advent of discussions on sustainable development. Due to their heterogeneity, ceramic products have enabled incorporating the most diverse types of waste into their starting formulations [7]. As an industry that consumes natural raw materials, this initiative appears as an alternative that extends the life of the deposits without changing the physical-

chemical characteristics of the manufactured products, in addition to reducing manufacturing costs [6]. The manufacture of glass-ceramics, polycrystalline materials generally obtained from the controlled crystallization of glass using various types of industrial waste, has also generated chemically stable products with improved mechanical properties compared to the original glasses [8–18].

Several studies have proven feasibility in using oil well drilling waste and kaolin waste as raw materials for manufacturing ceramics [4–7,19–22]. Kaolin and oil well drilling wastes have been evaluated separately and/or together with other industrial wastes, but there are no reports that contemplate the combined use of them to obtain glass-ceramics.

Glass-ceramics are polycrystalline, chemically stable materials obtained from the controlled crystallization of glasses [8]. Based on the urgent need of recycling the large amount of waste from petroleum and kaolin industries, this work is the

Table 2 – Composition of SACNKMg and CKN glass precursors.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>BaO</th>
<th>Others*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SACNKMg (wt.%)</td>
<td>52.81</td>
<td>12.14</td>
<td>8.92</td>
<td>14.71</td>
<td>1.66</td>
<td>9.76</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Calculated CKN (wt.%)</td>
<td>36.53</td>
<td>13.19</td>
<td>16.04</td>
<td>8.35</td>
<td>3.05</td>
<td>1.85</td>
<td>6.17</td>
<td>5.71</td>
<td>7.15</td>
</tr>
<tr>
<td>Formulated CKN (wt.%)</td>
<td>40.59</td>
<td>10.51</td>
<td>15.90</td>
<td>9.44</td>
<td>2.54</td>
<td>1.8</td>
<td>7.3</td>
<td>10.75</td>
<td>1.17</td>
</tr>
</tbody>
</table>

* Rb₂O, NbO₃, Y₂O₃, TiO₂, Sm₂O₃, MnO, ZnO, SO₃, SrO.
first report on the production of glass-ceramic materials from a mixture of kaolin and oil well drilling wastes.

2. Experimental

Oil well drilling waste from Potiguar Basin (Rio Grande do Norte-RN, Brazil) and kaolin waste from Equador city (RN, Brazil) were used as starting materials. The raw materials were wet milled in a ball mill for 5 h using a weight ratio of powder to alumina balls of 1:3. The suspensions were dried overnight and the resulting powders sieved through a 200 mesh (0.074 mm) sieve. Powder characterization was carried out by X-ray fluorescence (XRF) using a Shimadzu, EDX-700, and X-ray diffraction (XRD). XRD was performed using a Shimadzu XRD-6000 diffractometer (CuKα radiation, with 40 kV and 30 mA). The diffraction patterns were obtained within the angular range of $10 \leq 2\theta \leq 80^\circ$ in the step-scanning mode (0.02°/step, 2 s/step). After finding out the chemical and phase composition of each waste, a mixture corresponding to 10 g of
oil well drilling waste, 5 g of kaolin waste and 2.5 g of Na₂CO₃ was prepared aiming to produce a glass with the composition 52.81 wt.% SiO₂ – 12.14 wt.% Al₂O₃ – 8.92 wt.% CaO – 14.71 wt.% Na₂O – 1.66 wt.% K₂O – 9.76 wt.% MgO. Commercial powder of Na₂CO₃ was used to adjust the glass composition, decreasing its melting point. The glass precursor mixture, hereafter named CKN, was melted at 1500 °C for 1 h. The obtained glass was solidified at room temperature, pulverized in an agate mortar and passed through sieves of 200 (0.074 mm) and 400 mesh (0.038 mm). The resulting material was subjected to XRD and XRF analyses. XRD was recorded at 100 °C, 300 °C, 500 °C and 600 °C for step-by-step monitoring of the mineralogical composition. The glass precursor powder was uniaxially pressed at 100 MPa and further sintered at 850 °C for half an hour in air using heating and cooling rates of 5 and 10 °C/min, respectively. The glass-ceramic microstructure and energy dispersive spectroscopy (EDS) analysis were assessed using a field-emission scanning electron microscopy (FESEM, Carl Zeiss, Supra 35-VP Model).

3. Results and discussion

The chemical compositions of both raw materials, determined by XRF, are shown in Table 1. In the oil well drilling waste, CaO, SiO₂, Fe₂O₃ and BaO represent more than 70 wt.%. The high content of calcium oxide is characteristic of limestone rocks typical of the Potiguar basin. Barium oxide is attributed to the presence of barite (BaSO₄) used as the densifying agent

Fig. 7 – Detailed view of the dendritic-like structure of the CKN glass-ceramic.

Fig. 8 – FESEM/EDS analysis of a typical irregular crystal of the CKN glass-ceramic.
of the drilling mud. The kaolin waste is essentially made up of SiO₂ and Al₂O₃, together making up more than 90 wt.%. In this work, kaolin waste was used as a source of SiO₂, having its use limited due to the low concentration of fluxes, which could raise the melting temperature of the glass.

XRD patterns of both raw materials are shown in Figs. 1 and 2. The XRD pattern of the oil well drilling waste shows characteristic peaks of quartz, calcite, dolomite, and barite. The kaolin waste consists of quartz, kaolinite and muscovite.

Table 2 shows the chemical composition of a reference glass (SACNKMg) [23], calculated (calculated CKN) and formulated (formulated CKN) glass precursors. As can be seen, the Formulated CKN glass precursor contains a suitable SiO₂ content (>30 wt.%) to obtain glass-ceramic materials [9].

From the dilatometric analysis of the formulated CKN glass, shown in Fig. 3, one can estimate a thermal expansion coefficient of 12.3 × 10⁻⁶ K⁻¹ between room temperature and 550 °C (region I). From this point, a smooth change in the curve slope occurs and the coefficient of expansion increases to approximately 20.5 × 10⁻⁶ K⁻¹ (region II). Fig. 3 also shows that the glass transition temperature (Tg) is 575 °C.

The as-prepared glass powder and the respective pellet obtained after sintering at 850 °C for half an hour are shown in Fig. 4. The strong opacity and greenish color of the product may be related to the high iron content present in the composition. Fig. 5 exhibits the step-by-step XRD of the precursor glass (CKN) with increasing the measuring temperature up to 850 °C. It shows the evolution of the mineralogical structure of the material. The CKN glass is amorphous up to 600 °C. As the temperature increases between 700 and 850 °C, one can notice the formation of crystalline phases (intense diffraction peaks at 2θ = 25–35°). A large number of light signals were recorded in the glass-ceramic XRD patterns. Only few ones could be identified, which may be associated with the formation of unknown and/or unrecorded phases, since it has an innovative glass-ceramic material derived from two previously uncombined solid wastes. However, at the most intense formed peaks, signals of a calcium-silicon compound [Ca₁₄Si₁₉, (1 1 18), (PDF 87–861)], barium silicate [Ba₂SiO₄, (022) and (130), (PDF 55–580)] as well as magnesium silicate
Fig. 10 – EDS mapping of the dendritic structure of the CKN glass-ceramic.

[Mg$_2$SiO$_4$ (222), (PDF 34–189)] were detected, as indicated in Fig. 5.

FESEM images of the sintered CKN are shown in Fig. 6. Fig. 6(a,b) exhibits the presence of homogeneously distributed crystals (10 μm in length) throughout the entire microstructure. Fig. 6(c,d) shows the presence of crystalline phases combined with a dendritic-like structure in a glass matrix. One can observe the presence of two types of formed crystals: a first one with an undefined partially amorphous morphology, and a second one similar to a dendrite, shown in detail in Fig. 7. We can see the ordered growth of lamellae in different directions in the dendritic structure. The coverslips are separated by a rectilinear spacing similar to a contour. This kind of morphology is typical of nucleation processes involving an amorphous phase transformation in the crystalline phase. It usually starts by crystallizing some layers and then the liquid phase between them.

Figs. 8 and 9 show EDS analyses at selected points of the glass-ceramic microstructure. One crystal with irregular morphology was selected for the chemical analysis in Fig. 8. The elements found in the highest concentrations were Ba and O (Ba: 20.95 at.%, O: 76.12 at.%, Fe: 0.83 at.%, Na: 0.88 at.%, Si: 0.60 at.%, Al: 0.32 at.%, Ca: 0.19 at.%, K: 0.07 at.%, Mg: 0.004 at.%), confirming the barium silicate phase identified by XRD. These crystals can arise from preexisting phases that did not change during the sintering process. The EDS analysis in the center of the dendritic crystalline structure (point 2 in Fig. 9) indicates high concentrations of O, Ca and Si (O: 52.38 at.%, Ca: 18.47 at.%, Si: 19.69 at.%, Fe: 1.66 at.%, Na: 2.82 at.%, Al: 2.36 at.%, Mg: 2.22 at.%, Sr: 0.27 at.%, Ba: 0.10 at.%, K: 0.03 at.%).

EDS mapping of the dendritic structure (Fig. 10) indicated contains Ba, Fe, Si, O, and Fe.

4. Conclusions

This work proved the feasibility of obtaining a glass-ceramic material with dendritic structure from a mixture of oil well drilling and kaolin wastes. XRD and FESEM/EDS analyses confirmed the presence of Ba-containing crystals as the main constituent before sintering, indicating that they did not dissolve during the material’s production. Dilatometric analysis confirmed the low melting temperature of the glass precursor material. A pressed sample confirmed the melting process started before the temperature used for sintering (850 °C). This makes necessary to study possible applications that do not require high temperatures. It is recommended to test new glass compositions in order to obtain a wide range of thermal expansion coefficients for different applications.

Conflicts of interest

The authors declare no conflicts of interest.

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