

Research on Microstructure and Properties of Yellow Phosphorous Slag Glass-ceramics

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Abstract-The influence of the content of CaO on the crystallization behavior, microstructure and mechanical properties of yellow phosphorous slag (YPS) glass-ceramics was studied. XRD, TEM, SEM and so on were used to analyze the microstructure and properties of glass-ceramics. With the increasing content of CaO, the crystallization of β -wollastonite increased while the aspect ratio and the grain size decreased. The glass-ceramics with fine microstructure showed better mechanical properties. Yellow phosphorous slag waste appears to be well suited for being used as batch material for decorative architectural glass-ceramics.

Keywords-Yellow Phosphorous Slag; Glass-Ceramics; Microstructure; Mechanical Properties

I. INTRODUCTION

Glass-ceramic is a polycrystalline material, which contains glass phase and crystallization phase and it can be obtained by a process accomplished in two stages: glass melting and posterior controlled crystallization of glass by heat-treatment. Glass-ceramic materials for different applications in different fields have received increasing attention during last years. These materials have many outstanding properties comparing with glasses and ceramics [1–2]. With the rapid development of industry, there are many industry wastes which have been produced as the subsidiary materials, which are not utilized plenarily. It not only takes up a lot of land resource but also causes serious environment pollution. How we can take advantages of these industrial wastes and make the development of industry become sustainable has become increasingly important. In order to considerably minimize cost and recycle solid wastes, various solid wastes have been used as starting materials for glass-ceramics. Slag glass-ceramics was first made by the Soviet Union in the year of 1959 [3]. Recently, application of particles sintering technology to obtain high quality products from silicate waste materials has been explored [4–6]. Several combinations of wastes have been used in glass-ceramics, such as boiler ashes [7], steel making slag [8], phosphorus slag [9], blast-furnace slag [10], tailing and filter fly ashes [11–13].

In this work, the YPS from Hubei Province of China was used as the raw materials for glass-ceramics. The YPS is the emission of industrial waste in the production of phosphorus. It will emit 8~12t YPS when 1t yellow phosphorus was produced. There is more than 20 million ton YPS which is waiting for being utilized every year in China. The YPS is placed in the open space, therefore it wastes a lot of resources and contaminates the environment. Since the main chemical constituents of YPS consists of CaO, SiO₂ and Al₂O₃, and their contents are more than 85 mass%. CaO, SiO₂ and Al₂O₃ are the main oxide constituents in CaO-Al₂O₃-SiO₂ glass-ceramics. It is looking forward to having a high utilization rate of YPS in this glass-ceramics system, which is about 36-42 mass%. Therefore, it is necessary to investigate the relationship between the utilization rate of YPS and the structure, the characters of CaO-Al₂O₃-SiO₂ glass-ceramics. Overall, transforming industrial residue into slag glass ceramic products is a high quality added-value resource recovery technology.

II. EXPERIMENTAL PROCEDURES

A. Glass Preparation

The YPS was ground into particles less than 200 μ m in diameter, and atomic absorption spectroscopy was used to determine its composition (Table I). The instrument model is GBC AVANTA M. The sample was alkalescent slag which contained abundant CaO (about 44 wt%). Based on the YPS composition, we chose the CaO-Al₂O₃-SiO₂ glass system because it should accommodate a large quantity of slag. The full CaO content was supplied by the YPS, while the other components in Table I were necessarily included. An amount of these other components which came from YPS were fixed based on the CaO content and in general did not correspond to the desired composition of the base glasses, so the remainder was supplied by oxide and carbonate (analytical pure) reagents. The amount of YPS used in the glass batches was about 36-42 wt% of the total batch mixture.

TABLE I ORIGINAL COMPOSITION OF YPS.

YPS	SiO ₂	CaO	Al ₂ O ₃	BaO	Na ₂ O	K ₂ O	MgO	P ₂ O ₅	F	TiO ₂	ZrO ₂	SO ₃	Fe ₂ O ₃	Undetermined
Chemical composition(mass%)	39.950	44.050	3.720	0.180	0.700	0.880	2.340	2.970	2.640	0.210	0.077	1.350	0.058	0.975

The weighed batch materials, after being mixed, were melted in alumina crucible in an electric furnace at 1580 °C for 2h. The melts were then quenched in cold water to obtain frits which maintained glass phase structure and the size < 2.8 mm. The granular frits were present within refractory mold, and were heated in an electric furnace, according to the schedule which was gained by differential thermal analysis.

B. Analysis Methods

In order to determine the nucleation and crystallization temperatures of the primary glasses, DTA was performed in dry nitrogen by heating 30 mg powder samples in a Pt crucible with Al₂O₃ as the reference material within the temperature range from 20 °C to 1000 °C at a heated rate of 10 °C /min (Netzsch thermal analysis system). As the glass particles' size used to analyze was smaller than the size used to prepare the glass-ceramics sample, crystallization temperature of the glass samples should be higher than that of crystallization peak on the DTA curve.

X-ray diffraction was utilized to analyze which crystalline phases occurred in the produced samples. X-ray diffraction spectra were acquired by a D/MAX-RB X-ray diffraction system (RIGAKU) operating at 40 kV and 30 mA utilizing Cu K α radiation on powder samples passing through 240 grade meshes. The detector was scanned over a range from 5° to 75° for two theta angles, at a step size of 0.02° and a dwell time of 2s per step. The resulting powder diffraction patterns were analyzed utilizing a software package program.

The glass-ceramics sample fracture surface which had been etched for 40 s in 5 % HF (v%) solution were prepared beforehand for scanning electron microscopy (SEM). After the etched step, the samples were rinsed with excess distilled water immediately, and then were cleaned in ethanol for 3 min. Next the samples were gold-coated and observed with a JSM 600 microscope operating at 25kV. The volume and shape of crystals occurred in the microstructure of the glass-ceramic samples were determined. An irregularly-shaped blocky area was used to provide detailed microchemistry information. Elemental analysis was carried out using Energy Dispersive X-ray Spectroscopy (EDS) in scanning SEM mode.

A representative sample of glass-ceramics was analyzed for microstructure to investigate the scale and distribution of crystalline phases and their connectivity. Transmission electron microscopy (TEM) was on a JEOL JEM 2100F transmission electron microscope. The samples were prepared following traditional TEM sample preparation methods. The crystallized sample which was grinded in an agate mortar to a grain size < 65 μ m was used for TEM.

III. RESULTS AND DISCUSSION

A. Differential Thermal Analysis and Heat Treatment

The DTA results of the investigated glass samples are shown in Fig. 1. The glass transition temperature (T_g) is indicated about 657-668 °C, at which the sample changes from solid to liquid-like behavior [14]. The main endothermic peak around 902-917 °C is the dilatometric softening point of the low viscosity phase. Various exothermic effects at 954-966 °C indicating crystallization of the glasses are also recorded. As the content of CaO in the glass composition increased, the peak temperature of the crystallization endotherms decreased and the endothermic effects mentioned above were slightly displaced to lower temperatures. The nucleation temperature is an important factor for nucleus' formation. In general, the nucleation takes place in the range of 50~100 °C above glass transition temperature. In our work, the nucleation and the crystallization schedule of samples A₁ to A₄ were identified as T_n = 760 °C for 1h and T_c = 960 °C for 2h, respectively.

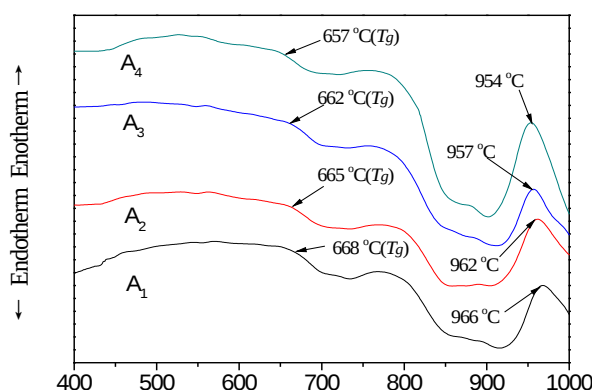


Fig.1 DTA results of the investigated glass samples

B. Microstructure of YPS Glass-Ceramics

Fig. 2 showed that the main phases of four samples were β -wollastonite despite of different CaO contents. The intensity of diffraction peaks increased with increased amount of CaO indicated that the amount of β -wollastonite increased.

When generating CaSiO_3 , the chemical equation was proposed to be $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$. The CaSiO_3 was composed of 48.28 percent of CaO and 51.72 percent of SiO_2 , so the amount of CaO was not enough compared with SiO_2 . Based on the chemical reaction, the amount of product- CaSiO_3 would increase by increasing the amount of reactant- CaO . CaO is the network modifying oxide, when the amount of CaO increased, the structure of the glass-ceramics was comparatively loose and then the particles' migration would be improved and the crystallization activation energy decreased, so more and more crystal nucleus would emerge under the same circumstances. In a word, the crystallization was boosted by increasing the amount of CaO .

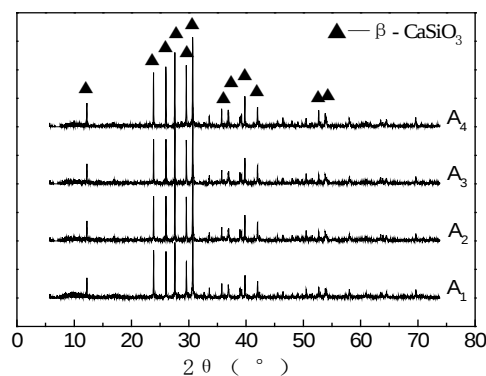


Fig. 2 XRD pattern of A series glass- ceramics

The microstructure of A series glass-ceramics were displayed in Fig. 3. When the amount of CaO increased, the grain morphology changed and the aspect ratio of gains decreased. The result of XRD indicated that the crystallization of β -wollastonite increased by increasing CaO . At the same space, the interaction enhanced with more crystals, so the growth of crystals were hindered and then couldn't grow into typical acicular crystals but developed into columnar crystals. The morphology of A_4 was randomly oriented, A_4 sample had the maximum crystallization and then the migration of particles and glass phase was hindered by those excess crystals, so the crystalline phase couldn't adjust to a regular, repeating pattern.

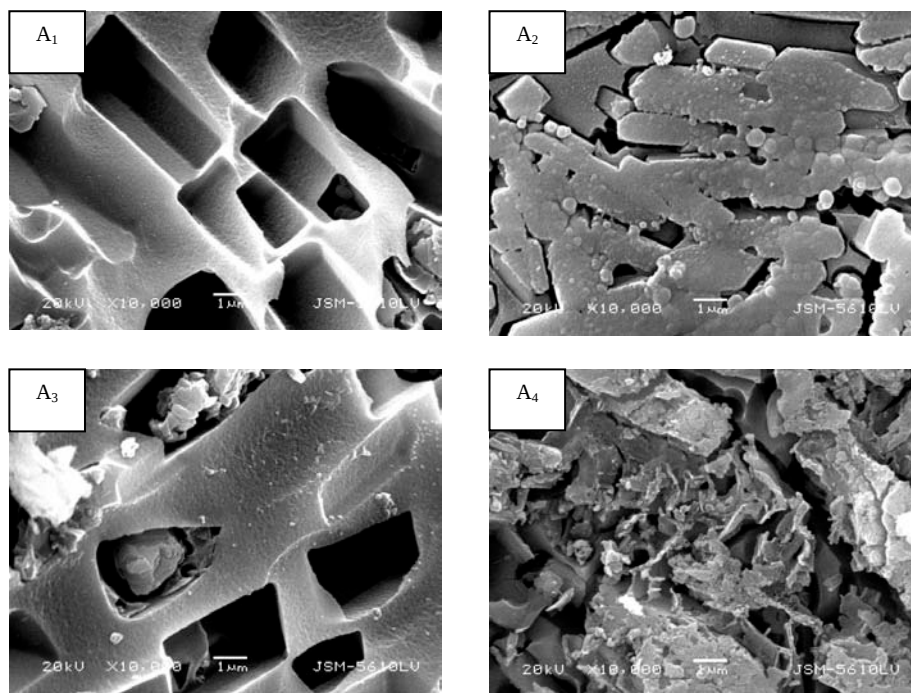
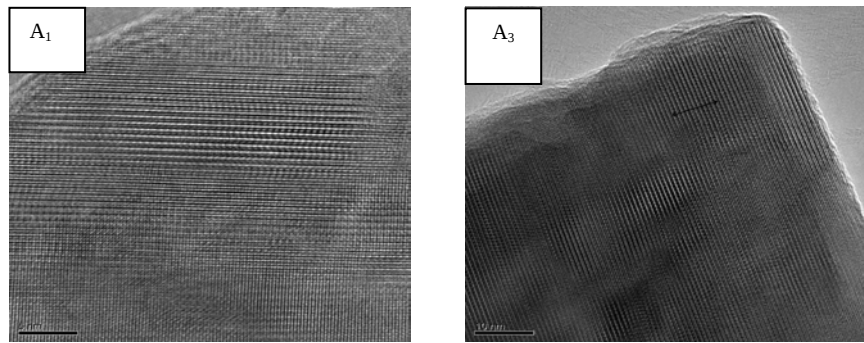


Fig. 3 SEM pattern of A series glass- ceramics

TEM (as shown in Fig. 4) analysis confirmed the phase structures and morphology. High-resolution TEM image (part A_3 of Fig. 4) showed us that the lattice spacing was 0.7752 nm, consistent with the lattice spacing of (100) planes of CaSiO_3 . Sample A_1 displayed the morphology. It clearly showed the grain boundary. On the one side, the orientation of lattice fringe was the same and it was stacked in a regular pattern and it was concluded to be crystal phase. On the other side, it was randomly oriented and it was glass phase. The crystal phase and glass phase were stacked alternately and perfectly connected.

Fig. 4 TEM pattern of A₁, A₃ glass- ceramics

C. The Mechanical Properties of YPS Glass-Ceramics

The bending strength signified the extent of resistance of the whole structure to the external forces. Fig. 5 displayed that the bending strength increased dramatically when the amount of CaO increased. By increasing CaO, the crystallization of main crystalline phase β -CaSiO₃ increased. Because of the regular chain structure of β -CaSiO₃ and the perfect connection of the crystal phase and glass phase, the strength of β -CaSiO₃ was also quite high, so more β -CaSiO₃ could increase the strength of whole structure.

As is seen from Fig. 5, the bending strength decreased abnormally when the content of CaO was 20 percent. The amounts of crystals in A₄ sample were the maximum. Particles' migration was hindered by those excess crystals with ordered, regular structure when heat-treated. Sintering would be restrained and then affected sintered density, so A₄ sample had more defects and closed stomata. What's worse, the result of SEM indicated that the crystalline is nonuniform. All these resulted in sample's bending strength decreased dramatically.

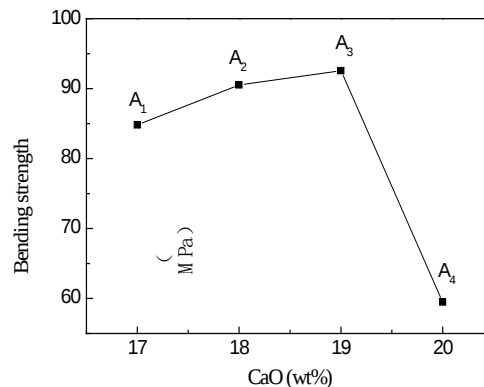


Fig. 5 The relation between bending strength and the content of CaO

As the amount of CaO increased, the vickers hardness of YPS Glass-Ceramics increased. This result was obtained from Fig.6. The result of XRD indicated that CaO enhanced the crystallization of β -wollastonite. The hardness of β -CaSiO₃ was quite higher than the glass phase, and the structure of β -CaSiO₃ was also more compact than glass phase and the crystal phase and glass phase were perfectly connected. Therefore the hardness of sample with more β -CaSiO₃ increased dramatically by increasing CaO.

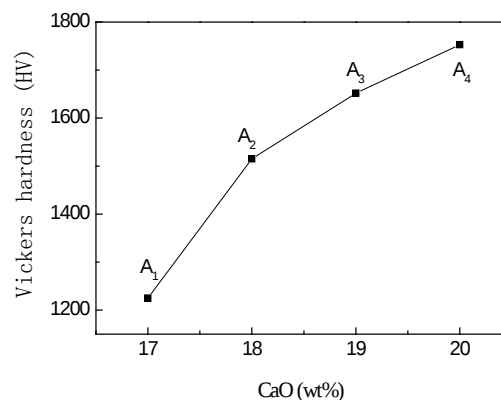


Fig. 6 The relation between micro-hardness and the content of CaO

Fig. 7 revealed that the thermal expansion coefficient of sample descended as CaO increased. The crystallization of β -wollastonite accelerated with increased content of CaO. The increasing amount of β -wollastonite resulted in more compact structure and its interlock structure resulted in lower thermal expansion coefficient.

The thermal expansion coefficient of sample A₄ was abnormal when the content of CaO increased to 20 percent. Although the amount of β -wollastonite in A₄ sample was larger than that of other samples, the result of SEM indicated that A₄ sample had a loose microstructure composed of crystals with nonuniform size and the sintered density was also the worst, therefore the thermal expansion coefficient of this sample increased suddenly.

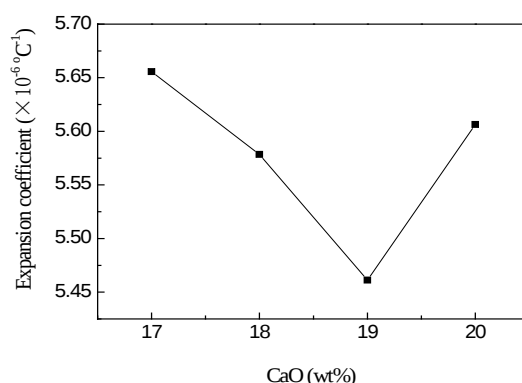


Fig. 7 The relation between thermal expansion coefficient and the content of CaO

IV. CONCLUSIONS

Glass-ceramic materials were successfully produced from yellow phosphorous slag in this study. The optimal amount of YPS used in the glass batch was about 36-42 wt% of the total batch mixture. XRD and SEM results revealed that the main crystalline phase is wollastonite (CaSiO_3). With the increasing amount of CaO, the crystallization of β -wollastonite increased while the aspect ratio and grain size decreased. The samples with higher content of CaO exhibited increased crystallization. The glass-ceramics with fine microstructure showed better mechanical properties. Therefore, yellow phosphorous slag waste appears to be well suited for being used as batch material for decorative architectural glass-ceramics.

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