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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.

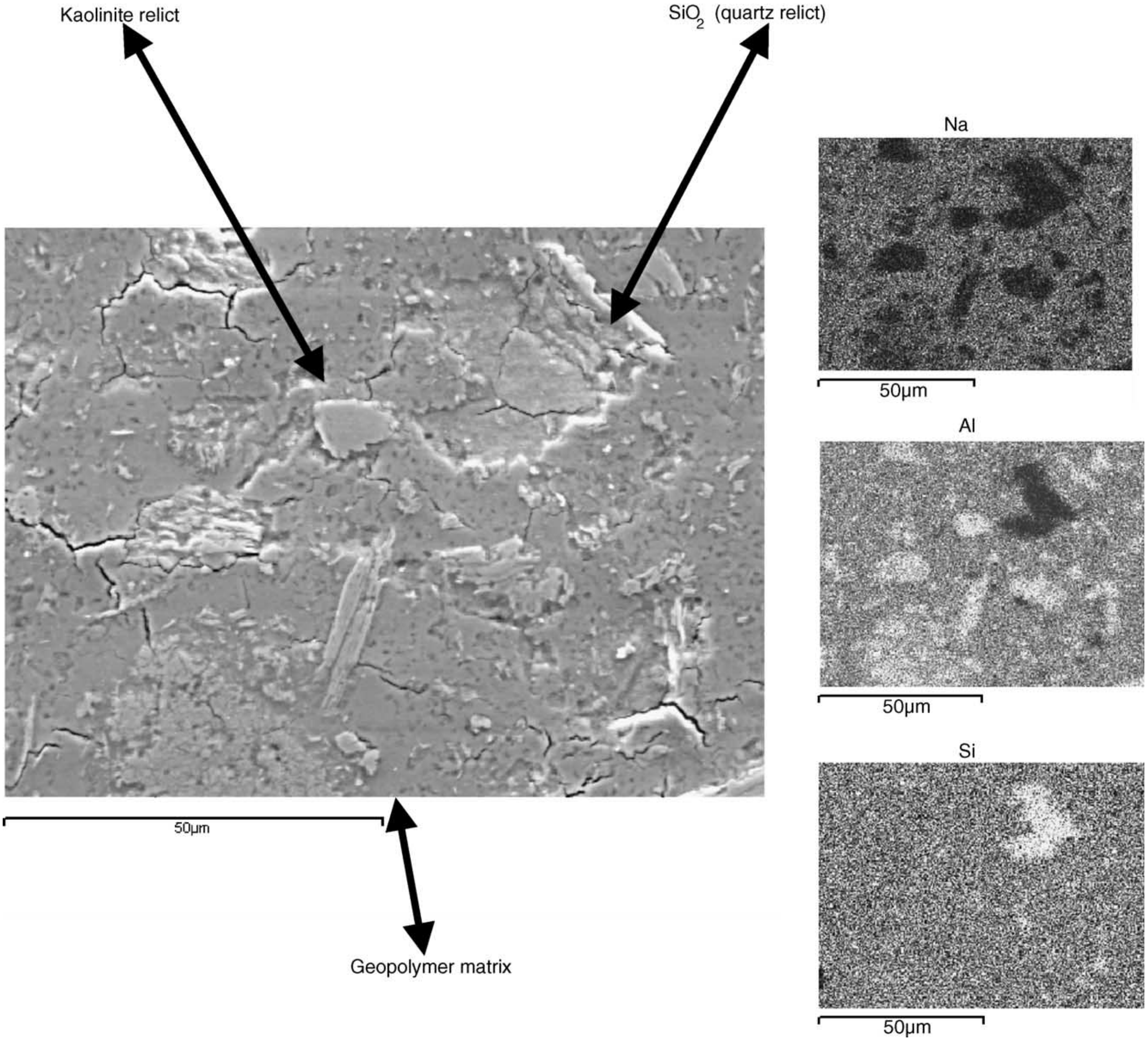

Fig. 1. SEM and element maps of the unheated geopolymer. Note that the sample heated at 300 °C shows similar SEM microstructural features.