Crystallization kinetics of glass-ceramics prepared from high-carbon ferrochromium slag

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Abstract

Glass-ceramics were successfully prepared from high-carbon ferrochromium slag (HCFS), and the optimum heat-treatment conditions were determined by analysis of the crystallization kinetics. The parent glass is first prepared in five different ratios of HCFS to waste glass (R(H/W)), then heat-treated separately at five heating rates (α) and monitored by DSC. As the value of R(H/W) increases from 0.60 to 1.67, the crystallization activation energy (E_c) decreases from 253.41 to 183.52 kJ/mol. The nucleation and crystallization temperatures decrease from 641.7 to 612.2°C, and 822.8 to 814.7°C, respectively, and both are lower than that of ordinary metallurgy slag. These results indicate that using HCFS to produce glass-ceramics both facilitates its production and saves energy. The crystallization index (n) increases with

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increasing $R(H/W)$, and when n exceeds 2.32, all of the parent glass samples with different $R(H/W)$ crystallize as bulk crystallization. The crystallization index (n) increases as the heating rate α decreases from 25 to 5 °C/min, with a maximum value of n (5.94) observed when α is 5 °C/min. These conditions produce the largest aspect ratio and highest density of the crystal grain in the glass-ceramics. Our results show the optimal HCFS-based glass-ceramics were obtained with a $R(H/W)$ of 1.29 and a 5 °C/min heating rate; under those conditions, the parent glass nucleates and crystallizes at 627.1 and 820.9 °C, respectively.

Keywords: Kinetics; High-carbon ferrochromium slag; Glass-ceramics; Activation energy; Crystallization index.

1. Introduction

High-carbon ferrochromium slag (HCFS) is an industrial by-product from the formation of high-carbon ferrochromium (HCFC); the production of one ton of HCFC generates 1.3 tons of HCFS [1,2]. HCFS is a heavy hazardous waste whose chromium content is approximately 1-10%, although it is showing promise as a secondary resource. The present work is concerned with the reuse of HCFS to produce glass-ceramics, which can be widely used as building materials such as wall tile, floor tile, and ceilings, etc. The production of glass-ceramics has utilized a variety of industrial wastes as raw materials, including coal fly ash [3-6], mud from zinc

hydrometallurgy [7-10], slag from steel production [11-16], ash and slag from waste incinerators [17-24], red mud from alumina production [25], waste glass from lamp and other glass products [26], as well as electric-arc furnace dust and foundry sands [27].

Little work has been reported on the immobilization of HCFS in glass and ceramic matrices [28,29], and recently, there has been some interest in the use of glass-ceramic matrices for this purpose [30,31]. It has been found that there are some high-melting-point materials (such as chromium sesquioxide, ringwoodite, and spinel) in the parent glass that do not completely melt during the melting process. Although trace amounts of these high-melting-point materials remain in the parent glass, they can act as nucleation agents and are thus beneficial [2]. However, one difficulty that has emerged in the preparation process is that there are too many nuclei seeds in the parent glass to be controlled during nucleation and crystallization, both of which directly affect the microstructure of glass-ceramics. Hence, to obtain glass-ceramics with homogenous and dense microstructure, the heat-treatment process should be investigated, with an emphasis on the nucleation temperature, the crystallization temperature, and the heating rate.

The preparation of HCFS-based glass-ceramics has been reported previously [2]. This work investigates the crystallization kinetics of these materials, such as the thermal stability, the crystallization activation energy, and the crystallization index, are further investigated.

2. Experimental procedure

2.1. Sample preparation

HCFS used in this study was received from a ferrochromium plant, and the HCFS mainly consisted of ringwoodite ((Mg,Fe)₂SiO₄), spinel (MgAl₂O₄), and ferrochromium (FeCr₄). Chromium was found to be contained mainly in the phases such as spinel and ferrochrome [1]. According to the calculated pentabasic phase diagram of CaO-Al₂O₃-SiO₂-Na₂O-Al₂O₃ (in which the content of Na₂O is 7.83-5.91 wt%, and Al₂O₃ is 7.31-11.68 wt%) [2], diopside, (CaMg(SiO₃)₂) and nepheline (KNa₃(AlSiO₄)₄) were determined to be the main phases of the glass-ceramics made from HCFS. Then, HCFS and waste glass (WG) were chosen as the main raw materials; fluorite (CaF₂) was used as flux; and limestone (CaCO₃) and soda (NaCO₃) were used as the modifier and clarifier, respectively. The parent glasses were prepared by five different ratios of HCFS to WG (R(H/W)), that is, 0.60, 0.78, 1.00, 1.29, 1.67, respectively. The mass percentages of each type of the raw materials are shown in Table 1 [2], in which, the mass of limestone (CaCO₃), soda (NaCO₃) and fluorite (CaF₂) in the five samples are 15 g, 5 g, and 5.26 g, respectively.

The HCFS-based parent glass was prepared as described previously [2]. The investigation on the crystallization kinetics of parent glass was carried out as follows: The parent glass sample was first ground into powder with the size below 75 µm and then investigated using differential scanning calorimetry (DSC). A 30 mg sample of the parent glass was placed in a crucible and put into the balance of the DSC

instrument using an empty crucible as a reference. They were heated from room temperature to 1000 °C at different heating rates α ($\alpha=5^{\circ}\text{C}/\text{min}$, $10^{\circ}\text{C}/\text{min}$, $15^{\circ}\text{C}/\text{min}$, $20^{\circ}\text{C}/\text{min}$, $25^{\circ}\text{C}/\text{min}$) under an N_2 atmosphere. Then, each sample was naturally cooled down to room temperature in the equipment under N_2 atmosphere.

Based on the analysis of the DSC data, the parent glass underwent a two-step process for the transformation to the glass-ceramics. The first stage is a low temperature heat-treatment to obtain a high density of nuclei seeds throughout the interior of the parent glass, and a higher temperature second step for the crystallization of nuclei seeds, which finally prepares the glass-ceramics.

2.2. Characterization and measurements

The chemical compositions of the raw materials were determined by wavelength dispersive X-ray fluorescence (XRF, Shimadzu-XRF-1800). Microstructural characterizations of the glass-ceramic samples were performed by a MLA250 scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) attachment. Differential scanning calorimetry (DSC, Model STA 4090, NETZSCH-Gerätebau GmbH, Selb, Germany) was used to determine the non-isothermal crystallization kinetics of the parent glass.

The leaching performance of each sample was tested by the toxicity characteristic leaching procedure (TCLP) developed by the U.S. Environmental Protection Agency (EPA) [32], with a pH 2.0 acetic acid solution as the leaching fluid. Glass-ceramics samples with five different R(H/W) values were all ground into

powder and put into the beaker, each leaching beaker was filled with 500 mL TCLP extraction fluid and 25 g powder, stirred for 24 hours at 1800 rpm. At the end of each agitation period, the leachates were filtered by a syringe filters (0.22 μ m, nylon). The concentrations of total chromium ions in the leachates was detected by inductively coupled plasma atomic emission spectrometry (ICP-AES, America, Varian).

3. Results

The transformation of parent glass to glass-ceramics involves two steps, nucleation and crystallization; therefore, two step heat-treatment was adopted on the parent glass. This transformation is monitored by DSC detection of the powdered parent glass samples from room temperature to 1000°C at different heating rates (α = 5°C/min, 10°C/min, 15°C/min, 20°C/min and 25°C/min). Nucleation is the initial process that forms a new phase during the two-step heat treatment. This step requires energy to overcome the resistance in the parent glass, and it appears as an endothermic peak in the DSC curve. In contrast, the crystallization process which ensures the attainment of the lowest energy of the system is an exothermic process. Thus, it is seen as a sharp exothermic peak in the DSC curve.

To study the crystallization kinetics of the parent glass, DSC curve analysis are performed. Several characteristic temperatures used during the kinetics analysis are defined and obtained from the DSC curves shown as Fig. 1. The temperature of the sharp exothermic peak in the DSC curves is defined as the crystallization temperature, T_p . In addition, the starting temperature of the crystallization, obtained by two tangent

lines, as shown in Fig. 1(a), is defined as T_c . The transformation temperature of the parent glass is defined as T_g ; it is the temperature for the polymer in the parent glass slack from the frozen to the thaw state and is also considered as the nucleation temperature. Finally, ΔT_f is the full width at half maximum (FWHM) of the exothermic peak. All the characteristic temperatures can be obtained from the DSC curves just as Fig. 1 shown, and the results obtained are all presented in Tables 2-5.

4. Discussions

4.1. Thermal stability of the parent glass

To a certain extent, the thermal stability of the HCFS-based parent glass reveals the trend of crystallization of the parent glass. Usually, the thermal stability is enhanced along with the increase of ΔT and $\Delta T'$, which are derived from T_c and T_g , as shown in Eq. 1 and 2, respectively [33,34].

$$\Delta T = T_c - T_g \quad (1)$$

$$\Delta T' = (T_c - T_g) / T_g \quad (2)$$

According to the T_c and T_g , as shown in Tables 2 and 3, ΔT and $\Delta T'$ can be calculated; the results are shown in Figs. 2 and 3. It is found that both ΔT and $\Delta T'$ increase with the increasing heating rate; hence, the parent glass becomes more stable. When the heating rate increases with constant $R(H/W)$, the heat and mass transfers become much more difficult in the parent glass, and the composition in the parent glass will require much more energy for nucleation and crystallization; therefore, the parent glass will crystallize at a higher temperature, and these results are seen in Table

4.

Figs. 2 and 3 also indicate that the thermal stability parameters (ΔT and $\Delta T'$) increase with decreasing $R(H/W)$ at the same heating rate. As the value of $R(H/W)$ decreases, the amount of nuclei seeds in the parent glass decreases, leading to the decrease of crystalline grains. When the $R(H/W)$ decreases to 0.6, the ΔT of the parent glass reaches 225.2 ($\Delta T'=0.355$), the parent glass sample obtained is the most stable. In contrast, when $R(H/W)$ increases to 1.67, ΔT decreases to 170.1 ($\Delta T'=0.265$), the parent glass turns into the easiest one to crystallize. Hence, it illustrates that the HCFS-based parent glass presents much more activity in crystallization when the amount of HCFS increases.

4.2. Crystallization activation energy calculation

The thermal stability only reveals the trend of crystallization of the parent glass; therefore, to investigate the crystallization mechanism of the parent glass, an analysis of crystallization kinetics was carried out, and the crystallization activation energy and crystallization index of the parent glass were subsequently calculated.

Thermal analysis has been used to study the crystallization kinetics of various glass systems [35-39]; therefore, Kissinger and Augis-Bennett equations were also adopted in this work to investigate the crystallization kinetics of the HCFS-based parent glass, namely, the crystallization activation energy (E_c) and the crystallization index (n).

Prior to calculating the crystallization index n , the crystallization activation

energy needed to be obtained first. Under the non-isothermal condition, the crystallization activation energy of the parent glass can be calculated by the Kissinger equation [40], shown as Eq. (3).

$$\ln(T_p^2/\alpha) = E_c/RT_p + \ln(E_c/R) - \ln v \quad (3)$$

where E_c (kJ/mol) stands for the crystallization activation energy, α ($^{\circ}\text{C}/\text{min}$) is the heating rate of the DSC, T_p ($^{\circ}\text{C}$) is the temperature of the exothermic peak in a DSC curve (Table 4), R is the gas constant per molecule, $8.314 \text{ J}/(\text{K}\cdot\text{mol})$, and v stands for the frequency factor. A plot of ' $\ln(T_p^2/\alpha)$ ' versus ' $1/T_p$ ', yields a line with a slope of ' E_c/R ' and an intercept of ' $\ln(E_c/R) - \ln v$ '; these results are shown in Fig. 4. The crystallization activation energies under different heating rates have been calculated from the fitting results and shown in Table 6.

When the value of $R(\text{H/W})$ increases from 0.60 to 1.67, the crystallization activation energy decreases from 253.41 to 183.52 kJ/mol, as shown in Table 6, because the heterogeneous nuclei seeds are almost all provided by the HCFS during the synthesis process. When the percentage of the HCFS in the raw materials increases, the number of nuclei seeds in the parent glass also increases; thus, the parent glass crystallizes much more easily, exhibiting an obvious decrease of the crystallization activation energy. As shown in Tables 3 and 4 the nucleation and crystallization temperatures decrease separately from 641.7 to 612.2 $^{\circ}\text{C}$, and 822.8 to 814.7 $^{\circ}\text{C}$, matching with the decrease of the crystallization activation energy. The crystallization activation energy of ordinary slag-based glass-ceramics, especially blast furnace slag or converter slag based glass-ceramics, are usually in the range of

300-400 kJ/mol [11-16], much higher than that of HCFS-based glass-ceramics (approximately 200 kJ/mol), indicating that the HCFS is much easier to be prepared into glass-ceramics than blast furnace slag or the converter slag. In addition, the nucleation and crystallization temperatures of the HCFS-based glass-ceramics are separately approximately 640°C and 850°C, again much lower than those of ordinary metallurgy slag-based glass-ceramics (the nucleation and crystallization temperatures are approximately 900 °C and 1100 °C, respectively) [11-16], thus producing HCFS-based glass-ceramics is much more energy-efficient, and industrially beneficial.

4.3. Crystallization index calculation

To date, two crystallization mechanisms have been developed for parent glass: surface crystallization and bulk crystallization. Bulk crystallization occurs when the parent glass is easy to crystallize and crystallization takes place both within the parent glass and at its surface. When crystallization occurs only at the surface of the parent glass, it is called surface crystallization [41,42]. Parameter n is defined as the crystallization index; it can reveal the mechanism and the degree of crystallization. Generally, when n becomes larger, the parent glass is easier to crystallize. When the value of n is above 3, the parent glass crystallizes as bulk crystallization; when the value of n ranges from 0-3, it crystallizes as surface crystallization [41,42]. Usually when the parent glass crystallizes as bulk crystallization, or n of the parent glass reaches a higher value, the glass-ceramics will present finer grain size and the higher

density.

The crystallization index n can be calculated by Augis-Bennett equation [43,44], shown as Eq. 4.

$$n = \frac{2.5T_p^2}{\Delta T_f \cdot E_c / R} \quad (4)$$

where T_p stands for the exothermic temperature in the DSC curves (Table 4); ΔT_f stands for FWHM of the exothermic crystallization peak (Table 5), and ' E_c/R ' is the slope in Fig. 4. The crystallization index n varies with the heating rate for different $R(H/W)$, as shown in Fig. 5.

Fig. 5 shows that when the heating rate is constant, the crystallization index increases with increasing $R(H/W)$. Based on the ordinary crystallization mechanism, if the value of n reaches above the red dot line, the sample crystallizes as bulk crystallization. Therefore, when the value of $R(H/W)$ is larger than 0.78, the samples crystallize as the bulk crystallization no matter how fast the heating rate is. In contrast, if the $R(H/W)$ is 0.60, the samples behave as surface crystallization regardless of the heating rate. However, both mechanisms were observed when for $R(H/W)=0.78$; when the heating rate exceeds 10 °C/min, surface crystallization was observed while heating rates of 10 °C/min or less resulted in bulk crystallization behavior.

When the $R(H/W)$ is constant, the crystallization index increases with the decrease of the heating rate. Especially when $\alpha=5$ °C/min, n reaches its maximum value ($n=5.98$), which is much higher than that of ordinary metallurgical slag-based parent glass without nucleation agents ($n=2.69$, and presenting as surface crystallization) [11-16].

4.4. Microstructure of glass-ceramics

Fig. 6 shows the microstructure of HCFS-based glass-ceramics of different heating rates for R(H/W) values of 0.60 and 1.29. Table 7 shows the EDS results of the sample in Fig. 6(j), which are the typical composition results for all the samples. It shows that the main phases of the glass-ceramics are $\text{CaMg}(\text{SiO}_3)_2$ and $\text{KNa}_3(\text{AlSiO}_4)_4$ as the experiment design.

Comparing the two groups of microstructures in Fig. 6, it can be seen that when the heating rate increases, the parent glass (R(H/W)=0.60) in Fig. 6(a)-(e) becomes even harder to crystallize. When $\alpha=5^\circ\text{C}/\text{min}$, the boundary of the crystallized grains can be obviously observed, but when the heating rate increases above $10^\circ\text{C}/\text{min}$, the grain boundary is hard to distinguish, and the samples are full of amorphous phase. Interestingly, the sample shown in Fig. 6(a) crystallizes as bulk crystallization, despite having an n value of 2.32, which indicates that incorporating HCFS into the parent glass allows for n values below 3.00. Conversely, all of the crystal grains of the samples (R(H/W)=1.29) in Fig. 6(f)-(j) present columnar structure, finer grain size and higher density. Especially when $\alpha=5^\circ\text{C}/\text{min}$, the sample in Fig. 6(f) exhibits a better crystal structure than others, and it shows the highest n value.

Fig. 7 presents the average aspect ratios of the crystalized grains in Fig. 6(f)-(j). It shows that when the heating rate decreases, the average aspect ratio of the crystalized grains in the glass-ceramic samples becomes larger. Especially when $\alpha=5^\circ\text{C}/\text{min}$, all the samples of different R(H/W) present the best crystal structure. It is generally known that the mechanical properties of the glass-ceramics are closely

related to the microstructure of the samples; glass-ceramics have better mechanical properties when the crystallized grains have a higher aspect ratio [45-49]. Hence, when the heating rate α reaches its minimum value ($\alpha = 5\text{ }^{\circ}\text{C/min}$), the average aspect ratio of the crystallized grains in the glass-ceramic samples (when $R(H/W)=1.29$) reaches its maximum, and the glass-ceramics obtain their optimal mechanical properties. Then, the optimum conditions for heat-treatment of the parent glass were determined to be as follows: the $R(H/W)$ of 1.29 and the heating rate of $5\text{ }^{\circ}\text{C/min}$, which resulted in nucleation and crystallization temperatures of 627.1 and 820.9°C respectively.

Compared to ordinary metallurgy slag-based parent glass, HCFS-based parent glass has a smaller E_c (approximately 200 kJ/mol), much lower nucleation and crystallization temperatures (approximately 640°C and 850°C respectively), and a higher average crystallization index (average $n=3.67$). Thus, the HCFS is not only easier to make into the glass-ceramics but also much more energy efficient than ordinary metallurgy slag, making it an advantageous material for use in the production of glass-ceramics.

4.5. Leaching performance of glass-ceramics

The ICP results of the glass-ceramics leaching performance are shown in Fig. 8. It can be found from Fig. 8 that, when the value of $R(H/W)$ increases, the concentration of total chromium ions in the leachates increases with it, and when the $R(H/W)$ reaches 1.67, the concentration of total chromium ions achieves its maximum

of 0.257 mg/L. According to the US EPA standards [32], the limits of the concentration of total chromium ions requested is 1.5 mg/L, meanwhile the limits of concentration of hexavalent chromium is 0.5 mg/L. It can be found from Fig.8 that the concentrations of total chromium ions of the glass-ceramics are all much lower than the limits requested by EPA. It further indicates that the potential of the proposed technology can stabilize large volumes of chromium, enabling the feasibility of HCFS reuse as glass-ceramic products.

5. Conclusions

The crystallization kinetics of HCFS-based glass-ceramics have been investigated in this work to determine the best heat-treatment conditions. The parent glass samples were prepared with five different ratios of HCFS to WG ($R(H/W)=0.60, 0.78, 1.00, 1.29, 1.67$), and each of the samples was heat-treated by five heating rates ($\alpha=5, 10, 15, 20, 25^\circ\text{C}/\text{min}$). DSC analysis was carried out to investigate the crystallization kinetics of these various samples.

The thermal stability of the HCFS-based parent glass was investigated first, and the results show enhanced thermal stability of parent glass along with the increasing ΔT ($\Delta T'$). The crystallization activation energy (E_c) and the crystallization index (n) of the parent glass were subsequently calculated and analyzed by Kissinger and Augis-Bennett equations, respectively. It revealed that as the $R(H/W)$ increased, the E_c decreased from 253.41 to 183.52 kJ/mol, and the nucleation and crystallization temperatures decreased from 641.7 to 612.2°C and from 822.8 to 814.7°C,

respectively. When α is constant, the n increases with the increasing $R(H/W)$, and it was found that when the n of the parent glass exceeds 2.32, all the parent glass samples with five different $R(H/W)$ crystallized as bulk crystallization. When $R(H/W)$ is constant, n increased with the decrease of α . Especially when $\alpha=5$ °C/min, n reached its maximum value 5.94, much higher than that of ordinary metallurgical slag-based parent glass, and the crystal grains in the glass-ceramics showed the largest aspect ratio and highest density. Hence, the optimum heat-treatment is as follows, $R(H/W)$ is 1.29, nucleation and crystallization temperature are separately 627.1 and 820.9°C, and the heating rate α is 5 °C/min. The kinetics analysis indicates that HCFS is not only easier to make into glass-ceramics but also much more energy efficient than ordinary metallurgy slag; therefore, HCFS has a significant advantage in producing glass-ceramics. Leaching performance indicates that concentrations of chromium ions in the extraction solutions are much lower than the limits requested by EPA, suggesting that the proposed strategy offers an environmentally safe method of treating large volumes of chromium slag.

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References

- [1]. Z.T. Bai, Z.A. Zhang, M. Guo, X.M. Hou and M. Zhang, Magnetic separation and extraction chrome from high carbon ferrochrome slag, *Materials Research Innovations*. 19(2015) 113-118.
- [2]. Zhitao Bai, Guibo Qiu, Ben Peng, Min Guo and Mei Zhang, Synthesis and characterization of glass-ceramics prepared from high-carbon ferrochromium slag, *RSC Adv*. 6 (2016) 52715-52719.
- [3]. S. Kumar, K.K. Singh and P. Ramachandrarao, Synthesis of cordierite from fly ash and its refractory properties, *J. Mater. Sci. Lett*. 19 (2000) 1263-.1268
- [4]. A.R. Boccaccini, M. Bucker and J. Bossert, Glass and glass ceramics from coal fly ash and waste glass, *Tile and Brick International*. 12 (1996) 515-519.
- [5]. R. Cioffi, P. Pernice, A. Aronne, M. Catauro and G. Quattroni, Glass-ceramics from fly ash with added Li_2O , *J. Euro. Ceramic Society*. 13 (1994) 143-146.
- [6]. M. Erol, S. Kucukbayrak, A. Ersoy-mericboyu and M.L. Ovecoglu, Crystallization behaviour of glasses produced from fly ash, *J. Europ. Ceram. Soc*. 21 (2001) 2835-2839.
- [7]. L. Montanaro, N. Bianchini, J.MA. Rincon and M. Romero, Sintering behaviour of pressed red mud wastes from zinc hydrometallurgy, *Ceram. Int*. 27 (2001) 29-34.
- [8]. M. Romero, J. MA. Rinc'on, S. Musik and V. Kozhukharov, Sintering behaviour of pressed red mud wastes from zinc hydrometallurgy, *Mater. Res. Bull*. 34 (1998) 1107-1110.

- [9]. A. Karamanov, M. Pelino, G. Taglieri and C. Cantalini, in “Proc. XVIII International Congress on Glass”, edited by M.K. Choudhary, N.T. Huff and Ch.H. Drummond III, (San Francisco (USA), The American Ceramic Society, Ohio, July 5-10, 1998).
- [10]. A. Karamanov, P. Piscicella, C. Cantalini and M. Pelino, Influence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on the crystallization of iron-rich glasses made with industrial wastes, J. Am. Ceram. Soc. 83 (2000) 3153-3157.
- [11]. L.I. Frantseyuk, I.V. Blintsova and A.E. Seredkin, Synthesis of slag-based glass-ceramics, Glass and Ceramics. 53 (1996) 356-360.
- [12]. E. Fidancevska, B. Mangutova, D. Milosevski, M. Milosevski and J. Bossert, Obtaining of dense and highly porous ceramic materials from metallurgical slag, Sci. Sintering. 35 (2003) 85-91.
- [13]. J.A. Topping, The fabrication of glass-ceramic materials based on blast-furnace slag-a review, J. Can. Ceram. Soc. 45 (1976) 63-70.
- [14]. T. Shaoqiu, L. Zhongjun and CH. Guorong, Studies of the crystallization of antimony-containing slag glass-ceramic, J. Am. Ceram. Soc. 75 (1992) 440-444.
- [15]. C.B. Ponton, R.D. Rawlings and P.S. Rogers, Mechanical properties of “silicram” glass-ceramics, Proc. Brit. Ceram. Soc. 37 (1986) 229-234.
- [16]. G.A. Khater, The use of Saudi slag for the production of glass-ceramic materials, Ceram. Inter. 28 (2002) 59-63.
- [17]. A.R. Boccaccini, M. Kopf and G. Ondracek, Neue Techniken der Abfallverwertung-zu den Möglichkeiten einer Verwertung von Filterstäuben aus

der Abfallverbrennung durch werkstofftechnische, Z. für angewandte Umweltforschung 7 (1994) 357.

- [18]. M. Romero, R.D. Rawlings and J.MA. Rincón, Development of a new glass-ceramic by means of controlled vitrification and crystallisation of inorganic wastes from urban incineration, J. Europ. Ceram. Soc. 19 (1999) 2049-2053.
- [19]. A.R. Boccaccini, M. Köpf and W. Stumpfe, Glass-ceramics from filter dusts from waste incinerators, Ceramics International. 21 (1995) 231-235.
- [20]. A.R. Boccaccini, M. Petitmermet and E. Wintermantel, Glass-ceramics from municipal incinerator fly ash, Am. Ceram. Soc. Bulletin. 76(11) (1997) 75-81.
- [21]. A.R. Boccaccini, H. Kern, J.MA. Rincon, M. Romero, M. Petitmermet and E. Wintermantel, in: "Proc. R'99" Recovery, Recycling, Re-integration" Conference", edited by A. Barrage, X. Edelmann (Published by EMPA, Switzerland, 1999) Vol. II, 152.
- [22]. J.MA. Rincón, M. Romero and A.R. Boccaccini, Microstructural characterisation of a glass and a glass-ceramic obtained from municipal incinerator fly ash, J. Mat. Sci. 34 (1999) 4413-4417.
- [23]. L. Barbieri, A. Corradi and I. Lancellotti, Thermal and chemical behaviour of different glasses containing steel fly ash and their transformation into glass-ceramics, J. Europ. Ceram. Soc. 22 (2002) 1759-1764.
- [24]. A. Polettini, R. Pomi, L. Trinci, A. Muntoni and S. Lomastro, Engineering and environmental properties of thermally treated mixtures containing MSWI fly ash and low-cost additives, Chemosphere. 56 (2004) 901-905.

- [25]. P. Zhang and J. Yan, Z. Metallk. 91 (2000) 764.
- [26]. M.M. Sokolova, V.S. Perunova, V.V. Sepanov and N.V. Kozlov, A glass ceramic material based on the waste from lamp production, Glass and Ceramics. 43 (1986) 133-139.
- [27]. Z. GAO III and C.H. Drummond, Thermal analysis of nucleation and growth of crystalline phases in vitrified industrial wastes, J. Am. Ceram. Soc. 82 (1999) 561-565.
- [28]. Z.Q. Wang, S.M. Yao, W.Y. Gao, Y.Y. Qu, Study on the ferrochromium based glass-ceramics, Journal of Dalian Institute of Light Industry. 19 (2000) 84-88.
- [29]. Z.Q. Wang, C. Ma, C.T. Han, Glass-Ceramics Prepared from C-Cr and Si-Mn Alloy Slag, Glass & Enamel. 29 (2001) 16-20.
- [30]. S.V. Raman, Microstructures and leach rates of glass–ceramic nuclear waste forms developed by partial vitrification in a hot isostatic press, J. Mater. Sci. 33 (1998) 1887-1892.
- [31]. P. Loiseau, D. Caurant, N. Baffier, L. Mazerolles and C. Fillet, Glass-ceramic nuclear waste forms obtained from $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-ZrO}_2\text{-TiO}_2$ glasses containing lanthanides (Ce, Nd, Eu, Gd, Yb) and actinides (Th): study of internal crystallization, J. Nucl. Mater. 335 (2004) 14-20.
- [32]. USEPA, Method 1311: Toxicity Characteristic Leaching Procedure. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, third ed., US Environmental Protection Agency, Office of Solid Waste, US Government Printing Office, Washington, DC, 1992.

- [33]. Qiuhong Yang, Zhonghong Jiang, The study of criterion for glass crystallization kinetics, Journal of The Chinese Ceramics Society. 22(1994), 419-426.
- [34]. M.M.A. Imran, Crystallization kinetics, glass transition kinetics, and thermal stability of $\text{Se}_{70-x}\text{Ga}_{30}\text{In}_x$ ($x = 5, 10, 15$, and 20) semiconducting glasses, Physica B. 406 (3) (2011) 482-487.
- [35]. H. Hosono, Y. Abe, Fast lithium conducting glass-ceramic in the $\text{CaO-Li}_2\text{O-TiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ system, Solid State Ionics. 44 (1991) 293-297.
- [36]. N. Anantharamulu, K. Koteswara Rao, G. Rambabu, B. Vijaya Kumar, V. Radha, M. Vithal, A wide-ranging review on Nasicon type materials, J. Mater. Sci. 46 (2011) 2821-2837.
- [37]. T. Ozawa, A new method of analyzing thermogravimetric data, Bull. Chem. Soc. Jpn. 38 (1965) 1881-1886.
- [38]. F. Branda, A. Buri, A. Marotta, S. Saiello, Kinetic of crystal growth in $\text{Na}_2\text{O-2SiO}_2$ glass: a DTA study, Thermochim. Acta. 77 (1-3) (1984) 13-18.
- [39]. I. Dyamant, E. Korin, J. Hormadaly, Non-isothermal crystallization kinetics of $\text{La}_2\text{CaB}_{10}\text{O}_{19}$ from glass, J. Non-Cryst. Solids. 357 (7) (2011) 1690-1695.
- [40]. H.E. Kissinger, Variation of peak temperature with heating rate in differential thermal analysis, J. Res. Natl. Bur. Stand. 57 (4) (1956) 217-221.
- [41]. H. Hosono, Y. Abe, Porous glass-ceramics with skeleton of the fast lithium conducting crystal $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$, J. Am. Ceram. Soc. 75 (1992) 2862-2864.
- [42]. H. Hosono, Y. Abe, Silver ion selective porous lithium phosphate glass-ceramics cation exchanger and its application to bacteriostatic materials, Mater. Res. Bull.

1994, 29(11), 1157-1160.

- [43]. K. Matusta, T Komatsu, R Yokota, Kinetics of non-isothermal crystallization process and activation energy for crystal growth in amorphous materials, J. Mater. Sci. 1984, 19(1), 283-292.
- [44]. J.E. Augis, J. Bennett, Calculation of the avrami parameters for heterogeneous solid state reactions using a modified the Kissinger method, J. Therm. Anal. 13 (1978) 283-292.
- [45]. M. Erol, S. Kucukbayrak, A. Ersoy-Mericboyu, Influence of particle size on the crystallization kinetics of glasses produced from waste materials, J. Non-Cryst. Solids. 357 (1) (2011) 211-219.
- [46]. S. Mahadevan, A. Giridhar, A.K. Singh, Calorimetric measurements on As-Sb-Se glasses, J. Non-Cryst. Solids. 88 (1986) 11-34.
- [47]. M. Saad, M. Poulin, Glass forming ability criteria, Mater. Sci. 19&20 (1987) 11-15.
- [48]. M. Avrami, Kinetics of phase change, J. Chem. Phys. 9 (1941) 177-180.
- [49]. W.A. Johnson, K.F. Mehl, Reaction kinetics in process of nucleation and growth, Trans. Am. Inst. Min. Metall. Pet. Eng. 135 (1939) 416-424.

Figure captions

Fig. 1. DSC curves of $R(H/W)=0.60$ samples at different heating rates.

Fig. 2 ΔT variation as a function of heating rate for different $R(H/W)$ ratios.

Fig. 3 $\Delta T'$ variation as a function of heating rate for different $R(H/W)$ ratios.

Fig. 4 Linear fitting results of $\ln(T_p^2/\alpha) \sim 1/T_p$, r is the Pearson correlation coefficient.

Fig. 5 Linear fitting of the crystallization index n to heating rate α with different $R(H/W)$ ratios; r is the Pearson correlation coefficient.

Fig. 6 Microstructure of the $R(H/W)=0.60$ and 1.29 glass-ceramics samples treated with different heating rates α :

(a)-(e), α is 5, 10, 15, 20, 25 °C/min, respectively, with $R(H/W)=0.60$;

(f)-(j), α is 5, 10, 15, 20, 25 °C/min, respectively, with $R(H/W)=1.29$.

Fig. 7 The average aspect ratios of $R(H/W)=1.29$ samples with different heating rates.

Fig. 8. The leaching concentration of total chromium ions within samples with different $R(H/W)$.

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Tables

Table 1 Raw material compositions.

Sample	HCFS /g	Waste glass /g	Mass ratio of HCFS and WG, R(H/W)
1	30.0	50.0	0.60
2	35.0	45.0	0.78
3	40.0	40.0	1.00
4	45.0	35.0	1.29
5	50.0	30.0	1.67

Table 2 Initial crystallization temperatures, T_c , with different heating rates ($^{\circ}\text{C}$).

Heating rate ($^{\circ}\text{C}/\text{min}$)	$T_c / ^{\circ}\text{C}$				
	R(H/W)=0.60	0.78	1.00	1.29	1.67
5	810.2	806.7	817.6	807.9	811.8
10	828.7	825.0	833.4	823.5	832.9
15	839.6	836.6	844.8	834.3	844.7
20	849.7	846.4	853.2	840.7	855.0
25	859.8	852.5	859.2	847.1	863.6

Table 3 Glass transformation temperatures, T_g , with different heating rates ($^{\circ}\text{C}$).

Heating rate ($^{\circ}\text{C}/\text{min}$)	$T_g / ^{\circ}\text{C}$				
	R(H/W)=0.60	0.78	1.00	1.29	1.67
5	612.2	624.1	629.3	627.1	641.7
10	620.3	621.9	635.8	636.5	652.8
15	626.8	623.4	636.4	647.0	652.8
20	634.6	633.3	629.8	645.6	656.6
25	634.6	633.6	645.1	646.0	662.7

Table 4 Crystallization temperatures, T_p , with different heating rates ($^{\circ}\text{C}$).

Heating rate ($^{\circ}\text{C}$ /min)	T_p / $^{\circ}\text{C}$				
	R(H/W)=0.60	0.78	1.00	1.29	1.67
5	814.7	815.7	818.6	820.9	822.8
10	828.7	833.7	839.4	844.5	852.9
15	839.6	846.6	849.8	850.3	856.7
20	845.7	854.4	859.2	860.7	864.0
25	850.8	863.5	870.8	875.1	877.6

Table 5 FWHM of the exothermic peak, ΔT_f , with different heating rates ($^{\circ}\text{C}$).

Heating rate ($^{\circ}\text{C}$ /min)	ΔT_f / $^{\circ}\text{C}$				
	R(H/W)=0.60	0.78	1.00	1.29	1.67
5	23.5	20.5	13.5	13.4	12.9
10	29.3	23.0	14.6	15.8	15.8
15	30.1	27.4	17.4	21.7	20.5
20	31.1	29.0	19.0	24.0	23.5
25	34.4	31.5	21.0	25.8	22.51

Table 6 Fitting results of samples with different R(H/W) ratios.

$\ln(T_p^2/\alpha)$	R(H/W)				
$=E_c/RT_p + \ln(E_c/R) - \ln v$	0.60	0.78	1.00	1.29	1.67
E_c/R	-3.05	-2.39	-2.26	-2.23	-2.20
$\ln(E_c/R) - \ln v$	39.03	30.95	29.28	28.81	28.40
E_c (kJ/mol)	253.41	198.81	188.17	185.47	183.52

Table 7 EDS analysis of the glass-ceramic samples in Fig. 6(j).

Point #	Element norm. C (wt %)								Phase
	O	Mg	Al	Ca	Na	Cr	Fe	Si	
1	47.15	22.78	1.38	6.16	1.57	0.29	0.61	20.60	CaMg(SiO₃)₂
2	45.37	19.58	1.88	8.99	1.54	0.00	1.80	20.19	
3	40.67	16.93	1.27	10.13	1.35	0.45	1.79	27.07	
4	43.49	2.21	13.61	1.96	13.00	0.57	1.25	23.47	(Na,K)AlSiO₄
5	39.85	1.36	17.17	1.98	14.20	0.03	0.00	24.66	
6	45.90	1.61	14.37	1.54	13.43	0.00	2.61	20.11	