




Treatment method of hazardous pickling sludge by reusing as glass–ceramics nucleation agent

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Abstract Heavy metal containing pickling sludge (PS) is one of the by-products of the stainless-steel-making industry, which has been considered hazardous due to contained chromium and nickel. Traditional methods of PS disposing are landfill and cement solidification. This research is aimed at disposing PS by solidification/stabilization and reusing it as a nucleation agent of glass–ceramics. The crystallization behavior and the properties of a glass in the $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3$ system were studied by considering PS as the nucleation agent. Experimental results confirm that introducing 14 wt% PS as the nucleation agent of glass–ceramics can decrease crystallization temperature by 110.8 °C, refine the grain size by forming isometric crystals with size of 2 μm , enhance Vickers hardness by 2690 MPa and decrease water absorption from (1.21 ± 0.10) wt% to (0.04 ± 0.01) wt%. Therefore, it is reasonable to conclude that PS can be utilized as a nucleation agent to improve the crystallization and mechanical properties of the glass–ceramics. The testing results of US EPA toxicity characteristic leaching procedure (TCLP) confirm the safety of this reusing method.

Keywords Glass–ceramics; Pickling sludge; Nucleation agent; Heavy metal stabilization

1 Introduction

Stainless steel pickling has been classified as an environmental hazard due to the potential hazardous nature of its sludge, which often contains substantial amounts of Cr and Ni [1]. The leaching concentration of some heavy metals in the pickling sludge (PS) is relatively high [2], making disposal an urgent issue from the environmental and social standpoints. Traditional methods of PS disposing include landfill and cement solidification [3], which have been utilized in some areas for many years, and are still adopted by many plants in China [4]. The negative environmental effects of these disposing methods have gradually been reflected in water safety and health issues caused by the heavy metal pollution [5]. Thus, alternative options need to be explored to solve the PS handling in a more environmentally friendly manner [1].

Glass–ceramics, composed of the glass phase and the microcrystalline phase with fine microstructure, is produced by controlled crystallization of glass [6, 7]. As a high value-added products, glass–ceramics attracted significant attention due to excellent solidification capacity of heavy metals, mechanical properties, along with the possibility of using solid waste as raw materials [8–10]. In recent years, many types of solid wastes, such as steelwork slag [11, 12], bottom ash [13], fly ash [14, 15], soda lime waste glass [16] and copper slag [17], have been widely tested as alternatives to produce glass–ceramics. Generally, the properties of glass–ceramics are defined by the chemical composition, microstructure and crystal [18]. Therefore, it is necessary to add some nucleation agents, such as pure CaF_2 , Fe_2O_3 and Cr_2O_3 into the formulations to improve the crystallization and mechanical properties of glass–ceramics in most cases [19–23].

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Stainless steel pickling is mainly carried out with an aggressive solution (nitric acid and hydrofluoric acid) [2, 24]. Precipitation with lime is one of the oldest methods applied to spent pickling liquor disposing, still used in many plants [25]. Owing to the chemical reaction of the spent pickling liquor with lime, CaF_2 , $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ are formed and become the main compositions of PS. Furthermore, these hydroxides can transform into oxides by heating the PS. Thus, the dried PS (the main components are CaF_2 , Fe_2O_3 and Cr_2O_3) can be obtained. In the glass–ceramics industry, CaF_2 is widely used to decrease the crystallization temperature of the parent glass by replacing the strong Si–O linkage with a weak Si–F pair [22, 26, 27]. The presence of Cr_2O_3 benefits the formation of fine-grained bulk crystallization in the glass matrix [28–30]. Besides, Wang [31] suggested that Fe_2O_3 has a significant effect on the crystallization of fly ash glass–ceramics, because it leads to phase separation of the glass and decreases the crystallization activation energy. Thus, CaF_2 , Fe_2O_3 , and Cr_2O_3 are widely used in the glass–ceramics industry in the form of effective nucleation agents. Furthermore, composite nucleating agents were more effective in some industrial waste glass–ceramics [22]. From the above viewpoint, it is clear that PS is a potential nucleation agent of glass–ceramics. Thus, utilization of PS as a nucleation agent of glass–ceramics is of great interest and significance. However, to the best of our knowledge, there are few researches aiming to reuse PS as a glass–ceramic nucleation agent.

Therefore, the objective of this paper was to study the use of stainless steel PS as a nucleation agent in CaO – MgO – SiO_2 – Al_2O_3 system glass–ceramics, based on stainless steel slag (SSS) and cullet, in order to improve the crystallization characteristics and properties. The PS was added in a glass–ceramics formulation maintaining its processing characteristics. The performance of different PS content glass–ceramics was measured in order to estimate the effect of the PS addition in the crystallization behavior and microstructure transition of the glass–ceramics samples. Moreover, to assess the safety and reliability of this reusing method, the obtained glass–ceramics were tested for heavy metals leaching.

2 Experimental

2.1 Raw materials

Pickling sludge (obtained from Baosteel Group Co., Ltd., Shanghai, China) was dried at 300 °C for 3 h to complete dehydration. Then it was ball-milled for 1 h and passed through 40-mesh sieve for complete mixing. Cullet was obtained by grinding down the waste glass from common soda glass and passing through 40-mesh sieves. Typical SSS (obtained from Qingshan Jinhui Stainless Steel Industry Co., Ltd., Henan, China) was completely mixed by ball-milling for 1 h and passed through 40-mesh sieves. Table 1 shows the details of PS, SSS and the cullet chemical composition, obtained by X-ray fluorescence (XRF, XRF-1800, shimadzu).

2.2 Glass–ceramics preparation

Glass–ceramics were prepared from SSS, cullet and PS without any additives. Four mixtures of SSS and cullet (SSS/cullet mass ratio of 0.78:1.00) were obtained with PS addition of 0 wt% (GC-0, standard), 7 wt% (GC-1), 14 wt% (GC-2) and 21 wt% (GC-3). These mixtures were mixed by dry ball-milling for 2 h. Then, the mixed powders were melted in an alumina crucible at 1460 °C for 2 h in a muffle furnace. After melting, one drop of the melt was poured in water and rapidly cooled down to room temperature. As-quenched products were pulverized and characterized by differential scanning calorimetry (DSC) to obtain the glass transition temperature (T_g) and the position of the exothermic peaks to guide the following heat treatment process.

The rest melt was poured on a piece of steel plate preheated to 600 °C and held for 0.5 h for residual stress relaxation. Then, the “single-stage” isothermal heat treatment process was applied to all parent glass. In this study, exothermal peak temperature (T_p) was chosen as the heat treatment temperature for each sample, held for 1 h. Finally, the samples were cooled slowly to room temperature to obtain glass–ceramics.

Table 1 Chemical compositions of raw materials measured by quantitative XRF (wt%)

Samples	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	CaF ₂	SO ₃	Cr ₂ O ₃	NiO	Others
SSS	36.97	26.11	21.46	6.46	2.51	0.08	2.12	1.22	0.99	–	2.08
Cullet	9.04	4.08	68.30	2.49	0.59	14.37	–	0.37	0.03	–	0.73
PS	–	1.17	9.30	2.72	25.52	1.74	45.71	–	5.01	1.84	6.99

Others: TiO₂, P₂O₅, K₂O, ZnO, BaO, CuO, MnO, BaO, Co₂O₃

2.3 Characterization techniques

Differential scanning calorimetry (DSC) scans were obtained with a NETZSCH STA 409 C/CD thermal analyzer in argon. The reference material was α -Al₂O₃ powder, and the parent glass powder samples were heated from room temperature to 1000 °C at a heating rate of 10 °C·min⁻¹. The crystalline phases in the glass–ceramics samples were identified from X-ray diffractometer (XRD, Philips APD-10, 40-kV and 150-mA, monochromatic Cu K α radiation) at a scan rate of 10 (°)·min⁻¹.

The fracture surfaces of glass–ceramics samples were examined by scanning electron microscopy (SEM, Carl Zeiss EVO 18) working in the secondary electron detector mode, at 10-kV acceleration voltage. The relative density was tested using conventional liquid displacement method, according to the Archimedes principle. Water absorption rate was measured as a percentage of weight increment. The Vickers hardness was measured according to the ASTM standard (ASTM E384-11, 2011). Samples were ground and polished with diamond paste. The maximum load of 2 N was applied, and the time of indentation was fixed at 10 s.

The leaching amounts of heavy metals (Cr, Ni, Cu, Mn) were tested by means of leaching experiment, according to toxicity characteristic leaching procedure (TCLP) test (EPA1311, 1992), with a pH-2.9 acid solution (extraction fluid 2) as the leaching fluid. Each leaching vial was filled with 100 ml TCLP extraction fluid and 5 g powder. The leaching vials were rotated end-over-end at 30 r·min⁻¹ for 18 h. To simulate long-term leaching potential of toxic metals regulated by USA government, the PS was subjected to multiple TCLP extractions four times. The concentrations of leached heavy metals were measured using inductive coupled plasma analyzer (iCPA 6300, Thermo Fisher Scientific America, USA).

3 Results and discussion

3.1 Extraction toxicity of heavy metals in PS

The PS was obtained from the open-air depot (Fig. 1a), and the color of the PS is tawny (Fig. 1b). The major constituents of PS are nucleation agent compounds (CaF₂, Fe₂O₃ and Cr₂O₃) of glass–ceramics. The total content of these compounds reaches 76.23 wt%, demonstrating the potential application in glass–ceramics preparation. However, the Cr₂O₃ and NiO contents detected in PS reach up to 5.01 wt% and 1.84 wt%, respectively, as shown in Table 1. Four sequential TCLP extractions were carried on the PS to evaluate its leaching characteristics for heavy metals. The leaching results are collected in Fig. 1c. The leaching concentration of Cr (117 mg·L⁻¹) in the first TCLP test is more than 23 times US EPA limitation of 5 mg·L⁻¹. The 101 mg·L⁻¹ Ni leachate concentration of the first leaching is 20 times the limitation of 5 mg·L⁻¹. The leaching concentration of Cr, after four sequential TCLP extractions, of 19 mg·L⁻¹ still exceeds the limits of the TCLP standards by a factor of four. Thus, it is urgent to dispose this tawny PS properly, rather than open-air storage, like in Fig. 1a.

3.2 Crystallization behavior of PS-doped glass–ceramics

DSC curves for the four glass samples with particle sizes of 75 μ m obtained at a heating rate of 10 °C·min⁻¹ are shown in Fig. 2. It can be seen from Fig. 2 that there is only one exothermal peak detected in GC-0 through GC-2. The crystallization peak temperature decreases from 889.8 to 779 °C with more PS additions. The PS is abundant in CaF₂, as seen in Table 1. The fluorine from PS may act as a network breaker in glass network by replacing strong Si–O bonds with Si–F bonds, resulting in the decrease of crystallization temperature in the glass [32]. Banijarmali et al.



Fig. 1 Open-air depot of PS **a**, dried PS **b**, and leaching concentration of heavy metals of the PS, depending on number of leaching times **c**

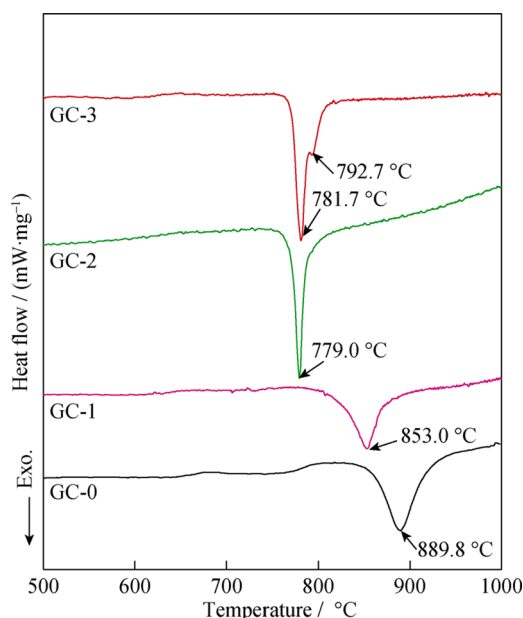


Fig. 2 DSC curves of PS-doped glass obtained at heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

[26] suggested that increasing fluorine content reduced the crystallization peak temperature via acceleration of the diffusion rate of the crystalline phase constituent. The crystallization peak temperature increases by $2\text{ }^{\circ}\text{C}$ from GC-2 to GC-3, indicating that adding 14 wt% PS is enough to reduce the crystallization temperature. Additionally, there is another exothermal peak in GC-3, located at $792.7\text{ }^{\circ}\text{C}$, which may be corresponding to the grain ripening.

In this study, XRD analysis was utilized to obtain crystal composition of powder glass-ceramics specimens. It can be seen from Fig. 3 that the main crystalline phases change from akermanite to augite by introducing PS into the formula of glass-ceramics. Unlike GC-0, there are no akermanite and sodium aluminum silicate phases detected in GC-1. Nevertheless, cuspidine and nepheline phases appear in XRD patterns with PS content increasing. These results suggest that PS plays an important role in the crystals formation process.

Khater [22] suggested that the glass network structure can be weakened by replacing Si–O band with Si–F. Thus, the solid solubility of the impurity ions, such as sodium, potassium and calcium, is improved in the residual glass phase, confirmed by the disappearance of akermanite and sodium aluminum silicate phases in XRD patterns of GC-1 and GC-2 samples. Besides, fluorine does not enter into the crystalline structure, but remains dissolved in the residual glass [32]. The fluorine content in the residual glass increases with higher PS amount. Thus, it aids the crystallization in the residual glass phase, obtaining cuspidine and nepheline phases in return, confirmed by XRD patterns of GC-2 and GC-3 samples.

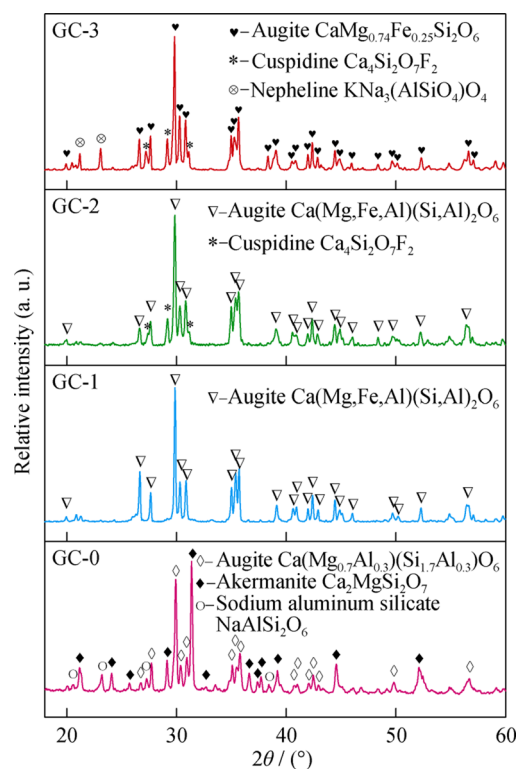


Fig. 3 XRD patterns of glass-ceramics with different PS contents

SEM analysis was conducted to understand the microstructure of glass-ceramics, as shown in Fig. 4. With PS content increasing, the microstructure of the glass-ceramics changes from columnar-shaped crystals (GC-0 with typical crystal microstructure of surface crystallization) to sheet-shaped crystals (GC-1), and afterward to granular crystals (GC-2 with typical crystal morphology of bulk crystallization, 1–2 μm in size, distributed homogeneously in the glass

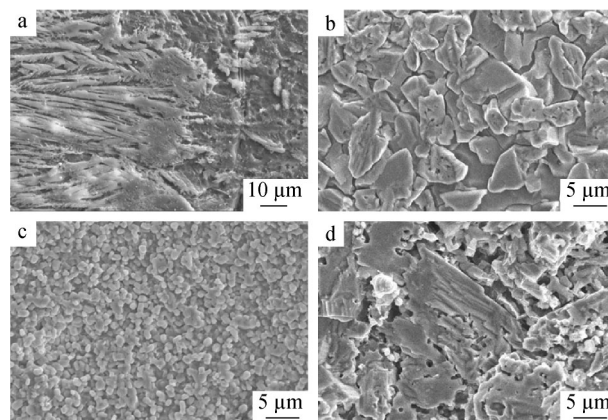


Fig. 4 SEM images of glass-ceramics with different PS contents: **a** GC-0 without PS, **b** GC-1 with 7 wt% PS, **c** GC-2 with 14 wt% PS, and **d** GC-3 with 21 wt% PS

Table 2 Physical characteristics of glass–ceramic products

Products	Relative density/(g·cm ⁻³)	Water absorption/wt%	Vickers hardness/MPa
GC-0	2.67 ± 0.02	1.21 ± 0.10	4890 ± 36
GC-1	3.03 ± 0.01	0.27 ± 0.01	7120 ± 110
GC-2	3.07 ± 0.01	0.04 ± 0.01	7580 ± 72
GC-3	3.01 ± 0.01	0.73 ± 0.02	6990 ± 85

matrix), and finally to non-uniform coarse grains (GC-3 with typical morphology of the abnormal grain growth).

Wang [31] suggested that Fe₂O₃ doped in glass–ceramics can induce the formation of small amorphous droplets distributed homogeneously in the glass matrix before nucleation. The interfaces between the amorphous droplets and glass matrix phases serve as the heterogeneous nucleation sites for the final crystallization. In terms of Cr₂O₃, Khater [22] pointed out that it has a similar mechanism with Fe₂O₃ for inducing nucleation. Besides, increasing fluorine content is responsible for more effective nucleation, probably via weakening the glass network structure and accelerating the diffusion of the crystalline phase constituents [26]. Based on the discussion above, adding more CaF₂, Cr₂O₃ and Fe₂O₃ (in the PS form) would bring more nucleation sites and promote grain refinement. This is corresponding to the changing trend of the crystalline microstructure in Fig. 4. However, there is excessive growth of the crystalline particles in GC-3 sample. This would be caused by the F⁻ overdose [22]. In summary, PS effectively promotes the nucleation and crystallization processes of the glass–ceramics. Granular crystals with the size of 1–2 μm are formed and distributed uniformly in glass–ceramics with 14 wt% PS.

3.3 Physical and mechanical properties evolution

The relative density, water absorption and Vickers hardness of all specimens were measured to evaluate the physical and mechanical properties of the PS-doped glass–ceramics. The results, summarized in Table 2, indicate that the water adsorption of the glass–ceramics decreases first and then increases with the increase in PS content. The varied tendencies of the density and Vickers hardness of these samples are on the contrary. GC-2 sample shows the

highest relative density of 3.07 g·cm⁻³ and the lowest water absorption of 0.04 wt% with peak value of Vickers hardness of 7580 MPa. Compared with GC-0, adding 14 wt% PS as the nucleation agent of SSS glass–ceramics enhances Vickers hardness by 2690 MPa, decreases water absorption by 1.17 wt% and increases the density by 0.4 g·cm⁻³. Thus, it is clear that adding PS as the nucleation agent improves the physical and mechanical properties to a great degree. Based on the above results, the GC-2 sample doped with 14 wt% PS is obviously the optimal glass–ceramic product.

3.4 TCLP tests of glass–ceramics

The leaching concentrations of heavy metals, based on the TCLP test, are shown in Table 3. These results indicate that the leaching concentration of heavy metals from the final glass–ceramic products is much lower than the US EPA regulatory standards. Vu et al. [13] suggested that the glass–ceramics have excellent stabilization capacity, because the heavy metals are bonded inside the lattice of the crystalline phase. Generally, the leaching concentrations of heavy metals in the glass–ceramics are all far below the US EPA regulatory limits, meaning that the final products are safe if they are used as construction materials.

4 Conclusion

This study confirms that introducing 14 wt% PS as the nucleation agent decreases the crystallization temperature by 110.8 °C, refines the grain size by forming isometric crystal with 2 μm in size, enhances Vickers hardness by 2690 MPa and decreases water absorption from (1.21 ± 0.10) wt% to (0.04 ± 0.01) wt%. These results indicate that PS can be utilized as a nucleation agent to improve the crystallization and mechanical properties of glass–ceramics. The TCLP test results confirm the safety of this reusing method. Therefore, the described technique of the PS disposal, reusing PS as a nucleation agent of glass–ceramics, is promising and reliable.

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Table 3 TCLP leaching concentrations of heavy metals in final products (mg·L⁻¹)

Metals Regulatory (US EPA)		GC-0	GC-1	GC-2	GC-3
Cr	5	0.12	0.14	0.13	0.61
Ni	5	0.01	0.03	0.04	0.14
Cu	15	0.13	0.32	0.25	0.36

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