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Microstructure of sodium polysialate siloxo geopolymer

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Abstract

Scanning electron micrographs of a well-cured polysialate siloxo geopolymer (silica:alumina ratio 2:1) prepared from metakaolinite reveal a microstructure consisting of a glass-like matrix containing metakaolinite relicts and impurity quartz grains. This inhomogeneity probably results from viscosity increases during preparation militating against efficient mixing of the components, but does not appear to seriously degrade the physical properties of the product. The matrix composition, determined by EDAX, conforms closely to the expected molar ratio and is unchanged by heating at 1200 °C, which however, brings about the crystallization of mullite needles in areas of the geopolymer matrix, the dissolution of the quartz impurities and the depletion of silica from the metakaolinite relicts, leaving behind fine alumina grains. These previously unsuspected thermal reactions help to explain the exceptional stability of the geopolymer matrix. Transmission electron micrographs confirm the essentially amorphous nature of both the as-prepared and heated geopolymer samples, but unexpectedly reveal in the latter nanometre-sized features resembling spinodal decomposition structures in glass.

Keywords: B. Microstructure; B. Electron microscopy; Ceramics; Geopolymers

1. Introduction

Aluminosilicate geopolymers have attracted considerable attention as energy-efficient ceramic-like materials which form and harden at ambient temperatures, yet are sufficiently durable and stable at high temperatures to be used in building and fireproof insulating applications as well as for imobilisation and storage of hazardous heavy metal-containing and radioactive materials. As originally described [1], polysialate geopolymers are prepared by reaction of a reactive aluminosilicate such as dehydroxylated kaolinite (metakaolinite) with an alkali silicate under highly alkaline conditions and controlled water content. After hardening, the resulting product is X-ray amorphous and is shown by solid state MAS NMR to contain tetrahedral AlO_4 and SiO_4 units randomly linked into a three-dimensional framework structure in which charge balance is maintained by the presence of the alkali cations [2]. This ‘‘structure’’ is largely unchanged by heating to >1000 °C, apart from the crystallisation of a small amount of mullite ($Al_6Si_2O_{13}$), thought to result from the thermal decomposition of traces of unreacted kaolinite [3]. Other geopolymeric systems have been proposed based on reaction of sodium silicate with other minerals such as flyash, but it has been suggested [4] that only materials with the general physical and structural characteristics described above should be properly be described as geopolymers.

The microstructure of geopolymers is important in view of the possible inhomogeneity suggested by their high-temperature behaviour [3], but despite the widespread interest in the potential applications of geopolymers, few electron microscope studies have been reported. One such study, of a kaolinite-based geopolymer composite containing the calcium aluminosilicate stilbite, $NaCa_4(Si_{27}Al_9)O_{72}\cdot 30H_2O$, was undertaken to determine the effect of calcium on the extent of dissolution of the crystalline filler [5], from the point of view that this is a

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cementitious system. The scarcity of high-resolution microstructural studies of conventional well-cured sodium polysialate geopolymers prepared from metakaolinite has led to the present work, which has the following aims:

(a) To investigate the compositional relationship between the amorphous geopolymer matrix and any unreacted grains;
(b) To study compositional and morphological changes in the geopolymer after heating to high temperatures.

2. Experimental

The geopolymer material was a conventional sodium polysialate siloxo, synthesized with an SiO_2:Al_2O_3 ratio of 3.3, a Na_2O:SiO_2 ratio of 0.25 and an H_2O:Na_2O ratio of 10 (this composition has previously been found to yield a well-cured product [2]).The geopolymer was prepared by reacting kaolinite previously dehydroxylated at 700 °C with the calculated amount of sodium silicate (Gessy Lever) and sodium hydroxide (Vetec, Grade PA) dissolved in the calculated amount of water, After mixing to a stiff paste, the geopolymer was placed in a cylindrical plastic mould, sealed with polyethylene film to retain the water, allowed to stand at room temperature for 60 min. and cured at 65 °C for 90 min. The plastic film was then removed and the sample dried at 65 °C for 60 min. The resulting sample displayed all the expected properties of a well-cured aluminosilicate geopolymer; it was amorphous to X-rays, showed typical ^{29}Si and ^{27}Al MAS NMR spectra [4], possessed a Mohs hardness of >7, a Vickers hardness of about 54 and a compressive strength of 48 MPa.

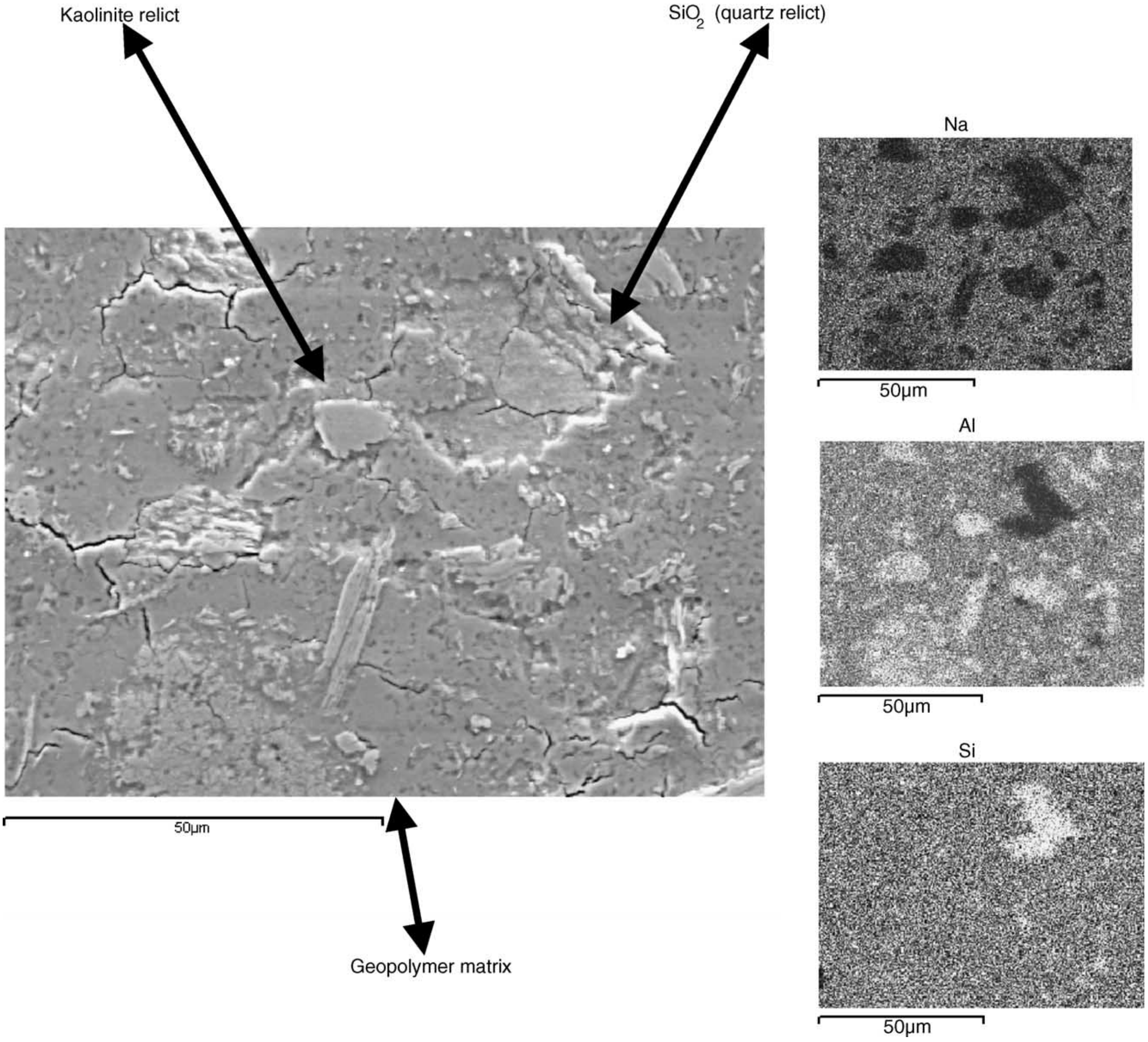

Fig. 1. SEM and element maps of the unheated geopolymer. Note that the sample heated at 300 °C shows similar SEM microstructural features.

Coupons were cut by diamond saw from the cured and dried billet. One sample was heat-treated in air at 300 °C for 4 h, under which conditions a small amount of shrinkage has previously been shown to occur, with concomitant dehydration of the hydrated Na^+ indicated by ^{23}Na MAS NMR [3]. Another sample, heated in air at 1200 °C for 4 h, was shown by XRD and MAS NMR to retain its essentially amorphous character and tetrahedral AlO_4 and SiO_4 structural units, but with the additional presence of some crystalline mullite.

Conventional techniques were used to prepare polished sections of the geopolymer samples for electron microscopy. A LEO Gemini DSM 982 microscope equipped with a field emission gun (FEG) and an Oxford INCA EDX-System was employed. Transmission electron microscopy was performed by means of a FEI F30 microscope equipped with a STEM unit and an EDAX analytical system. Preparation of the TEM samples was rendered exceedingly difficult by the presence of numerous cracks crossing the samples. Only in the case of the 1200 °C sample was thin foil preparation by grinding, polishing and ion beam milling successful, and powder samples of the as-prepared geopolymer had to be used instead. In general, the analysis of sodium by EDX presents problems since Na evaporation may be induced by the electron beam, especially when a FEG is used. To minimize this effect the electron beam was rastered rapidly over the analysed area. However, the possibility that the Na analyses may all be slightly low cannot be ruled out.

3. Results and discussion

3.1. Microstructure of the unheated geoplymer

The SEM micrograph of the cured and dried sample is shown in Fig. 1. This reveals areas of inhomogeneity, in the few grains of crystalline appearance within the glassy aluminosilicate matrix. EDX analysis of these grains (Fig. 1) shows that some of these areas contain only alumina and silica in an atomic ratio of approximately 1:1, suggesting that these are unreacted relicts of the original dehydroxylated kaolinite. Other grains were found to contain only silicon, and thus correspond to the quartz impurities known from XRD to be present in the original kaolinite; these quartz grains survived the highly alkaline conditions of geopolymerisation. The geopolymer matrix was the only part of the sample to contain sodium, and was found by EDX to correspond to the atomic composition Al ~ 25 at.%, Si ~ 55 at.%, Na ~ 20 at.%. Analyses made of a number of matrix regions and show this same composition with considerable consistency. The presence of inclusions and unreacted relicts in the unheated geopolymeric material undoubtedly arises from incomplete mixing of the original batch, which becomes progressively more difficult as the material stiffens before being placed in the mould, but since the mechanical and physical properties of this particular geopolymer sample after curing is consistent with the results of previous studies [2], it appears that the sample integrity is not significantly degraded by the presence of these granular inclusions.

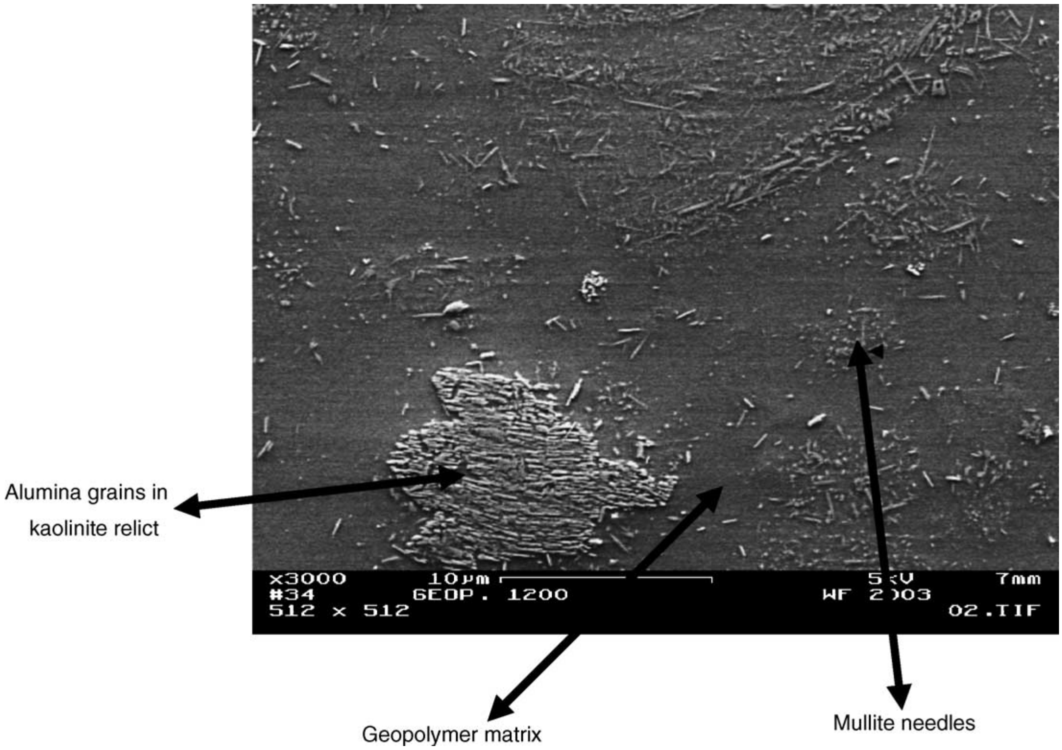

Fig. 2. SEM of geopolymer heated at 1200 °C.

The SEM results for the sample heated at 300 °C are identical with the unheated sample, indicating that dehydration does not change the geopolymer composition nor the morphology and composition of the granular inclusions. This observation is consistent with the previous conclusion [3] that the hydration water in the dried but unheated sample is associated with the charge-balancing alkali metal ions located in the aluminosilicate network.

3.2. Geopolymer heated at 1200 °C

After heating at 1200 °C, the sample retains its essentially X-ray amorphous character, evidenced by he persistence of the broad hump in the baseline of the X-ray diffractogram, but also shows weak X-ray peaks of mullite ($Al_6Si_2O_{13}$) and α-Al_2O_3 superimposed on this amorphous background. These crystalline phases have previously been observed in a well-cured geopolymer of this composition heated at 1300 °C [3], and were thought to be the thermal reaction products of the unreacted metakaolinite relicts [3]. The SEM micrograph of the sample heated at 1200 °C (Fig. 2) does not support this suggestion, showing instead evidence that the needle-like grains of mullite are formed within the geopolymer matrix rather than within the metkaolinite relicts which are still identifiable by their angular shape. EDX analyses of the Al:Si ratio of these needle-like crystals confirm their identification as mullite. The angular metakaolinite relicts also contain fine crystals (Fig. 2), identifiable by EDX as pure alumina, and thus also indicate the presence of grains of pure alumina formed within relicts of the original metakaolinite grains, identified on the basis of their morphology. That the decomposition product of the metakaolinite is alumina rather than mullite suggests that the reactive silica component of these relicts has been taken up at 1200 °C by the geopolymer, as have the impurity quartz grains, which are no longer detected in this sample by either XRD or SEM. The α-alumina previously detected by XRD and ^{27}Al MAS NMR in samples heated to 1300 °C [3] was explained as a thermal decomposition product of the unreacted metakaolinite rather than originating from the geopolymer matrix; the present SEM observations confirm this suggestion. The thermal stability of the glassy geopolymer matrix is confirmed by the fact that its composition in areas unaffected by mullite formation is identical to the as-prepared composition, within the limits of the analysis. The identification of the alumina grains with the crystalline inclusions is also confirmed by the fact that these were also detected in the SEM micrographs of the unheated sample, but in concentrations too small to be detected by XRD or ^{27}Al MAS NMR.

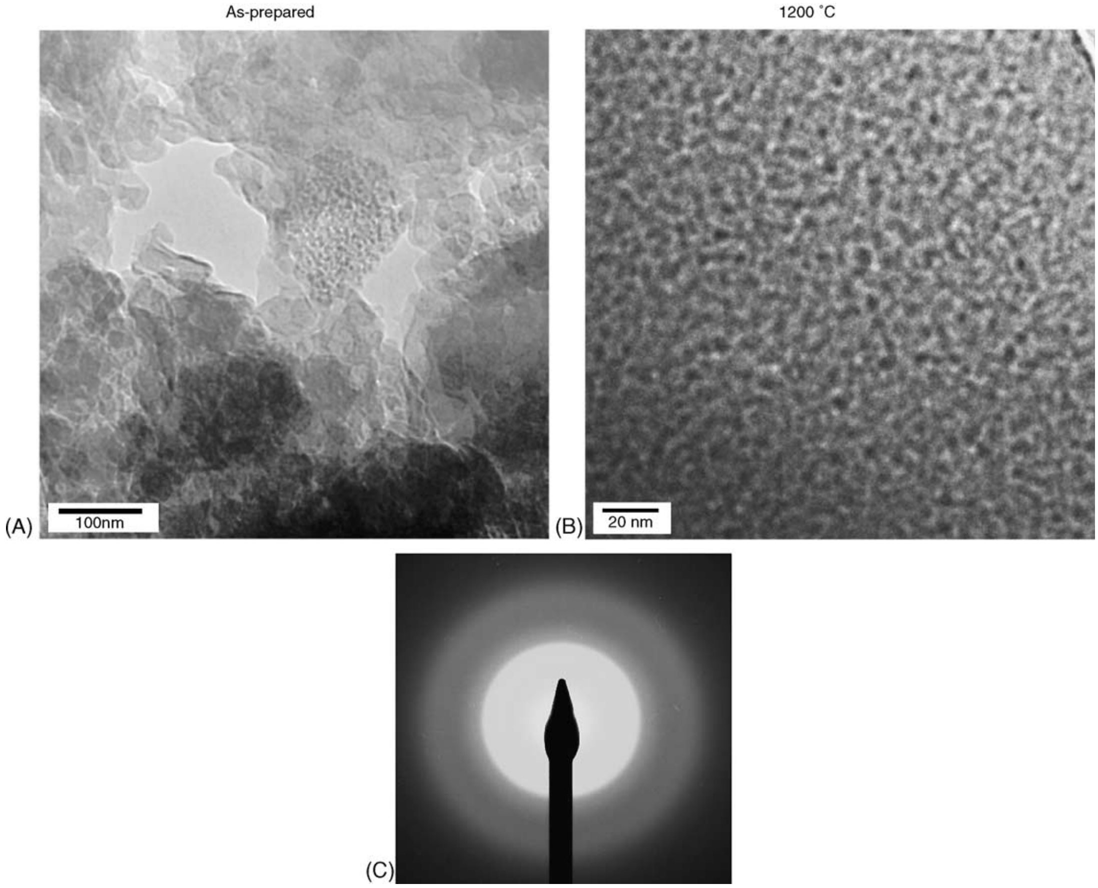

Fig. 3. TEM of (A) unheated geopolymer, (B) geopolymer heated at 1200 °C, (C) a typical diffraction pattern from the geopolymer matrix area of both unheated samples and samples heated at 1200 °C.

These results suggest that the present well-cured aluminosilicate geopolymer structure has the ability to accommodate changes in its silica content, and at higher temperatures actively scavenges any available silica, whether in the form of crystalline impurity quartz grains or the silica component of unpolymerised metakaolinite (depletion of the silica from the metakaolinite relicts leaves behind the small grains of alumina observed in the microstructure of the heated sample). Offsetting this effect is a tendency to maintain the overall composition of the geopolymer matrix, evidenced by the EDX analyses of the geopolymer matrix of the heated sample. This appears to be accomplished in the heated sample by the precipitation of some of the excess silica in combination with alumina as the aluminosilicate phase mullite in some regions of the geopolymer matrix. These observations, although unforeseen, may help to explain the thermal stability of the amorphous geopolymer structures and their tolerance of high temperatures.

3.3. High-resolution TEM

High-resolution TEM micrographs of the matrix regions of the unheated and heated geopolymer samples are shown in Fig. 3. The unheated geopolymer matrix (Fig. 3A) shows particle-like structures of approximately 50 nm, reminiscent of a particulate gel. Some of these particles also show signs of incipient demixing, which after heat treatment at 1200 °C (Fig. 3B) has progressed throughout the matrix, which essentially retains its initial composition. The TEM of the heated geopolymer matrix has the appearance of a glass, which has undergone spinodal decomposition. The diffraction pattern (Fig. 3C) is similar for both the unheated sample and that heated to 1200 °C, indicating by its halo-like appearance and absence of spots the essentially amorphous character of both samples.

4. Conclusions

These microstructural observations confirm earlier indirect conclusions regarding the presence of regions of inhomogeneity in polysialate geopolymers, but also reveal a surprising consistency in the composition of the matrix material, even after heating at 1200 °C. A further unexpected observation that on heating at >1000 °C, alumina grains occur in the relicts of unpolymerised metakaolinite, suggesting that the geopolymer matrix acts as a sink for silica, but that the matrix composition is maintained by the crystallization of the aluminosilicate mullite. The origin of this mullite is the geopolymer matrix itself, not the metakaolinite relicts as previously supposed. Thus, the mechanism by which the geopolymer maintains its stable composition appears to involve a balance between the high-temperature reactions tending to increase the silica content (dissolution of the labile silica component of the unreacted metakaolinite and the quartz impurities) and removal of silica by the crystallization of mullite. These previously unsuspected buffering reactions may hold the key to the thermal stability of these aluminosilicate geopolymers.

The essentially glassy nature of the geopolymer structure is also confirmed by TEM, which reveals a nanostructure development after heating to high temperature.

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