Utilization of fly ash and red mud for thermal storage ceramics

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The solid wastes Red mud and fly ash were used as the raw materials in the production of thermal storage ceramics. Red mud was used to lower the firing temperature and fly ash powders were introduced to improve the mechanical properties. The physical properties of samples, including firing behavior, thermal storage properties and thermal shock resistance were evaluated. Also, the effects of fly ash and red mud on the properties of ceramics were investigated. The results showed that the thermal shock resistance of the sample improved by the addition of fly ash powders in the preparation of thermal storage ceramics. Besides, the addition of red mud promoted the formation of liquid phase. In particularly, sample R3 (40 wt % fly ash, 15 wt % clay shale, 20 wt % feldspar, 25 wt % quartz and addition of 15 wt % red mud) fired at 1140°C exhibited the best performance, in which the open porosity, bulk density, bending strength, thermal conductivity at 500°C and theoretical heat storage density (room temperature-500°C) were 0.37%, 2.54 g/cm³, 89.81 MPa, 3.62 W/(m·K), 1.56 KJ/cm³, respectively. Despite the bending strength of R3 sample fired at 1140°C decreased by 20.29% after 30 thermal shock cycles, it still maintained a flexural strength of 73.78 MPa.

Key-words: Fly ash, Red mud, Thermal shock resistance, Thermal storage ceramics

1. Introduction

Human beings are facing the danger of running out of energy resources due to the rapidly growth of world’s population. Renewable sources of energy will become progressively more important as time goes on and must be used where practical. As a clean energy, solar energy is regarded as valued resource. Many countries in the world have a growing presence in solar power generation and the thermal storage system is the kernel of solar power plant.

Solid wastes arise along with the rapid development of industry, which is a major issue for urgent solution. Fly ash is collected from the flue gas of thermal power plants during the combustion of coal for energy production, which is recognized as a kind of environmental pollutant. Most of fly ash is directly discharged into landfill, which is hazardous due to the volatile toxic metals that it contains.¹ Hence, it’s necessary to explore new possibilities for their utilization as raw materials for industrial production. Nowadays, the comprehensive utilization of fly ash is mainly concentrated in the field of building materials, especially in the form of addition to cement and concrete products, fly ash minerals-based bricks, roadway and pavement materials.⁵⁻⁶ Besides, a small quantity of fly ash is used as adsorbents for flue gas, wastewater and soil improvement, also utilized for synthesis of zeolite, mullite whiskers and α-cordierite glass-ceramics.⁷⁻⁹ The physical and chemical properties of fly ash vary with the type of coal used and the combustion conditions. Fly ash, which exists in different particle sizes (between 1 and 100 μm) and shapes, is mainly made up of tiny glass beads. Since the main chemical composition of fly ash is SiO₂ and Al₂O₃, it is considered as a low cost material resource for the ceramic industry.

Red mud is the major solid waste discharged in the process of alumina extraction from bauxite, the production of 1 ton of alumina generally results in the creation of 1–1.5 ton of red mud.¹⁰ According to the different refining processes, red mud can be divided into Bayer Process red mud and bauxite calcination red mud. The physical, chemical and mineralogical properties are fluctuated with preparation processes.¹¹ The main chemical composition is SiO₂, Al₂O₃, Fe₂O₃ and CaO. In recent years, many researchers have explored the resource utilization of red mud, these applications include heavy metal immobilization, production of Portland cement clinker, coagulant, adsorbent and catalyst for environmentally benign processes.¹²⁻¹⁴

This work aims to use the solid wastes as raw materials to synthesize the thermal storage material with high thermal conductivity and high heat storage density for medium temperature based on the previous research.¹⁵ The fly ash powders are added to improve the thermal shock resistance...
of the thermal storage ceramic. Further on, a certain amount of red mud is added on the basis of the fly ash-based ceramics to further enhance the thermal conductivity and heat storage density of the sample. The mechanism of adding fly ash in the improvement of thermal shock resistance of ceramic is discussed in this study. Meanwhile, the effect of the red mud on the ceramic properties is also evaluated.

2. Experiment

2.1 Raw materials

In this study, fly ash, red mud and clay shale were used as main raw materials in the preparation of thermal storage ceramics. The chemical composition, microstructural and mineralogical analysis of clay shale was presented in the previous study. Only the properties of fly ash and red mud were characterized in this study. The chemical compositions of those raw materials were analyzed by X-ray Fluorescence analyzer (Axios-Advanced, PANalytical B.V., Netherlands) before experiment. The powders of fly ash and red mud were subjected to X-ray Diffraction (XRD) to identify the phases of those solid wastes. The chemical composition of raw materials was listed in Table 1.

The fly ash powders are regarded as glassy phases surrounded by different crystalline and mainly contain silicon-aluminum amorphous phase, mineral microcrystals and a few unburned carbon particles. The data in Table 1 revealed that the content of SiO$_2$ and Al$_2$O$_3$ was 46.40 and 42.66 wt % in fly ash respectively. However, the content of Fe$_2$O$_3$ was only 1.52 wt %. Table 1 also shows the main chemical composition of red mud is Fe$_2$O$_3$, Al$_2$O$_3$, SiO$_2$, Na$_2$O and TiO$_2$. In particular, because the red mud is derived from Bayer process, the content of Na$_2$O is quite high, which could be regarded as the flux agent of ceramics. The XRD analysis of the fly ash powders shows that three phases were identified by the pattern, namely mullite, quartz and corundum.

The XRD patterns of red mud and fly ash powders were presented in Fig. 1. The main phases of red mud were hematite, anatase, sodalite, gibbsite and some amorphous phases. The XRD analysis of the fly ash powders shows that three phases were identified by the pattern, namely mullite, quartz and corundum.

Fly ash-based ceramic were designed as 40 wt % fly ash, 15 wt % shale, 20 wt % soda feldspar and 25 wt % quartz. The fly ash-based ceramic was considered to use as many fly ash powders as possible and was also considered with excellent physical properties. A certain content of red mud was added to the batch formula of fly ash-based ceramic. The batch formulas of the samples with red mud addition were given in Table 2.

2.2 Sample preparation

All of the raw materials were grinded into small powders and sifted through a 250 mesh (63 μm) sieve. All the starting materials were dry-mixed by a ball mill for 30 min according to the batch formula. The mixture was pelleted by adding 5 wt % of polyvinyl alcohol (PVA) aqueous

| Table 1. Chemical composition of raw materials (wt %) |
|-----------------------------------------------|
| Chemical composition | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ | CaO | MgO | K$_2$O | Na$_2$O | Others | I.L. | Total |
| Fly ash | 46.40 | 42.66 | 1.52 | 2.10 | 2.06 | 0.13 | 0.48 | 0.09 | 1.01 | 3.55 | 100.00 |
| Clay shale | 56.88 | 21.14 | 7.22 | 0.89 | 0.89 | 1.42 | 2.11 | 0.17 | 0.53 | 8.75 | 100.00 |
| Feldspar | 66.52 | 18.66 | 0.06 | 0.02 | 0.94 | 0.21 | 0.33 | 12.48 | 0.37 | 0.41 | 100.00 |
| Quartz | 98.35 | 0.89 | 0.08 | 0.05 | 0.04 | 0.00 | 0.17 | 0.00 | 0.12 | 0.30 | 100.00 |
| Red mud | 13.54 | 21.43 | 33.88 | 7.52 | 0.66 | 0.00 | 0.09 | 10.83 | 1.18 | 10.87 | 100.00 |

| Table 2. The batch formula of series R samples (wt %) |
|-----------------------------------------------|
| Sample | Fly ash | Clay shale | Feldspar | Quartz | Red mud (addition) |
| R1 | 40 | 15 | 20 | 25 | 5 |
| R2 | 40 | 15 | 20 | 25 | 10 |
| R3 | 40 | 15 | 20 | 25 | 15 |
solution (7 wt% content of PVA) and aged for 24 h. After that, those mixtures were pressed into disk (Ø30 mm × 5 mm) and rectangular bar (37 mm × 6.5 mm × 6.5 mm) at under the pressure of 60 and 40 MPa respectively through the uniaxial pressing machine (Model NYL-500, Wuxi machine factory, China). The green bodies were dried at 110°C for 24 h and then fired in box furnace. The firing schedule of samples was as follows: The heating rate was 5°C/min when the temperature of the furnace was lower than 1000°C and 3°C/min when the temperature of the furnace was higher than 1000°C. The samples were soaked for 30 min at every 100°C and heated up to the maximum temperature with a holding time of 2 h.

2.3 Characterization

For thermal storage ceramics, the densification, thermal physical properties and thermal shock resistance are the main performance indicators. Firing linear shrinkage was determined by the change rate of diameter of the sample before and after firing. Water absorption rate (Wa), open porosity (Pa), and bulk density (D) of the samples were measured via Archimedes Method. The bending strength of the samples was measured by using a computer-controlled electronic universal testing machine (REGER-4100, produced by Shenzhen Rui Geer, China), and the span for the testing was 28 mm and the loading rate was 0.5 mm/min. In addition, the thermal shock resistance of the samples was evaluated by the loss of bending strength before and after certain thermal shock cycles. A detailed description of a cycle of thermal shock was given in earlier previous publication. Only the main feature of experimental procedure is presented in this article to orientate the reader:

The samples were carried into a furnace with a certain temperature of 600°C, and then soaked for 15 min. After that, the samples were taken out and cooled by a fan to room temperature. The thermal physical properties of a thermal storage ceramics mainly focus on the thermal conductivity and thermal storage density. Thermal conductivity (K) was calculated through the expression (1)

\[ K = \alpha C_p \rho \]  
(1)

and thermal storage density (Q) was obtained by the expression (2):

\[ Q = \int_{T_i}^{T_f} \rho C_p dT \]  
(2)

\( \alpha \): thermal diffusivity of the samples; 
\( C_p \): specific heat of the samples; 
\( \rho \): density of the samples (replaced by bulk density here); 
\( T_i \): initial temperature, room temperature (25°C) was chosen here; 
\( T_f \): final temperature, maximum usage temperature (500°C), the thermal storage material investigated in this study was pre-designed as medium-temperature group, and the target temperature is 500°C was adopted here;

Thermal diffusivity was tested by the laser-flash method (LFA 457 MicroFlash, NETZSCH, German) using specimens of 10 mm in diameter and 1.5 mm in thickness. Specific heat of the sample was measured by C80 micro calorimeter (SETARAM, France).

XRD and Scanning Electron Microscope (SEM) were carried out in order to reveal the relationships between the chemical compositions, preparation process, structure and properties. The mineralogical phases of the specimen were identified by XRD using a D/MAX-IIA diffractometer (Rigaku Corporation, Japan). The microstructure and morphology of the samples was observed by SEM (JSM-5610LV, JEOL Ltd., Japan). To reveal the morphology of the crystalline structure, the samples after experiments were etched in hydrofluoric acid solution (HF acid, 5 wt%) for 60 s.

3. Results

3.1 Firing properties

The firing properties are plotted as functions of firing temperatures for the 3 types of samples in Fig. 2. As shown in Fig. 2(a), rapid densification takes place at high temperatures along with large shrinkage for all types of samples. Figures 2(b) and 2(c) show that from 1120–1140°C, the generation of large amount of liquid phase in the samples closes the apparent pores resulting in a rather low water absorption and high bulk density of samples. The data in Fig. 2(b) reveals that the samples become porcelain after fired at 1140°C. A plateau is seen in each curve of the sample fired in the range 1140–1180°C. However, when the firing temperature is over 1180°C, the sample starts to expand with a sharp decrease of bulk density and firing shrinkages. The dramatic changes in firing properties indicate the sample is over-burned at 1200°C. Regardless of the sample type, the best firing temperature here is 1140°C, which corresponds to the best comprehensive performance. The chemical compositions of raw materials reveal that the red mud contains lots of sodium oxides, so red mud can be regarded as flux agent somehow. In this case, the experimental data verify that additional red mud measure has succeeded in lowering the firing temperature and reducing the energy consumption.

3.2 Estimation of the thermal storage properties

Figures 3(a)–3(c) present the specific heats as the function of temperature. Both the experimental data and the fitting line are presented in the figure. The specific heats of all types of samples fired at 1140°C are approximately linear with testing temperature and can be written as following equation:

\[ C_p = aT + b \]  
(3)

The constants a and b are determined by the characteristics of the materials, which includes but not be limited to thermal vibration, defect formation, electron thermal excitation and phase transition. The thermal properties of those samples are all listed in Table 3. The thermal conductivity values are calculated according to expression (1). The thermal storage density is calculated according to the Eq. (2).
The thermal conductivity of 2.33 W/(m·K) of sample at 500°C in previous study\(^{15}\) had been gained but a sharp decline of bending strength of the sample after 30 times thermal shock cycles have been noticed (125.76 MPa before thermal shock test and only 22.05 MPa after 30 times thermal shock cycles.), which in influence the guarantee for the stable operation of a solar system.

Those drawbacks have been improved in this study. A thermal conductivity of 3.62 W/(m·K) (tested at 500°C) of Sample R3 fired at 1140°C has been attained in this study, which has been improved dramatically. Meanwhile, this sample with very high thermal storage density enables the final products to store more heat. On the other hand, the thermal shock resistance is essentially important for a thermal storage ceramic. The good thermal shock resistance of the materials is the guarantee for the stable operation of a solar system. Figure 4 presents the bending strength of series R samples before and after 30 thermal shock cycles.

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Fig. 2. Different firing properties of different samples as a function of firing temperature: (a) Firing shrinkage (Sf); (b) Porosity (Pa); (c) Bulk density (Db).

Fig. 3. The specific heats as the function of temperature: (a) R1 fired at 1140°C; (b) R2 fired at 1140°C; (c) R3 fired at 1140°C.
However, in this study, regardless the type of sample, the loss in bending strength of the sample after 30 times thermal shock cycles is no more than 25%. The largest reduction (20.29%) in bending strength after thermal shock resistance test happens on sample R3. On the other hand, due to the high original bending strength of sample, the residual bending strength of 73.78 MPa has still been obtained.

### 3.3 Phase composition and microstructure of the samples

To gain an insight into the thermal properties of the samples, the samples after fired at 1140°C are sent to XRD and SEM analysis. Figure 5 presents the XRD patterns obtained from the powder of those samples. The four phases are identified by the patterns, namely mullite, feldspar, quartz and hematite. The distribution of those phases in sample R3 is presented in Fig. 6. Figures 6(a) and 6(b) present the microstructure of sample under the low magnification and high magnification respectively. Figure 6(a) visually denotes the densification of the sample. Due to the high content of liquid phase generation at high temperature, only some isolated pores are in the sample. Those pores strongly relate to the thermal shock resistance. Mullite phases are found around pores, as shown in Fig. 6(b). The increased content of red mud in the sample will bring more Fe₂O₃ in the system which strongly lowers the viscosity of liquid phase at high temperature, thus the pore in Fig. 6 is out of shape. However, the short column shaped phases agglomerate around pores and those phases were already identified as mullite phases. Some quartz phases exist in the glassy phase. Figure 7 shows the SEM image (both secondary electron and back scattered electron images) and element mappings in the area of the sample R3 fracture. Some areas made up of small dots are found to be with Fe enrichment, so hematite is identified combined with XRD and SEM analysis. To understand the improvement of thermal shock resistance of sample, the attention is fixed on the microstructure of the pores. To avoid the influence of hematite on the observation of the pores morphology, the morphology of the pores in detail of the sample without red mud addition is shown in Fig. 8. The spherical pits along with mullite phases are observed. The mullite phases are found to be agglomerated in the pits.

### 4. Discussion

#### 4.1 Densification mechanism

The ceramics produced in this study can be regarded as clay-based ceramics which is a complicated system. During the firing process, different solid phases and liquid...
phase co-exist in the system. The kernel of a thermal storage material is the heat transfer efficiency, thus, thermal conductivity and thermal density of the ceramics are essentially important. However, those two factors are related to the volume fraction of pores, discontinuous solid phase and glassy phase of the material. Only few apparent pores locate in the clay based ceramics in this study and this kind of ceramic contains about 50–70 wt% of glassy phase.\(^\text{20}\) The glassy phase is liquid phase at high temperature and the liquid phase fills in the gaps of the solid particles and closes the apparent pores. Consequently, the glassy phase is regarded as continuous solid phase and the other solid particles are considered to be embedded in the glassy phase. Meanwhile, some isolated pores still remain. Those pores not only deduce the density but also affect the thermal conductivity of the ceramics. The relation of small pore volume fraction and thermal conductivity is described as follows:\(^\text{21}\)

\[
\frac{k_{\text{eff}}}{k_0} = 1 + \frac{3\phi}{\left(\frac{k_1 + 2k_0}{k_1 - k_0}\right) - \phi}
\]

where \(k_{\text{eff}}\) is the effective thermal conductivity of material, \(k_0\) is thermal conductivity of a continuous solid phase, \(k_1\) is thermal conductivity of discontinuous phase and \(\phi\) is small fraction of the discontinuous phase.

The isolated pores in this study are from two aspects. First, some of the pores come from the decomposition of organics which exist in the clay. During the heating, the grains grow and liquid phase generates, which makes some of the pores close. On the other hand, not all the pores are

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**Fig. 6.** Micro structure of sample R3 fired at 1140°C: (a) low magnification, (b) high magnification.

**Fig. 7.** SEM image and element mappings in the area of fracture of sample R3.
eliminated due to the extremely high viscosity of the liquid phase. Second, the fly ash powders are used in this study. Figure 9 illustrates the formation process of those isolated pores. Many small floaters of the fly ash powders are mixed with other raw materials. Fly ash powders contain mullite crystal nuclei and some of the mullite nuclei locate on the surface of those floaters.19) With the temperature rising, the nuclei start to grow and form as long strips. At around 1000°C, the liquid phase starts to generate. The liquid phase envelopes the solid particles as well as the floaters. It should be mentioned that the chemical compositions of fly ash powders are mostly Al2O3 and SiO2,19) on the other hand, the ternary system Al2O3–SiO2–Na2O is easy to form as eutectics according to the phase diagram.21) Thus, with the temperature arising, the wall of the floater melts and the shape of the floater remains.

Many alkali oxides are introduced by the addition of red mud, which increase the amount of liquid phase and lower the viscosity of the generated liquid phase.22) The velocity of gas escaping can be calculated according to the Stokes equation.22)

\[ \eta = \frac{2}{9} \frac{R^2(\rho - \rho_s)g}{v_t} \]  

Where \( \eta \) is the viscosity of liquid phase, \( v_t \) is the terminal velocity of a sphere, \( R \) is the radius of the sphere, \( \rho \) is the density of liquid phase, \( \rho_s \) is the density of gas and \( g \) is the gravitational acceleration.

The low viscosity of the liquid phase and big pore will accelerate the emission of gas in the hole, according to Eq. (5). Alkali oxides lower the viscosity of silica melts. Consequently, with the addition of red mud, the density of the sample increases. However, as the content of silicate in the sample still keeps a high level, the viscosity of liquid phase cannot reduce to a great extent. Thus, due to the high viscosity of liquid phase, the gas is hard to be discharged from small pores. The pits exist after cooling consequently.

4.2 The improvement of thermal shock resistance

The introduction of fly-ash powders is manifest in the improvement of thermal shock resistance of sample. Although the bending strength of sample decreases at the thirtieth time thermal shock cycle, the loss in bending strength of the sample after 30 times thermal shock cycles is within a controllable range in present study.

The improvement of thermal shock resistance is mainly due to the increasing of thermal conductivity and the existence of the pores.

The clay based ceramics is with low rates of heat transfer, so the expression of thermal resistance is described as follows:23)

\[ R \propto \frac{k(1 - \mu)}{Es} \]  

Where \( R \) is thermal stress resistance factor, \( k \) is thermal conductivity, \( s \) is thermal stress, \( \mu \) is Poisson ratio and \( E \) is Young’s modulus. The thermal conductivity in this study is improved significantly. According to Eq. (6), the result has been a giant leap in thermal stress resistance and thermal shock resistance consequently.

With the accumulation of thermal shock cycles, the micro cracks also accumulate and form as propagation. The microstructure of the pores introduced by the floaters is another reason of the improvement of thermal shock resistance.

The pores can release the thermal stress and arrest the propagation of micro-cracks.24,25) Many isolated pores are introduced by the floaters in fly ash. On the other hand, as shown in Fig. 8, those pores are surrounded by the mullite phases and the formation mechanism is described as Fig. 9. The reinforcing mullite particles also contribute to improving the anti-heat shock performance of the material. Moreover, those mullite particles present a large and elongated shape, which provides effective shielding for crack propagation.26) Overall, the pore along with mullite phase effectively protect sample from thermal shock. Consequently, the considerable residual strength of the samples still remains after thermal shock test.

5. Conclusion

In this paper, the fly ash and red mud were used to prepare the thermal storage ceramics and the effects of fly
ash and red mud on the properties of ceramics were studied. The R3 sample (40 wt% fly ash, 15 wt% shale, 20 wt% soda feldspar, 25 wt% quartz and addition of 15 wt% red mud) fired at 1140°C showed the best comprehensive properties and the bending strength, theoretical thermal conductivity and thermal conductivity at 500°C were 89.81 MPa, 3.62 W/(m·K) and 1.56 kJ/cm³, respectively. The floaters in the fly ash were used as templates for the synthesis of mullite and then the rod-like mullite crystals staggered into a nested structure. The nested structure could easily absorb and release the thermal stress, which endowed the sample a good thermal shock resistance. The addition of red mud promoted the formation of liquid phase, a large amount of liquid phase filled the closed pores in the body, thereby improving the heat storage performance of samples.

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