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Thermal evolution and crystallization kinetics of potassium-based geopolymer

Peigang He, Dechang Jia *, Meirong Wang, Yu Zhou

Institute for Advanced Ceramics, Harbin Institute of Technology, Harbin 150080, PR China

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Abstract

In this paper crystallization kinetics of potassium-based geopolymer (Si/Al = 2.5, denoted as KG2.5) upon heating are investigated by differential thermal analysis (DTA) under non-isothermal conditions at various heating rates. From 35 to 700 °C KG2.5 shows a significant weight loss due to both evaporation of free water and condensation of hydroxyl groups. Crystallization of KG2.5 starts at a low temperature of ~960 °C according to XRD and DTA analysis. KG2.5 also exhibits a low onset temperature of viscous sintering stage and on heating to 950 °C the sintering is completed. In the DTA graphs, the exothermic peaks which are caused by leucite crystallization shift to higher temperatures with increasing heating rate. The activation energy value of crystallization for leucite is found to be 455.9 kJ/mol and the corresponding Avarami constant is 3.89 indicating the three-dimensional crystal growth mechanism.

Keywords: Geopolymer; Thermal evolution; Crystallization kinetics; Avrami exponent

1. Introduction

Leucite ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) is an important material of dental ceramics as it possesses high coefficient of thermal expansion which enables the leucite dental ceramics to be compatible with most metals used in prosthodontics [1–3]. Leucite ceramics also tolerate a high degree of ionic substitution, and the thermal expansion of leucite can be lowered by the incorporation of cesium [4,5], making them excellent candidates for ceramic matrix composites.

Usually, leucite is prepared by the conventional solid-state reaction which requires mechanical mixing and extensive heat treatment at temperatures of >1600 °C with a prolonged heating period to achieve the desired phase purity [6,7]. Conventional methods suffer from problems of agglomeration, abnormal grain growth, furnace contamination, etc. In this objective, sol–gel technique has been widely used [8–11]. However, there may be some disadvantage such as high cost and severe preparation conditions. Geopolymer technology provides a novel way to synthesis leucite and with the proper processing procedure geopolymer can be directly converted into the final structural ceramic part of interest.

The geopolymer technique invented by Glukhovsky [12] and adequately developed by Davidovits [13,14] is initially applied for preparation of monolithic materials, starting from metakaolin and reactive silica under the presence of strong alkaline solutions such as KOH. Though geopolymer is generally X-ray amorphous if cured at standard pressures and temperatures, it will convert into crystalline ceramic phases like leucite or pollucite upon heating. At present, the effects of different Si/Al ratios ($1.15 \leq Si/Al \leq 2.15$) and alkali cations ($Na^+$, K^+, Cs^+) on the physical evolution, phase transitions, or microstructural development of geopolymers have been studied [15–20]. To date, however, effects of different raw materials and higher Si/Al ratio (especially in the range from 2.15 to 3) on the thermal evolution of geopolymer have not been reported yet. Meanwhile, little attention has been paid to the crystallization kinetics which would be quite useful for designers and practitioners.

In this paper, therefore, potassium-based geopolymer ($K_2O{\cdot}Al_2O_3{\cdot}5SiO_2{\cdot}11H_2O$, KG2.5) was prepared and crystallization kinetics was studied. The Si/Al ratio of KG2.5 is much higher than those in the literature [15–20] besides using

* Corresponding author at: P.O. Box 3022, No. 2 Yikuang Street, Institute for Advanced Ceramics, HIT Science Park, Harbin Institute of Technology, Harbin 150080, PR China. Tel.: +86 451 86418792; fax: +86 451 86414291.
E-mail address: dcjia@hit.edu.cn (D. Jia).

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Table 1
Chemical composition of metakaolin (wt.%).

Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Fe_2O_3	$\sum$
42.53	54.64	0.16	0.11	0.48	0.12	0.80	0.97	99.81

different raw metakaolin materials, so thermal evolution of KG2.5 was also investigated, which was beneficial to its practical application.

2. Experimental

2.1. Preparation of potassium-based geopolymer

KG2.5 with composition of $SiO_2/Al_2O_3 = 5$, $K_2O/SiO_2 = 0.2$ and $H_2O/K_2O = 11$ (mole ratio) was obtained by mixing metakaolin with a potassium silicate solution. These ratios were chosen based on our previous work, as it allowed for optimal mechanical and thermal properties. Chemical compositions of the metakaolin (800 °C calcined kaolin, Shanghai Fengxian Indus., China) are given in Table 1. The main phase of metakaolin was amorphous with a characteristic hump in X-ray diffractometry patterns centered at about 23° in 2θ and its minor phase was quartz. The potassium silicate solution was prepared by dissolving amorphous silica (Shanghai Dixiang Indus, China) into a KOH (Tianjin Fuchen Indus., China) solution. The solution was then allowed to mature under stirring for 48 h in order to dissolve the silica completely. The resultant slurry was cast into polystyrene containers (70 mm in diameter and 80 mm in height), sealed, and cured at 70 °C for 48 h. After demoulding, the hardened KG2.5 was further cured at 70 °C for 24 h. Samples for XRD analysis were first fractured and then heated at a temperature between 700 and 1025 °C in air. These samples were heated and cooled at 5 °C/min, with no isothermal soak.

2.2. Characterization

Phase compositions of the samples were examined by XRD (Rigaku, RINT–2000). Simultaneous TGA and DTA (Netzsh STA 409 instrument) were carried out in an atmosphere of flowing air in alumina crucibles over a temperature range from 35 to 1200 °C. Specimens were prepared for dilatometry by cutting hardened KG2.5 cylinders (4 mm in diameter) to 15 mm in length, and were analyzed in a Netzch dilatometer (Model DIL 402 C) up to 1200 °C at 5 °C/min in air. The crystallization behaviour of KG2.5 was investigated by DTA at different heating rates of 10, 15, 20, 25 and 30 °C/min, respectively, in a continuous air flow. The Avarami constant was obtained by the Ozawa method, and the activation energy of leucite crystallization was determined by the modified Kissinger method.

3. Results and discussion

3.1. Thermal evolution

X-ray patterns for unheated KG2.5 and after being heated to a variety of temperature are shown in Fig. 1. KG2.5 showed a characteristic amorphous hump at ~28° 2θ between RT ~900 °C and several reflections from quartz present introduced by the raw metakaolin. The major reflections for leucite ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) first appeared at 16.36°, 26.04° and 27.42° 2θ when the sample was heated at 950 °C. When sample was heated at 1025 °C, a substantial amount of leucite crystallites formed according to the distinct and strong leucite peaks observed. The starting crystallization temperature was much lower than that observed by Bell et al who reported that upon 1050 °C the major reflection for leucite first appeared [18]. Our previous work also proved that potassium-based geopolymer (Si/Al = 2) crystallized fully to leucite phase after 800 °C soaking for 2 h [21]. The lower crystallization temperature might be attributed to the existence of quartz in the starting metakaolin. The quartz content was about 10 wt.% and homogeneously distributed in the metakaolin. It would be served as the crystallization seeds and thus promote a heterogeneous nucleation of the leucite phase under heat treatment. Similar phenomenon has also been evidenced in other seeded-gel to ceramic transformation [22,23]. The XRD analysis also indicated that a very little amount of kalsilite appeared (corresponding to 27.4° 2θ) after the sample being heated to 950 °C and the major reflection for kalsilite grew only slightly in samples heated to higher temperatures. Previous research works [6,7,11] proved that crystallization of kalsilite was inevitable during the heat treatment when leucite was synthesized by either a wet chemical method or a high temperature melting and crystallization method. As for geopolymer, it is known that metakaolin used in making geopolymer was not completely dissolved leading to compositional heterogeneities on molecular level [17,18]. At the position where the silicon content around aluminum was lower than that of the leucite stoichiometric composition, kalsilite would crystallize as the common metastable intergrowth. Kalsilite would disappear after being treated at a higher temperature or for prolonged heat treatment [24].

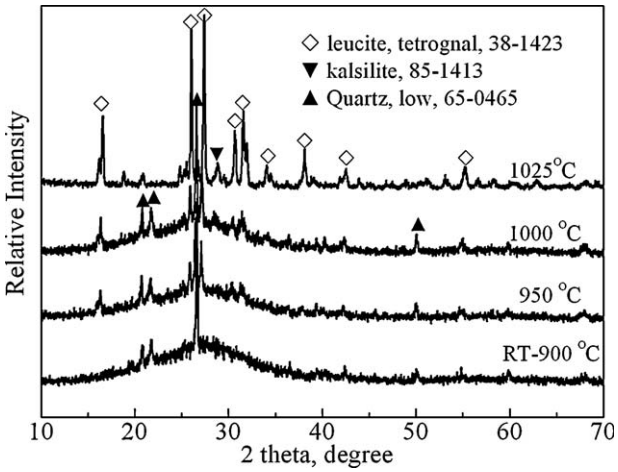

Fig. 1. XRD analysis for unheated KG2.5 and after being heated to the specified temperature without isothermal soaks.

The TG/DTA and thermal shrinkage results are shown in Figs. 2 and 3. They were consistent with the observation in a variety of geopolymer, regardless of alkali choice (Cs, K, and

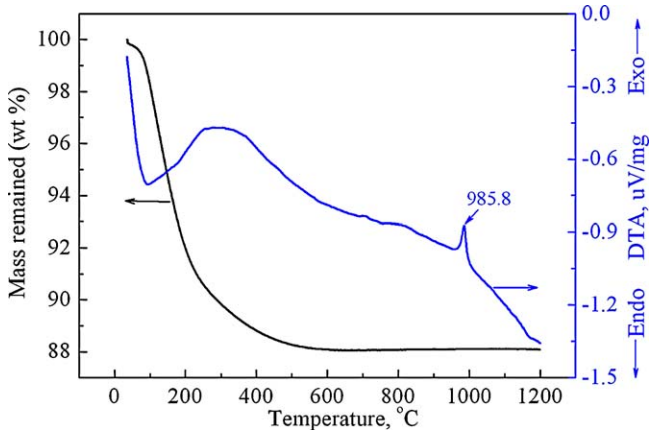

Fig. 2. TG/DTA of KG2.5. Sample was heated at 5 °C/min up to 1200 °C.

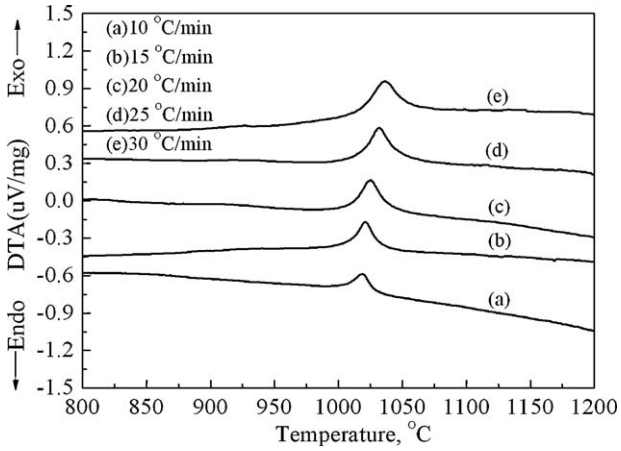

Fig. 4. DTA curves of KG2.5, using different heating rates of 10, 15, 20 and 25 and 30 °C/min, respectively.

Na) or Si/Al ratio [17–20]. The major weight loss before 700 °C from KGP2.5 was a result of water loss, by both evaporation of free water and condensation/polymerization of T–OH groups (T = Si, Al). The DTA pattern of KG2.5 had an exotherm centered at 985 °C over the range of 960–1006 °C. According to the XRD analysis, the exothermic peak was due to leucite crystallization. Thermal shrinkage of the KG2.5 can also be divided into four stages, as reported by Bell et al. [18] and Duxson et al. [20]. When temperature was lower than 100 °C (stage I), KG2.5 kept approximately dimensionally stable as only free water from large pores and surfaces was lost in this stage. Shrinkage in stage II (100–300 °C), stage III (300–700 °C) and stage IV (700–950 °C) were caused by capillary strain, physical contraction during polymerization of T–OH groups, and viscous sintering, respectively. On heating to 950 °C the shrinkage was fully completed and the overall shrinkage value was about 0.19 (dL/L_0). The DTA results showed that KG2.5 did not crystallize into leucite until 960 °C, which was above the temperature range of stage IV. The higher crystallization temperature was helpful to the densification of KG2.5 because the presence of crystallites before or during sintering would slow down the sintering rate by raising the viscosity of the matrix [25]. The KG2.5 investigated in our study was found to be much more easily densified than potassium-based geopolymer analyzed by Bell et al. [18] and Duxson et al. [20] who reported the respective stage IV onset temperature of 850 and 780 °C. The lower onset temperature observed for KG2.5 in this study (700 °C) was expected to be primarily related to its composition, $K_2O{\cdot}Al_2O_3{\cdot}5SiO_2$. In the K_2O–Al_2O_3–SiO_2 system [26], higher SiO_2 content deviating from leucite ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) composition would resulted in the liquid formation at high temperature and thus facilitate the geopolymer densification. The easy densification behavior was beneficial to its application in composites especially those reinforced with carbon fibers, due to their lower fabrication temperature [27].

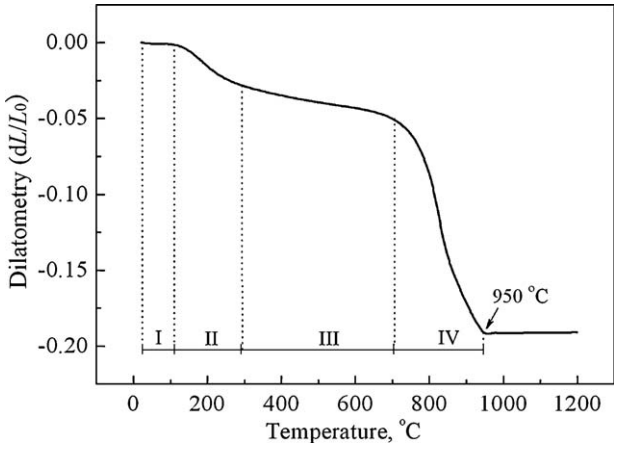

Fig. 3. Dilatometry of KG2.5. Sample was heated at 5 °C/min up to 1200 °C.

3.2. Crystallization kinetics analysis

KG2.5 crystallization kinetics was investigated based on the non-isothermal DTA analysis. Fig. 4 shows the DTA curves of KG2.5 with different heating rates ranging from 10 to 30 °C/min. With increasing heating rate, the exothermic peaks shifted to higher temperatures.

$$\frac{d\ln[-\ln(1-\chi)]}{d(\ln\beta)} = -n \quad (1)$$

The value of the Avarami parameter n, which is a measurement of the dimensionality of crystal growth, was determined using the following Ozawa equation (1) [28]:In this equation, χ is the crystallized volume fraction at a given temperature T, and β is the heating rate (°C/min). Fig. 5 depicts the DTA traces for the crystallized peak of KG2.5 at β = 20 °C/min and χ is given by $\chi = S_T/S$, where S is the total area of the exothermic peak between the temperature T_i (the initial of crystallization) and T_f (the completion of crystallization), and S_T is the area between T_i and T [29]. The graphical representation of the crystallized volume fraction depicted the typical sigmoidal curve as a function of temperature for different heating rates, as shown in Fig. 6.

The plot of $\ln[-\ln(1-\chi)]$ vs. $\ln\beta$ can be linearized and n can be calculated from the slope. The Ozawa plot of $\ln[-\ln(1-\chi)]$

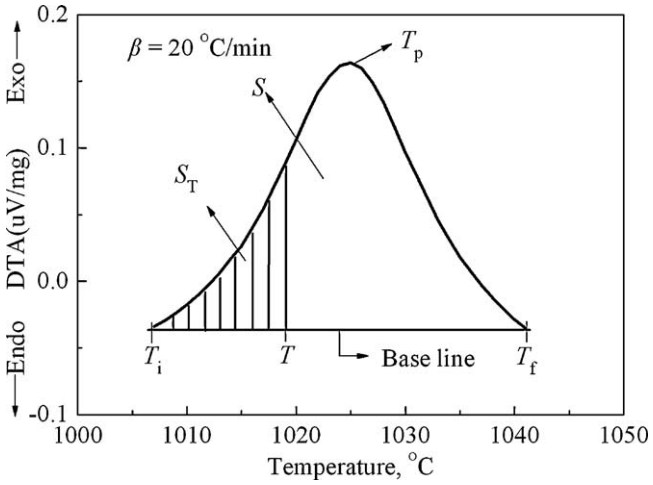

Fig. 5. DTA traces for the crystallized peak of KG2.5 at $\beta = 20$ °C/min.

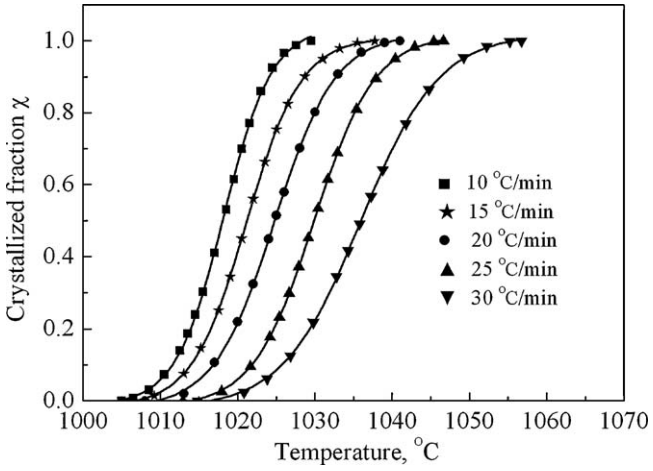

Fig. 6. Crystallized fraction as a function of temperature for the crystallization peak of KG2.5 at different heating rates.

vs. lnβ for KG2.5 is shown in Fig. 7, where the volume fraction crystallized is calculated at the fixed temperatures of 1027 °C. In the investigated system, n determined from the slope was 3.89 indicating that the crystallization of KG2.5 was controlled by a three-dimensional growth mechanism [30].

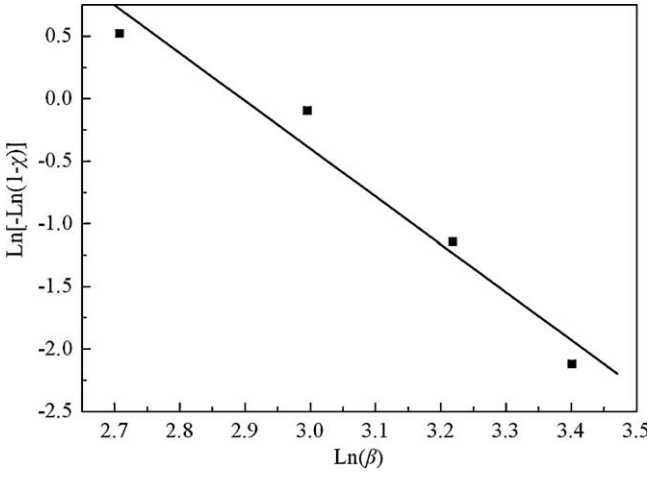

Fig. 7. The Ozawa plot of ln[−ln(1 − χ)] vs. lnβ.

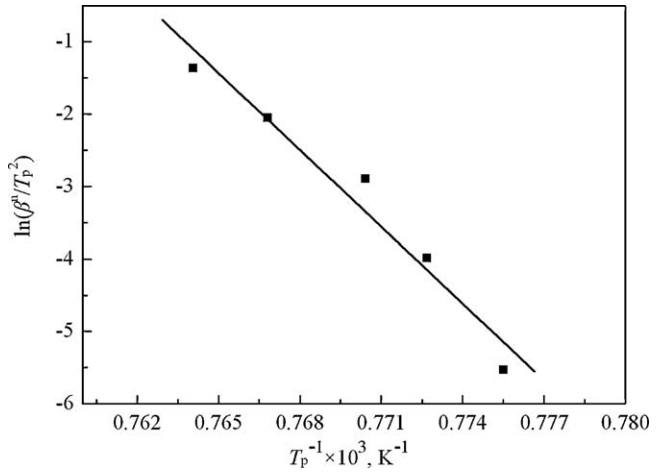

Fig. 8. The modified Kissinger plot of $\ln(\beta^n/T_p^2)$ vs. $1/T_p$.

The activation energy value for the crystallization was estimated using the modified Kissinger equation (2) through the changes in the peak crystallization temperature with respect to the heating rate [31].

$$\ln\left(\frac{\beta^n}{T_p^2}\right) = -\frac{mE_c}{RT_p} + \text{constant} \quad (2)$$

where T_p is the temperature corresponding to the maximum in the DTA crystallization peak (°C); R is the gas constant (8.314 J/mol); E_C is the activation energy for crystallization (kJ/mol); and m represents the dimensionality of the crystalline phase and is determined through the relationship $m = n - 1$. The modified Kissinger plot is shown in Fig. 8 and the slope of the plot of $\ln(\beta^n/T_p^2)$ vs. $1/T_p$ gives the value of E_C. Activation energies obtained from the modified Kissinger plot was 455.9 kJ/mol for the as-synthesized KG2.5.

The activation energy of leucite crystallization may be different for various preparation methods. Zhang et al. [24] reported that the activation energy of leucite prepared by hydrothermal synthesis method was only 125 kJ/mol, which was much lower than that calculated in our study. The hydrothermal method was advantageous in uniformly mixing the starting materials at a molecular level, but this was not the case for geopolymer technology. Due to the existence of unreacted metakaolin [18], geopolymer was inhomogeneous at the molecular level. Thus a higher energy was required for the structural rearrangement during the change from amorphous to crystallized phase. Similar trends were also observed during the crystallization process of mullite [32].

4. Conclusions

Potassium-based geopolymer ($K_2O{\cdot}Al_2O_3{\cdot}5SiO_2{\cdot}11H_2O$, denoted as KG2.5) was prepared using potassium silicate and metakaolin. Crystallization kinetics together with thermal evolution of the KG2.5 on heating was investigated. KG2.5 exhibited a low onset temperature of both crystallization and viscous sintering. After it was fully densified, leucite crystallization occurred gradually upon heating and exhibited an

obvious exotherm in the DTA curve. Using the Ozawa method and modified Kissinger method, the crystal growth was found to be controlled by a three-dimensional mechanism and the activation energy value for leucite crystallization was 455.9 kJ/mol.

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