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Journal of the European Ceramic Society 31 (2011) 1513–1516

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Short communication

Development of alkali activated borosilicate inorganic polymers (AABSIP)

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Received 14 October 2010; received in revised form 8 February 2011; accepted 14 February 2011

Abstract

A new class of materials is presented namely, alkali activated borosilicate inorganic polymers (AABSIP), which are similar to alkali activated aluminosilicate polymers (geopolymers). The pastes made with this new material ($Na_{1.10}BSi_{1.70}O_{8.88}\cdot 4.65(H_2O)$) were found to have a compressive strength of up to 56(7) MPa and a Young's modulus of 1.95(7) GPa. The microstructure is composed of a glassy matrix with many sub micron pores with some remnant precursor material. The AABSIP materials have been identified as suitable for structural and non-structural applications, particularly neutron shielding.

Keywords: Electron microscopy; Microstructure-final; Strength; Nuclear applications; Geopolymers

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1. Introduction

Alkali activated aluminosilicate inorganic polymers or geopolymers have been the focus of many investigations,[1–15] for applications varying from Portland cement replacement, radioactive waste containment, fireproof barriers, ceramic precursors and biological implants. Despite many groups worldwide producing reliable products from feedstocks such as fly ash, the fundamental structure of geopolymers and formation mechanisms are not completely understood. In model clay based geopolymer systems the basic reaction mechanisms can be mathematically modelled.[16] This process can be simplified to a dissolution–reorientation–solidification process. The physical properties of the geopolymers depend primarily on the ratio of Si/Al, Na/Al and the water content.[4,8] Often these ratios are investigated indirectly, for example, by varying the activation solution to solids ratio. The metakaolin geopolymer formulations optimised for maximum compressive strength are achieved when the nominal composition is Si/Al = 1.8–2.2 and Na/Al = 0.9–1.2.[3,8,13] Therefore a typical geopolymer might be $NaAlSi_2O_6$–5.5(H_2O).

We have substituted boron for aluminium in the inorganic polymer structure to produce a new class of material. The challenge was finding a form of boron to use that had suitable composition, coordination chemistry and alkali dissolution kinetics. There are a number of choices for the boron feedstock, the most available being boric acid (H_3BO_3) and borax ($Na_2B_4O_7\cdot 10H_2O$) which can be converted to boron oxide (B_2O_3) or borax with varying degrees of hydration. It should be noted that inorganic boron has been added to geopolymers previously but in this case to control setting time,[17] this research did not attempt to eliminate Al from the structure and so produced a boroaluminosilicate.

Typically a geopolymer is synthesized by alkali activating an aluminosilicate solid with an alkali silicate solution. However, this method is not overly suitable for this study as the boron containing feedstocks typically have a high water content; boric acid and borax have 43 wt% and 47 wt% water, respectively. This high water content can be problematic when designing geopolymer mixtures as the bound water is not available initially, making the mixture unworkable (very dry and stiff). One alternative is to add the extra water required to have a workable mixture, however ultimately there is too much water, resulting in low pH in the solution and subsequently a weak solid. Another problem identified with borax-like materials is that the Na/B = 0.5, thus if the geopolymers are to have Na/B = 1, half the Na is supplied by the borax, meaning the solution pH will be lower than if it was wholly supplied by sodium hydroxide solution. Dehydration of borax decahydrate ($Na_2B_4O_7\cdot 10H_2O$) to borax pentahydrate ($Na_2B_4O_7\cdot 5H_2O$) is preferred as half the structural

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doi:10.1016/j.jeurceramsoc.2011.02.021

Table 1
Formulations of the AABSIP samples.

Material	Supplier	Mix 1	Mix 2
Silica Fume SF98	Australian fused materials	40.5%	40.5%
Borax		–	37.1%
Anhydrous borax	Heated at 300 °C	19.5%	–
NaOH (AR Grade)	ChemSupply	9.3%	9.3%
Deionised water		30.6%	13.1%

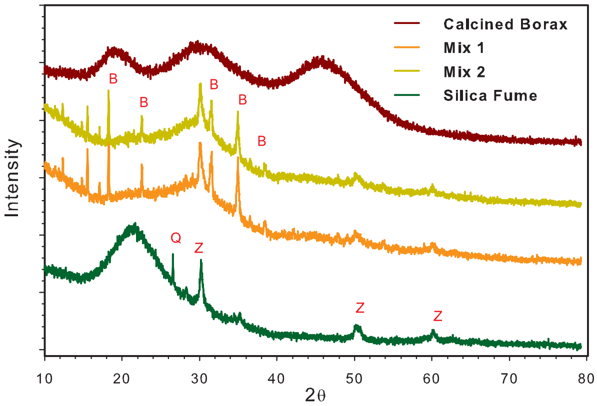

Fig. 1. X-ray diffraction patterns of the silica fume and the anhydrous borax feedstocks that were used to produce the AABSIP samples mix 1 and mix 2. The crystalline peaks in the silica fume are zirconia (Z) and quartz (Q). The crystalline phase formed in the AABSIP samples was Borax decahydrate (B). Patterns offset for visibility.

water has been removed, reducing the structural water content to 31 wt%. Although this process reduces the amount of structural water, the mix still maintains a starting Na/B = 0.5. The borax pentahydrate can be further heated to dehydroxylate it to anhydrous borax ($Na_2B_4O_7$) at 300 °C. Although the boron in borax is both 3-fold and 4-fold coordinated, it is likely to reorganise during the reorientation stage of the reaction; resulting in 4-fold coordinated boron in the inorganic polymer. If a sodium borate solution is used, the boron can more readily reorder during the polymerisation reaction. Using borax rather than the anhydrous borax to produce the sodium borate solution resulted in a more viscous solution.

Adequate neutron shielding is required for facilities such as medical linear accelerators, cyclotrons, synchrotrons, nuclear research facilities and nuclear power stations. The most suitable composition for neutron shielding depends on the neutron energy. Low atomic mass isotopes are best at slowing down high energy neutrons as they have high microscopic removal cross sections. In contrast, the isotopes that best capture lower energy (thermal) neutrons are those with high microscopic absorption cross-sections, however this property does not vary smoothly with atomic mass.[18,19] Elements with stable isotopes with particularly high absorption cross-sections include[20]: B, Rh, Cd, In, Pm, Sm, Eu, Gd, Dy, Er, Tm, Hf, Ir, Au, Hg, Pa, Np. Hydrogenous material is often used to slow down high energy (fast) neutrons so that they can interact with the other isotopes in the shielding. Boron-10 is extensively used to capture thermal neutrons as it has a high capture cross-section and is abundant (19.4% of naturally occurring boron).[20] The macroscopic cross-section for both removal of fast neutrons and absorption of thermal neutrons is the product of the relevant microscopic cross-section and the number of atoms per unit volume of each isotope, this value can then be summed for all isotopes in a material.

2. Materials and methods

The boron starting materials utilised to manufacture AABSIP were borax ($Na_2B_4O_7 \cdot 10H_2O$) and anhydrous borax ($Na_2B_4O_7$). The anhydrous borax was produced by dehydrating borax at 150 °C for 30 min followed by further dehydration at 300 °C for 15 h. The diffraction pattern of the anhydrous borax is shown in Fig. 1. The formulations of the AABSIP samples are presented in Table 1. Given the low solubility of borax and sodium hydroxide in water, a formulation of $Na_{1.10}BSi_{1.70}O_{8.88} \cdot 4.65(H_2O)$ was selected for both mix 1 and mix 2. The boron containing feedstocks were dissolved in the sodium hydroxide solution. This solution was then mixed with the silica fume in an ARE-250 Orbital Planetary Mixer (Thinky, Japan) at 1300 rpm for 5 min followed by a deaeration cycle of 2100 rpm for 0.5 min. The resulting slurry was cured at 70 °C for 24 h in 24 mm diameter polypropylene vials. Compressive strength testing was conducted after cutting sample ends perpendicular to the long axis and air drying for approximately 1 h prior. An EZ50 (Lloyds, England) was used to apply a constant stress rate of 0.25 MPa/s, after a 50 N preload until the samples failed.

The ring milled fracture pieces were drifted into top loading plastic XRD sample holders. The X-ray diffraction patterns were collected on a D8 Advance (Bruker-AXS, Germany) with copper anode (40 kV, 40 mA) with a Lynxeye Position Sensitive detector (covering 3° 2θ). The patterns were collected from 10° to 100° 2θ with a nominal step size of 0.02° at 0.5 s. The Bragg peaks from the crystalline phases were identified by search/match using EVA 11 (Bruker-AXS, Germany) to search the JCPDF Database. The morphology of the fracture surfaces were analysed with a Zeiss EVO-40 (Carl-Zeiss, Germany) scanning electron microscope (SEM).

3. Results and discussion

The anhydrous borax dissolved more rapidly than the hydrated borax in the sodium hydroxide solution and with a lower viscosity. The geopolymer slurry of mix 1 resulted in a lower viscosity than mix 2. After 7 days the samples from mix 1 and mix 2 produced samples that appeared dense, with a smooth surface finish and khaki colour. The compressive strength testing indicated that samples underwent elastic deformation followed by brittle fracture similar to behaviour exhibited by geopolymer pastes.[15] The compressive strength and Young's modulus of both mixes were equal within uncertainties, Table 2. The strength and deformation mode indicate that this new class of material would be suitable for structural applications, similar to that of Portland cement or Geopolymers. The spread of com-

Table 2
Compressive strength and Young's modulus of AABSIP samples. Uncertainties quoted are the standard deviation of 4 replicate samples.

	Compressive strength (MPa)	Young's modulus (GPa)
Mix 1	56(7)	1.95(7)
Mix 2	45(16)	1.71(7)

pressive strength results for mix 2 was significantly greater than for mix 1, believed to be caused by increased heterogeneity of mix 2.

The microstructure of the AABSIP samples is similar to that of geopolymers; a glassy matrix with some pores.[1,8,13,15] Fig. 2 illustrates the microstructure of a fracture surface of mix 1 which is also typical of mix 2. The micrograph shows a porous glassy matrix with some undissolved silica fume spheres and a ∼3 μm borax crystal (assumed from morphology, EDS and the XRD results).

The samples were found to be predominantly X-ray amorphous with minor concentrations of borax (Fig. 1). Samples from both mixes had similar X-ray diffraction patterns. The XRD data indicates that there has been a reaction, as the patterns of the AABSIP samples are not a linear combination of the calcined borax (amorphous) and the silica fume (amorphous).

The AABSIP samples were sound materials with high strength indicating a useful novel material has been developed. It is considered that the reaction mechanisms for AABSIP materials are similar to that of geopolymers (alkali activated aluminosilicate inorganic polymer) and alkali activated boroaluminosilicate.[17] In the alkali activated boroaluminosilicate materials the boron was incorporated into the geopolymer matrix in Q4 sites.[17] Synthesis of a strong stable material implies that boron was incorporated into a stable structure alongside the alkali and silicate, suggesting that boron can substitute for aluminium.

This new class of material, AABSIP, is ideal for neutron shielding: castable, strong and with relatively high macroscopic neutron cross-sections for both fast and thermal neutrons. Table 3 shows the macroscopic cross-section for absorption and removal of thermal and fast neutrons respectively. An increase in macroscopic cross-sections results in more effective neutron shielding. For thermal neutrons the AABSIP samples have comparable abilities (per unit length) to that of borated polyethylene and superior to that of water. For fast neutrons the AABSIP samples have comparable abilities to both borated polyethylene and water.

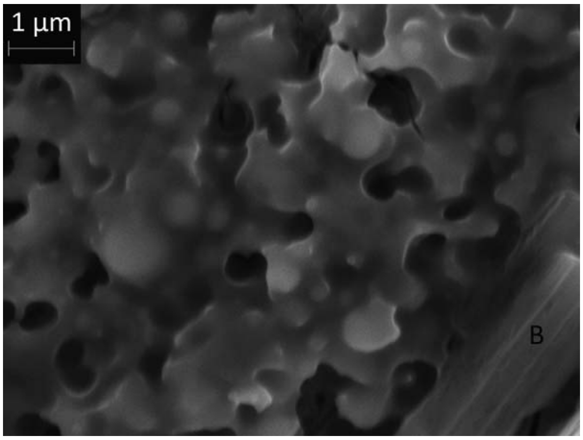

Fig. 2. Microstructure of mix 1, a porous glassy matrix, with a crystallised borax crystal (B).

Table 3
Comparison of the calculated neutron shielding properties of the AABSIP and other shielding materials. Increased macroscopic cross-section results in improved neutron stopping power. References are for the composition of the material. The cross-section data is from published data.[18,20]

	(Thermal) macroscopic absorption cross-section (cm^{-1})	(Fast) macroscopic removal cross-section (cm^{-1})
AABSIP	2.8	0.11
AABSIP (50% dehydroxilation)	3.3	0.10
AABSIP (100% dehydroxilation)	4.1	0.08
Magnetite concrete[19]	0.06	0.11
Borated polyethylene[18] (8 wt% B_4C)	2.6	0.13
Borated polyethylene[21] (SWX-207HD5)	3.8	0.06
Water	0.02	0.11

The bound water content of the AABSIP is useful to moderate (slow down) the fast neutrons, although in some situations the water will need to be removed from the structure when radiolitic hydrogen is problematic. Removal of the water from the samples will reduce the effectiveness of shielding fast neutrons but increase the effectiveness of shielding thermal neutrons. The maximum working temperature of AABSIP is likely to be significantly higher than that of borated polyethylene (<90 °C); this will be investigated in future work. AABSIP can be cast into moulds of various shapes and sizes, it can even be cast in situ making it one of the most versatile neutron shielding materials available. The material's high compressive strength indicates that structural walls can be constructed with AABSIP, making this material ideal for outer walls of nuclear facilities. AABSIP also has the advantage that it will not become significantly radioactive from neutron activation, reducing the need for secondary shielding for gamma radiation, particularly if potassium is substituted for sodium.

4. Conclusions

A new class of material has been presented—alkali activated borosilicate inorganic polymer (AABSIP). The microstructure is composed of a glassy matrix with many sub micron pores and some remnant precursor material. It has been identified as suitable for structural and non-structural applications, particularly for neutron shielding applications, based on the compressive strength and boron content.

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