

# Effect of $Al_2O_3$ on migration and distribution of chromium and chromium fixation effect in stainless-steel slag glass-ceramics

Chuanbo Zhang<sup>1</sup>, Zhifang Tong<sup>1,\*</sup>, Congcong Xu<sup>1</sup>, Jiaxing Wang<sup>1</sup>, Zhiheng Jia<sup>2</sup>

<sup>1</sup>Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou, Jiangxi 341000, P.R. China

<sup>2</sup>Changchun Gold Deign Institute Co., Ltd., Changchun, Jilin 130000, P.R. China

Received 1 November 2022; Received in revised form 27 January 2023; Accepted 21 February 2023

## Abstract

Stainless-steel slag was used to prepare glass-ceramics, which could solidify chromium (Cr) in the slag. The migration and distribution state of chromium in the slag during the preparation of the glass-ceramics have a great influence on the chromium fixation ability of the glass-ceramics. In this paper, the effects of  $Al_2O_3$  content in the glass-ceramics on the migration and distribution of chromium during the nucleation and crystallization steps, and on the chromium fixation effect of the glass-ceramics were systematically studied. The results show that in the nucleation stage, with the increase of  $Al_2O_3$  content, the number of chromium spinel (Cr-spinel) nanocrystals formed in the glass first increases and then decreases, and Cr in the glass phase gradually migrates to Cr-spinel nanocrystals. TEM and XPS analyses show that during crystallization, part of Cr in Cr-spinel diffuses into diopside lattice, and the other part of Cr still exists in Cr-spinel wrapped by diopside. Cr in the glass phase also diffuses and migrates into the diopside lattice with the formation of diopside crystals. The optimal  $Al_2O_3$  content is 11.8 wt.%, which results in 97.94 wt.% of the total Cr being fixed in the diopside crystalline phase. The ability of chromium fixation is very high giving a very low Cr leaching concentration of 0.004 mg/l. The research results provide theoretical and technical support for increased chromium fixation and realizing harmless and high-value utilization of stainless-steel slag.

Keywords: stainless-steel slag, glass-ceramics, Cr migration and distribution, chromium fixation

## I. Introduction

Stainless-steel is widely used in various industries due to its excellent performance [1–3]. A large amount of Cr-containing stainless-steel slag is being obtained in production of stainless-steel. When it is stored in openair for a long time,  $Cr^{3+}$  in the slag will be oxidized to form toxic  $Cr^{6+}$ .  $Cr^{6+}$  dissolved in water will cause harm to the natural environment and human health [4,5]. The toxicity of stainless-steel slag has become a bottleneck restricting the sustainable development of stainless-steel production industry. The glass-ceramics can be prepared with stainless-steel slag, which can solidify Cr in the slag. It is an effective way to realize the harmless and high-value utilization of stainless-steel slag [6–9].

In recent years, research on the preparation of glass-ceramics from metallurgical slag has gradually

increased [10-15]. During the preparation of glassceramics, it is found that as the main component of basic glass, Al<sub>2</sub>O<sub>3</sub> has a great influence on the crystallization and properties of glass-ceramics. Zhao et al. [16] studied the influence of Al2O3 on the structure and properties of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass-ceramics. The results showed that with the increase of Al<sub>2</sub>O<sub>3</sub> content from 3.20% to 9.62%, the initial crystallization temperature and crystallization temperature of the glass-ceramics gradually increased, crystal precipitation became difficult and the crystallization rate decreased. The hardness, wear resistance and thermal expansion coefficient of the glass-ceramics first increased and then decreased. Xu et al. [17] prepared the glass-ceramics with cordierite as the main crystal phase. It was found that with the increase of Al<sub>2</sub>O<sub>3</sub> content, the viscosity of the glass increased, which hindered the growth of the crystal. More glass phases led to the decrease of the strength of the glass-ceramics.

<sup>\*</sup>Corresponding author: tel: +86 13879715231

e-mail: tongzhifang1998@126.com

Raw material	CaO	MgO	$Al_2O_3$	SiO <sub>2</sub>	$Cr_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
Stainless steel slag	38.82	10.01	4.83	39.67	2.03	1.25	1.61	0.22	0.04
Fly ash	5.16	0.60	34.02	48.71	-	5.40	1.81	1.29	0.47
Quartz sand	-	-	0.23	98.32	-	0.25	-	-	-
Light magnesium oxide	0.75	98.44	0.06	-	-	0.05	-	-	-
Soda ash	-	-	-	-	-	-	-	56.86	-
Industrial iron oxide	-	-	-	-	-	99.00	-	-	-
Industrial alumina	-	-	98.6	0.5	-	0.3	-	0.6	-
<b>T</b> 11			•		- 1	• (			

Table 1. Main chemical compositions of the glass-ceramics raw materials (wt.%)

Table 2. Chemical composition of the A1-A5 glass-ceramics (wt.%)									
Samples	CaO	MgO	$Al_2O_3$	SiO <sub>2</sub>	$Cr_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O
A1	25.0	12.4	10.0	44.8	1.3	3.9	1.4	1.1	0.1
A2	24.8	12.3	10.9	44.3	1.2	3.9	1.4	1.1	0.1
A3	24.5	12.2	11.8	43.9	1.2	3.8	1.3	1.0	0.1
A4	24.3	12.1	12.7	43.4	1.2	3.8	1.3	1.0	0.1
A5	24.0	12.0	13.5	43.0	1.2	3.8	1.3	1.0	0.1

Using stainless-steel slag to prepare glass-ceramics can fix Cr in the slag. The migration and distribution of Cr during the preparation of glass-ceramics have a great influence on the Cr fixation effect of glassceramics. Therefore, it is of great significance to investigate the migration behaviour of Cr in the prepared glassceramics and conditions for chromium fixation. As the main component of basic glass, the influence of  $Al_2O_3$ on the occurrence, distribution and migration behaviour of Cr during nucleation and crystallization has not been reported yet.

In the present study, stainless-steel slag was used as the main raw material for glass-ceramics preparation using the melting method. The effects of  $Al_2O_3$  on the types and morphology of the nuclei and the distribution and migration behaviour of Cr between the nuclei and glass phase in the nucleation stage were investigated. In the crystallization stage, the migration behaviour of Cr from nuclei to crystal and the effect of  $Al_2O_3$  on the occurrence and distribution of Cr between the crystal and glass phase were studied. Finally, the Cr-fixation effect of the glass-ceramics was verified. The research results provided theoretical and technical support for strengthening Cr fixation and realizing harmless and high-value utilization of stainless-steel slag.

## **II. Experimental**

#### 2.1. Raw materials and formulas

Stainless-steel slag was used as the main raw material for the glass-ceramics preparation, together with fly ash, a small amount of quartz sand, light magnesium oxide, soda ash, industrial iron oxide and an industrial alumina for adjusting its composition. X-ray fluorescence spectrometer (XRF, Axios Max, Netherlands) was used to detect the main chemical components of the raw materials, as listed in Table 1.

In this study, CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) glassceramics with diopside as the main crystalline phase was prepared. By referring to relevant literature [5,1821] and the previous research work of our research group [22], A1 composition (Table 2) was used as the basic glass formula in which the added amount of stainless-steel slag was 60 wt.% and that of fly ash was 20 wt.%. Al<sub>2</sub>O<sub>3</sub> content in the basic A1 formula was varied by adding an industrial alumina to obtain five groups of glass-ceramics formulas, namely, A1, A2, A3, A4 and A5 (A1-A5). The added amount of the raw materials remained unchanged. Their chemical compositions are listed in Table 2.

#### 2.2. Glass sample preparation

All raw materials were crushed, dried at 100 °C for 24 h and sieved using a 200-mesh sieve. The raw materials were weighed according to the formula. They were then ball-milled in a ball mill for 3 h (the ball-tomaterial ratio was 10:1). The mixed raw materials were put into a 200-ml alumina crucible and subsequently placed in a tubular furnace. They were then heated to 1550 °C at 10 °C/min and kept at this temperature for 1 h. Nitrogen was injected into the entire process for protection. Simultaneously, a stainless-steel mould was put into the muffle furnace and heated to 550 °C. The molten glasses were poured into the mould, placed in the muffle furnace, annealed at 550 °C for 1 h and cooled in the furnace to prepare the parent glass. The parent glasses were placed in an isothermal-gradient furnace and heated according to the heat-treatment system to obtain a nucleation glass and crystallized glass-ceramics.

#### 2.3. Testing and characterization

The glasses were cut into  $20 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$  strips. The thermal-expansion curve of the parent glass was measured using a thermal-expansion analyser (CTE, ZRPY-1000, China) and the transformation temperatures ( $T_g$ ) of the glasses were analysed. The test temperature ranged from room temperature to 780 °C and the heating rate was 5 °C/min. The crystallization temperatures of the parent glasses in argon atmosphere were measured using a differential scanning calorimeter (DSC, NETZSCH STA449F5, Germany) at a heating rate of  $10 \,^{\circ}$ C/min and the measurement temperature range was  $30-1000 \,^{\circ}$ C.

The glass samples were ground to less than 200-mesh size and analysed using XRD (D/max 2500 PC, Japan) under Cu-K $\alpha$  radiation at a working voltage of 40 kV and working current of 30 mA. The scanning range was 10°–90° and the scanning angular velocity was 0.2 °/s.

The internal crystal morphology of the glass samples was observed using SEM (Philips XL30, America). The samples were immersed in HF solution (5 vol.%) for 20 s, immediately washed with distilled water, subsequently washed with ethanol and finally dried. Before the test, gold was sprayed on the sample surface, which was fixed on the stage using a conductive adhesive.

The types and morphology of nanocrystals in the nucleation glasses were analysed by TEM (Tecnai G2-20, USA). The sample to be tested was thoroughly ground in an agate mortar, then 10 mg was taken and placed in a centrifugal tube containing 10 ml ethanol solution and ultrasonically dispersed in an ultrasonic disperser for 30 min. After 20 min, small volume of the solution was dropped on the copper net with a dropper and irradiated with a baking lamp for 5 min. The accelerating voltage of TEM was 300 kV and the point resolution was 0.24 nm.

The nucleation glass and glass-ceramics powders were tested by XPS (ESCALAB 250XI, USA). The radiation source was Al K $\alpha$  X-ray (1486.6 eV), the passing energy of high-resolution scanning was 30.0 eV, the step was 0.05 eV and the peak position was calibrated with the standard C 1s peak (284.8 eV).

In this study, a liquid-solid ratio of 10:1 (l/kg) was used to leach Cr from the glass-ceramics using the overturning oscillation method to investigate the Cr-fixation effect of the glass-ceramics. The samples were shaken for 1, 3, 5, 7 and 24 h and allowed to stand for 4 h. Then, a pressure filter (0.45- $\mu$ m filter membrane) was used to extract the leachate and stored it at 25 °C. The Cr concentration in the leaching solution was measured using an inductively coupled plasma mass spectrometer (ICP, Thermo ICAP 6300, USA).

## III. Results and discussion

#### 3.1. Determination of heat treatment conditions

CTE and DSC tests were performed to determine the nucleation and crystallization heat-treatment conditions for preparation of the A1-A5 glass-ceramics. Figures 1a and 1b show the thermal-expansion curve and DSC curves of the A1-A5 parent glasses, respectively. It can be seen that  $T_g$  of the parent glass (Fig. 1a) and the temperature corresponding to the exothermic peak (Fig. 1b) are changed with the amount of added  $Al_2O_3$ . Studies have shown that the nucleation temperature of glassceramics is generally 30–50 °C above  $T_g$  [23–25]. In conjunction with our previous research, the nucleation heat treatment schedule for the A1-A5 glass-ceramics is selected as dwell temperature of 715, 700, 650, 665 and 688 °C for 2 h. As it can be seen from Fig. 1b, the DSC curves of the five groups of parent glasses show obvious endothermic peaks at about 800 °C, indicating that a large number of crystals begin to precipitate inside the glass at this temperature. Therefore, the crystallization heat treatment parameters for the A1-A5 glass-ceramics were selected as follows: 833, 824, 810, 826 and 833 °C for 2.5 h.

#### 3.2. Internal micro morphology of glass

The samples of A1-A5 glasses after nucleation and crystallization heat treatment were analysed by SEM and the results are shown in Figs. 2 and 3. It can be seen from Fig. 2 that with the increase of  $Al_2O_3$  content, nanocrystals are formed in the nucleated glasses and the number of nanocrystals increases first and then decreases. When the amount of  $Al_2O_3$  is 11.8 wt.% (A3), the number of nanocrystals is the largest and the particle size is the smallest. With the increase of  $Al_2O_3$  content, the number of nanocrystals decreases and the average size increases to about 60 nm. This is because  $Al_2O_3$ 



Figure 1. CTE (a) and DSC curves (b) of the A1-A5 parent glass



Figure 2. SEM images of A1-A5 glasses with the different amounts of added  $Al_2O_3$ 



Figure 3. SEM image of the glass-ceramics with different  $\mathrm{Al}_2\mathrm{O}_3$  contents

is an amphoteric oxide, which can exist in the form of tetrahedral structure  $[AlO_4]^{5-}$  or octahedral structure  $[AIO_6]^{9-}$  [26]. Some studies have pointed out that the existing form of Al<sub>2</sub>O<sub>3</sub> is related to the content of alkali metal and alkaline earth metal oxides in glass [16]. In this study, the content of alkali metal and alkaline earth metal oxides is higher than that of  $Al_2O_3$ . Therefore, as a network forming body in glass, Al<sub>2</sub>O<sub>3</sub> mainly exists in the form of tetrahedral structure  $[AlO_4]^{5-}$ . When the content of  $Al_2O_2$  is too high, amount of the formed Al-O-Si bonds will increase, the glass network will be tightly connected, the viscosity will increase and the ion migration rate will slow down. The nucleation rate of nanocrystals is lower than the growth rate of nanocrystals, which shows that the size of nanocrystals increases and their number decreases.

Figure 3 shows SEM images of the A1-A5 crystalline glasses. As it can be seen from Fig. 3, when the  $Al_2O_3$ content increased from 10 wt.% (A1) to 11.8 wt.% (A3), the number of precipitated crystals increased gradually and their particle size decreased from 1.2 to 0.6 µm. When the  $Al_2O_3$  content continued to increase, the number of crystals decreased and the particle size increased. The reason was that the number of nanocrystals generated in the nucleation stage directly affected the number and particle size of the precipitated crystals during the crystallization process. When the content of  $Al_2O_2$ is 11.8 wt.%, the number of spinel nanocrystals is the largest (Fig. 2) and in the crystallization stage, precipitated crystals nucleate and grow with nanocrystals in the nucleation stage as heterogeneous nuclei. The growth interfaces of the precipitated crystals quickly touch each other and stop growing, resulting in the smallest particle size and the largest number of precipitated crystals.

## 3.3. Distribution of Cr in the nucleation stage

The distribution state of Cr between the glass phase and the formed nanocrystalline nucleus in the nucleated



Figure 4. XRD diffraction patterns of A1-A5 nucleation glasses

glass will directly affect the distribution of Cr during the crystallization process and then affect the chromium fixation effect of the glass-ceramics. In order to determine the phase of nanocrystalline nuclei, XRD was performed on the A1-A5 nucleated glass samples and the results are shown in Fig. 4. At  $2\theta$  between 20° and 40°, only the typical wide glass peak of inorganic glass appeared and no obvious crystal diffraction peak was observed. The reason may be that the size of the nanocrystals generated is small and the dispersion of the nanocrystals in the glass is high. The diffraction peaks of the crystals are broadened, overlapped and blurred, showing the characteristics of amorphous diffraction peaks.

Because the nanocrystals formed in the nucleation stage were relatively small and highly dispersed, their phases were difficult to analyse by XRD. In the present study, TEM analysis was conducted on the A1-A5 nucleation glass powders to determine the phase type of the nanocrystals. We considered the A3 nucleation glass as an example. Figure 5a shows the TEM bright-field image of the A3 nucleation glass. It can be observed from Fig. 5a that the nanocrystals were precipitated in zones 1 and 2. Figure 5b shows the HRTEM image of zone 1 in Fig. 5a. Lattice fringes can clearly be observed in the nanocrystals in HRTEM, whereas the region without lattice fringes was an amorphous glass phase. The crystal lattice fringes of zones 1 and 2 shown in Fig. 5a were analysed. The calibration results of the crystal plane spacing are shown in Figs. 6 and 7. Fourier transform was applied to the HRTEM images of the crystals shown in Figs. 6a and 7a to obtain the diffraction patterns, as shown in Figs. 6b and 7b. After the measurement, distance  $l_1$  from the diffraction spot to the diffraction centre in the reciprocal lattice was obtained. The calculation formula for crystal plane spacing d is expressed as follows:

$$d = \frac{1}{l_1} \times \frac{l_0}{scale} \tag{1}$$

where  $l_0$  is 10 nm<sup>-1</sup>,  $l_1$  represents the actual measured lengths shown in Figs. 6b and 7b, which were 3.991 and 4.02 nm<sup>-1</sup> respectively, and "scale" is 10 nm<sup>-1</sup>. According to Eq. 1, the crystal-plane-spacing values of the nanocrystals in zones 1 and 2 were 0.25056 and 0.249 nm, respectively. To verify the accuracy of the calculation results, the calibration-diagram profile of the lattice stripes was measured and analysed and the results are shown in Figs. 6c and 7c, which show that the measured results of the crystal plane spacing were 0.2506 and 0.2491 nm, respectively. The calculation results were consistent with the measurement and analysis results of the calibration-diagram profile.

Thus, the crystal plane spacing of the crystal in zone 1 of Fig. 6 is d = 0.2506 nm. Based on the ICDD-PDF database, the plane spacing of the crystal in zone 1 (Fig. 6) corresponded to the (311) cryst



Figure 5. TEM (a) and HRTEM (b) images of the A3 nucleation glass sample



Figure 6. MgCr<sub>2</sub>O<sub>4</sub> nanocrystals in the A3 nucleation glass (a), Fourier-transform diffraction pattern (b) and profile of the calibration diagram (c)



Figure 7. (Mg,Fe)(Cr,Al)<sub>2</sub>O<sub>4</sub> nanocrystals in the A3 nucleation glass (a), Fourier-transform diffraction pattern (b) and profile of the calibration diagram (c)

tal plane of  $MgCr_2O_4$  (PDF#: 77-0007), indicating that the nanocrystal phase in zone 1 was  $MgCr_2O_4$ . Figure 7 shows that the crystal plane spacing in zone 2 was 0.249 nm, which corresponded to the (311) crystal plane of  $(Mg,Fe)(Cr,Al)_2O_4$  (PDF#: 09-0353), indicating that the nanocrystal phase in zone 2 was  $(Mg,Fe)(Cr,Al)_2O_4$ .

TEM test results show that the nanocrystals formed in the nucleation stage are mainly chrome spinel nanocrystals and the research results are consistent with the results indirectly inferred by many researchers based on theoretical analysis and combined with EDS detection results [27–29].

The chemical state of  $Cr^{3+}$  in the A1-A5 nucleation glasses was analysed using XPS and the effect of the different Al<sub>2</sub>O<sub>3</sub> contents on the occurrence and distribution of Cr in the Cr spinel and glass phase was investigated. Dïngkun *et al.* [30] found that due to the different ligands of  $Cr^{3+}$  in a glass,  $Cr^{3+}$  may exist in the form of isolated  $Cr^{3+}$  ions and exchange coupled  $Cr^{3+}$  pairs that form Cr spinels. Different forms of existence correspond



Figure 8. XRD spectrum of pure MgCr<sub>2</sub>O<sub>4</sub> (a), electron binding-energy spectrum of Cr in MgCr<sub>2</sub>O<sub>4</sub> (b) and electron binding-energy spectrum of Cr in the parent glass (c)



Figure 9. Fitted XPS peak-splitting spectra of Cr in the A1-A5 nucleation glasses

Table 3. Proportion of the Cr distribution in the Cr spinel/glass phase to the total Cr content in the A1-A5 nucleation glass

	Samples	Peak [ev]	Area [a.u.]	Sum [a.u.]	Proportion of Cr in spinel [%]	
A1	Glass phase Cr $2p_{1/2}$	588.8	897.58	2508 58		
	Glass phase Cr $2p_{3/2}$	577.8	1161	2308.38	74.03	
	Spinel Cr $2p_{1/2}$	586.5	2944.13	7407 57	74.95	
	Spinel Cr $2p_{1/2}$	576.1	4553.44	1491.31		
	Glass phase Cr $2p_{1/2}$	588.8	624	1266.46		
12	Glass phase Cr $2p_{3/2}$	577.8	1560.89	1200.40	78.63	
A2	Spinel Cr $2p_{1/2}$	586.5	2798.42	8040 21		
	Spinel Cr $2p_{1/2}$	576.1	5241.79	8040.21		
A3	Glass phase Cr $2p_{1/2}$	588.8	581.31	1623 72		
	Glass phase Cr $2p_{3/2}$	577.8	1042.41	1023.72	85.01	
	Spinel Cr $2p_{1/2}$	586.5	3261.85	0207 55	65.01	
	Spinel Cr $2p_{1/2}$	576.1	5945.7	9207.55		
A4	Glass phase Cr $2p_{1/2}$	588.8	696.57	1800.06	82.12	
	Glass phase Cr $2p_{3/2}$	577.8	1203.39	1099.90		
	Spinel Cr $2p_{1/2}$	586.5	3056.86	8726 81	02.12	
	Spinel Cr $2p_{1/2}$	576.1	5669.98	0720.04		
A5	Glass phase Cr $2p_{1/2}$	588.8	717.02	1085 27		
	Glass phase Cr $2p_{3/2}$	577.8	1268.25	1903.27	81.08	
	Spinel Cr $2p_{1/2}$	586.5	2988.53	5520.00	61.06	
	Spinel Cr $2p_{1/2}$	576.1	5520.99	5520.99		

to different line widths and symmetries of ESR spectral resonance. In this study, we considered that  $Cr^{3+}$  existed as exchange-coupled  $Cr^{3+}$  pairs in the Cr-spinel crystals and free  $Cr^{3+}$  ions in the glass matrix. The binding energy of  $Cr^{3+}$  was different in the two different chemical environments. In this paper, pure MgCr<sub>2</sub>O<sub>4</sub> is synthesized firstly. The phase XRD test results are shown in Fig. 8a, and the XPS test results of Cr in pure MgCr<sub>2</sub>O<sub>4</sub> and A3 parent glass are shown in Figs. 8b and 8c.

It can be seen from Fig. 8a that there is only the diffraction peak of MgCr<sub>2</sub>O<sub>4</sub> in the spectrum without other impurities, indicating that the pure MgCr<sub>2</sub>O<sub>4</sub> has been synthesized. According to Figs. 8b and 8c, the binding energies of  $2p_{1/2}$  and  $2p_{3/2}$  of Cr in MgCr<sub>2</sub>O<sub>4</sub> are 586.5 and 576.1 eV. The binding energies of  $2p_{1/2}$ and  $2p_{3/2}$  of Cr in the A3 parent glass are 588.8 and 577.8 eV respectively. Since the electron binding energies of Cr in (Mg,Fe)(Cr,Al)<sub>2</sub>O<sub>4</sub> and Cr in MgCr<sub>2</sub>O<sub>4</sub> are similar, taking the XPS electron binding energy spectra of Cr in the MgCr<sub>2</sub>O<sub>4</sub> and parent glass as a reference, the XPS electron binding energy spectra of Cr in the A1-A5 nucleation glasses are fitted and divided into peaks, and the peak area is integrated. The area ratio of the fitted peak represents the percentage of Cr in spinel crystal and glass phase; the distribution behaviour of Cr between spinel crystal and glass phase is discussed. The results are shown in Fig. 9 and Table 3. It can be seen from Table 3 that with the increase of Al<sub>2</sub>O<sub>3</sub> content, the proportion of Cr distributed in Cr-spinel grains to the total Cr first gradually increases and then decreases. When the content of  $Al_2O_3$  is 11.8 wt.%, the proportion is 85.01 wt.%, reaching the maximum.

Let us analyse the cause firstly from the perspective of spinel structure. Its chemical formula is  $MeIO \cdot MeII_2O_3$ , in which MeI are divalent metal ions, usually  $Mg^{2+}$ ,  $Fe^{2+}$  and  $Mn^{2+}$ , and MeII are trivalent metal ions, usually  $Cr^{3+}$ ,  $Al^{3+}$  and  $Fe^{3+}$ . When the content of  $Cr^{3+}$  is constant, increasing  $Al^{3+}$  will increase the



Figure 10. XRD patterns of the A3 glass-ceramics crystallized for 10, 20, 30 and 60 min

precipitation of spinel. Rezvani et al. [18] also pointed out that trivalent ions can enter the spinel structure and promote the formation of spinel nuclei. It can be seen from Figs. 2, 6 and 7 that Cr-spinel nanocrystals are mainly precipitated in the nucleation stage. XRD in Fig. 10 can further prove that it is Cr-spinel rather than MgAl<sub>2</sub>O<sub>4</sub>. With the increase of Al<sub>2</sub>O<sub>3</sub> content, Al<sup>3+</sup> enters the Cr-spinel structure to form (Mg,Fe)(Cr,Al)<sub>2</sub>O<sub>4</sub> nanocrystals, which shows that the number of nanocrystals increases (Fig. 2). Secondly, with the increase of the number of nanocrystals, the amount of glass phase gradually decreases and the Cr in the glass phase gradually diffuses and migrates into the nanocrystals, so the proportion of Cr distributed in Cr-spinel to the total content of Cr increases gradually. When the Al<sub>2</sub>O<sub>3</sub> content is too high, the glass viscosity increases, the ion migration rate slows down, the number of nanocrystals decreases and the Cr content distributed in Cr-spinel grains decreases.

#### 3.4. Distribution of Cr in the crystallization stage

The A3 sample is taken as an example. Four A3 nucleation glasses were kept at 810 °C for 10, 20, 30 and 60 min. The glass-ceramics at different times was examined by XRD (Fig. 10). The phase transformation pattern of the nano-spinel in the glass after different crystallization times was investigated and the migration behaviour of the Cr element in the crystallization stage was analysed.

Figure 10 shows that when the nucleated glass was crystallized for 10 min, a small diffraction peak of  $MgCr_2O_4$  appeared in the diffraction pattern, which indicated that the nanocrystals formed in the nucleation stage were mainly MgCr<sub>2</sub>O<sub>4</sub> (including a small amount of (Mg,Fe)(Cr,Al)<sub>2</sub>O<sub>4</sub>, since its characteristic peak is similar to that of  $MgCr_2O_4$ ). After the 20-min crystallization, a diopside crystal phase was formed and  $MgCr_2O_4$  still existed. After the 30-min crystallization,  $MgCr_2O_4$  disappeared in the XRD pattern and only the diopside crystalline phase remained. After the 60-min crystallization, the type of crystal phase in the glass was consistent with that of the 30-min crystallization and the XRD peak intensities of the crystal increased, which indicated that the crystallization degree of the crystal after 60 min was higher than that after 30 min. The XRD results showed that because of the similar lattice constants of  $MgCr_2O_4$  and diopside, the diopside nucleated and grew with MgCr<sub>2</sub>O<sub>4</sub> as a heterogeneous core during the crystallization process.

To explore the transformation relationship between the Cr spinel and diopside, the glass-ceramics crystallized for 2.5 h was investigated using TEM and the result is shown in Fig. 11. Figure 11a shows the highangle annular dark field image (HAADF) of the A3 glass-ceramics powder under transmission electron microscope. When observing the image with high resolution, it is found that there are two different lattice stripes in zone 1 and zone 2, in which the crystal of zone 1 is wrapped by the crystal of zone 2.



Figure 11. HAADF image of the A3 glass-ceramics (a) and TEM mapping diagram of Cr (b)



Figure 12. XPS fitting peak-splitting spectrum of Cr in the A1-A5 glass-ceramics

After calibrating the lattice fringes of the crystals in zones 1 and 2 in Fig. 11a, we obtained that the crystal plane spacing of the crystals in zone 1 was d =0.2506 nm. The query shows that the crystal plane spacing corresponds to the (311) crystal plane of MgCr<sub>2</sub>O<sub>4</sub> (PDF#: 77-0007), indicating that the crystal in zone 1 is MgCr<sub>2</sub>O<sub>4</sub>. The crystal plane spacing of the crystal in zone 2 is d = 0.2993 nm, which corresponds to the (221) crystal plane of CaMgSi<sub>2</sub>O<sub>6</sub> (PDF#: 78-1390), indicating that the crystal in zone 2 is diopside. Distribution of Cr element in Fig. 11a is tested by TEM mapping and the results are shown in Fig. 11b. As it can be seen from Fig. 11b, the distribution of Cr in zone 1 is relatively concentrated, which is  $MgCr_2O_4$  wrapped by diopside. The distribution of Cr outside zone 1 is relatively dispersed, which can be considered as diffusion of Cr into diopside lattice. TEM analysis shows that in the crystallization stage of the glass-ceramics, with the extension of crystallization time, diopside nucleates and grows with Cr-spinel as heterogeneous core, part of Crspinel disappears, while Cr and other components diffuse into diopside crystal lattice, and part of Cr-spinel is still preserved and wrapped by diopside.

XPS was used to analyse the chemical state of Cr ion in the A1-A5 glass-ceramics and the influence of different content of Al2O3 on the occurrence and distribution of Cr between crystal phase and glass phase was investigated. It can be seen from Fig. 12 and Table 4 that when the added amount of  $Al_2O_3$  is 11.8 wt.%, the proportion of Cr in diopside is the largest, accounting for 97.94 wt.% of the total Cr, indicating that more and more Cr exists in diopside crystal phase. By comparing the content of Cr in Cr-spinel during the nucleation stage, it can be seen that during the crystallization of glass-ceramics, with the growth of diopside crystal phase, in addition to the Cr from spinel entering diopside crystal phase, Cr in glass phase also gradually diffuses and migrates to diopside crystal phase. This induces the content of Cr in diopside phase to be significantly higher than that in Cr-spinel, so as to realize the purpose of increased Cr fixation.

## 3.5. Curing effect of chromium on glass-ceramics

Toxicity-leaching experiments of the A1-A5 glassceramics were carried out for 1, 3, 5, 7 and 24 h to investigate the Cr-fixation effect of the glass-ceramics. The Cr-ion concentration in the leaching solution was detected using ICP, and the results are listed in Table 5. It shows that when the leaching time was extended, the Cr leaching concentration increased and tended to stabi-

	Samples	Peak [ev]	Area [a.u.]	Sum [a.u.]	Proportion of Cr in diopside [%]	
A1	Glass phase Cr $2p_{1/2}$	588.8	120.41	337.02	94.06	
	Glass phase Cr $2p_{3/2}$	577.8	217.51	551.92		
	Diopside Cr $2p_{1/2}$	586.5	1901.14	5252 22		
	Diopside Cr $2p_{3/2}$	576.1	3451.09	3332.23		
	Glass phase Cr $2p_{1/2}$	588.8	88.23	242 73		
A2	Glass phase Cr $2p_{3/2}$	577.8	154.50	242.75	96.21	
	Diopside Cr $2p_{1/2}$	586.5	2119.71	6161.07		
	Diopside Cr $2p_{3/2}$	576.1	4041.36	0101.07		
	Glass phase Cr $2p_{1/2}$	588.8	48.34	137.76		
A3	Glass phase Cr $2p_{3/2}$	577.8	89.42	137.70	07.04	
	Diopside Cr $2p_{1/2}$	586.5	2276.40	6544 41	27.94	
	Diopside Cr $2p_{3/2}$	576.1	4268.01	0344.41		
. 4	Glass phase Cr $2p_{1/2}$	588.8	111.04	202 57	05.47	
	Glass phase Cr $2p_{3/2}$	577.8	182.53	293.37		
A4	Diopside Cr $2p_{1/2}$	586.5	2151.44	6102.24	95.47	
	Diopside Cr $2p_{3/2}$	576.1	4040.80	0192.24		
A5	Glass phase Cr $2p_{1/2}$	588.8	91.14	224.24		
	Glass phase Cr $2p_{3/2}$	577.8	133.10	224.24	06 58	
	Diopside Cr $2p_{1/2}$	586.5	2218.27	6222 77	90.30	
	Diopside Cr $2p_{3/2}$	576.1	4105.50	0323.11		

Table 4. Proportion of the Cr distribution in the diopside/glass phase to the total Cr content in the A1-A5 glass-ceramics

Table 5. Leaching concentration of Cr in the A1-A5 glass-ceramics after different times (mg/l)

Samples	1 h	3 h	5 h	7 h	24 h
A1	0.014	0.013	0.017	0.018	0.019
A2	0.009	0.011	0.010	0.012	0.013
A3	0.003	0.004	0.003	0.004	0.004
A4	0.008	0.006	0.006	0.007	0.007
A5	0.006	0.007	0.008	0.008	0.008

lize after 24 h. When the  $Al_2O_3$  content was 11.8 wt.%, the lowest Cr leaching concentration of only 0.004 mg/l was achieved, which indicated that the glass-ceramics prepared in this study offered a good Cr-fixation ability.

## **IV.** Conclusions

In this study, glass-ceramics were prepared from stainless-steel slag. The effects of  $Al_2O_3$  on the occurrence, distribution, and migration of Cr in the nucleation and crystallization stages of the glass-ceramics were systematically studied and the Cr-fixation ability of the glass-ceramics was verified. The conclusions are enumerated as follows:

(1) Stainless-steel slag was used as the main raw material (60 wt.%) to prepare glass-ceramics. In the nucleation stage of the glass-ceramics, Cr mainly existed in Cr-spinel nanocrystals. Increased  $Al_2O_3$  content promoted the precipitation of Cr-spinel grains, and Cr in the glass phase gradually migrated to spinel grains. The highest number of Cr-spinel nanocrystals was produced with the  $Al_2O_3$  content of 11.8 wt.%.

(2) During the transition from the nucleation to the crystallization stage, Cr spinel nuclei gradually generated the diopside with prolonged crystallization time. The TEM analysis demonstrated that during the transformation from the Cr spinel to diopside, some of the

crystal structures of the Cr spinel were destroyed and the components were integrated into the diopside crystal. Some Cr spinels remained preserved and wrapped in the diopside shell.

(3) In the crystallization stage, with increasing  $Al_2O_3$  content, the number of diopside crystals first increased and then decreased, and Cr in the glass phase diffused and migrated to the diopside phase. When the content of  $Al_2O_3$  was 11.8 wt.%, the largest amount of the diopside grains with fine size was generated in the glass-ceramics and the content of Cr in the diopside phase was the highest (i.e. 97.94 wt.% of the total Cr in the sample).

(4) By adjusting the  $Al_2O_3$  content, glass-ceramics realized good Cr-fixation effect. When the  $Al_2O_3$  content was 11.8 wt.%, the Cr leaching concentration was 0.004 mg/l.

Acknowledgements: This study was supported by the National Natural Science Foundation of China (No. 52064019) and the natural science foundation of Jiangxi Province (No. 2019acbl20015).

## References

 F.Q. Gu, Y.B. Zhang, Z.J. Su, Y.K. Tu, S. Liu, T. Jiang, "Recovery of chromium from chromium-bearing slags produced in the stainless-steel smelting: A review", *J. Clean. Prod.*, **296** (2021) 126467.

- A. Zaffora, F.D. Franco, M. Santamaria, "Corrosion of stainless steel in food and pharmaceutical industry", *Curr. Opin. Electrochem.*, **29** (2021) 100760.
- K.D. Ramkumar, A. Singh, S. Raghuvanshi, A. Bajpai, T. Solanki, M. Arivarasu, N. Arivazhagan, S. Narayanan, "Metallurgical and mechanical characterization of dissimilar welds of austenitic stainless steel and super-duplex stainless steel–A comparative study", *J. Manufac. Process.*, 19 (2015) 212–232.
- U. Bulut, A. Ozverdi, M. Erdem, "Leaching behavior of pollutants in ferrochrome arc furnace dust and its stabilization/solidification using ferrous sulphate and portland cement", *J. Hazard. Mater.*, 162 (2009) 893–898.
- C.Z. Liao, Y.Y. Tang, C.S. Liu, K. Shih, F.B. Li, "Doublebarrier mechanism for chromium immobilization: A quantitative study of crystallization and leachability", *J. Hazard. Mater.*, **311** (2016) 246–253.
- S.Y. Liu, Y.X. Chen, S.L. Ouyang, H.R. Li, X. Li, B.W. Li, "Microstructural transformation of stainless steel slagbased CAMS glass ceramics prepared by SPS", *Ceram. Int.*, 47 (2021) 1284-1293.
- Z.J. Wang, I. Sohn, "Influence of the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> mass ratio and gas composition on the viscous behavior and structure of Cr-containing stainless steel slags", *Ceram. Int.*, 46 (2020) 903–912.
- S.G. Zhang, J. Yang, B. Liu, D.A. Pan, C.L. Wu, A.A. Volinsky, "One-step crystallization kinetic parameters of the glass-ceramics prepared from stainless steel slag and pickling sludge", *J. Iron. Steel Res. Int.*, 23 (2016) 220–224.
- S.L. Ouyang, Y.X. Zhang, Y.X. Chen, Z.W. Zhao, M. Wen, B.W. Li, Y. Shi, M.Z. Zhang, S.L. Liu, "Preparation of glass-ceramics using chromium-containing stainless steel slag: crystal structure and solidification of heavy metal chromium", *Sci. Rep.*, 9 (2019) 1964.
- K.Y. Chen, Y. Li, X.Y. Meng, L. Meng, Z.C. Guo, "New integrated method to recover the TiO<sub>2</sub> component and prepare glass-ceramics from molten titanium-bearing blast furnace slag", *Ceram. Int.*, 45 (2019) 24236–24243.
- M. Erol, S. Küçükbayrak, M.A. Ersoy, "Production of glass-ceramics obtained from industrial wastes by means of controlled nucleation and crystallization", *Chem. Eng. J.*, **132** (2007) 335–343.
- V.O. Soares, F.C. Serbena, G.S. Oliveira, C. Cruz, R.F. Muniz, E.D. Zanotto, "Highly translucent nanostructured glass-ceramic", *Ceram. Int.*, 47 (2021) 4707–4714.
- H.T. Gao, X.H. Liu, J.Q. Chen, J.L. Qi, Y.B. Wang, Z.R. Ai, "Preparation of glass-ceramics with low density and high strength using blast furnace slag, glass fiber and water glass", *Ceram.Int.*, 44 (2018) 6044–6053.
- M.J. Cattell, C. Patzig, S. Bissasu, A. Tsoutsos, N. Karpukhina, "Nucleation efficacy and flexural strength of novel leucite glass-ceramics", *Dent. Mater.*, **36** (2020) 592–602.
- S. Jang, S. Kang, "Influence of MgO/CaO ratio on the properties of MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass-ceramics for LED packages", *Ceram. Int.*, **38** (2012) S543–S546.
- 16. X.W. Zhao, Z.Y. Gao, X.M. Chang, Q.Y. Liu, "Effect of

 $Al_2O_3$  on structure and properties of glass-ceramics containing rare-earth tailings", *China Ceram.*, **49** (2013) 59– 62. [in Chinese].

- X.Y. Xu, X.B. Lao, "Effect of MgO/SiO<sub>2</sub> ratio and Al<sub>2</sub>O<sub>3</sub> content on crystallization behavior and properties of cordierite-based glass-ceramics", *J. Eur. Ceram. Soc.*, **41** (2021) 1593–1602.
- M. Rezvani, Y.B. Eftekhari, H.M. Solati, V.K. Marghussian, "Effect of Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> nucleants on the crystallization behaviour of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-MgO(R<sub>2</sub>O) glass-ceramics", *Ceram. Int.*, **31** (2005) 75–80.
- X.Z. Guo, X.B. Cai, J. Song, G.Y. Yang, H. Yang, "Crystallization and microstructure of CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass–ceramics containing complex nucleation agents", *J. Non-Cryst. Solids.*, **405** (2014) 63–67.
- D. Kim, H.J. Kim, S.I. Yoo, "Effects of microstructures on the mechanical properties of lithium disilicate glass-ceramics for the SiO<sub>2</sub>-Li<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O-ZnO system", *Mater. Sci. Eng. A*, **804** (2021) 140564.
- Y. Shi, B.W. Li, M. Zhao, M.X. Zhang, "Growth of diopside crystals in CMAS glass-ceramics using Cr<sub>2</sub>O<sub>3</sub> as a nucleating agent", *J. Am. Ceram. Soc.*, **101** (2018) 3968–3978.
- Z.F. Tong, Z.H. Jia, Q.P. Zeng, C.C. Xu, "Thermodynamics of the effects of slag compositions on the precipitation of chromium spinel in CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Cr<sub>2</sub>O<sub>3</sub>-FeO-TiO<sub>2</sub> slag system", *Nonferrous Met. Sci. Eng.*, **11** (2020) 1–10. [in Chinese].
- 23. C.S. Ray, D.E. Day, "Determining the nucleation rate curve for lithium disilicate glass by differential thermal analysis", *J. Am. Ceram. Soc.*, **73** (1990) 439–442.
- 24. A. Karamanov, M. Pelino, "Evaluation of the degree of crystallisation in glass-ceramics by density measurements", *J. Eur. Ceram. Soc.*, **19** (1999) 649–654.
- E. Kleebusch, C. Patzigb, T. Höcheb, C. Rüssel, "Phase formation during crystallization of a Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass with ZrO<sub>2</sub> as nucleating agent- An X-ray diffraction and (S)TEM-study", *Ceram. Int.*, 43 (2017) 9769–9777.
- Z.Q. Zhou, F. He, M.J. Shi, J.L. Xie, P. Wan, D.H. Cao, B. Zhang, "Influences of Al<sub>2</sub>O<sub>3</sub> content on crystallization and physical properties of LAS glass-ceramics prepared from spodumene", *J. Non-Cryst. Solids*, **576** (2022) 121256.
- V.K. Marghussian, U. Balazadegan, Y.B. Eftekhari, "The effect of BaO and Al<sub>2</sub>O<sub>3</sub> addition on the crystallization behaviour of cordierite glass ceramics in the presence of V<sub>2</sub>O<sub>5</sub> nucleant", *J. Eur. Ceram. Soc.*, **29** (2009) 39–46.
- Y.X. Zhang, S.L. Liu, S.L. Ouyang, X.F. Zhang, Z.W. Zhao, X.L. Jia, Y.S. Du, L.B. Deng, B.W. Li, "Transformation of unstable heavy metals in solid waste into stable state by the preparation of glass-ceramics", *Mater. Chem. Phys.*, 252 (2020) 123061.
- L. Barbieri, C. Leonelli, T. Manfredini, G.C. Pellacanl, C. Siligardi, "Solubility, reactivity and nucleation effect of Cr<sub>2</sub>O<sub>3</sub> in the CaO-MgO-AI<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glassy system", *J. Mater. Sci.*, **29** (1994) 6273–6280.
- S. Dïngkun, L.A. Orlova, "Mechanism of the catalytic effect of Cr<sub>2</sub>O<sub>3</sub> on the crystallization of glasses", *J. Non-Cryst. Solids*, **112** (1989) 207–210.