

Article

One-Step Microcrystalline Glass Preparation Using Smelting Slag from Waste Automobile Three-Way Catalysts through Iron Collection

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Abstract: The smelting slag obtained through iron collection from waste automobile three-way catalysts was used as a raw material to prepare microcrystalline glass through a one-step crystallization heat treatment. The phase composition and microstructure of the prepared glass were analyzed through X-ray diffraction and scanning electron microscopy–energy dispersive X-ray spectroscopy, respectively. Single-factor experiments were conducted to investigate the effects of crystallization temperature from 900 to 950 °C and crystallization time from 0.5 to 4 h on the physical and chemical properties of the microcrystalline glass. The results indicated that the optimum crystallization temperature and time for preparing microcrystalline glass with glass smelting slag through the proposed one-step crystallization heat treatment process were 950 °C and 3 h, respectively. Under these experimental conditions, the number of crystalline phases of the microcrystalline glass was high, the grains were mainly spherical and columnar particles, the sample structure was dense, and the best results were obtained: the density was 2.72 g/cm³, the water absorption was 1.55%, the porosity was 4.2%, the Vickers hardness was 618 HV, the acid resistance was 2.6%, and the alkali resistance was 0.04%. In addition, the results of the toxicity characteristic leaching procedure indicated that the leaching concentrations of heavy metals such as Zn, Cr, and Pb in the microcrystalline glass were lower than those in the base glass and were considerably lower than the acceptable limits. The microcrystalline glass obtained from final smelting slag through heat treatment can enhance the stabilization of harmful elements. The findings of this study can be applied to the treatment of bulk solid waste.

Keywords: waste catalyst; resource-oriented; one-step treatment; microcrystalline glass; stabilization



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1. Introduction

In recent years, waste catalyst resource utilization technology, including pyro-technology, wet technology, and biotechnology, has received extensive attention. In particular, the pyrometallurgical enrichment technique has been remarkably developed and has been used to efficiently recover valuable metals. However, green and sustainable technologies for utilizing enriched smelting slag have yet to be developed. In the process of recovering platinum group metals from three-way catalysts (SACs-3) through iron collection, the final glassy slag is mainly constituted by high contents of silicon or silicon aluminum glassy slag, which can be used as raw materials for aluminosilicate- or silicate-series microcrystalline glass [1–3]. Furthermore, B₂O₃, flux agent, added to the smelting process can be used as the nucleating agent in the preparation of microcrystalline glass [4,5].

A large amount of final glassy residue is generated in the process of iron capture and the recovery of platinum group metals from SACs, though the corresponding comprehensive utilization and treatment capacity is relatively weak. The low value-added treatment methods of pit landfill, open pile, paving, or use as raw material for cement are still the

main treatment methods of final slag, which also contains toxic heavy metal elements such as chromium, lead and cadmium. Therefore, the accumulation and retention of a large amount of metallurgical solid waste will certainly bring continuous potential risks and threats to the surrounding natural environment and human survival. The use of final slag as a raw material for the preparation of microcrystalline glass can not only realize the resource utilization of smelting final slag and generate additional economic benefits but also result in zero solid waste in the whole recycling process, which is a win-win situation for both economic and environmental protection [6–8].

In recent years, techniques for preparing microcrystalline glass using metallurgical final slag after heat treatment have attracted extensive attention [9–13]. Zheng et al. [9] studied the effect of the amount (mass fraction) of pickling sludge on the properties of microcrystalline glass prepared from smelting slag with silica aluminate as the main component, and the results demonstrated the best overall performance of microcrystalline glass with 21% (mass fraction) of pickling sludge. The sample obtained by heat treatment at 900 °C for 1.2 h had a density of 3.04 g/cm³, a water absorption of 0.11%, a Vickers hardness of 742.72 HV, a flexural strength of 119.32 MPa, and an acid and alkali resistance of 99.16% and 99.79%, respectively. Nan et al. [11] used the sintering method to prepare microcrystalline glass with iron tailings as the main raw material, and the results showed that the performance of the base glass melted under a melting temperature of 1400 °C and a holding time of 2 h was strong, the performance of the microcrystalline glass specimens obtained by crystallization treatment under a crystallization temperature of 900 °C and a holding time of 2 h was better, and both specimens' compressive strength was 158.32 MPa, their density was 2.74 g/cm³, and their coefficient of thermal expansion was $6.8 \times 10^{-6} \text{ K}^{-1}$. Wang et al. [12] prepared microcrystalline glass by adding TiO₂ as a nucleating agent in a one-step process in laterite; with the increase in TiO₂, the main crystalline phase started to change from μ -cordierite to the pseudosapphire phase and the crystallinity, grain size, and acid and alkali resistance of the microcrystalline glass were improved. Shi et al. [13] successfully produced CaO-Al₂O₃-SiO₂(CAS) glass-ceramic materials from molybdenum tailings (MTs). A large volume of raw MTs, 41–49 wt%, can be recycled. The main crystalline phase of CAS glass-ceramic is wollastonite (CaSiO₃), and the content of the crystal phase increases with the addition of MTs in CAS glass-ceramic materials.

Microcrystalline glass not only has the excellent properties of both ceramics and glass but also has properties (mechanical properties, chemical corrosion resistance, acid and alkaline resistance, etc.) superior to those of similar ceramics and glass [14–16]. There are three main processes for preparing microcrystalline glass: the melting method involves adding a certain amount of a nucleating agent to a solid waste raw material, melting and homogenizing it under high-temperature conditions to form a glass melt. Then, the melt is cast and shaped, and after a little cooling and shaping, it is then annealed. After the annealing process, nucleation and crystallization are carried out under certain temperature conditions to obtain finished microcrystalline glass. The melting-sintering method is a process in which raw materials are melted and quenched by water to obtain a glass powder that is then further ground and pressed into shape and finally sintered at a high temperature to obtain the desired microcrystalline glass products. In the one-step method, one directly mixes and grinds raw materials in the glassy or crystalline state and then sinters them to make solidly soluble raw powder materials to form glass [17–19].

At present, a large amount of waste SACs-3 is generated and a large amount of slag obtained from the melting and trapping processes is accumulated, but there have been few studies related to the treatment methods for this slag. In the present study, the smelting glass slag obtained from waste automobile three-way catalysts through iron collection was used as the raw material. Microcrystalline glass heat treatments were compared and analyzed to develop a one-step precrystallization heat treatment suitable for the obtained melting slag and to finally prepare microcrystalline glass. The studied method showed the advantages of a short process flow and energy saving compared with the commonly used nucleation-crystallization treatment process. A new process of slag vitrification in

the smelting process was proposed, and the influence of the vitrification process on the harmless treatment of hazardous solid wastes such as SACs was studied. Thereafter, X-ray diffraction (XRD) and scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) were used to analyze the phase composition and microstructure of the as-prepared microcrystalline glass, and the physical and chemical properties of the glass were investigated. Furthermore, the effects of crystallization time and temperature on the physical and chemical properties of the microcrystalline glass were investigated, and the optimal heat treatment system was determined.

2. Experiment

2.1. Experimental Materials and Equipment

The base glass was obtained through the water quenching of an upper glass residue formed in the late stage of the iron smelting process to recover PGMs from SACs-3. X-ray fluorescence spectrum (XRF) analysis results showed that its main chemical components were: SiO₂ (30.26%), CaO (18.84%), Al₂O₃ (30.68%), MgO (6.78%), B₂O₃ (8.32%), TFe (0.75%), and TiO₂ (2.82%).

The following chemical reagents were used during the experiments: sodium hydroxide (analytical grade), nitric acid (analytical grade), acetic acid (analytical grade), and hydrofluoric acid (10%).

The equipment used in the experimental procedures included the following: a box resistance furnace, a temperature control instrument, a thermocouple, a constant-temperature drying oven, a differential thermal analyzer, a scanning electron microscope, a Vickers hardness tester, an X-ray diffractometer, and an ICP plasma emission spectrometer.

Tables 1 and 2 show the chemical reagents and instruments used in the experiments, respectively.

Table 1. Experiment reagents.

Reagents	Specification	Manufacturers
sodium hydroxide	analytical grade	Sinopharm Chemical Reagent Co., Shanghai, China
nitric acid	analytical grade	Sinopharm Chemical Reagent Co.
acetic acid	analytical grade	Sinopharm Chemical Reagent Co.
hydrofluoric acid	C(HF) = 10%	Xiamen HaiBiao Technology Co. Xiamen, China

Table 2. Experiment apparatus.

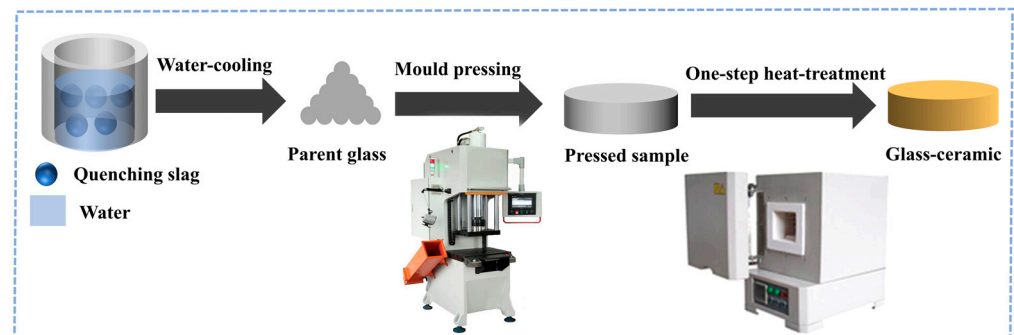
Apparatus Name	Specification/Model	Manufacturers
box resistance furnace	SX2-4-10	Sinopharm Chemical Reagent Co.
temperature control instrument	CKW-3100	Beijing Chaoyang Automatic Instrument Factory, Beijing, China
thermocouple	Platinum-Rhodium Couple(S type)	Shenyang Dongda Sensing Technology Co. Shenyang, China
constant-temperature drying oven	HG101-1A	Nanjing Experimental Instrument Factory, Beijing, China

Table 2. *Cont.*

Apparatus Name	Specification/Model	Manufacturers
differential thermal analyzer	SDTQ600	Ta Corporation, Singapore
scanning electron microscope	SU-8010	Hitachi, Japan
Vickers hardness tester	THVP-50	Shenyang Times Testing Technology Co. Shenyang, China
X-ray diffractometer	D8 Advance	Bruker, Bremen, Germany
ICP plasma emission spectrometer	ICP-5000	China Spotlight Technology Co., Beijing, China

2.2. Experimental Procedure

Figure 1 illustrates the preparation of microcrystalline glass through one-step heat treatment. The slag was dried at 105 °C for 12 h after water cooling; some of the microcrystalline glass obtained after drying was taken, crushed, and ground into a fine powder; and regular-shaped blocks of microcrystalline glass were taken and finely ground with an agate mortar and sieved through No. 200 mesh to obtain a fine powder. To obtain the glass transition temperature (T_g) and crystallization temperature (T_c) of the base glass, 10 mg of the sieved fine powder was placed in a platinum crucible, which was transferred to a differential thermal analyzer and heated up to 1100 °C under air at a heating rate of 10 °C/min [20–22]. The fine powder was sieved without adding any binder and was directly pressed into a cylinder with a diameter of 30 mm and a height of 10 mm under 50 MPa of pressure and held at 105 °C for 4 h. Thereafter, the powder was removed and stored in a sealed container for subsequent heat treatment experiments.

**Figure 1.** Schematic of the preparation of microcrystalline glass through one-step heat treatment.

The prepared column base glass was placed in a corundum boat and moved into a chamber resistance furnace, and the temperature was increased at a rate of 10 °C/min. First, the holding time was set to 3 h and the target treatment temperatures were set to 900 °C, 925 °C, and 950 °C to investigate the best crystallization temperature of the microcrystalline glass, and then the holding time was adjusted to 0.5 h, 1 h, 2 h, 3 h, and 4 h at these temperatures. The results showed that the best performance of the microcrystalline glass was achieved at 3 h of crystallization time.

2.3. Analysis

The microstructure of the microcrystalline glass was analyzed using a scanning electron microscope (SEM, SU-8010). The acid and alkali resistance of the microcrystalline glass samples were determined according to the M. Erol method [23]. The density and water absorptivity of the microcrystalline glass were determined through the Archimedes drainage method [24]. A Vickers hardness tester (THVP-50; Shenyang Times Testing Technology Limited Company, Shenyang, China) was used to test the Vickers hardness of the

microcrystalline glass samples [25]. The standard toxicity characteristic leaching (TCLP) method was used to determine the leaching concentrations of heavy metals in the prepared microcrystalline glass [26].

3. Results and Discussion

3.1. Basic Glass Differential Thermal Analysis

Figure 2 displays the differential thermal analysis results for the base glass. The glass transition temperature (T_g) of the base glass was approximately 697.42 °C, and the crystallization temperature (T_c) was approximately 948.93 °C. In particular, this differential heat curve obtained through DSC exhibited a heat absorption peak at 958.49 °C, indicating the melting temperature (T_m) of the base glass. Therefore, the maximum crystallization temperature in this experiment was 950 °C.

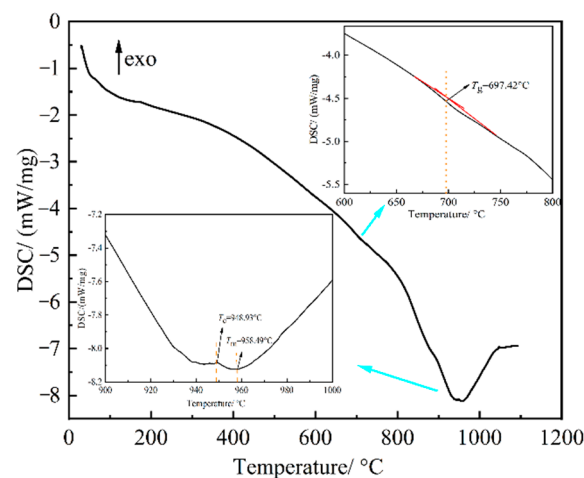


Figure 2. DSC curves of the base glass.

3.2. Effects of Heat Treatment Temperature on the Crystal Precipitation of Microcrystalline Glass and Its Properties

The results of the differential heat curve of the base glass showed that the crystallization exothermic peak of the base glass was 948.93 °C, that is, the maximum crystallization temperature of the base glass was 948.93 °C. Therefore, three heat treatment temperatures of 900 °C, 925 °C, and 950 °C were selected to analyze the effects of heat treatment temperature on the crystal precipitation of the microcrystalline glass and its properties.

Figure 3 displays the XRD patterns of the microcrystalline glass obtained after holding it at different crystallization temperatures for 3 h each. The base glass was precrystallized at three crystallization temperatures of 900 °C, 925 °C, and 950 °C, and the diffraction peaks of the obtained microcrystalline glass were stronger at 950 °C than those at 900 °C, indicating that the higher the crystallization temperature, the greater the precrystallization of the base glass. Within the range of the crystallization temperature from 900 °C to 950 °C, the crystalline phases of the microcrystalline glass were all dominated by calcium feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The main precipitation phase of the microcrystalline glass within the range of 900–950 °C was independent of temperature; however, the degree of crystallization of the prepared microcrystalline glass increased with increasing temperature.

Figure 4 displays the SEM images of the microcrystalline glass obtained after the heat treatment of the base glass at different crystallization temperatures. The crystallization temperature notably influenced the microstructure of the microcrystalline glass. When the crystallization temperature was 900 °C, the number of crystalline phases in the microcrystalline glass was small, the degree of crystallization was low, the size of the grains varied, and the number of glassy phases was greater; furthermore, obvious cracks and pores appeared after corrosion by hydrofluoric acid. When the crystallization temperature increased to 925 °C, the glass phase in the microcrystalline glass disappeared, the number of

crystalline phases sharply increased, the grain size increased, the crystal became spherical, and the density of the microcrystalline structure increased. When the crystallization temperature increased to 950 °C, some spherical grains transformed into columnar grains and the structure became denser, thereby improving the performance of the microcrystalline glass. With the increase in temperature, the degree of crystallization of the microcrystalline glass rapidly increased, the precipitation of the crystalline phase rapidly increased the viscosity of the microcrystalline glass, and the resistance to crystallization became significant, which inhibited the further sintering process and formed a supercooled liquid that could not be nucleated. At the same time, due to the fastest heat dissipation in the direction perpendicular to the shape wall, the crystal grew in the opposite direction and the anisotropy of crystal growth made part of the grain shape turn into a column. The degree of crystallization of the microcrystalline glass within the range of 900–950 °C increased with increases in temperature.

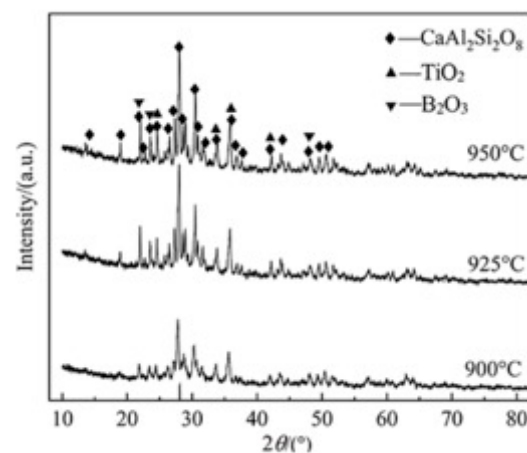


Figure 3. XRD patterns of microcrystalline glass products obtained at different crystallization temperatures.

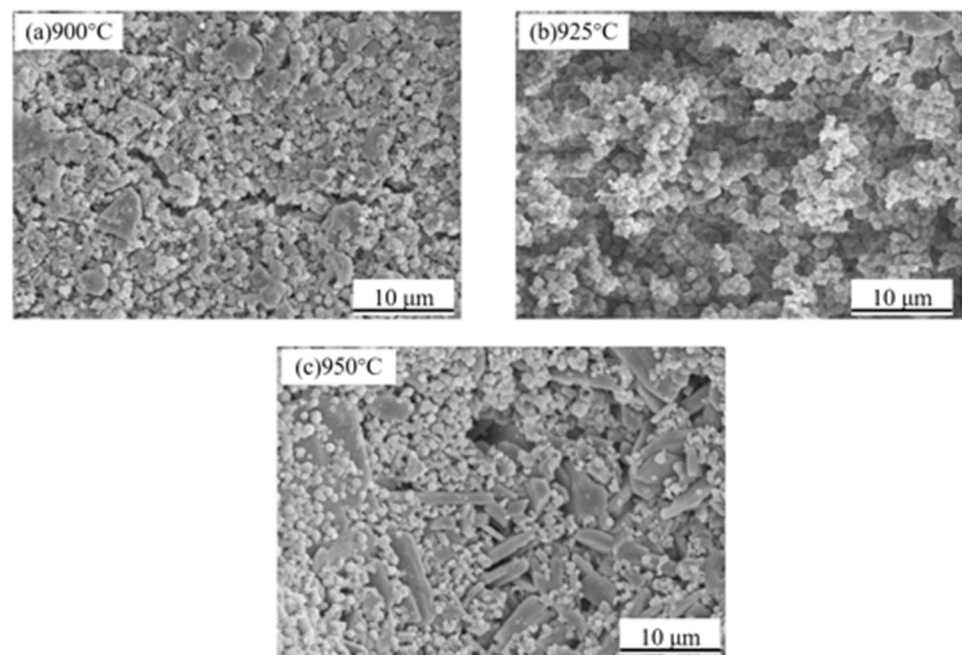


Figure 4. SEM images of microcrystalline glass samples at different crystallization temperatures: (a) 900 °C, (b) 925 °C, and (c) 950 °C.

The determination of parameters such as the strength, coefficient of thermal expansion, and optical and dielectric properties of microcrystalline glass is costly and time-consuming,

while the measurement of density is relatively simple and low-cost. Therefore, the evaluation of material density can be used to analyze the phase changes in microcrystalline glass to indirectly examine its properties and to realize the control of glass composition and the microcrystallization process. Density testing is commonly used in practical production as one of the means of glass quality inspection. Figure 5 illustrates the results of the effects of crystallization temperature on the density of the microcrystalline glass. As illustrated in Figure 5, the density of the prepared microcrystalline glass gradually increased with the increase in crystallization temperature, thereby reaching a maximum density of 2.72 g/cm^3 at 950°C . The increase in temperature promoted the precrystallization of the base glass and increased the number of crystals, improved the crystallization degree, increased the density of the crystal structure, and increased the density of the microcrystalline glass.

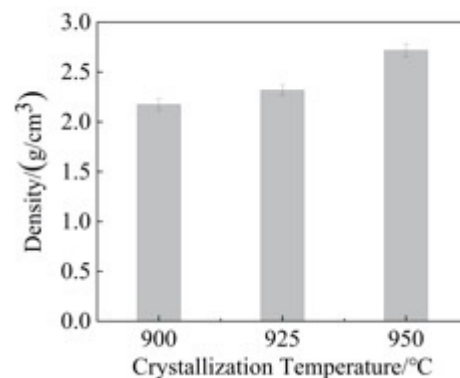


Figure 5. Effects of crystallization temperature on the density of the microcrystalline glass.

Water absorption is a physical quantity that indicates the degree of water absorption of an object. A low water absorption rate could inhibit the adsorption of a leaching solution into the interior of a curing body, thus inhibiting the leaching of heavy metals. Therefore, reducing the water absorption rate of microcrystalline glass is important for product quality improvement. Figure 6 illustrates the results of the effect of crystallization temperature on the water absorption of the studied microcrystalline glass. The trend of the water absorption of the microcrystalline glass with the increase in the crystallization temperature and the trend of density with the increase in the temperature were opposite. This may be attributed to the increase in the number of crystalline phases precipitated from the microcrystalline glass with increasing temperature. Moreover, the crystalline grains primarily had spherical and columnar shapes; therefore, the number of pores between the crystals gradually decreased and the densities of the crystals increased. As displayed in Figure 4, with the increase in the crystallization temperature, the number of crystalline phases gradually increased, the densities of the crystalline phases increased, and the water absorption rate of the microcrystalline glass decreased.

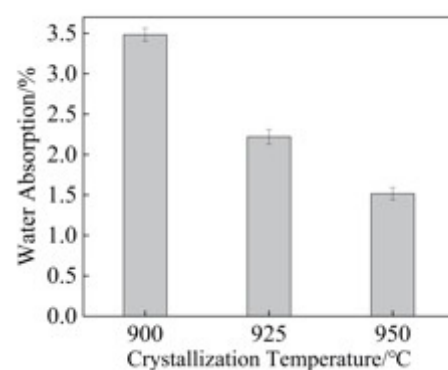


Figure 6. Effects of crystallization temperature on the water absorption of the microcrystalline glass.

Porosity refers to the percentage of the volume of pores contained in a refractory product compared with the total volume of the product. It is used to identify the degree of sintering of products such as ceramics and refractory materials, to determine the adsorption capacity of porous substances such as activated carbon, and to measure the technical properties of foams, among others. The excessive porosity of microcrystalline glass could lead to an uneven surface and thus affect the strength of the product. Figure 7 illustrates the results of the effects of crystallization temperature on the porosity of the studied microcrystalline glass. When the crystallization temperature was 900 °C, the number of crystalline phases in the microcrystalline glass was small because the lower crystallization temperature hindered the precipitation process and the growth of the precipitated grains was incomplete. Moreover, a large number of pores were observed between the crystalline phases, thereby resulting in a high porosity of the samples. For example, the porosity was as high as 7.43% at 900 °C. With the increase in temperature, the precrystallization process was strengthened, the number of crystalline phases increased, the degree of crystallization was high, the pores and gaps between the crystals gradually decreased, the density of the microcrystalline glass increased, and the porosity of the microcrystalline glass decreased.

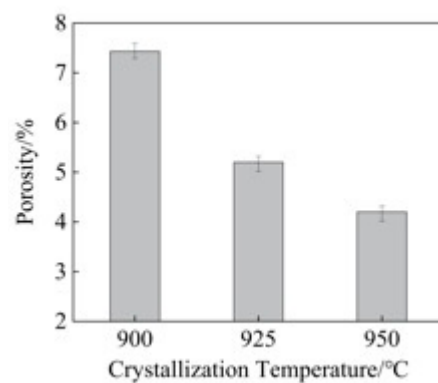


Figure 7. Effects of crystallization temperature on porosity of the microcrystalline glass.

Figure 8 illustrates the results of the effects of crystallization temperature on the Vickers hardness of the prepared microcrystalline glass. The Vickers hardness of the microcrystalline glass increased with increasing crystallization temperature. When the crystallization temperature was 950 °C, the Vickers hardness of the microcrystalline glass was 618 HV. The lower the crystallization temperature, the less the crystalline phase precipitation and the larger the glassy phase in the microcrystalline glass; thus, the internal densities and microhardness were low. With increasing temperature, a large number of crystalline phases precipitated inside the microcrystalline glass and the grains bit each other more; the porosity of the microcrystalline glass decreased, thus increasing the density and Vickers hardness of the microcrystalline glass.

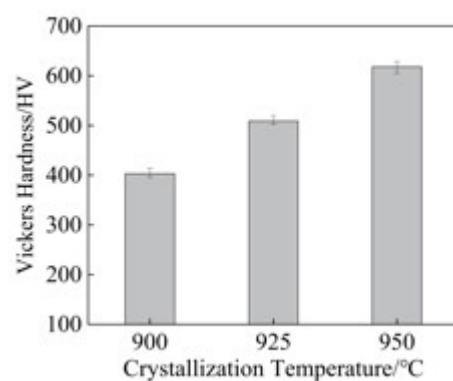


Figure 8. Effects of crystallization temperature on the Vickers hardness of the microcrystalline glass.

Industrial microcrystalline glass often needs to serve in acidic and alkaline environments, and the acid and alkaline resistance of microcrystalline glass materials significantly affect their service life, so it is important to study the acid and alkaline resistance of microcrystalline glass to expand its use field. The possible reactions between the main crystalline phase of the microcrystalline glass and acidic and alkaline substances in this study are shown in Equations (1)–(3). Figure 9 displays a plot of the acid and alkali resistance of the microcrystalline glass versus crystallization temperature. Overall, the alkali resistance of the microcrystalline glass was stronger than its acid resistance because the glass phase leaches more easily in acidic solutions. However, the variation trends of the acid and alkali resistances of the microcrystalline glass with temperature were identical; both resistances decreased with increasing temperature. With increasing crystallization temperature, the number of crystals in the microcrystalline glass gradually increased, the number of complete grains increased, the density increased, and the acid and alkali resistances increased. As illustrated in Figure 9, the acid and alkali resistances of the prepared microcrystalline glass were the highest (by 2.36% and 0.4%, respectively) at a crystallization temperature of 950 °C.

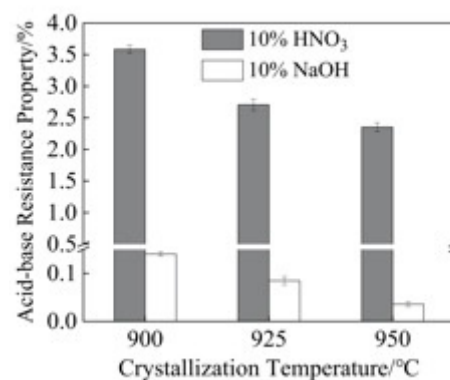
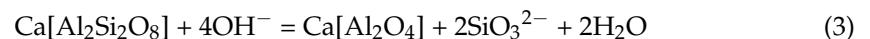
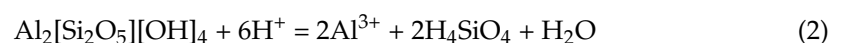


Figure 9. Effects of the crystallization temperature on the acid and alkali resistances of the microcrystalline glass.

In summary, the optimal crystallization temperature for preparing the microcrystalline glass in this experiment was 950 °C.



3.3. Effect of Crystallization Time on Precrystallization and the Properties of the Microcrystalline Glass

The crystallization time notably influenced the performance of the microcrystalline glass, and a reasonable crystallization time was crucial to achieve superior performance. The prepared cylinders were placed in corundum boats and transferred to a high-temperature furnace, the temperature was increased to 950 °C in one step at a rate of 10 °C/min, and the microcrystalline glass samples were obtained by cooling in the furnace after holding for 0.5, 1, 2, 3 and 4 h.

The XRD patterns for the microcrystalline glass products prepared by holding for different times at the optimal crystallization temperature are displayed in Figure 10. The crystalline phase species of the microcrystalline glass did not change with the increase in the crystallization time from 0.5 h to 4 h. The main crystalline phases of the microcrystalline glass obtained at different crystallization times all constituted the anorthite phase ($\text{CaAl}_2\text{Si}_2\text{O}_8$). However, when the crystallization time was increased to 1 h and more, the diffraction peak of the chalcocite feldspar was enhanced compared with that at a crystallization time of 0.5 h. This indicated that the content or crystallization degree of

the crystalline phase of the microcrystalline glass increased, while the peak intensity of the chalcocite feldspar was slightly enhanced after 1 h. Thus, the crystallization degree of the crystalline phase was slowly enhanced by the continuing extension of the crystallization time after 1 h. The extension of the crystallization time did not affect the crystalline phase type of the microcrystalline glass; however, a reasonable extension of the crystallization time improved the degree of crystallization of the microcrystalline glass.

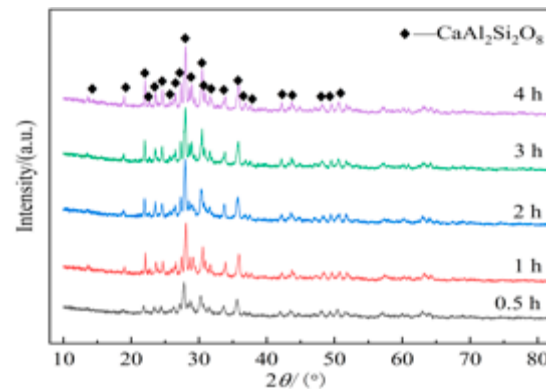


Figure 10. XRD patterns of microcrystalline glass product samples prepared at different crystallization times.

Figure 11 displays SEM images of the microcrystalline glass prepared at different crystallization times. When the crystallization time was 0.5 h, the crystallization degree of the sample was low, the number of glassy phases was larger, the grain size was uneven and the number was small, the grains were irregularly distributed, and the internal structure of the microcrystalline glass was random and contained defects such as pores. This can be attributed to the short crystallization time, the small number of grains, and the incomplete growth of the nuclei, which resulted in an insufficient crystallization of the prepared microcrystalline glass. With the extension of the crystallization time, the crystallization drive of the sample was enhanced, the number of crystals increased, and the growth of the nuclei was complete [27]. When the crystallization time was extended to 1 h, the glass phase in the microcrystalline glass sample disappeared and a large number of spherical grains with different sizes ranging within 100–200 nm was generated. The grains generated in the samples were more closely arranged and tended to gather into clusters; however, small holes were observed in the samples. When the crystallization time was further extended to 3 h, some spherical grains in the sample transformed into rods, thereby increasing the density of the sample structure and enhancing the performance of the microcrystalline glass. However, when the crystallization time was extended to 4 h, the spherical grains and rod-like grains in the sample disappeared. In addition, a mesh structure formed in the sample increased the contact area of the glass with the acidic and alkaline solutions and considerably reduced the acid and alkali resistances of the sample, thereby resulting in a decrease in its chemical stability.

Figure 12 illustrates the effects of crystallization time on the density of the prepared microcrystalline glass. The density of the microcrystalline glass first increased and then decreased with the extension of the crystallization time. When the crystallization time was extended to 3 h, the density reached its maximum value of 2.72 g/cm³; when the crystallization temperature was further extended to 4 h, the density of the microcrystalline glass decreased. These results can be attributed to the gradual increase in the number of precipitated phases (chalcocite feldspar) in the microcrystalline glass with the extension of the crystallization time, especially at 3 h of crystallization. Furthermore, the density of the prepared microcrystalline glass increased because a considerable number of columnar crystals were generated and the density of the chalcocite feldspar was between 2.6 and 2.76 g/cm³. However, when the crystallization time was extended to 4 h, the density of the microcrystalline glass decreased because a large number of reticular structures were

generated in the microcrystalline glass. Moreover, the spherical and columnar crystal phases in the crystal disappeared and holes started to appear. Therefore, the density of the microcrystalline glass was maximum at a crystallization time of 3 h.

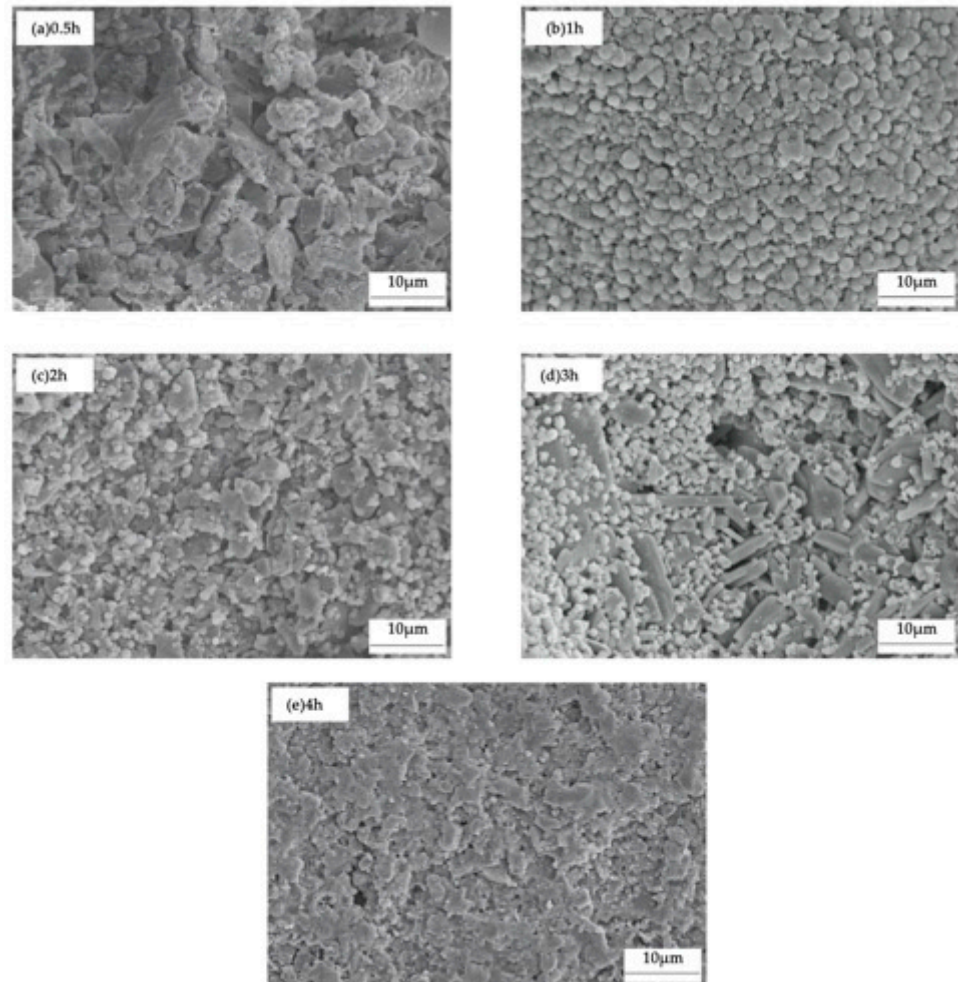


Figure 11. SEM images of microcrystalline glass samples at different crystallization times: (a) 0.5 h, (b) 1 h, (c) 2 h, (d) 3 h, and (e) 4 h.

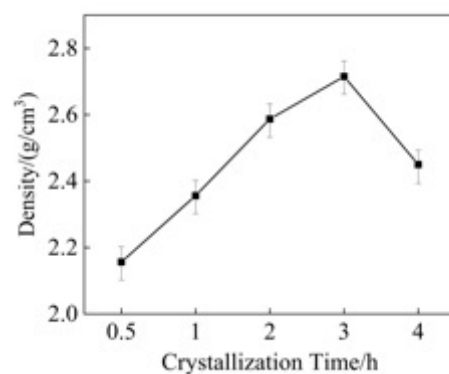


Figure 12. Effects of crystallization time on the density of microcrystalline glass.

Figure 13 displays the relationship between the crystallization time and the water absorption of the microcrystalline glass. The variation trend of the water absorption of the microcrystalline glass was opposite to the variation trend of density. The water absorption of the microcrystalline glass first decreased and then increased with the extension of the

crystallization time and reached a minimum of 1.55% at 3 h. This may be attributed to the extension of crystallization time, the increase in the number of crystalline phases of the microcrystalline glass, the complete growth of more grains, and the higher mutual adherence between grains, which increased the crystal densification and thereby reduced the number of pores in the microcrystalline glass and decreased the water absorption rate of the microcrystalline glass. However, an excessively long crystallization time may cause the aggregation of crystals in microcrystalline glass and form a mesh structure, thus resulting in a large number of pores in a sample and increasing the water absorption of microcrystalline glass. As illustrated in Figure 13, when the crystallization time was extended from 3 h to 4 h, the water absorption of the microcrystalline glass increased from 1.55% to 2%.

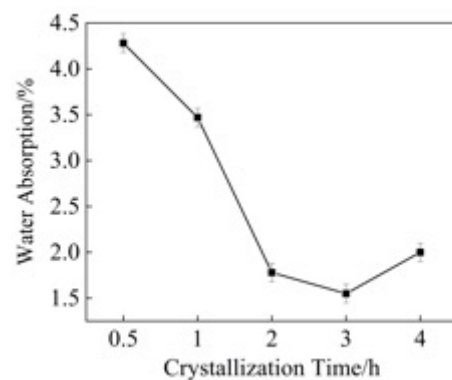


Figure 13. Effects of crystallization time on the water absorption of the microcrystalline glass.

Figure 14 illustrates the effects of crystallization time on the porosity of the microcrystalline glass. For the crystallization time of 0.5 h, the porosity of the microcrystalline glass was as high as 9.23%, which can be attributed to the nonuniform distribution of grains in the matrix due to insufficient crystallization time. Moreover, the microcrystalline glass was not dense enough to produce a large number of pores and gaps inside the crystal; this increased the porosity of the microcrystalline glass. With the extension of the crystallization time, the number of crystalline phases increased and the bonding of the glass phase with the crystalline phase was enhanced. Moreover, the density of the samples increased, so the porosity of the microcrystalline glass decreased. Furthermore, the porosity of the microcrystalline glass decreased to 4.2% when the crystallization time was extended to 3 h. However, a further extension of the crystallization time resulted in the agglomeration of crystals in the microcrystalline glass and the simultaneous arrangement of spherical and columnar grains in networks. Consequently, a large number of pores were generated in the sample, thereby increasing the porosity of the microcrystalline glass.

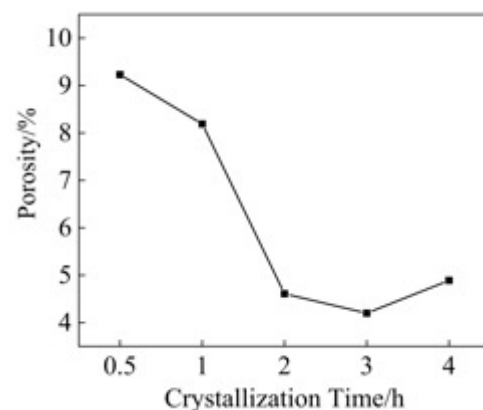


Figure 14. Effect of crystallization time on the porosity of the microcrystalline glass.

Figure 15 illustrates the effects of crystallization time on the Vickers hardness of the prepared microcrystalline glass. The Vickers hardness of the microcrystalline glass samples first increased and then decreased with increases in the crystallization time. The Vickers hardness of the microcrystalline glass was maximum (618 HV) after 3 h of crystallization. When the crystallization time was exceedingly long (4 h), the Vickers hardness of the sample decreased to 592 HV. The crystallization time was not sufficient, the crystal precipitation inside the microcrystalline glass was less, and the grain shape was irregular and incompletely developed; thus, the number of pores in the microcrystalline glass increased and the hardness of the glass decreased. With the extension of the crystallization time, the precipitation was more complete, the grain growth was more adequate, and the shape was transformed to spherical and columnar, thereby strengthening the mutual bonding between the grains, considerably reducing the number of pores inside the microcrystalline glass, and increasing the hardness of the microcrystalline glass. However, an excessively long crystallization time caused an abnormal increase in the grain size and the aggregation of the grains into clusters. This weakened the effects of fine crystal strengthening and reduced the hardness of the microcrystalline glass.

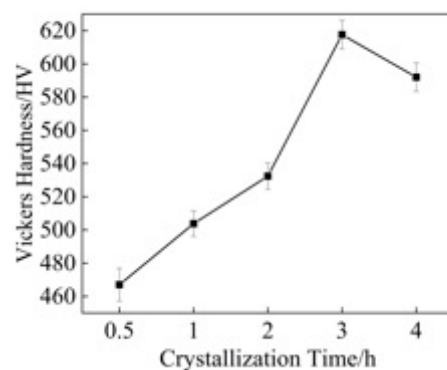


Figure 15. Effects of crystallization time on the Vickers hardness of the microcrystalline glass.

Figure 16 illustrates the relationship between crystallization time and the acid and alkali resistances of the prepared microcrystalline glass. The alkali resistance of the microcrystalline glass was stronger than its acid resistance, likely because the glass phase is more easily leached in acidic solutions [28]. The acid and alkali resistances of the microcrystalline glass were optimal at 2.36% and 0.04%, respectively, after 3 h of crystallization. When the crystallization time was shorter, the number of crystals of the microcrystalline glass was small and the residual glass phase was dominant; thus, the corrosion resistance of the microcrystalline glass was low. When the crystallization time was extended, the degree of crystallization of the microcrystalline glass was higher, the grain growth was more complete, the crystal structure was denser, and the constituent glass phase was lesser, thereby increasing the acid and alkali resistances of the microcrystalline glass. However, the crystallization time was exceedingly long, so the grains accumulated into clusters, thereby resulting in the destruction of the dense structure between the crystalline phases, the generation of a large number of holes and gaps, and the arrangement of spherical and columnar grains in a network-like structure. The two aforementioned conditions resulted in an increase in the contact range of the microcrystalline glass with the acid and alkali solutions; thus, the acid and alkali resistance of the microcrystalline glass decreased. As displayed in Figure 16, when the crystallization time was extended to 4 h, the acid and alkali resistances of the microcrystalline glass decreased compared with those when the crystallization time was 3 h; the acid and alkali resistances were 0.27% and 0.13%, respectively.

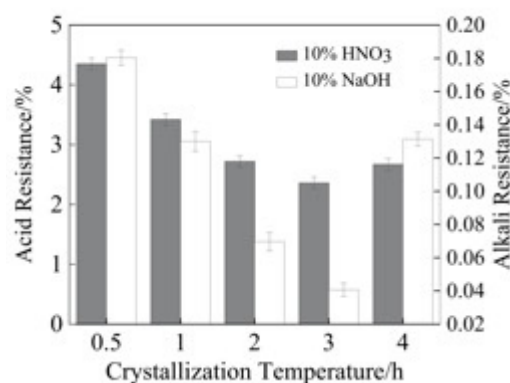


Figure 16. Effects of crystallization time on the acid and alkali resistances of the microcrystalline glass.

3.4. Effects of Microcrystallization on the Toxic Leaching Characteristics of Heavy Metals

To determine whether the leaching concentrations of heavy metal ions from the final smelting slag after microcrystallization satisfied the requirements, we analyzed the leaching characteristics of heavy metals such as Zn, Cr, Mn, and Pb in the prepared microcrystalline glass under optimal conditions; Table 3 summarizes the results. The leaching concentrations of heavy metal ions from the base glass leachate were lower than the limits stipulated by the U.S. Environmental Protection Agency (US-EPA), indicating that the glass slag obtained from the melting and collection process was non-toxic. Moreover, the leaching concentrations of heavy metal ions, especially Zn, Cr, and Pb ions, in the microcrystalline glass obtained after microcrystallization were lower than the US-EPA limits. The leaching concentrations of heavy metals in the microcrystalline glass were lower than those in the base glass, indicating that microcrystallization can effectively immobilize heavy metal ions in microcrystalline glass. Therefore, the microcrystalline glass prepared with the proposed one-step heat treatment process is an environmentally friendly and harmless material.

Table 3. Heavy metal leaching characteristics of the microcrystalline glass prepared under optimal conditions (mg/L).

	Zn	Cr	Mn	Pb
Base glass	1	0.072	4.7	BDL
Microcrystalline glass	0.28	BDL	2.48	BDL
Limit value	500	5	5	5

BDL: below instrument detection limit.

4. Conclusions

This study proposed a one-step method for the preparation of microcrystalline glass using the iron smelting slag of SACs-3. We investigated the effects of crystallization temperature and crystallization time on the physical and chemical properties of microcrystalline glass prepared using the proposed method. Furthermore, the toxicity and leaching characteristics of heavy metals in the microcrystalline glass were investigated. The main conclusions of the study are as follows:

- (1) The differential thermal analysis of the base glass and the XRD analysis of the microcrystalline glass samples indicated that the main crystalline phase of the microcrystalline glass was constant and constituted by chalcocite feldspar. A suitable range of variables was determined. The crystallization temperature varied between 900 and 950 °C, and the crystallization time varied between 0.5 and 4 h.
- (2) Single-factor experiments were performed to analyze changes in the degree of crystallization, number of crystalline phases, grain shape, and physical and chemical properties of the microcrystalline glass, with crystallization temperature and time as

variables. The optimal parameters for the heat treatment process were determined as follows: a crystallization temperature of 950 °C and a crystallization time of 3 h.

- (3) The physicochemical properties of the microcrystalline glass prepared with the proposed one-step method were determined: the bulk density was 2.72 g/cm³, the water absorption rate was 1.55%, the porosity was 4.2%, the Vickers hardness was 618 HV, the acid resistance was 2.6%, and the alkali resistance was 0.04%. The leaching concentrations of heavy metal ions were lower than those of the base glass and were considerably lower than the stipulated limits, and the harmful components were stabilized for disposal.

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