

Thermal properties of spray-coated geopolymer-type compositions

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Abstract Thermal properties (DTA-TG and thermal expansion) of spray-coated fly ash-based geopolymer have been studied. The geopolymer composition selected for thermal spray coating had Si:Al = 3.3 and Na:Al = 1.45. To improve the fire resistant characteristics, fine- and coarse-milled vermiculite powder was added at 10 mass percent. Water:geopolymer ratios varied from 0.35 to 0.41 depending on vermiculite content and method of coating. Water added into a starting mixture to increase the flow ability also decreased the geopolymerisation reaction.

Keywords Geopolymer · Thermal properties · Fly ash · Fire resistant coatings

Introduction

Geopolymer is a unique material that exhibits many exceptional properties such as high compressive strength, low shrinkage plus acid and fire resistance. Geopolymers are prepared by activating aluminosilicate sources such as fly ash, furnace slag or metakaolin with alkaline liquids (sodium hydroxide and/or sodium silicate) and curing at a moderate temperature.

Geopolymer properties can be tailored by varying the Si:Al ratio, and Davidovits [1] noted that by increasing the Si:Al ratio the fire and heat resistant characteristics can be

improved. Fire resistant geopolymer panels and metal coatings have been prepared by using granulated furnace slags [2] and metakaolin [3] as the main raw materials. The latter was described as an intumescent-type coating based on crystallisation and expansion of the low temperature zeolitic compounds. It has also been demonstrated that metakaolin and fly ash-based geopolymer type material have the potential to be used as fire resistant coatings on metal substrates [4, 5]. Particularly, we have shown that fly ash-based compositions with a molar ratio of Si:Al = 3.5 exhibit strong adhesion to steel substrates and has promising fire resistant characteristics [5].

Metal coatings can be made fire resistant by:

- The presence of a porous heat insulating layer.
- Designing the coating to release a fire protective atmosphere by including $(\text{NH}_4)_2\text{CO}_3$, $\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, etc.
- Inducing endothermic processes that lower the surface temperature (adding gypsum and concrete).

As mentioned above, fire resistant properties are often achieved by the release of protective gases or water. Thus, design of new fire resistant materials should increase the amount of gaseous component released upon heating or exhibit other properties that make the material superior in withstanding exposure to high temperatures.

The response of fly ash-based geopolymer compositions to fire has been studied by numerous researchers. Kong et al. [6] observed that fly ash geopolymer lost about 11 mass% upon heating with the main mass loss occurring before 130 °C.

Rickard et al. [7] observed up to 10% mass loss in geopolymers prepared from Collie fly ash (Western Australia). They also observed a large exothermic effect at 410 °C which was proposed to be due to the transition of

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ferrhydrite present in Collie fly ash to haematite. Mass loss due to the evaporation of the structural water and dehydroxylation of ferrhydrite of the Collie fly ash-based geopolymer stabilised at around 500 °C with most of the mass loss occurring before 200 °C. For thermal resistant properties, it is preferable if dehydroxylation happened at a higher temperature, for instance, after 500 °C where steel loses 50% of its room temperature yield stress [8]. Although, the thermal property (DTA/TG) of Collie fly ash-based geopolymers has been studied by Rickard et al. [7], it is obvious that the mass loss of geopolymers depends on its chemical composition. Rickard et al., used a low Si:Al ratio to optimise bulk properties [7] while for fire-resistant coating, it is necessary to use higher Si:Al ratios [5]. Moreover, the chemical and mineralogical composition of the fly ash varies even within a thermal power station forcing the adjustment to the geopolymer formulation on a regular basis.

In a previous article, we reported the use of a dip coating method for fire resistant coatings [5]. However, for practical application, it is preferable to use a coating method such as spray coating. Preliminary research has shown that by spraying, a strong uniform coating can be applied to a steel substrate.

In this article, we report our results on the thermal properties of spray-coated geopolymer-type compositions. Fine- and coarse-ground vermiculite with a dehydroxylation temperature up to 800 °C were added as a fire proofing agent to geopolymer-type composition. Vermiculite, when heated above 300 °C, expands and becomes a highly efficient heat-insulating material. The expanded vermiculite has low bulk density, low heat conductivity, high melting point and chemical inertness [9]. Our proposition was to combine the inherently impressive properties of geopolymer with vermiculite to produce a superior fire-resistant product.

Experimental

Geopolymer compositions prepared from Collie fly ash were used as starting materials. For fly ash-based geopolymer preparations, the chemical and mineralogical compositions of the fly ash are very important. Fly ashes consist of crystalline and amorphous components, and the amorphous composition is expected to readily react with the alkaline liquids. Therefore, the amorphous composition of the fly ash is used as the reactive component. The amorphous composition of fly ash is calculated by subtracting the chemical compositions of the crystalline compounds determined by Rietveld refinement with X-ray diffraction data from the chemical composition of bulk fly ash determined by X-ray fluorescence. A detailed

description of this procedure has been reported in a previous article [10]. The chemical composition of the bulk fly ash and its amorphous part are shown in Table 1.

For fire resistant applications, the adhesive force of the coating to the metal substrate is very important achieving the highest value for compositions with Si:Al and Na:Al molar ratios of 3.5 and 1.0, respectively [5]. For previous dip coating applications, the water:cement ratios were varied from 0.25 to 0.35. For the present experiments, the Collie fly ash was found to have chemical and mineralogical compositions that were a little different than those presented in our previous articles. However, the molar Si:Al ratio was maintained, but the Na:Al ratio was forced higher due to the combination of the selected alkaline liquids (sodium silicate and sodium hydroxide) and fly ash. To obtain sprayable compositions, we used industrially available sodium silicate N42 (Coogee, Australia) solution with $\text{SiO}_2:\text{Na}_2\text{O} = 3.1$ and density 1.42 g/cm^3 . The water:cement mass ratio is very important when applying coatings by spraying. Therefore, the main variable in the present research was the water:cement ratio. The optimum water:cement ratio was determined by trial and error using a spray gun with 0.5-mm-diameter nozzle. Air pressure was maintained by a laboratory air compressor. Air pressure regulation was not performed.

For comparison, we also prepared coatings by dipping the steel into the geopolymer formulation. These coatings were prepared with lower water content than the spray coatings.

Fine- and coarse-ground vermiculite powders were added to some of the formulations to improve thermal

Table 1 Chemical composition of bulk and amorphous component of Collie fly ash

| Oxide | XRF mass/% | Amorphous mass/% |
|--|------------|------------------|
| SiO ₂ | 49.88(16) | 21.00(2) |
| Al ₂ O ₃ | 24.80(20) | 15.00(1) |
| Fe ₂ O ₃ | 16.60(4) | 5.5(8) |
| CaO | 1.79(10) | 1.8(1) |
| K ₂ O | 0.61(8) | 0.61(8) |
| TiO ₂ | 1.36(2) | 1.36(2) |
| MgO | 1.31(6) | 1.31(6) |
| Na ₂ O | 0.37(10) | 0.4(1) |
| P ₂ O ₅ | 1.52(4) | 1.52(4) |
| SrO | 0.33(1) | 0.33(1) |
| BaO | 0.45(1) | 0.45(1) |
| Other | 0.70(12) | 0.7(1) |
| Sum of aluminosilicates | 74.68(26) | 36.30(25) |
| Sum of alkali | 0.98(13) | 0.98(13) |
| SiO ₂ /Al ₂ O ₃ | 2.01(2) | 1.39(19) |
| Si/Al (molar) | 1.71(1) | 1.18(13) |

resistance. Vermiculite samples were from South Africa provided by Perlite and Vermiculite Factory (Perth, Western Australia). Samples were milled for 5 min in a vibration mill, then sieved through a 63 μm sieve and designated as fine-milled vermiculite. The vermiculite left in the sieve was designated as coarse ground. The coarse-ground sample was found to be generally less than 250 μm size as measured by sieve analysis. The chemical composition of the original vermiculite sample as measured by ICP is shown in Table 2.

Based on the chemical composition, the structural formula is estimated to be (ignoring impurities): $[\text{Ca}_{0.98}\text{K}_{0.88}\text{Na}_{0.03}\text{Mg}_{1.39}](\text{Si}_{5.91}\text{Al}_{1.53}\text{Fe}_{0.56})(\text{Mg}_{3.56}\text{Fe}_{0.29}\text{Ti}_{0.15})\text{O}_{20}(\text{OH})_4$.

The compositions of coatings described in this article are shown in Table 3.

As spray-coated compositions have a higher water:cement ratio than dip-coated compositions, the alkalinity of the formulated mix is reduced for spray coatings. For the purposes of this exercise, single pass spray coats on metal were used. This resulted in thin coatings (0.5–0.7 mm), which could be increased by making several passes with the spray gun.

To study the thermal characteristics of each composition, samples were cast in 5-mm-high cylindrical plastic moulds. The moulded, but un-capped, samples were kept at ambient to simulate the curing of spray coatings on an outdoor metal structure. After 10 days, the samples were milled and prepared for DTA/TG and X-ray measurements. Dilatometer samples were cast into a 1 mL syringe and cut to length to obtain a cylinder of 10–15 mm length and 5 mm diameter.

Characterisation

X-ray diffraction (XRD) patterns of the powders were obtained with a Bruker D8 Advance Diffractometer using $\text{Cu-K}\alpha$ radiation. Crystalline phases were identified by EVA2 (Bruker) software.

Pushrod dilatometry was performed on a DI-24 Adamel Lhomargy dilatometer (Roissy En Brie, France). In order to make the sample hard enough for cutting with a diamond-tipped blade, the cast samples were cured at 70 $^{\circ}\text{C}$ overnight. Measurements were conducted according to ASTM E831 over a temperature range of 20–900 $^{\circ}\text{C}$ with a heating rate of 5 $^{\circ}\text{C}/\text{min}$. The average of the three measurements was used as the representative dilatometric curves, and all results lay within a 15% standard deviation.

The DTA/TG measurements were performed on TGA/DSC1 Mettler Toledo equipment. Approximately, 20 mg of crushed powder was used for heating up to 1,000 $^{\circ}\text{C}$ using a heating rate and starting temperature at 10 $^{\circ}\text{C}/\text{min}$ and 50 $^{\circ}\text{C}$, respectively. Measurements were performed in air.

Platinum-coated fracture surfaces of the geopolymer compositions were observed by a Zeiss EVO 40XVP scanning electron microscope.

Results and discussion

Microstructure

XRD revealed (not shown here) that the <63 μm vermiculite has been largely amorphised, while coarse-ground vermiculite maintained its crystalline state. Fig. 1 shows

Table 2 Chemical composition of vermiculite, mass%

| | SiO_2 | Al_2O_3 | CaO | Fe_2O_3 | K_2O | MgO | Na_2O | P_2O_5 | TiO_2 | ZrO_2 | LOI 1,000/ $^{\circ}\text{C}$ |
|-------------|----------------|-------------------------|--------------|-------------------------|----------------------|--------------|-----------------------|------------------------|----------------|----------------|-------------------------------|
| Vermiculite | 39.7 | 8.72 | 6.16 | 7.75 | 4.66 | 22.3 | 0.13 | 2.23 | 0.94 | 0.01 | 6.33 |

Table 3 Compositions of the geopolymer-type coatings

| | Dip coating composition | Spray coating composition | Spray coating composition with fine vermiculite | Spray coating composition with coarse vermiculite |
|---|-------------------------|---------------------------|---|---|
| Si:Al (molar) | 3.5 | 3.5 | 3.5 | 3.5 |
| Na:Al (molar) | 1.45 | 1.45 | 1.45 | 1.45 |
| $\text{H}_2\text{O}/\text{total mass}$ | 0.35 | 0.389 | 0.402 | 0.402 |
| Sodium silicate, N42/g | 68.6 | 68.6 | 68.6 | 68.6 |
| NaOH pellets/g | 0.04 | 0.04 | 0.04 | 0.04 |
| De-ionised water/g | 1.84 | 6.56 | 8.09 | 8.09 |
| Vermiculite, <63 $\mu\text{m}/\text{g}$ | – | – | 14.08 | – |
| Vermiculite, >63 $\mu\text{m}/\text{g}$ | – | – | – | 14.08 |

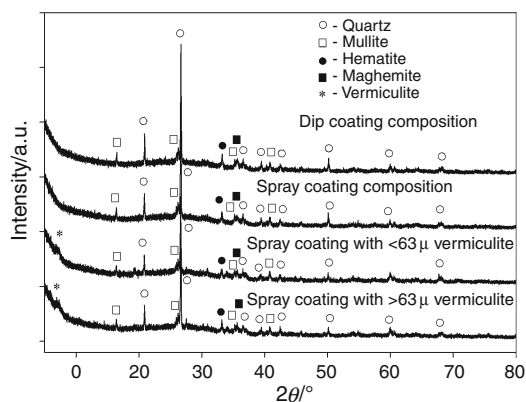


Fig. 1 XRD patterns of the dip-coated and spray-coated compositions

XRD patterns of the experimental compositions. There are no obvious differences in the crystalline signature of the dip and spray coating compositions other than a small vermiculite reflection. Although, it was difficult to find differences between fine- and coarse-milled vermiculite, it is proposed that alkaline liquids will react more readily with the fine-milled vermiculite.

Figure 2 shows SEM micrographs of the geopolymer compositions. SEM micrographs suggest that the coating represents a mixture of semi-reacted amorphous glassy phase and fly ash microspheres. The dip-coated composition shows the same microstructure (not shown here as it is included in our previous article [5]).

In the fine-ground vermiculite coating, the vermiculite particles appear severely damaged, while in the coarse-ground vermiculite coating the vermiculite particles are still clearly visible. There is no evidence that the coarse-ground vermiculite has interacted with the alkaline liquids.

Thermal characteristics

Figure 3 shows dilatometer curves of the geopolymer compositions.

The thermal expansion curve of the pure spray-coated composition is similar to that observed for the dip-coated composition reported in our previous article [5]. A sharp expansion at about 130 °C was observed for both the dip-coated sample (water:cement ratio of 0.35) and spray-coated sample (water:cement ratio of 0.389). This initial sharp expansion is believed to be related to the release of free water. Although the vermiculite containing samples have a high water:cement ratio, the presence of the vermiculite particles appears to have constrained the expansion caused by the free water. In general, geopolymers intended for structural applications, with low Si:Al ratio, shrink with heating, however, the geopolymer-type coatings described here expand with heating. The expansion characteristics of

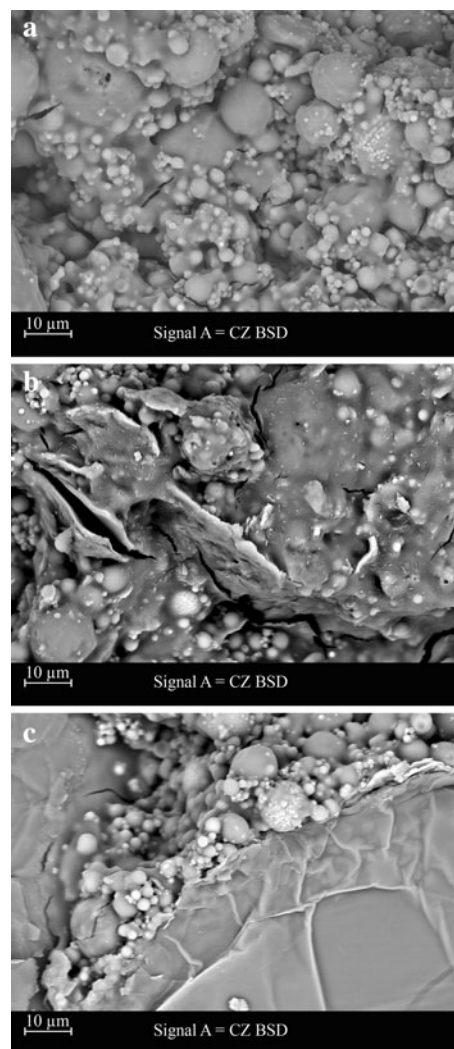


Fig. 2 SEM micrographs of the geopolymer coatings, **a** spray coating, **b** coating with <63 μ vermiculite, **c** coating with >63 μ ground vermiculite

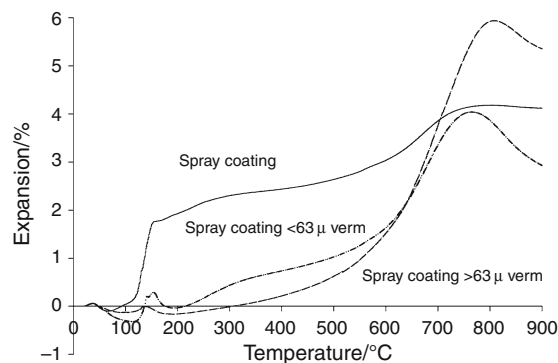


Fig. 3 Dilatometer curves of the spray compositions

the geopolymer-type coatings strongly depend on the composition. High Si:Al ratio samples usually show expansion, regardless of the starting materials used [4, 5, 11].

Since, the geopolymer-type coatings have high silica content, the expansion of the spray coating most likely depends on the presence of a silica-rich phase within the geopolymeric gel structure. The expansion of the vermiculite containing samples started at higher temperatures than pure spray coating composition. The samples with vermiculite show the highest expansion at 800–850 °C which is similar to that observed for dip-coated samples but with exaggerated expansion most likely due to the presence of vermiculite. Vermiculite is known to exfoliate (expand) from 300 to 850 °C beyond which new silicate phases form. The formation of crystalline phases from vermiculite, after the release of structural OH groups has been reported elsewhere [12]. Approximately, 6% expansion observed for the sample with >63 μm vermiculite at about 800 °C is a convolution of the expansion of the geopolymer and coarse vermiculite.

Figure 4 shows DTA/TG analysis of the coating compositions.

DTA/TG results revealed that the dip coating composition has greater mass loss caused by the presence of structural water in the geopolymer composition. The mass loss of the spray-coated composition is less than the dip-coated sample, but higher than the samples containing vermiculite. This result is unexpected because the dip coating composition has a lower water:cement ratio. Most of the mass loss of the dip coating composition occurred before 400 °C after which there was a slight mass gain. The mass gain is believed to be related with the oxidation of the iron oxides. DTA/TG traces of the spray coating composition are similar to the trace for the dip coating composition. The vermiculite containing samples show continuous mass loss up to 1,000 °C, and it is likely that mass loss caused by dehydroxylation of vermiculite was greater than the mass gain caused by the oxidation of the iron-containing species.

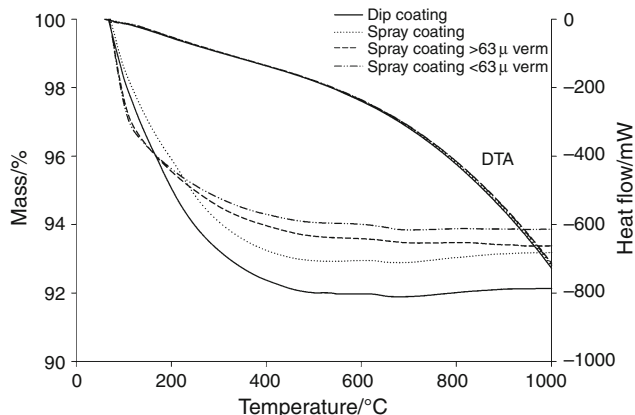


Fig. 4 DTA/TG analysis of the coating compositions

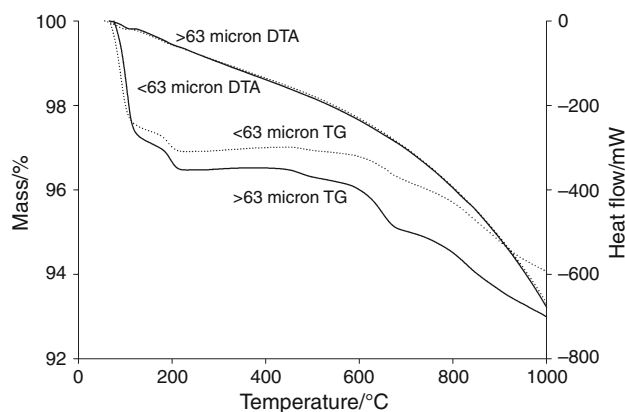


Fig. 5 DTA/TG graph of fine- and coarse-ground vermiculite

The mass loss measured by DTA/TG (Fig. 5) indicates that fine-ground vermiculite had a mass loss of 5.95% at 1,000 °C, while coarse-ground vermiculite lost 6.97% at 1,000 °C. The difference in mass loss is believed to be due to the partial structural distortion of the fine-ground vermiculite and agrees with XRD data (not shown). However, there is no difference in the thermal reaction of fine and coarse-ground vermiculite. Coarse-ground vermiculite shows a distinct three step mass loss as is usually observed for raw vermiculite [13].

The present research indicates that the structure of the coating composition results in a profound effect on its thermal reaction. It is proposed that the dip coating composition has a more condensed structure due to high alkalinity achieved through use of less water. A more condensed geopolymer structure contains structural water in the cavities, while in a less condensed structure water is present mostly as free water and is released during drying. The presence of additional water results in a decreased condensed geopolymer structure and also did not give beneficial thermal-resistant properties. For geopolymer coating preparation, it is important not to increase water content to increase flow ability instead it may be better to use additives such as superplasticizers. Although, the present research shows that the spray coating composition contains less structural water, the presence of the vermiculite caused mass loss to occur continuously up to 1,000 °C which is important for thermal resistance properties of metal coatings.

Conclusions

Thermal properties (DTA-TG and thermal expansion) of spray-coated fly ash-based geopolymer strongly depend on the internal structure of geopolymers. Increasing water contents of the spray-coated composition decreased its geopolymerisation reaction rate. A more condensed

geopolymer structure contains higher structural water which is beneficial for fire-resistant properties. The addition of the coarse-ground vermiculite to the geopolymer showed greater improvement of fire-resistant properties than the addition of the fine-ground vermiculite.

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