Effect of Cr$_2$O$_3$ on Crystallization of Diopside Glass–Ceramics

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Abstract: CaO–MgO–Al$_2$O$_3$–SiO$_2$–Cr$_2$O$_3$ diopside glass–cereamics were prepared from blast furnace slag, low-carbon ferrochromium alloy slag, and quartz sand by the melting method. The prepared glass–ceramics were characterized by differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS). The effect of Cr$_2$O$_3$, a nucleating agent, in the crystallization process of diopside glass–cereamics was studied. The results show that chromium is present in glass–ceramics as Cr$^{3+}$ and Cr$^{6+}$, and Cr$^{3+}$ accounts for more than 80% of the chromium contents. When the mass percentage of Cr$_2$O$_3$ in glass–ceramics is less than 1.60%, a small amount of diopside phase is precipitated during heat treatment, and Cr$^{3+}$ is dispersed in the diopside phase. When the mass percentage of Cr$_2$O$_3$ reaches or exceeds 1.60%, Cr$^{3+}$ preferentially forms the magnesia chrome spinel phase, which further induces the in situ growth of diopside. The leaching concentration of chromium meets the Chinese national standard, indicating that diopside glass–cereamics can effectively solidify the heavy metal chromium, and this fact makes the application of glass–cereamics feasible.

Keywords: Cr$_2$O$_3$; diopside; magnesia chrome spinel; glass–cereamics; in situ growth

1. Introduction

Glass–cereamics of the pyroxene class have the advantages of high hardness and chemical corrosion resistance, and are usually used as building decoration materials [1,2]. Similar to other glass–cereamics, the crystals in glass–cereamics of the pyroxene class are formed by the controllable crystallization of glass [3]. When the glass–cereamics of the pyroxene class of CaO–MgO–Al$_2$O$_3$–SiO$_2$ system were prepared by melting method, it was necessary to add nucleating agent. The proper amount of nucleating agent can promote the overall crystallization of the glass–cereamics, improve the crystallization efficiency, and shorten the crystallization time, which can ensure that the ideal microstructure and excellent physical and chemical properties of the glass–cereamics are obtained [4]. The research results of Zhao and others show that Cr$_2$O$_3$ is an effective nucleating agent for the preparation of glass–cereamics of the pyroxene class [5]. This provides an innovative way to deal with toxic chromium-containing solid wastes, so it is necessary to study the effect of Cr$_2$O$_3$ on glass–cereamics crystallization. The rapid development of China’s industry has produced a large amount of industrial solid waste, such as blast furnace slag (BFS) and low-carbon ferrochromium alloy slag (LFAS). These metallurgical slags have the potential for reuse in glass–cereamics manufacturing [6]. The main components of BFS and LFAS are CaO, MgO, Al$_2$O$_3$ and SiO$_2$ (the sum of the mass percentages of these four chemical components is more than 90%), glass–cereamics of the pyroxene class belongs to the CaO–MgO–Al$_2$O$_3$–SiO$_2$ system, and LFAS contains the nucleating agent composition Cr$_2$O$_3$, so the production of glass–cereamics of the pyroxene class with excellent properties is one of the best ways to comprehensively utilize these industrial solid wastes.

According to a large amount of research in the literature, most of the current studies use analytical pure reagents to explore the effect of Cr$_2$O$_3$ on the crystallization of glass–cereamics. For example, Shi et al. designed the raw material ratio according to the actual composition of most iron ore tailings, used analytical pure reagents to simulate the actual
slag composition, and explored the actual grain growth mechanism in glass-ceramics containing Cr$_2$O$_3$ [7]. Zhang et al. used analytical reagents to simulate chromium-containing waste to prepare diopside glass-ceramics, and explored the crystallization of chromium-doped diopside [8]. However, the chemical composition of actual slag is more complex, and using slag to prepare glass-ceramics has more practical significance. Therefore, in this study, BFS and LFAS were directly used as the main raw materials to prepare glass-ceramics. The solid metallurgical wastes account for 75–79% of the raw materials of glass-ceramics, and the components of CaO, MgO, Al$_2$O$_3$, and SiO$_2$ in the two metallurgical wastes are fully utilized. In this study, the effect of Cr$_2$O$_3$ on the formation of the diopside phase was explored, and the presence of Cr$_2$O$_3$ in diopside glass-ceramics was discussed from the perspective of ions. In addition, due to the crystallization and solidification of the diopside phase, the concentration of chromium leaching is greatly reduced, which has important theoretical significance and practical value for the treatment of chromium-containing solid wastes from the perspective of environmental protection and the development of preparation technology of diopside glass-ceramics by making full use of metallurgical solid wastes.

2. Experimental Materials and Schemes

2.1. Samples Preparation

BFS and LFAS were used as the main raw materials, and a certain amount of quartz sand (QS) was added as a supplementary silicon source [9]. The BFS used was from Baotou Iron and Steel Works, and the LFAS was from a ferrochromium alloy plant in Inner Mongolia. The chemical composition of each raw material determined by X-ray fluorescence (XRF) is shown in Table 1.

Table 1. Main chemical components of raw materials (mass fraction, %).

| Component | BFS | LFAS | QS  |
|-----------|-----|------|-----|
| CaO       | 34.43 | 48.64 | 0.029 |
| SiO$_2$   | 34.21 | 29.46 | 98.200 |
| Al$_2$O$_3$ | 13.84 | 7.36  | 0.120 |
| MgO       | 9.15  | 7.23  | 0.005 |
| Cr$_2$O$_3$ | -     | 3.48  | -   |
| CaF$_2$   | 0.78  | -     | -   |
| CaS       | 3.2   | -     | -   |
| MnO       | 0.52  | -     | -   |
| Fe$_2$O$_3$ | -     | 0.58  | 0.037 |
| FeO       | 0.69  | 0.5   | -   |
| K$_2$O    | 0.48  | -     | -   |
| Na$_2$O   | 0.54  | -     | 0.018 |
| TiO$_2$   | 0.89  | -     | -   |
| Other     | 1.27  | 2.75  | 1.591 |

Due to the excellent physical and chemical properties of glass-ceramics with pyroxene as the main crystalline phase, the phase diagram of the CaO–Al$_2$O$_3$–SiO$_2$ ternary system with 5% MgO mass fraction (see Figure 1) was made using Factsage software. The composition content of the base glass was selected in the pyroxene area of the ternary phase diagram, and a total of four base glass composition points were selected. The Cr$_2$O$_3$ in each raw material was carried by LFAS, and the mass fraction of Cr$_2$O$_3$ was 1.11%, 1.36%, 1.60%, and 1.83% by adjusting the ratio. The mass proportion and main components of the four groups of base glass raw materials are shown in Table 2 (other components in the raw materials account for a relatively small proportion and can be neglected).
Figure 1. CaO–Al₂O₃–SiO₂ ternary phase diagram with 5% MgO.

| Numbering | Composition LFAS:BFS:QS | CaO       | SiO₂      | Al₂O₃    | MgO   | Cr₂O₃   | Other |
|-----------|-------------------------|-----------|-----------|----------|-------|---------|-------|
| 1         | 40:60:26.23             | 31.90     | 46.18     | 8.94     | 6.67  | 1.11    | 5.20  |
| 2         | 50:50:28.78             | 32.38     | 46.85     | 8.26     | 6.39  | 1.36    | 4.76  |
| 3         | 60:40:31.33             | 32.85     | 47.51     | 7.61     | 6.12  | 1.60    | 4.31  |
| 4         | 70:30:33.88             | 33.30     | 48.14     | 6.98     | 5.86  | 1.83    | 3.89  |

Table 2. Mass proportion and main composition of base glass raw materials (mass fraction, %).

The raw materials were crushed, weighed, and mixed, then put into corundum crucible, and placed in MoSi₂ high-temperature atmosphere furnace to raise the temperature to 1500 °C and left in isothermal conditions for 3 h. In order to avoid the glass cracking due to rapid cooling, and to eliminate the stress inside the glass, the majority of the molten glass was poured into a 600 °C stainless steel mold and annealed at 600 °C for 2 h to obtain the base glass. A part of it was taken out and ground for differential thermal analysis (DTA).

2.2. Techniques of Characterization

The crystal phase types in glass–ceramics were identified by an UltimaIV X X-ray diffractometer (the scanning angle range was 10°–90°, and the scanning rate was 0.02°/min). The French Sellam Labsys Evo-type differential scanning calorimetry analyzer was used for differential thermal analysis (DTA), the base glass sample was crushed and ground through a 200 mesh sieve, and an alumina crucible was used as a reference substance, the heating rate was 10 K/min, and the protective atmosphere was nitrogen. The samples to be observed were etched in 5% HF solution for 50 s. After drying and spraying with gold, the micro morphology of the samples was observed with Hitachi SU5000 field emission scanning electron microscope. The microscope was equipped with an X-ray energy-dispersive spectrometer (EDS), which was used to semi-quantitatively analyze the chemical composition of the crystal phase. XPS patterns were obtained by a Thermo ESCALAB 250XI X-ray photoelectron spectrometer, involving C1s and Cr2p orbitals. The XPS energy calibration was based on the surface-contaminated carbon C1s, which was corrected to 284.8 eV [10,11]. Avantage 5.938 software was used for fitting and peak splitting analysis of the XPS fine-scanning spectral line. The concentration of the heavy metal chromium in glass–ceramics was determined by an Icap6000 inductively coupled plasma emission spectrometer. The specific operation was as follows. The buffer solution of acetic acid (pH 4.93) was mixed with the glass–ceramics powder (particle size less than 75 μm) at the liquid–solid mass ratio of 20:1 (L/kg), and the solution was oscillated at 23 ± 2 °C for 18 ± 2 h. Finally, the leaching solution was filtered and tested.

3. Results and Discussion

3.1. Determination of Heat Treatment System for Glass–Ceramics

DTA results (see Figure 2) show that the starting temperature of glass transition, Tg, is between 778 °C and 780 °C. According to the study of Beall et al., crystal nucleation
generally occurs at temperature range of 50–100 °C higher than the Tg [12]. Therefore, the nucleation of the base glass in each group was carried out at 828 °C, 830 °C, 830 °C, and 830 °C, and maintained for 90 min. Normally, exothermic peak temperature, Tp, is selected as the crystallization temperature, but there are two obvious exothermic peaks on the curve in Figure 2. In order to obtain the optimal crystallization temperature, the #3 base glass samples were randomly selected for two groups of heat treatment experiments. The first group (denoted as A) was nucleation temperature at 830 °C and the crystallization temperature at 960 °C, and the second group (denoted as B) was nucleation temperature at 830 °C and crystallization temperature at 1024 °C. The holding time of both groups was 90 min. XRD test was conducted on the samples after heat treatment (see Figure 3). Compared to the diopside facies characteristic peaks shown in the PDF card (PDF#41-1370) and the phonotephrite facies characteristic peaks shown in the PDF card (PDF#88-0854), the diopside phase is precipitated from glass–ceramics in group A, while the phonotephrite phase is precipitated from glass–ceramics in group B. According to the physical and chemical performance requirements of the building glass–ceramics, such as wear resistance and corrosion resistance, the main crystal of glass–ceramics is corresponding to pyroxene phase, and diopside phase belongs to a type of pyroxene phase. Therefore, group A glass–ceramics meet the requirements, while group B glass–ceramics do not meet the requirements. Therefore, the highest temperature of the first exothermic peak on the DTA curve of each group was selected as the crystallization temperature, and the heat treatment system of #1–#4 glass–ceramics was obtained as follows: 954 °C, 963 °C, 960 °C, and 957 °C, were respectively, used as the crystallization temperatures for 90 min, and 828 °C, 830 °C, 830 °C, and 830 °C were, respectively, used as the nucleation temperatures for 90 min.

Figure 2. DTA curve of base glass.

Figure 3. XRD results of A and B experiments.
3.2. Type and Morphology Analysis of Crystallization Minerals

It is necessary to determine the amorphous properties of the base glass before heat treatment, and the #3 base glass sample is randomly selected, and the results after XRD detection are shown in Figure 4. There is no obvious crystallization peak in the figure, indicating that the base glass is amorphous. After heat treatment of the base glass, dark green glass–ceramics were obtained, as shown in Figure 5. XRD analysis of glass–ceramics samples is shown in Figure 6. Compared with the standard PDF card of diopside (PDF#41-1370), it can be determined that the crystal phase of each group of glass–ceramics is diopside, which belongs to pyroxene minerals, consistent with the designed crystal type, and should have good mechanical and chemical properties. Combined with the appearance of color, glass–ceramics samples can be used as wall tiles, floor tiles, and other building decoration materials.

![Figure 4. XRD results for base glass #3.](image)

![Figure 5. Samples of glass–ceramics.](image)

![Figure 6. XRD pattern of the glass–ceramics samples.](image)

In this study, glass–ceramics samples #1–#4 were observed by scanning electron microscopy (SEM, the image mode is SEI). See Figure 7a–d. Figure 7 shows that the crystal
morphology and distribution change with increasing Cr$_2$O$_3$ mass percentage. When the mass fraction of Cr$_2$O$_3$ is 1.11% or 1.36% (see Figure 7a,b), irregular bulk crystals are precipitated in the glass phase, and the distribution is sparse. When the mass fraction of Cr$_2$O$_3$ is 1.60% or 1.83%, in addition to the precipitation of irregular bulk crystals, long strip crystals with significantly different shapes appear in the central area of the bulk crystals, and the closely connected bulk crystals around the long strip crystals in Figure 7c,d are clearly denser, larger, or even connected into pieces.

Figure 7. SEM photos of glass–ceramics samples #1~#4 (The mass fraction of Cr$_2$O$_3$ in (a–d) is 1.11%, 1.36%, 1.60%, and 1.83%).

EDS analysis was carried out on three points. A, B, and C in the bulk crystal region and D in the long strip crystal region are shown in Figure 7, and EDS spectra are shown in Figure 8.

Figure 8. EDS spectra of points A, B, C, and D.
The results in Figure 8 show that the crystal phases precipitated at three points, A, B, and C in the bulk crystal region are of the same type, containing elements such as O, Mg, Al, Si, Ca, and Cr. According to the above XRD results and element composition, points, A, B, and C seem to be the diopside phase \( \text{CaMg(SiO}_3\text{)}_2 \) [13]. In order to further analyze the crystal phase types, the elemental composition and atomic fraction determination results at two points, C and D, with different EDS spectra are listed in Table 3.

Table 3. Element composition and atomic fraction of points C and D.

| Element | O      | Mg     | Al     | Si     | Ca     | Cr     | Fe     |
|---------|--------|--------|--------|--------|--------|--------|--------|
| Atomic fraction at point C/% | 54.27  | 6.66   | 8.16   | 16.24  | 14.36  | 0.32   | -      |
| Atomic fraction at point D/% | 48.96  | 13.97  | 8.22   | -      | 2.79   | 25.65  | 0.41   |

Table 3 shows that, except for the Ca, Mg, Si, and O elements that make up diopside, point C also has a high Al content. This is the result of partial substitution of \( \text{Mg}^{2+} \) and \( \text{Si}^{4+} \) by \( \text{Al}^{3+} \) to form a solid solution, which makes the chemical formula of crystal at C \( \text{Ca}_{0.14}(\text{Mg}_{0.07}\text{Al}_{0.04})(\text{Si}_{0.16}\text{Al}_{0.04})\text{O}_{0.54} \) [14,15]. The atomic ratio in this chemical formula is equivalent to \( \text{Ca}:\text{Mg} \) (some \( \text{Mg} \) was replaced by \( \text{Al} \)):\( \text{Si} \) (some \( \text{Si} \) was replaced by \( \text{Al} \))\( :\)O\( = 1.4:1.1:2.0:5.4 \), which is very close to the atomic ratio of the diopside chemical formula \( \text{Ca}_{0.14}\text{Mg}_{0.07}\text{Al}_{0.04}\text{Si}_{0.16}\text{Al}_{0.04}\text{O}_{0.54} \). Therefore, it can be judged that the region at point C is the diopside phase. Since the EDS spectra of, A, B, and C in the bulk crystal region are the same, the bulk crystal region is the diopside phase.

In addition, a study has shown that \( \text{Cr}_2\text{O}_3 \) and \( \text{MgO} \) in glass easily generate \( \text{MgCr}_2\text{O}_4 \) [16]. Table 3 shows that point D in the long strip crystal region contains O, Mg, Al, Ca, Cr, and Fe elements. Here, \( \text{Fe}^{2+} \) partially replaces \( \text{Mg}^{2+} \), and \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) partially replace \( \text{Cr}^{3+} \) to form a solid solution, which makes the chemical formula of crystal at D \( \text{Mg}_{0.14}\text{Fe}_{0.002}(\text{Al}_{0.08}\text{Fe}_{0.002}\text{Cr}_{0.26})\text{O}_{0.49} \) [17]. The atomic ratio in this chemical formula is equivalent to \( \text{Mg} \) (some \( \text{Mg} \) was replaced by \( \text{Fe} \)):\( \text{Cr} \) (some \( \text{Cr} \) was replaced by \( \text{Al} \) and \( \text{Fe} \))\( :\)O\( = 1.42:3.42:4.90 \), which is more close to the atomic ratio \( \text{Mg}:\text{Cr}:\text{O} = 1:2:4 \) in the chemical formula of magnesia chrome spinel. Therefore, it can be judged that the long strip crystal is magnesia chrome spinel. Due to its low content, the characteristic peak of the magnesia chrome spinel phase is not found in the XRD curve in Figure 5. Rezvani et al. demonstrate that the similarity between the lattice parameters of the main crystal phase and the nucleating agent has a good catalytic effect on the crystallization [18]. Shen et al. demonstrate that the lattice parameters of magnesia chrome spinel and diopside are similar in one dimension [19]. Therefore, the diopside phase nucleates and crystallizes first on the plane of spinel, which is consistent with the findings of this study.

3.3. Dissolution Behavior of \( \text{Cr}_2\text{O}_3 \) in the Diopside Phase

SEM result (see Figure 7c) shows that the diopside phase and magnesia chrome spinel phase coexist when 1.60% \( \text{Cr}_2\text{O}_3 \) is added. It can be seen from the EDS data in Table 3 that the diopside phase also contains a certain amount of chromium, which may be related to the fact that a certain amount of \( \text{Cr}_2\text{O}_3 \) in the glass phase enters the diopside phase during the crystallization process. According to the research of Zhang et al., the concentration of \( \text{Cr}_2\text{O}_3 \) in diopside phase is determined by the characteristic behavior of \( \text{Cr}^{3+} \) in the crystal field [8]. Therefore, it is necessary to study the valence state of chromium in glass–ceramics.

XPS spectra of Cr elements were measured in #3 glass–ceramics with sufficient crystallization. The peak splitting results of the XPS fine spectrum of Cr2p are shown in Figure 9. Due to the spin-orbit coupling effect of electrons, the orbital energy levels are “tiny” split, and Cr2p is split into two peaks, Cr2p1/2 and Cr2p3/2 [20,21]. For the p orbital, the intensity ratio of its splitting peak has a fixed proportion, which is \( \text{Cr}2\text{p}_{1/2}:\text{Cr}2\text{p}_{3/2} = 1:2 \), as shown in Figure 9 [22].
For the Cr$_2$p$_{3/2}$, the binding energies of the fitting peaks are 575.98 eV and 578.56 eV, respectively. According to the XPS database, the 2p$_{3/2}$ orbital binding energy of Cr$^{3+}$ is generally not greater than 576 eV, and the 2p$_{3/2}$ orbital binding energy of Cr$^{6+}$ is generally not greater than 579 eV. Therefore, the peaks at 575.98 eV and 578.56 eV represent Cr$^{5+}$ and Cr$^{6+}$, respectively. With increasing valence state, the binding energy increases, and the experimental results are highly consistent with the theoretical values. After peak splitting, the area enclosed by the fitting peak and baseline of Cr$^{3+}$ and Cr$^{6+}$ at Cr$_2$p$_{3/2}$ was calculated, and the proportion of each area was calculated to estimate the proportion of the amount of Cr$^{3+}$ and Cr$^{6+}$ in the glass–ceramics [23]. The results show that in the Cr$_2$p$_{3/2}$ peak, the peak area allocated to Cr$^{3+}$ after normalization is 87.03%, and that allocated to Cr$^{6+}$ is 12.97%. The results of the peak distribution show that Cr$^{3+}$ and Cr$^{6+}$ coexist, but the large difference in peak area confirms that Cr$^{3+}$ is the main form of chromium ions in glass–ceramics.

After verifying that there is more than 80% Cr$^{3+}$ in the glass–ceramics, the dissolution of Cr$_2$O$_3$ can be explained in the following aspects. Cr is a transition group element, and the characteristic behavior of Cr$^{3+}$ in the crystal field can be explained by crystal field theory [24]. When Cr$^{3+}$ is in the electrostatic field formed by the charged ligand, Cr$^{3+}$ will strongly occupy the octahedral position of the crystal field, making Cr$_2$O$_3$ exist in diopside [25].

EDS spectra of A and B in Figure 8 show that chromium is also found in the diopside region of glass–ceramics with mass fraction of Cr$_2$O$_3$ of 1.11% and 1.36%, while no single chromium enrichment phase is found in SEM photos (Figure 7a,b), indicating that the amount of Cr$_2$O$_3$ entering diopside phase during crystallization has not reached the maximum limit at this concentration. In addition to a certain amount of chromium dispersing in the diopside phase (see Table 3), magnesium–chromium spinel phase enriched in chromium also appears in the sample supplemented with 1.60% Cr$_2$O$_3$, which significantly indicates that the maximum concentration limit of Cr$_2$O$_3$ in diopside is exceeded at this time. As Cr$_2$O$_3$ is only the most effective nucleating agent component brought in by slag raw materials, in addition, slag also brings a small amount of common nucleating agent components, such as CaF$_2$, Fe$_2$O$_3$, FeO, TiO$_2$, etc. Under the combined action of these composite nucleating agents, diopside main crystal phase is precipitated. As the effect of composite nucleating agents, mainly Cr$_2$O$_3$, on promoting crystallization is more significant than that of single nucleating agent, Cr$_2$O$_3$, when the mass fraction of Cr$_2$O$_3$ is 1.60%, it reaches the upper limit of solubility in the diopside phase.

### 3.4. Precipitation of Magnesia Chrome Spinel

Figure 10 presents the backscattered electron (BSE) image of glass–ceramics sample #3, which shows that the wrapped phase of magnesia chrome spinel is diopside, and a
large amount of chromium is enriched in magnesia chrome spinel phase (see Figure 10a). Amplifying the Figure 10a box area produces Figure 10b, which shows that a small amount of chromium is dispersed (dissolved) in diopside phase (see the circle area of Figure 10b), which is consistent with the above EDS results. For CaO–MgO–Al₂O₃–SiO₂–Cr₂O₃ system glass–ceramics, during crystallization, when the mass fraction of Cr₂O₃ in the glass–ceramics is lower than 1.60%, a small amount of diopside phase is precipitated during heat treatment. At this point, Cr³⁺ disperses in the diopside phase. When the mass fraction of Cr₂O₃ is higher than 1.60%, the interaction between Cr³⁺, Mg²⁺, and O²⁻ in the glass matrix gives priority to the formation of MgCr₂O₄ magnesia chrome spinel phase, and these magnesia chrome spinel phases can further induce the in situ growth of the diopside phase.

Figure 10. SEM image of the cross-section of glass–ceramics #3 and their X-ray mapping ((a) is Cr element, (b) is an enlarged view of the part of (a)).

Figure 11 schematically shows the nucleation and growth process of diopside with magnesia chrome spinel phase as a base. In the nucleation stage, the magnesia chrome spinel phase is only a few nanometers in size. At this time, its nucleation density is large, which can not only promote crystallization, but also serve as the center of diopside heterogeneous nucleation (see Figure 11a). Diopside grains in the crystallization stage grow continuously and grow around magnesia chrome spinel (see Figure 11b), while the increase in Cr₂O₃ concentration accelerates this process, making diopside grains wrapped around magnesia chrome spinel grow significantly with increasing Cr₂O₃ content (see Figure 7).

Figure 11. Schematic diagram of the diopside phase and magnesia chrome spinel phase ((a) is the magnesia chrome spinel phase and diopside phase in the nucleation stage, (b) is the magnesia chrome spinel phase and diopside phase in the crystallization stage).

XPS results show that Cr³⁺ and Cr⁶⁺ coexist in glass–ceramics. About 87% of chromium ions exist in the form of Cr³⁺, and 13% of chromium ions exist in the form of Cr⁶⁺, but Cr⁶⁺ is harmful to human health. Therefore, it was necessary to test the chromium leachability of #3 and #4 glass–ceramics with high content of Cr₂O₃, and the chromium leaching concentration was 1.22 mg/L and 2.39 mg/L, respectively, which were lower than the...
10mg/L required by the Chinese national standard GB5085.3-2007 [26]. The results show that the chromium leaching concentration meets the requirements of building decoration materials, which makes the application of glass–ceramics feasible. From the microscopic point of view, during the entire heat treatment stage of glass–ceramics, the formation of magnesia chrome spinel phase can solidify most chromium elements, and a large number of diopside phases can grow around magnesia chrome spinel and form a secondary wrap for chromium elements. Therefore, using low-carbon ferrochrome alloy slag and furnace slag as raw materials to prepare glass–ceramics can solidify the chromium element and realize the harmless treatment of heavy metal chromium in low-carbon ferrochrome alloy slag.

4. Conclusions

Glass–ceramics with Cr$_2$O$_3$ mass fraction of 1.11%, 1.36%, 1.60%, and 1.83% were prepared by BFS and LFAS, respectively. The main crystal phase is diopside. When the mass fraction of Cr$_2$O$_3$ increases to 1.60%, the magnesia chrome spinel phase can be seen in the SEM photos, and the diopside phase wraps around the magnesia chrome spinel phase. When the mass fraction of Cr$_2$O$_3$ continues to increase to 1.83%, the diopside grain grows considerably. XPS results of glass–ceramics show that chromium ions exist in glass–ceramics in the form of Cr$^{3+}$ and Cr$^{6+}$. In the Cr2p$_{3/2}$ peak, the peak area allocated to Cr$^{3+}$ is 87.03%, and the peak area allocated to Cr$^{6+}$ is 12.97%, that is, Cr$^{3+}$ is the main form of chromium ions in microcrystalline glass. During the crystallization process, when the mass percentage of nucleating agent Cr$_2$O$_3$ in glass–ceramics is less than 1.60%, Cr$^{3+}$ is dispersed in the diopside phase. When Cr$_2$O$_3$ reaches or exceeds 1.60%, chromium is enriched in the magnesia chrome spinel phase, and magnesia chrome spinel further induces the in situ growth of diopside. From the microscopic point of view, the formation of the magnesia chrome spinel phase and the secondary wrapping of the diopside phase can effectively solidify most chromium elements. From the macroscopic point of view, the leaching of chromium in glass–ceramics meets the Chinese national standards. Therefore, the preparation of glass–ceramics from LFAS and BFS can effectively solidify heavy metal chromium elements.

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References

1. Rathore, M.; Dalvi, A. Electrical transport in Li$_2$SO$_4$–Li$_2$O–P$_2$O$_5$ ionic glasses and glass–ceramic composites: A comparative study. Solid State Ion. 2013, 239, 50–55. [CrossRef]
2. Gao, H.; Liu, X.; Chen, J.; Qi, J.; Wang, Y.; Ai, Z. Preparation of glass-ceramics with low density and high strength using blast furnace slag, glass fiber and water glass. Ceram. Int. 2018, 44, 6044–6053. [CrossRef]
3. Mastelaro, V.R.; Bayer, P.S.; Zanotto, E.D. Crystallization mechanism and kinetics of a Fe-diopside (25CaO·25MgO·50SiO$_2$) glass–ceramic. J. Mater. Sci. 2019, 54, 9313–9320. [CrossRef]
4. Liu, H.; Wang, Y.; Wang, T.; Yang, R.; Liu, S. Enhanced surface crystallization of glass by adding traditional oxide nucleating agents. Ceram. Int. 2014, 40, 453–457. [CrossRef]
5. Zhao, W.; Huang, X.; Yan, B.; Hu, S.; Guo, H.; Chen, D. Recycling of Blast Furnace Slag and Fluorite Tailings into Diopside-Based Glass-Ceramics with Various Nucleating Agents’ Addition. Sustainability 2021, 13, 11144. [CrossRef]
6. Yekta, B.E.; Alizadeh, P. The effect of CaF$_2$ and Cr$_2$O$_3$ on the crystallisation and mechanical properties of SiO$_2$–CaO–Fe$_2$O$_3$–(Al$_2$O$_3$) glasses. Glass Technol. 2005, 46, 347–350. [CrossRef]

7. Shi, Y.; Li, B.; Zhao, M.; Zhang, M. Growth of diopside crystals in CMAS-glass-ceramics using Cr$_2$O$_3$ as a nucleating agent. J. Am. Ceram. Soc. 2018, 101, 3968–3978. [CrossRef]

8. Zhang, S.; Zhang, Y.; Wu, T. Effect of Cr$_2$O$_3$ on the crystallization behavior of synthetic diopside and characterization of Cr-doped diopside glass ceramics. Ceram. Int. 2018, 44, 10119–10129. [CrossRef]

9. Li, Z.; Luo, Z.; Li, X.; Liu, T.; Guan, L.; Wu, T.; Lu, A. Preparation and characterization of glass-ceramic foams with waste quartz sand and coal gangue in different proportions. J. Porous Mater. 2015, 23, 231–238. [CrossRef]

10. Shah, D.; Patel, D.I.; Roychowdhury, T.; Rayner, G.B.; O'Toole, N.; Baer, D.R.; Linford, M.R. Tutorial on interpreting X-ray photoelectron spectroscopy survey spectra: Questions and answers on spectra from the atomic layer deposition of Al$_2$O$_3$ on silicon. J. Vac. Sci. Technol. B 2018, 36, 062902. [CrossRef]

11. Stevie, F.A.; Donley, C.L. Introduction to X-ray photoelectron spectroscopy. J. Vac. Sci. Technol. A Vac. Surf. Film. 2020, 38, 063204. [CrossRef]

12. Beall, G.H.; Pinckney, L.R. Nanophase Glass-Ceramics. J. Am. Ceram. Soc. 2004, 82, 5–16. [CrossRef]

13. Ito, M.; Morioka, M. Growth of diopside (CaMgSi$_2$O$_6$) single crystal by the Czochralski technique. Geochim. J. 2006, 40, 625–629. [CrossRef]

14. Liu, P.; Kai, W.; Zhu, C.; Tang, Y.; Zhao, W.; Cai, Y.; Cai, J.; Ji, J. Hydrothermal synthesis of chloride from saponite: Mechanisms of smectite-chlorite conversion and influence of Mg$^{2+}$ and Al$^{3+}$ supplies. Appl. Clay Sci. 2019, 184, 105357. [CrossRef]

15. Chen, H.; Geng, J.; Zhang, Z.; Jiang, R.; Zhai, J.; Zhang, J. The Structure and Properties of Sepiolite with Partial Lattice Ions Substituted by Aluminum Ions. Front. Chem. 2021, 9, 637. [CrossRef]

16. Wang, M.C.; Hsu, C.C.; Hon, M.H. The reaction between the magnesia–chrome brick and the molten slag of MgO–Al$_2$O$_3$–SiO$_2$–CaO–Fe$_2$O$_3$ and the resulting microstructure. Ceram. Int. 2009, 35, 1501–1508. [CrossRef]

17. Lenaz, D.; Lughi, V. Raman study of MgCr$_2$O$_4$–Fe$^{2+}$Cr$_2$O$_4$ and MgCr$_2$O$_4$–MgFe$_2$O$_4$ synthetic series: The effects of Fe$^{2+}$ and Fe$^{3+}$ on Raman shifts. Phys. Chem. Miner. 2013, 40, 491–498. [CrossRef]

18. Rezvani, M.; Eftekhar-Yekta, B.; Solati-Hashjin, M.; Marghussian, V. Effect of Cr$_2$O$_3$, Fe$_2$O$_3$ and TiO$_2$ nucleants on the crystallization behaviour of SiO$_2$–Al$_2$O$_3$–CaO–MgO(R$_2$O) glass-ceramics. Ceram. Int. 2005, 31, 75–80. [CrossRef]

19. Dengkun, S.; Orlolova, L. Mechanism of the catalytic effect of Cr$_2$O$_3$ on the crystallization of glasses. J. Non-Cryst. Solids 1989, 112, 207–210. [CrossRef]

20. Mogulkoc, A. Effects of electron–acoustic phonon interaction in the presence of spin–orbit couplings in graphene. Phys. B Condens. Matter 2015, 473, 20–25. [CrossRef]

21. Nath, M.; Song, S.; Liu, H.; Li, Y. CaAl$_2$Cr$_2$O$_7$: Formation, synthesis, and characterization of a new Cr(III) compound under air atmosphere in the Al$_2$O$_3$–CaO–Cr$_2$O$_3$ system. Ceram. Int. 2019, 45, 16476–16481. [CrossRef]

22. Kochur, A.; Kozakov, A.; Mikheykin, A.; Torgashev, V.; Bush, A.; Nikolskii, A. Chemical bonding and valence state of 3d-metal ions in Ni$_{1-x}$Co$_x$Cr$_2$O$_4$ spinels from X-ray diffraction and X-ray photoelectron spectroscopy data. J. Electron Spectrosc. Relat. Phenom. 2014, 195, 208–219. [CrossRef]

23. Shi, Y.; Han, X.X.; Li, B.W.; Chen, Y.X.; Zhang, M.X. Modification of glass network and crystallization of CaO–Al$_2$O$_3$–MgO–SiO$_2$ based glass ceramics with addition of iron oxide. Ceram. Int. 2020, 46, 9207–9217. [CrossRef]

24. Feng, W.L.; Yang, W.; Zheng, W.C. Studies of the local compressibility of Cr$^{3+}$-centered octahedron in LiSc (WO$_4$)$_2$ crystal from the pressure dependence of the optical spectra. Radiat. Eff. Defects Solids 2011, 166, 160–163. [CrossRef]

25. Alyabyeva, L.; Burkov, V.I.; Kotov, V.A. Luminescence of disordered crystals with langasite structure doped with chromium ions. J. Commun. Technol. Electron. 2017, 62, 175–177. [CrossRef]

26. Song, Z.; Zeng, J.; Wang, C.; Zhang, J.; Zhou, J.; Pan, Y.; Xu, Y.; Liu, Q.; Qian, G. Application and mechanism of an ore-washing sludge in the remediation of chromium (III) and copper (II)-contaminated soils. J. Mater. Cycles Waste Manag. 2020, 22, 897–906. [CrossRef]