Fly ash based geopolymer thin coatings on metal substrates and its thermal evaluation

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ARTICLE INFO

ABSTRACT

Class F fly ash based Na-geopolymer formulations have been applied as fire resistant coatings on steel. The main variables for the coating formulations were Si: Al molar and water: cement weight ratios. We have determined that the adhesive strength of the coatings strongly depend on geopolymer composition. The ease with which geopolymer can be applied onto metal surfaces and the resultant thickness depend on the water content of the formulation. Adhesive strengths of greater than 3.5 MPa have been achieved on mild steel surfaces for compositions with Si:Al of 3.5. Microstructure evolution and thermal properties of the optimised coating formulations show that they have very promising fire resistant characteristics.

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1. Introduction

Since the 1920s when wide scale coal fired power generation began, millions of tonnes of fly ash and bottom ash have been created. Most of the fly ash was disposed of as landfill requiring extensive land area. To suppress dust the fly ash is usually stored wet raising environmental concerns about possible leaching of toxic elements into the water table. In the 2001 around 480 Mt (million tonnes) of coal combustion products (CCP) were produced worldwide [1], while in Australasia (Australia and New Zealand) 13.5 Mt of CCP were produced in 2006/2007 [2]. From both environmental and economic perspectives the disposal of fly ash in tailings dams will soon be too costly creating a driver to find alternative means to disposing of ash [3]. During the 1930s in the USA fly ash began to be used as a supplementary cementitious material (SCM) [4]. Currently, in Australasia around 13% of the CCP or 1.74 Mt is being used as SCM for concrete manufacture [2]. Recently Jha et al. [5] reviewed the potential of fly ash for the extraction of valuable metals, ceramic applications, synthesis of zeolite and manufacture of fire resistant materials.

Research is also being conducted into the use of fly ash for production of geopolymer cement and concrete [6–8]. Geopolymers are amorphous to semi-crystalline three-dimensional silica–aluminate materials prepared by alkaline hydroxide and/or alkaline silicate activation of an aluminosilicate source. Since 1972 research into geopolymers has identified their excellent mechanical properties, ability to encapsulate hazardous waste and high resistance to chemical attack [9–11]. Commonly used aluminosilicate sources include metakaolin, fly ash and slag. Fly ash has an advantage over metakaolin in terms of lower cost [12]. Fly ash geopolymers are being used in structural applications such as large concrete columns [13] and railway sleepers [14] and have demonstrated excellent mechanical properties and durability. Geopolymer also has the potential to be manufactured into fire resistant panels [15] or as fire resistant coatings on metal [16]. Geopolymer coatings can be designed to keep temperatures below 550 °C where steel loses about 50% of its yield strength [17]. Although there are reports on the preparation of fire resistant metakaolin based coatings on steel substrates [18], to the best of our knowledge, there are no reports on the application of fly ash based geopolymer fire resistant coating on metal substrates.

The aim of the present research is to examine the feasibility of using fly ash for the manufacture of geopolymer fire resistant coatings on metal substrates.

2. Experimental procedures

2.1. Preparation

Fly ash from the Collie thermal power station (Western Australia) was used to manufacture the geopolymer coatings. The chemical and mineralogical composition, the content of its reactive

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Table 1
Composition of geopolymer coatings with Na: Al = 1 (mol).

	Si:Al (mol)	Water: cement (wt.)
FA1	1.0	0.35
FA2	2.0	0.35
FA3	3.0	0.35
FA3.5a	3.5	0.35
FA3.5b	3.5	0.30
FA3.5c	3.5	0.25

component and average particle size has been reported in previous papers [19,20]. The content and composition of the amorphous part of fly ash were used for calculating coating formulations. Adhesion of thermal resistant coating to metal substrates is a critical property believed to be strongly influenced by the formulation of the geopolymer [18]. To investigate the influence of adhesion with formulation change two parameters were varied, namely molar Si:Al and water content. The water content is very important for geopolymer workability. The molar Na:Al ratio of all compositions was fixed at 1 while the Si:Al was varied from 1 to 3.5. Compositions were denoted as FA*n*, where *n* is the Si:Al ratio. The composition and weight ratio of water:cement of geopolymer mixes are shown in Table 1.

To achieve the various geopolymer compositions sodium hydroxide was added to sodium aluminate or sodium silicate solutions. To maintain Na:Al = 1 the maximum achievable Si:Al was found to be 3.5. Details of the starting materials for each formulation are summarised in Table 2.

According to the supplier's data sheets the composition of the sodium aluminate (Coogee, Australia) was Al_2O_3 – 19%, NaOH – 25.5%, bulk density 1.45 g/cm^3; the composition of the sodium silicate (PQ, Australia) D-51 was Na_2O – 14.7%, SiO_2 – 29.4%, H_2O – 55.9%, density 1.50–1.53 g/cm^3; the composition of the Coogee N42 sodium silicate was SiO_2:Na_2O = 3.1, water content 60.5% w/w and density 1.42 g/cm^3.

Weighed starting materials were mixed in 300 ml plastic containers by a high speed Thinky mixer (Thinky Co., Japan) for 5 min followed by de-foaming for 30 s. The mixing and de-foaming speeds were 1400 and 2100 rpm, respectively. Mild and stainless steel plates with approximate dimensions of 5 × 5 cm (or 15 × 15 cm for fire tests) were cleaned with corundum abrasive paper (grade 80) followed by washing with detergent, de-ionised water and acetone. Energy dispersive X-ray spectra revealed the presence of a minor amount of Mn in the mild steel while Cr was present as the main alloying element in the stainless steels. Quantitative analysis of the steel substrates was not undertaken. Geopolymer compositions were applied to metal surfaces by dipping. After dip coating metal plates were placed in plastic bag and cured at 70 °C for 24 h. In addition to the preceding preparation, some of the metal plates were polished to a 3 μm finish before washing. The two different finishes were included to enable the effect of surface roughness on the adhesion strength to be determined.

Coating thickness depends on water content, resulting in a 0.5 mm thick coat for compositions with water:geopolymer of 0.35. Additionally, each geopolymer composition was poured in plas-

tic moulds (25 mm diameter and 50 mm long), sealed and cured under the same conditions as the thin coatings. The bulk samples when de-moulded were used to determine compressive strength and thermal crystallisation characteristics.

2.2. Characterisation

Crystalline phases were identified from X-ray diffraction (XRD) patterns obtained with a Bruker D8 Advance Diffractometer equipped with a LynxEye detector using Cu-Kα radiation. Diffraction patterns were collected from 10° to 80° 2θ. The step size was 0.02° 2θ with a scan rate of 0.6° 2θ per minute. Automated phase identification software (EVA2, Bruker) was used to analyse the diffraction patterns.

Geopolymer fracture surfaces were studied with a Zeiss EVO 40XVP scanning electron microscope with EDS X-ray detector (Energy Dispersive Spectroscopy, Oxford Instruments). Geopolymer-steel interfaces were studied by embedding samples in epoxy resin followed by polishing.

The adhesive strength of the coated samples was measured with an Elcometer 106, adhesion tester according to ASTM D4541. The average of at least 2 measurements was presented as adhesion strength.

Australian standard 1530.4 was used for measuring the heat insulating characteristics of the coatings. Using a custom made gas heating rig, the standard time/temperature curve (Eq. (1)) was followed as closely as possible.

$$T = 345 \ \log_{10}(8t + 1) + 20 \tag{1}$$

where T is device temperature in °C at time t (min) from ignition of the heating rig. Measurements were performed on coated mild steel with dimensions of 15 × 15 cm. Coating thicknesses of FA3.5a and FA3.5c were 0.6 mm and 1.5 mm, respectively.

Thermal expansion or shrinkage of geopolymer samples was measured with a DI-24 Adamel Lhomargy dilatometer. The measurements were conducted up to 900 °C at a heating rate of 5 °C/min. The average of the three measurements was used as the representative dilatometric curve. Compressive strength of the compositions was measured after 7 days using an Instron-5500R testing machine. All reported compressive strength results are the average of four separate measurements.

3. Results and discussion

While, the coated metal plates cured normally and hardened within 24 h, those cured in plastic tubes behaved differently depending on the Si:Al and water content. As expected, compressive strength of the samples was much lower than geopolymers with similar composition but lower water content. Compressive strength of cylinders and adhesive strength of coatings to the metal substrates are presented in Table 3.

Samples FA3 and FA3.5a were too soft to de-mould thus preventing measurement of compressive strength. After opening the plastic moulds and curing at ambient temperature for several days a glassy phase was found to have formed on top of the samples indicating a

Table 2
Starting materials used for each of the coating compositions.

|	Fly ash, mass %	Sodium aluminate, Coogee, mass %	Sodium silicate, PQ, D-A53, mass %	Sodium silicate, Coogee, N42, mass %	Sodium hydroxide pellet, mass %	De-ionised water, mass %
FA1	54.03	31.40	–	–	1.52	13.02
FA2	67.57	–	1.06	–	5.86	25.50
FA3	56.92	–	–	26.67	1.80	14.60
FA3.5a	52.84	–	–	36.72	0.20	10.23
FA3.5b	55.38	–	–	38.45	0.20	5.95
FA3.5c	58.09	–	–	40.37	0.20	1.30

Table 3
Compressive strength and adhesive strength of geopolymers.

	Compressive strength (MPa)	Adhesion strength to mild steel (MPa)	Adhesion strength to stainless steel (MPa)
FA1	2.6 (0.4)	0.25 (0.1)	0.40 (0.25)
FA2	0.8 (0.2)	0.5 (0.15)	0.75 (0.25)
FA3	–	2.9 (0.1)	0.50 (0.25)
FA3.5a	–	≥3.5	1.4 (0.25)
FA3.5b	2.2 (0.1)	≥3.5	1.2 (0.25)
FA3.5c	3.9 (0.3)	≥3.5	1.4 (0.25)

Note: A dash indicates strength was too low to measure; the figures in brackets are standard deviations obtained from multiple measurements.

level of inhomogeneity for these compositions. However, adhesive strength for FA3 and FA3.5 to metal substrates was much higher than for FA1 and FA2. Sample FA3.5c coated onto polished mild steel showed an adhesive strength of 2.7 (0.5) MPa i.e. lower than non polished mild steel substrates indicating that surface roughness influences adhesion strength. It should be noted that the Elcometer adhesion tester has an upper limit of 3.5 MPa which prevents determination of high adhesive strength coatings. For some FA3.5 samples failure occurred through the geopolymer rather than at the geopolymer-metal interface preventing measurement of true adhesive strength. Therefore, the adhesive strength values presented in Table 3 should be regarded as relative values rather than absolute values albeit the adhesive strength values being in the same range as that reported between metakaolin geopolymer and steel [21]. No evidence of chemical bonding was observed by SEM/EDS analysis however the adhesive strength of the geopolymer to stainless steel was much lower than for mild steel suggesting the presence of both physical and chemical bonding. The lower adhesive strength to stainless steel is not just related to a smoother surface finish, because the adhesion strength for the polished mild steel was higher than for stainless steel. On the other hand, we have observed strong adhesion of metakaolin based geopolymer (approximately 3.5 MPa) on both stainless and mild steel substrates [18]. Yong et al. suggested that the growth of synthetic geopolymeric gel is more rapid when placed on an iron substrate due to chemical bonding [22]. However, the presence of Cr in stainless steel was thought to inhibit the growth of the geopolymeric gel on the steel substrate and weak bonding was observed [22]. Latella et al. suggested that for metakaolin based geopolymer on stainless steel the bonding appears to be purely mechanical rather than chemical [23]. From these references there is no clear consensus on the mechanism responsible for adhesion of geopolymeric gel to steel. Clearly the adhesive strength of geopolymeric gel to a metal substrate depends on chemical composition and experimental procedures for preparation of the geopolymeric gel, starting materials and substrate types etc. It is speculated that adhesion of the geopolymer compositions to stainless steel is likely to be physical; while the bonding to mild steel may have a component of chemical adhesion. However, as discussed before, we do not have direct evidence of the chemical bonding between geopolymer composition and mild steel substrates. Based on adhesive strength, the best coating composition was FA3.5. The composition FA3.5 represents a mixture of a partly reacted fly ash in sodium silicate. As sodium silicate solutions are used for corrosion resistant and thermal insulating coatings its presence may be the reason for strong adhesion of the geopolymer to the metal substrates [18]. The detailed mechanism(s) of the fly ash geopolymer bonding to mild steel substrates is subject to further investigation.

From XRD patterns the main crystalline phases of the geopolymer samples are quartz, mullite and maghemite, all introduced from the fly ash (Fig. 1). For Si:Al = 1 and 2 zeolitic compounds with compositions close to sodium aluminium silicate hydrate
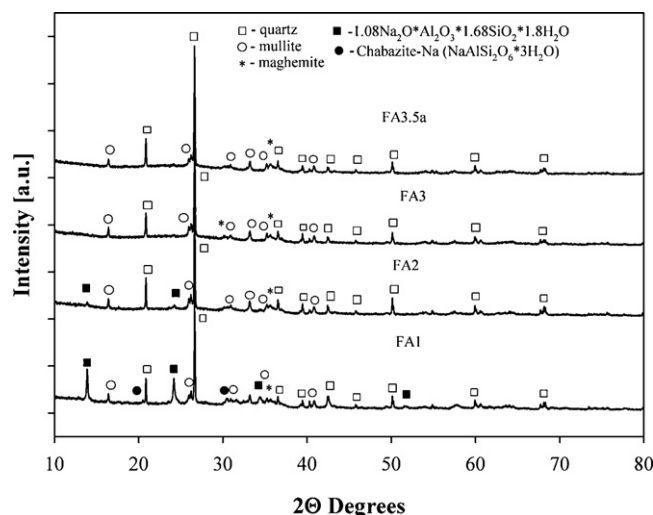

Fig. 1. XRD patterns of the geopolymer compositions.

and chabazite-Na (PDF 31-1271 and PDF 19-1178) were identified. Crystallisation of zeolitic compounds at Si:Al and Na:Al of 1 were observed for metakaolin based compositions [18]. XRD patterns showed that the FA3.5 coating is composed of an amorphous component and unreacted fly ash. Since the alkalinity is lower for FA3.5 mixtures the dissolution rate of the aluminium from fly ash is clearly lower which is consistent with observations for metakaolin based compositions [18].

SEM images (Fig. 2) also support the previous statement that coating FA3.5 is a composite of an amorphous glassy phase and residual fly ash.

While FA2 and FA3 compositions exhibited shrinkage with temperature increase, the FA1 composition showed expansion up 820 °C (Fig. 3). Generally for thermal resistant coatings, the thermal expansion should match the substrate to maintain structural integrity during heating and cooling. When heated, metal expands while generally geopolymers shrink creating a thermal mismatch that could lead to cracking of the coating and loss of adhesion. Aside from deterioration of the coating, formation of cracks during heating is undesirable because heat can flow directly to the metal substrate with concomitant loss of strength and possible failure. Therefore the FA1 composition is preferable for thermal resistant coatings. However, it has been found to only weakly adhere to metal substrates, possibly because of zeolite crystallisation.
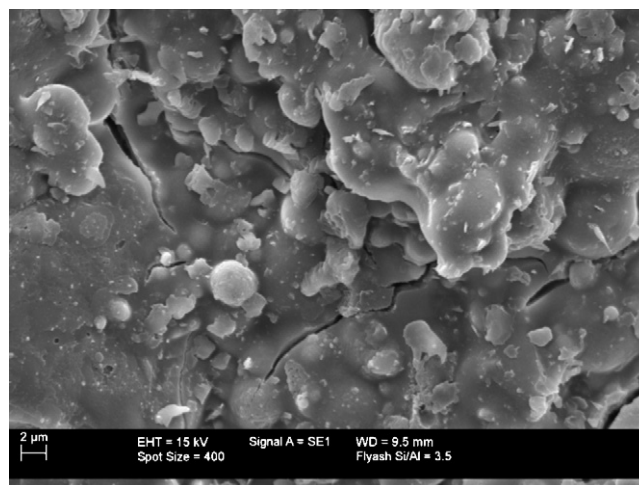
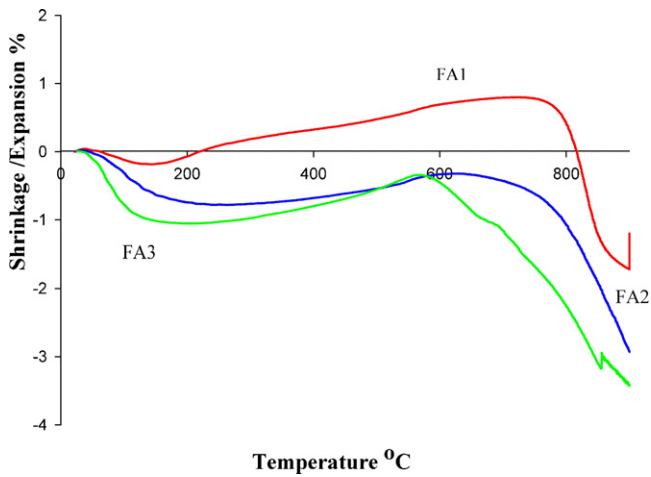**Fig. 2.** SEM micrograph of the FA3.5a sample.

Fig. 3. Thermal expansion and shrinkage of the geopolymer samples.

Fig. 5. Thermal test of the coated samples.

Zeolitised fly ash plates have been recognised for their fire resistant properties and potential for use as passive fire protection in doors and firewalls [24]. Similarly, Krivenko et al. noted directed crystallisation of the Na-zeolitic compounds from metakaolin and sodium silicate on metal substrates and observed an intumescent (expansion) behaviour when heated [16]. Within the FA3.5 sample series, the highest expansion was observed for FA3.5c while shrinkage occurred in FA3.5a and FA3.5b samples (Fig. 4). Initial shrinkage of the FA3.5a and FA3.5b is believed to be due to water release. The expansion of FA3.5c is higher than FA3.5a and FA3.5b as there is less water in the structure and thus the dehydration shrinkage is not observed. A peak in expansion is observed at approximately 700 °C for FA3.5b and FA3.5c. Provis et al. propose that this peak is caused by swelling of a high silica phase present as pockets within the geopolymeric gel structure [25]. Rickard et al. observed a broader peak at 800 °C that was ascribed to one or more of the following reasons: crack formation, crystallisation of the paste, or an increase in porosity [26]. It is likely that the feature at 800 °C in dilatometry curves observed by Provis et al. is different from that presented in this paper as the percentage change in expansion is considerably larger.

Fig. 5 shows the fire test curves for FA3.5a and FA3.5c samples. The insulating capacity of the samples was calculated by measuring the time necessary for the unexposed side to reach a temperature of 180 °C above the ambient temperature when the exposed side is subjected to the standard fire temperature curve.
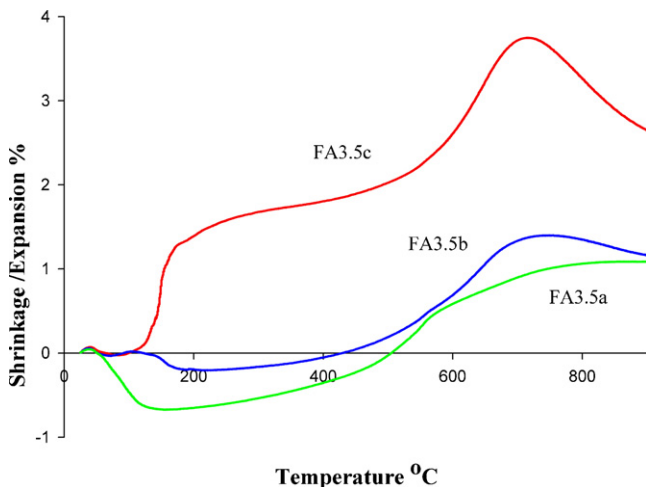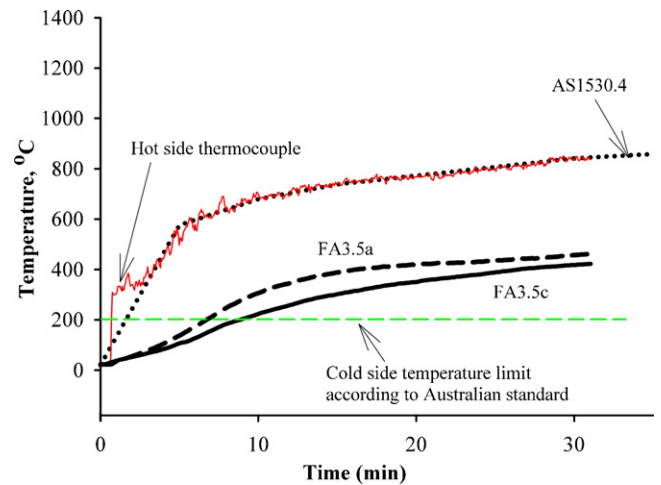
The coating thicknesses for FA3.5a and FA3.5c were 0.6 mm and 1.5 mm, respectively. The cold side temperature curve shows that the insulation capacity of FA3.5a to be ≈7 min while for FA3.5c it was ≈9 min. The difference in the insulation capacity of the FA3.5a and FA3.5c samples is thought to be mainly due to the difference in coating thickness as composition and microstructure are similar. The insulating capacity of the zeolitised fly ash prepared by Leiva et
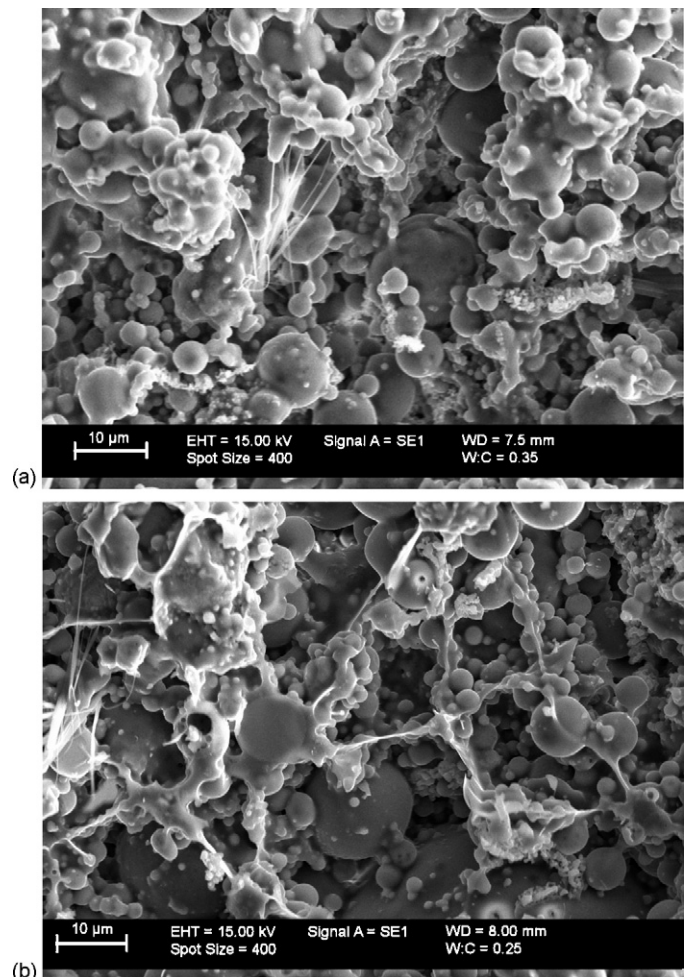

Fig. 6. SEM micrographs of the FA3.5a (a) and FA3.5c (b) coatings after thermal testing.

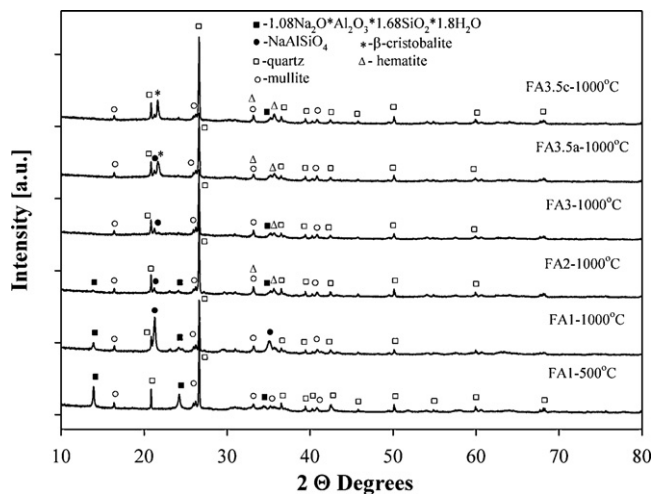**Fig. 4.** Change of the thermal expansion and shrinkage with water content.

Fig. 7. XRD patterns of the calcined samples.

al. [24] was found to be 46 min while for the fly ash based vacuum filtered panel prepared by Viches et al. [27] was more than 60 min for 20 mm thick panels (note: although the testing was performed to various European standards, the fire curve applied to the sample was exactly the same as the Australian standard). As thermal conductivity is proportional to thickness this suggests that if the thickness of FA3.5a and FA3.5c coatings were increased to 20 mm their insulating capacity may exceed 100 min.

The SEM micrographs of fracture surfaces of the FA3.5a and FA3.5c coatings after thermal testing are shown in Fig. 6. Both samples show increased porosity within the unreacted fly ash matrix compared to the matrix present in Fig. 2. Both samples show an appearance of some needle shaped material, possibly crystallisation from the glassy phase.

Coatings can be made fire resistant by designing the material to respond to high temperatures to: (i) form a porous heat insulating layer, (ii) evolve a fire protective atmosphere (formed by $(NH_2)_2CO$, $Al(NH_4)(SO_4)_2 \cdot 12H_2O$, $NaH_2PO_4 \cdot 2H_2O$ etc.) or (iii) initiate endothermic processes that lower the surface temperature ($CaSO_4 \cdot 2H_2O$, concrete). For the work presented here the fire resistance characteristics were due to the dehydration of the water from the geopolymer type composition and evolution of a porous structure. The effectiveness of the current coatings can be increased by making the coatings thicker or by adding different fireproofing agents.

Fig. 7 shows XRD patterns of the calcined samples. The zeolitic compound in FA1 is stable up to 500 °C and traces were still observed at 1000 °C. It is believed that this zeolitic compound was responsible for expansion up to 820 °C. When heated, low silica containing samples transformed from an amorphous structure to crystallised sodium aluminosilicate. However, the intensity of the sodium aluminosilicate reflection was low in FA3.5 samples. Since sodium aluminosilicate could crystallise more readily from amorphous geopolymeric gel, it is an indication of the lower dissolution of the fly ash into the sodium silicate solution. When FA3.5 samples were heated up to 1000 °C a cristobalite reflection appears which suggests the presence of excess amorphous silica.

4. Conclusions

Fire resistant geopolymer type coatings have been prepared by using fly ash as the main starting constituent. The adhesive strength of the coating to steel strongly depends on the chemical composition of the coating. The best adhesive strength was observed for high silica containing compositions which were >3.5 MPa. A

1.5 mm thick coating with Si:Al and water:cement of 3.5 and 0.25, respectively had a 9 min insulating capacity. Increasing coating thicknesses will result in greater fire insulating capacity.

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