

Article

Microstructure Evolution Mechanism of Geopolymers with Exposure to High-Temperature Environment

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Abstract: The investigation on geopolymers has intrigued broad interests in the past decades, due to the requirements for the recycling of aluminosilicate solid wastes, such as red mud, slags, sludges and demolished concrete. Previous studies have demonstrated the feasibility of reusing this Aluminosilicate as a resource to prepare cementitious materials and indicated their promising properties at ambient temperature. However, when this material was exposed to high temperatures, especially above 1000 °C, the microstructure evolution mechanisms were not systematically investigated. In this study, the microstructural evolution process of metakaolin-based K geopolymer (molar ratio of K:Al:Si was 1:1:4) is investigated. The crystallized leucite originated from the geopolymer precursor was detected above 1000 °C. The SEM results indicate that the microstructure of the geopolymer before heating was composed of non-reacted metakaolin with a typical layered structure and reacted amorphous binder phase. As the geopolymer heated to 1000 °C, the microstructure of the geopolymer changed to a porous structure with an average pore size from 10 to 30 μm. When the heating temperature reached 1100 °C, the pores started to close along with the leucite crystallization process. As the heating temperature reached 1200 °C, most of the pores were closed. The TEM results show that the microstructure of the geopolymer, after being heated to 1400 °C, was composed of an amorphous glassy phase and crystallized leucite phase. The crystallized leucite grains originated from the nano-sized crystal nuclei, with an average size of 2–3 nm. The TEM-EDS results indicate that the chemical composition of the glassy phase was complicated. It varied from area to area because of the movement and uneven distribution of K.

Keywords: microstructure; geopolymer; high temperature; crystallization; glassy phase



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1. Introduction

As is well-known, the traditional manufacturing of concrete constructions and cementitious building materials has brought severe negative environmental impacts. The production of portland cement, the most commonly used binder material in cement concrete constructions and products, is an energy-intensive process that accounts for a large amount of global CO₂ emissions and other greenhouse gas. Apart from portland cement, various industrialization activities, such as metallurgy and chemical production, also pose significant greenhouse gases emissions and landfilling problems, due to the by-produced solid waste materials, such as red mud, fly ash, slag and many types of sludges. As a result, the use of environmentally-friendly low carbon cementitious materials to achieve

the goal of the green construction industry is a promising way to reduce the consumption of natural resources and energy consumption and is essential for achieving the goal of sustainable constructions. To eliminate the severe negative environmental burden from portland cement manufacturing, the utilization of industrial solid wastes as a resource to manufacture low-carbon cementitious materials without sacrificing the long-term performance and reliability is a promising approach to not only abate carbon emissions but also realize the innocuous treatment of industrial solid waste [1,2].

In many solid wastes, aluminosilicate is one of the main components from a chemical perspective. Although the composing elements are similar to portland cement, the inert nature of the aluminosilicate in solid waste has significantly limited their practical applications. To activate the non-active aluminosilicate, the express of “geopolymer” was patented by Joseph Davidovits through the alkali-activation method. From then on, the research of geopolymer materials burgeoned rapidly. In the most recent decade, using industrial solid wastes to prepare geopolymer-based cementitious materials intrigued great interests [3–5]. It was pointed out that geopolymers can be used as cementitious material to replace portland cement and manufacture low carbon concentrations [6].

It was reported that the hydration products of aluminosilicate cementitious materials were mainly composed of C-S-H, C-A-S-H and N-A-S-H and the hydration products were gradually transformed into a stable zeolite structure [7]. Campbell studied the durability of ancient Egyptian pyramids and verified that the hydration products contained zeolite-like structural compounds [8]. Zivica believed that using water glass as an activator can provide more silica tetrahedral monomers, which is beneficial to the formation of the final hydration product C-S-H gel, and previous studies have demonstrated that the activation and hydration process of aluminosilicate cementitious materials is mainly composed of the bond breaking and recombination of Mg-O, Ca-O, Si-O-Si, Al-O-Al and Al-O-Si in raw materials [9].

Krizan explored the hydration characteristics of a slag-based geopolymer. It was found that the degree of hydration was affected by the molar ratio and the alkali content of the activator. The testing results indicated that the hydration degree was proportional to the molar ratio and alkali contents [10]. The molar ratio of the Si:Al:K can be varied from 1:1:1 to 1:x:y (x and y can be varied from 1 to 4), depending on diverse applications [11,12]. It was reported that with a Si:Al molar ratio of 1:1.4 and a K:Si ratio of 1:1.8, the K-based geopolymer can be used as an anti-corrosion inorganic coating [11]. Another study demonstrated that with a Si:Al ratio of 3.5, the adhesive strength of a class F fly ash-based geopolymer can reach 3.5 MPa [12].

Except for the low-carbon emission benefit, another important merit of geopolymers is their outstanding fire-resistance performance. When concrete constructions and organic ones are exposed to a high-temperature environment, such as fires in city buildings or tunnel linings [13], sewer pipes [14] and refractory coatings [15], traditional concrete structures or organic coatings show catastrophic failure which results in massive economic loss and even endanger human lives. As a result, geopolymers can be potentially used as fire and heat resistance cementitious materials or inorganic coatings to enhance the durability and stability of concrete constructions.

To investigate the effect of molar ratio on the fire and heat resistance properties of geopolymers, the internal reaction mechanism of Na, Al, Si and Fe was explored by using red mud as a raw material to prepare single-component geopolymers. In this study, red mud was mixed with 0, 5, 10 and 15 wt% Na₂O, then calcined at 800 °C, cooled to room temperature and ground for 3 min, then passed through a 0.30 mm mesh. The leaching test, X-ray photoelectron spectroscopy (XPS), Mossbauer spectroscopy (Mossbauer) and nitrogen isothermal adsorption (NIA) were used to study the role of each element in the polymer. The experiment found that the pretreated RM dissolves in water to form an alkaline environment and releases a large number of elements for polymerization, but to form a stable geopolymer gel, more soluble Si is needed, so the addition of SF helps to form a stable gel. At the same time, the aluminosilicate structure in the original RM

is destroyed in an alkaline environment and the bonding energy of the Al-O and Si-O bonds was reduced, thereby improving the activity of Al_2O_3 and SiO_2 . A further study investigated the single elements of iron and found that alkali thermal activation affected the coordination of iron ions, changed the coordination structure and distribution position of iron ions so that Al^{3+} was replaced by Fe^{3+} in the aluminosilicate structure in RM. It had no obvious effect on polymerization [16].

Reinforced by fibers, Samal's studies systematically investigated the synergistic effects of carbon fibers, E-glass fibers and basalt fibers on the fire resistance of geopolymer composites [17]. It was found that the thermal resistance of geopolymers can be significantly enhanced by using fiber reinforcement. A Si:Al molar ratio as high as 15.6 was used as the parameter to manufacture the geopolymer [18]. Another study from the same researcher claimed that the thermal shrinkage of geopolymers can be affected by the increasing molar ratio of Si:Al [19].

Although those technologies and potential activation and hydration studies have shed some light on developing geopolymers, a majority of previous studies on geopolymer systems focused on the change in properties with increasing temperature. The microstructure evolution mechanism remains unclear from the perspective of the durability of geopolymers with exposure to high temperatures. This work aims to explore the potential microstructural evolution mechanism when the geopolymer is heated to high temperatures. To simplify the impact from the impurities of geopolymers on the phase change mechanisms, the metakaolin-based K geopolymer was used as the precursor rather than aluminosilicate solid waste geopolymer.

2. Experimental Procedure

The geopolymer was prepared according to previous studies [20]. The amorphous silica fume, KOH were obtained from Sinopharm. The TEM morphology and corresponding diffraction pattern of the silica fume are shown in Figure 1. As can be seen from this figure, the silica fume has an amorphous structure with an agglomeration of nano-sized particles. The metakaolin was used directly without further purification and calcination. The KOH solution was prepared by dissolving 1 mol of K_2O into 11 mol of water. The silica fume was added into the KOH solution with the molar ratio of $\text{K}_2\text{O}/\text{SiO}_2 = 1:2$ and followed by magnetic stirring for 24 h in a stainless-steel flask at room temperature. After the silica fume was completely dissolved in the KOH solution, the metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) powder was mixed with the $\text{KOH}/\text{SiO}_2/5.5\text{H}_2\text{O}$ solution; the final chemical molar ratio of K:Al:Si was 1:1:4. After mixing for 5 min in a high-energy mixer with a mixing rate of 1000 rpm, the gel solution was poured into a plastic petri dish and vibrated for 30 s to remove the air bubbles. After that, the petri dish was wrapped with plastic film and cured for 48 h at 50 °C. The final cured body was then removed from the petri dish carefully and was calcinated in a high-temperature furnace. The target temperatures ranged from 1000 °C to 1400 °C with 100 °C intervals, soaking 3 h after reaching the targeted temperature, and the heating and cooling rate was 2 °C/min.

The calcined samples were characterized using a Rigaku D/Max-b (Phillips) X-ray diffractometer. X-ray diffraction (XRD) was performed using a copper target at 45 kV and 20 mA. Diffraction scans were performed from 5 to 75° at a rate of 1°/min with a step size of 0.02°. Samples for the microstructure observation were sputter-coated with a gold-palladium alloy using a K575 Sputter Coater (Emitech, Houston, TX, USA) before the scanning electron microscopy (SEM) observation with an S-4700 SEM (Hitachi, Tokyo, Japan). For the SEM microstructure observation, the fracture surfaces of the calcined K geopolymer were etched using 3 wt% HF at room temperature for 20 s. The HRTEM and EDS analysis were manipulated on JEOL 2100 cryo and the accelerating voltage was 120 kV.

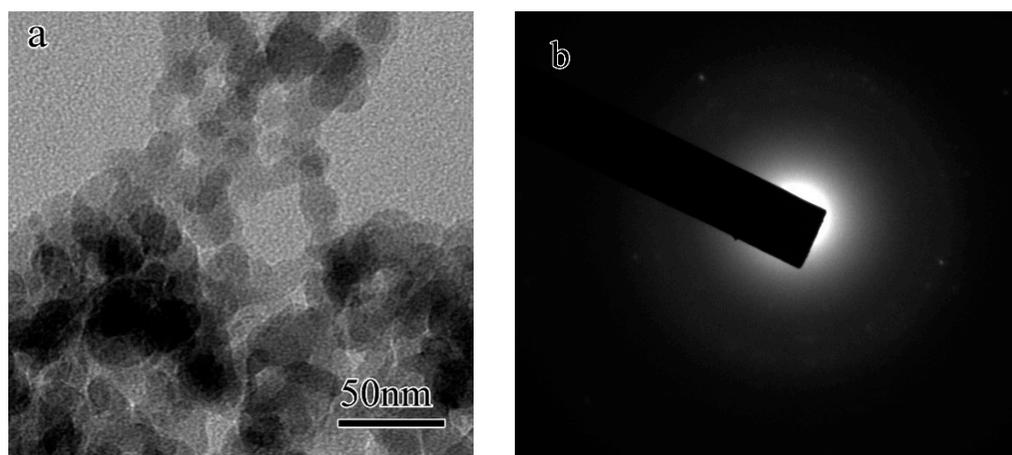


Figure 1. TEM morphology (a) and the corresponding diffraction pattern (b) of silica fume.

3. Results and Discussion

Figure 2 gives the XRD pattern of the metakaolin-based K geopolymer after calcination at different temperatures. As shown in this figure, only quartz peaks can be observed on geopolymer after heating it to 1000 °C and 1050 °C for 3 h, namely, the geopolymer was mostly composed of glassy phase. After it was heated to 1100 °C, palpable leucite peaks could be observed. Previous studies have demonstrated that the crystallization starting temperature of the geopolymer is sensitive to the chemical composition of the precursors. As a result, in this study, the crystallization temperature of the metakaolin-based geopolymer was higher than that in He's study, due to the fact that the molar ratio of K:Al:Si in He's study was 1:1:2.5 rather than 1:1:4, as in this study. From the crystal structure perspective, the ideal molar ratio of K:Al:Si should be 1:1:2 in leucite, according to the formula of leucite (KAlSi_2O_6). As a result, the extra Si content in this system significantly hindered the crystallization phase transformation process of the geopolymer into leucite ceramics. The extra Si content had an impact on the pozzolanic reaction when the geopolymer was prepared and the higher silica content contributed to the decline of mechanical properties which lead to the unreacted material acting as defects [21]. After the heating process, the extra silica content became the cause for the formation of more glassy phase content in the geopolymer-based leucite/glass composites and, finally, also impacted the mechanical properties [22,23].

Figure 3 shows the SEM fracture surface morphology of the metakaolin-based K geopolymer before and after calcination from 1000 °C to 1200 °C, with 100 °C intervals. As can be seen in Figure 3a, before the calcination process, distinctive unreacted metakaolin with typical layered structure (shown as the red-circled areas) and the reacted amorphous binder phase (shown as the blue-circled areas) could be observed, which well agrees with the expression of kaolinite from Provis [24]. After calcination at 1000 °C, a large number of observable pores with an average size in the range of 10–30 μm could be detected (Figure 3b) and the pores started to disappear with the formation of a continuous glassy phase when the heating temperature reached 1100 °C and there was a distinctive interface of the dense area and high porosity area, as shown in Figure 3c. After the heating temperature reached 1200 °C and 1400 °C, the microstructure showed a complete dense morphology and no pores could be observed on the fracture surface of the samples, as shown in Figure 3d,e.

The TEM morphologies of the K-based geopolymer before calcination are shown in Figure 4. In this figure, the round dark areas are the nano-sized crystal groups, as shown in Figure 4b, the bright area is the amorphous binder phase and the white small circles are the nanopores with average sizes varyin from 5 to 30 nm, shown as Figure 4c, and the crystallized grains originated from the nano-sized crystal nuclei with an average size of 2–3 nm, as shown in Figure 4d. This well agrees with the previous statement of the

formation of geopolymers. It was claimed that the formation process of geopolymers can be divided into four steps. First, the alkaline solution reacts with the metakaolin to form the silicate and aluminate-rich solution. In this process, the 5- or 6-coordinated Al are converted into 4-coordination. Second, the aluminosilicate oligomers are formed, due to the solution of the silicate, by the activating solution. Third, with the increasing concentration of aluminate, the stabilized aluminosilicate is dissolved to form a gel commence. Last, the geopolymer gel grows at the location where the slurry solidifies. It was also claimed that the nano-sized nuclei are the zeolite precursors which is beneficial to form leucite once the geopolymer is heated above the crystallization temperature [23].

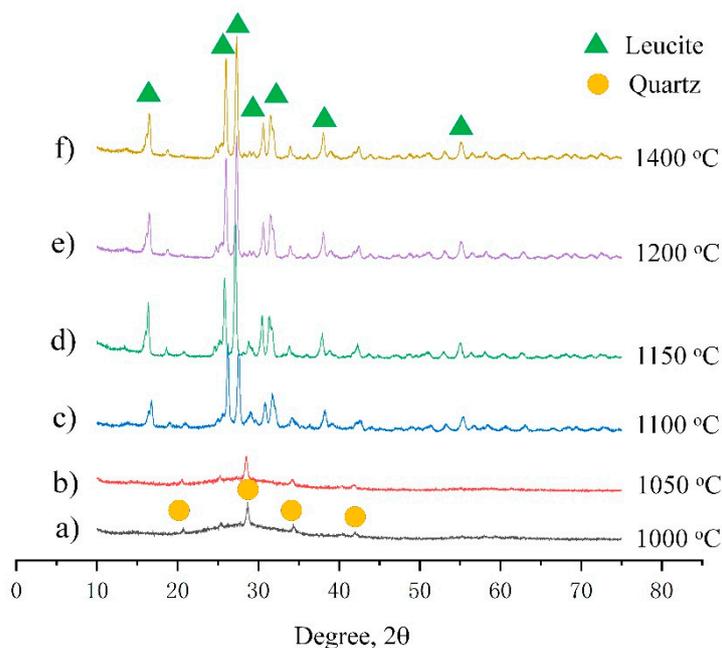


Figure 2. XRD pattern of the geopolymer materials calcined at various temperatures. (a) 1000 °C, (b) 1050 °C, (c) 1100 °C, (d) 1150 °C, (e) 1200 °C, and (f) 1400 °C.

He and Jia investigated the microstructure change of the metakaolin-based geopolymer with a Si:Al molar ratio that varied from 2 to 4 and a K:Al molar ratio of 1:1 at 800 °C [22]. It was found that, after the heat treatment, part of the geopolymer precursor formed leucite ceramics with a crystal size of about 4 μm . The HRTEM observation indicated that the grains were either lamellar- or needle-shaped twins, which was originated from the phase transformation from cubic to tetragonal symmetry at high temperature [25]. In addition, the exothermic peaks of the leucite crystallization shifted to high temperatures with increasing heating rates. The crystallization activation energy of leucite crystallization is about 455.9 kJ/mol and the corresponding Avrami constant is 3.89 [26]. Figure 5 depicts the HRTEM morphologies of the glassy phase and the crystal phase of the geopolymer after calcination at 1400 °C. It can be detected that the microstructure of the geopolymer, after being heated to 1400 °C, is composed of an amorphous glassy phase and crystallized leucite phase. Figure 5a shows a typical non-crystallized structure, which represents that this area is an amorphous glassy phase. Figure 5b presents a clear crystallized structure and the lattice agrees well with the tetragonal leucite.

Table 1 lists the TEM-EDS results of the atom fraction of the chemical composition of the glass phase at different areas corresponding to Figure 6. As can be seen in this table, the atom fractions of the glassy phase of geopolymer after calcination were different in different areas. For the ratio of K:Al:Si, the difference was not very obvious in different areas. In area A, it was approximately 1:1:1.5; in area B and E, the ratio changed to 1.5:1:2; in areas C and D, it was approximately 1:1:2. There is one thing that has to be noted; although the ratio of K:Al:Si was similar in areas B and E and C and E, respectively, the O contents

were significantly diverse. The ratio of K:O varied from 1:2 to 3:2. As can be deduced from the TEM-EDS results, the chemical composition of the glass phase was very complicated and the atoms were not evenly distributed due to the migration of these atoms.

Table 1. TEM-EDS results of atom fraction of chemical composition of the glass phase in calcined K geopolymer.

Chemical Elements	Area A	Area B	Area C	Area D	Area E
K	19.7	25.1	20.0	18.2	26.5
Al	21.7	17.5	17.5	17.1	17.2
Si	28.9	33.9	34.8	35.3	38.2
O	29.7	23.5	27.7	29.4	18.1

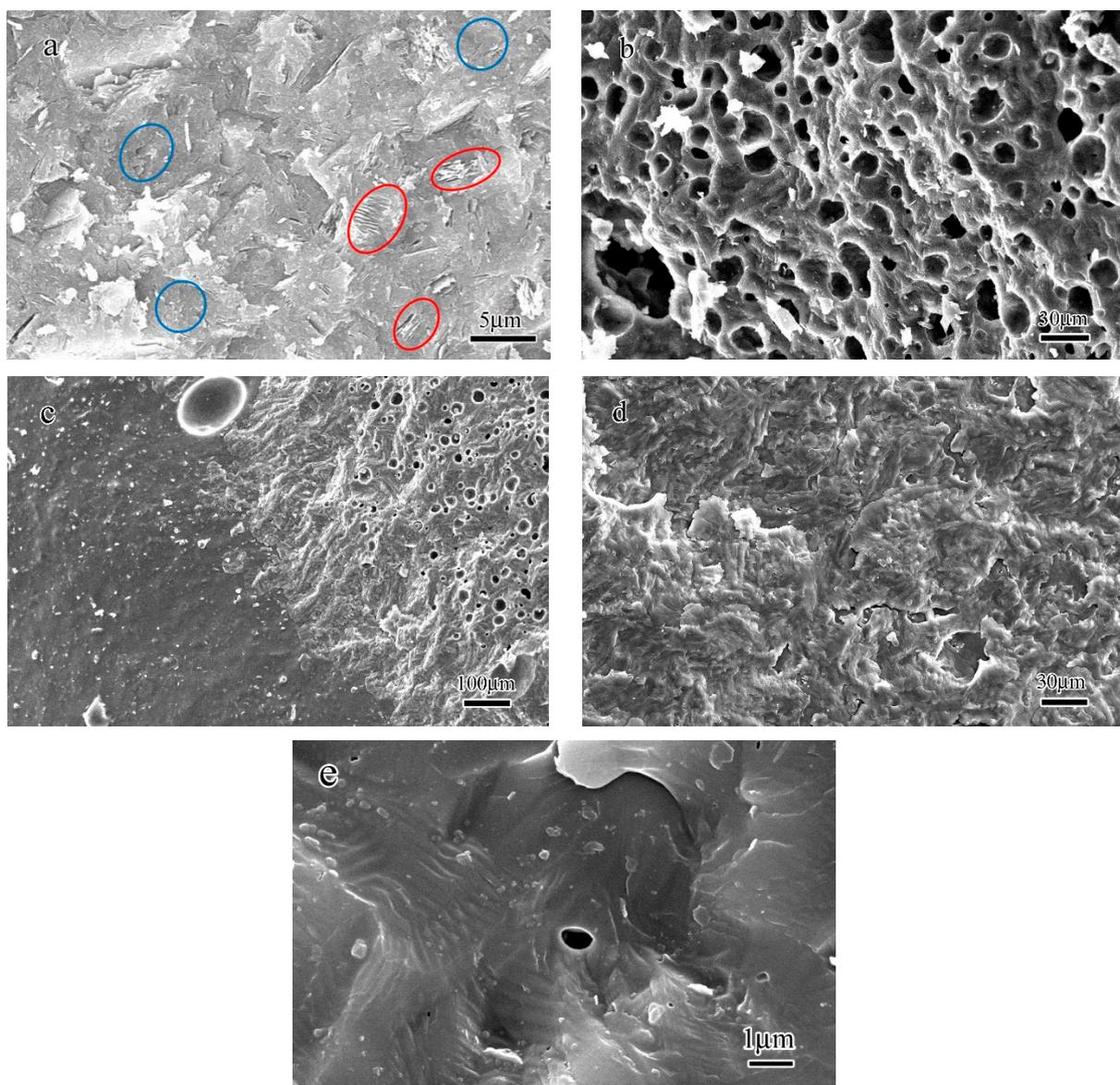


Figure 3. Fracture surface SEM images of the GP (a) before and after calcination at (b) 1000 °C, (c) 1100 °C, (d) 1200 °C and (e) 1400 °C.

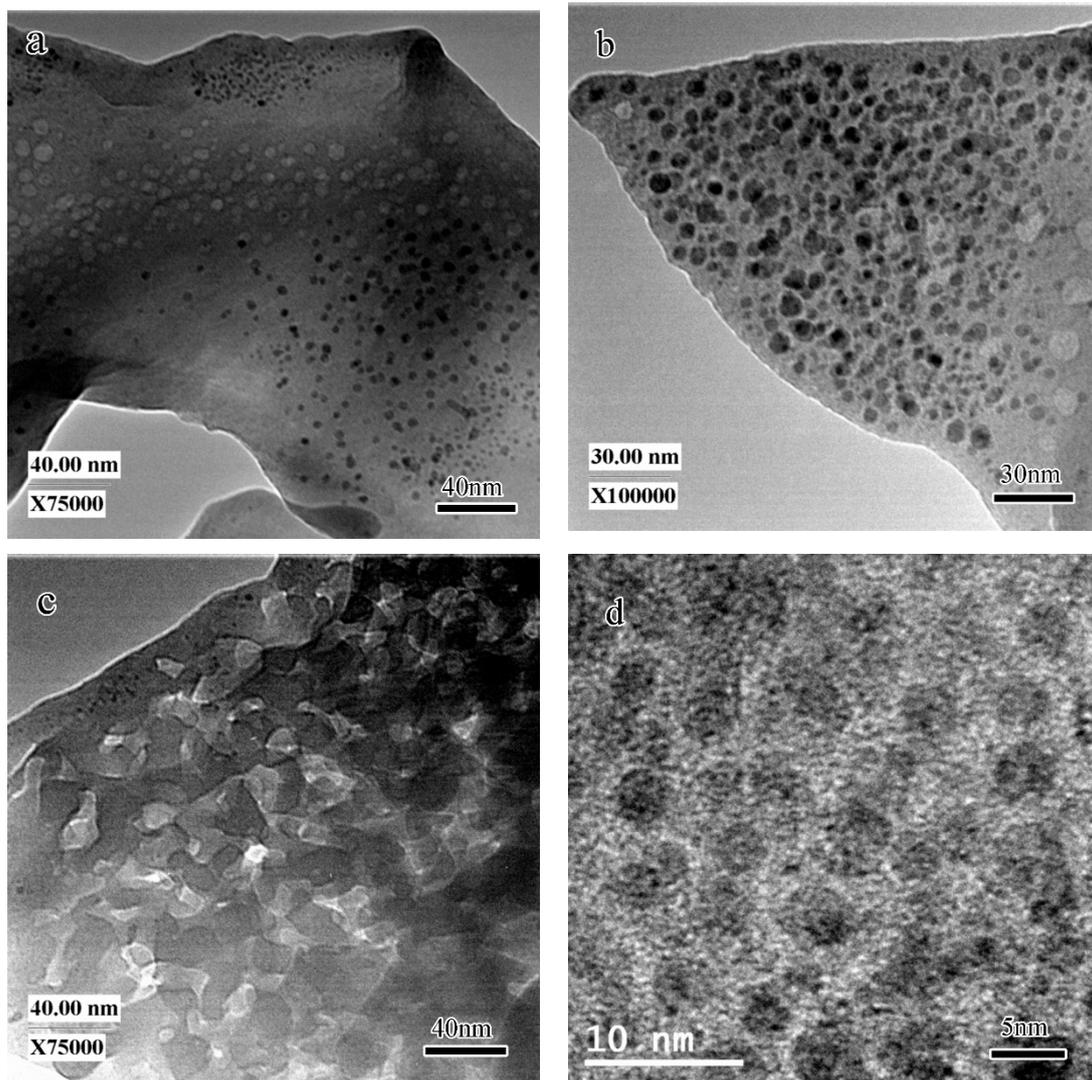


Figure 4. TEM images of the unheated GP: (a) the typical morphology of the amorphous hydration products (area A), nano crystals (area B) and nano pores (area C); (b) the agglomeration of the nano crystals; (c) the high-magnification image of the nano pores; (d) the high-magnification image of the nano crystals.

Due to the thermal diffusion of K, some places are rich in K and some places are poor in K, as mentioned above. The leucite nucleation happened in those areas with the ratio of the atoms of K/Al/Si/O = 1:1:2:6. Moreover, in those areas where the ratio of the atoms was not the same as leucite, the formation of a glassy phase was easier than that of a leucite crystal. During the calcination processing, the thermal migration degree of the atoms increased with the increase in calcination temperature, namely, it increased the probability to have the atoms ratio of K/Al/Si/O = 1:1:2:6 and form the leucite crystal.

Figure 7 gives the schematic illustration of the curing process which demonstrates the two potential reasons of the uneven distribution of the glassy phase. The first one is that the K_2O has a lower melting point (800 °C) than the amorphous Al_2O_3 and SiO_2 in the metakaolin, which does not have a specific melting point; therefore, the K_2O was evaporated from the surface of the samples during heating, which made the non-equilibrium of K in the bulk of the material. Consequently, K diffused from the center to the surface, that lead to the uneven chemical distribution. The second reason is that the geopolymer was made of $K_2O \cdot H_2O/SiO_2$ solution plus metakaolin and H_2O slowly evaporated from the bulk materials during the curing procedure. During this process, part of K_2O diffused with

H₂O in the samples and concentrated on the wall of the channel of water evaporation; this also lead to the uneven chemical distribution of the final glass phase.

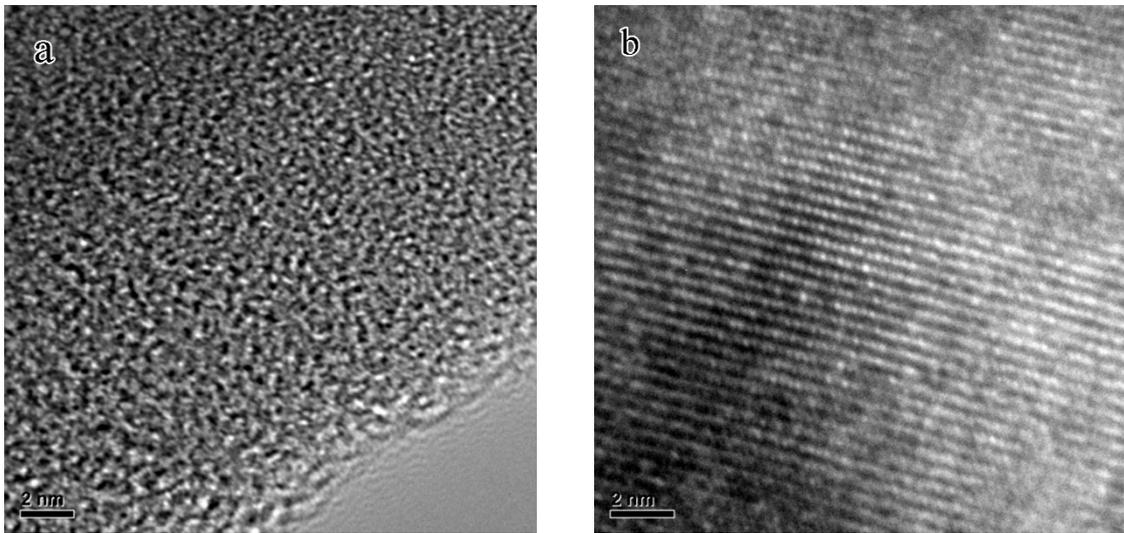


Figure 5. HRTEM images of K-based GP calcined at 1400 °C for 3 h: (a) amorphous glassy phase structure; (b) the crystallized leucite structure.

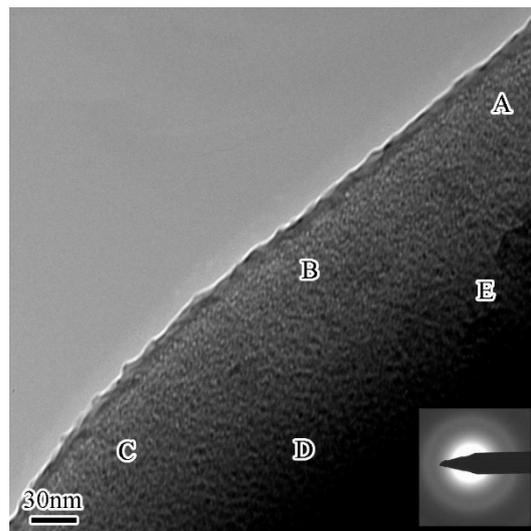


Figure 6. TEM morphology and the corresponding selected area diffraction pattern of the glassy phase.

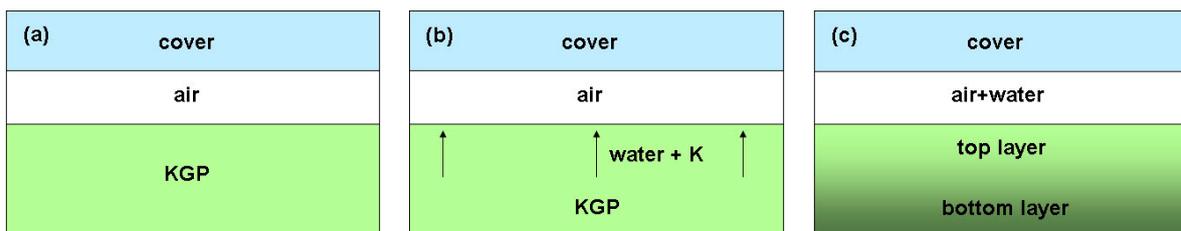


Figure 7. Schematic demonstration of the GP curing process. (a) before curing, (b) during the curing process, and (c) after curing process.

4. Concluding Remarks

In summary, the crystallization process of the metakaolin-based K geopolymer with the Si:Al:K molar ratio of 1:1:4 and with the heating temperature up to 1400 °C was investigated. The following conclusions were obtained.

1. The XRD results show that the crystallization did not occur until the heating temperature reached 1100 °C.
2. The SEM observation indicated that the microstructure of the fracture surface of the geopolymer before heating was composed of non-reacted metakaolin with a typical layered structure and reacted amorphous binder phase. The TEM result indicates that the unheated geopolymer was composed of an amorphous hydration product phase, nano-sized pores with size varying from 5 to 30 nm and agglomeration of nanocrystals with an average size of 2–3 nm.
3. After the geopolymer was heated to 1000 °C, the microstructure of the geopolymer started to become porous with an average pore size in the range of 5 to 30 µm. When the heating temperature reached 1100 °C, the pores closed along with the leucite crystallization process and the sintering effect and a distinctive interface between the densified microstructure and porous structure could be observed. When the heating temperature reached 1200 °C, most of the pores closed. The TEM results demonstrate that the components of the geopolymer after being heated to 1400 °C were composed of an amorphous glassy phase and crystallized leucite phase.
4. The crystallized leucite grains originated from the nano-sized crystal nuclei with an average size of 2–3 nm. The TEM-EDS results indicate that the chemical composition of the glassy phase was complicated. It varied from area to area because of the movement and uneven distribution of K.

Author Contributions: Y.L. and Y.X. prepared most of this manuscript. J.L. and C.X. organized the Figures and Tables. D.W. revised the manuscript and organized the outline and the whole contents. N.C. and N.X. supervised the analysis part. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Some or all data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

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