Microstructural control of CaO–Al₂O₃–SiO₂ glass-ceramics by the amounts of tungsten oxide and carbon added as nucleation agent sources

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Microstructural control of CaO–Al₂O₃–SiO₂ (CAS) glass-ceramics (GCs) bearing metastable CaAl₂Si₂O₈, a layered crystal, from a parent glass having a single composition was achieved by increasing the amounts of WO₃ and carbon as sources of metallic W particle nucleation agents. The average crystal size increased from 9.3 to 49 µm when the amount of WO₃ and carbon were increased fivefold in the preparation of CAS GCs. To investigate the effect of WO₃ and carbon separately, glass cullet containing WO₃ was mixed with glass batches containing carbon and then melted to form glass specimens with different amounts of WO₃ and carbon. Upon crystallization of these glass specimens, the average crystal size increased from 9.0 µm to 49 µm when the amount of WO₃ or carbon was increased fivefold, respectively. The results indicate that changing the amounts of WO₃ and carbon is necessary to control the CAS GC microstructure.

Key-words: Glass-ceramics, Layered crystals, Nucleation agents, Microstructural control

1. Introduction

Initial report on glass-ceramics (GCs)¹ prompted investigations into their superior properties, such as their high fracture toughness compared with that of normal glass.²⁻¹³ The fracture behavior of lower-fracture-toughness GCs has also been studied because GC microstructures such as house-of-card structures comprising layered crystals have exhibit unique crack-like defects and microcracks in Vickers indentation experiments.¹⁰ Such subsurface cracks in house-of-cards type structures were recently observed in synchrotron X-ray multiscale tomography experiments conducted to elucidate the toughening mechanisms.¹⁰⁻¹³ In a previous study,¹² a relatively high fracture toughness was found for a house-of-cards structure with a relatively low crystal fraction in CaO–Al₂O₃–SiO₂ (CAS) GCs precipitated with hexagonal plate-like particles of metastable-CaAl₂Si₂O₈ layered crystals (CAS GC-H). However, this previous study focused on comparing different types of microstructures and parent glass compositions. Therefore, from the perspective of potential future applications, obtaining a single microstructure on various size scales using a parent glass with a single composition is important for elucidating the fracture mechanism/toughening process of GCs with a house-of-cards structure.

Herein, we demonstrate microstructural control of CAS GCs by increasing the amounts of nucleation agent sources. An increase in the amount of nucleation agents generally results in the growth of smaller crystal.⁴⁻⁵,¹⁴ However, we found that the crystal size in CAS-GC-H can be increased by increasing the amount of nucleation agent sources. These crystals can precipitate in CAS glass when a relatively small amounts of metallic particles is present as nucleation agents.¹⁰⁻¹³,¹⁴⁻¹⁶ These particles form by the reduction of oxides by carbon when the system is in the molten-glass state.¹²⁻¹⁶ The nucleation process of CAS-GC-H thus proceeds during glass melting. The effects of the amounts of nucleation agent sources are therefore worth investigating. The present study mainly focuses on comparing glass specimens prepared with different amounts of WO₃/carbon as sources of metallic W particle nucleation agents added to glass batches/cullet, and feasible mechanisms are discussed.

2. Experimental section

2.1 General information

The WO₃ particle morphology was characterized by field-emission scanning electron microscopy (FE-SEM; Supra40, Zeiss). Before being observed, the samples were sputter-coated with Pt. The crystalline phases and microstructure of the glass specimens after crystallization were characterized by powder X-ray diffraction (XRD) analysis (XRD-6100, Shimadzu) and SEM, respectively. Binarized
SEM images were used to approximate the volume fractions in the glass specimens after crystallization. SEM images of CAS-GC-H showed a needle-like morphology representing a cross-section of a house-of-cards structure comprising hexagonal plate-like particles of metastable CaAl2Si2O8.10,13) For simplicity, we refer to the crystalline phase observed in the SEM images of CAS-GC-H as “needle-like particles.” In addition, we define the particle size as the well-defined longer length of the needle-like particles that corresponds to the lateral size of layered crystals of metastable-CaAl2Si2O8 along the b-axis direction.17) Note that the stacking direction of layered crystals of metastable-CaAl2Si2O8 corresponds to the c-axis direction.17) The number of particles in an area of at least 500,000 μm² was counted and averaged. The presence of metallic W particles was investigated using a transmission spectrophotometer (V670 equipped with ARSN-733, JASCO). The profiles in the wavelength ranges of 420–460 and 670–690 nm were instrumentally derived. The mechanical properties of the GC specimens in this study were briefly evaluated by Vickers hardness tests (HMVG20, Shimadzu) with a 1 kgf load and a 15 s holding time. Vickers hardness values were estimated using the average of at least fifteen indentations measurements. These measurements were in a manner similar to that reported in the previous study12) because of the compassion of this study with the previous study.12) The glass specimens before and after crystallization were cut and polished to obtain appropriately sized samples for each analysis method. For the glass specimens after crystallization, the surface layers were removed by polishing.

### 2.2 Materials

Calcium carbonate (CaCO₃), aluminum oxide (Al₂O₃), silicon dioxide (SiO₂), and tungsten oxide (WO₃) were obtained from Wako Pure Chemical. Carbon was obtained from Kojundo Chemical Laboratory. For the comparisons described later, plate-like particles of WO₃ (denoted as WO₃-P) were prepared as another type of WO₃ via previously reported procedures without the expansion of protonated tungstate.18) FE-SEM images of the two WO₃ particle types are shown in Fig. 1.

### 2.3 Sample preparation

The CAS-GC-H samples were prepared according to a previously reported procedure.12)–16) The samples were melted at 1550 °C for 1 h under air in an alumina crucible. The melts were annealed at 850 °C for 30 min. Heat treatment of the glass specimens was conducted at 1050 °C for 2 h at a heating rate of 100 °C/h to achieve crystallization. Batches were prepared by mixing CaCO₃, Al₂O₃, and SiO₂ to form 50 g of 25CaO·20Al₂O₃·55SiO₂ glass (wt %). Glass batches with 0.40, 0.24, or 0.080 wt % WO₃ and 2.0, 1.2, 0.40, or 0.060 wt % carbon were melted to obtain glass cullet, which was subsequently remelted.

To investigate the effect of the nucleation agents, following melting of glass batches with 0.60 or 0.12 wt % WO₃, the resultant glass cullet was remelted after the addition of glass batches with the same composition and weight containing 3.0 or 0.60 wt % carbon. To elucidate the mechanisms presented above, the glass specimens were prepared using glass batches with 0.080 wt % WO₃ or WO₃-P and 0.40 wt % carbon. In addition, a glass cullet with 0.080 wt % WO₃ and 0.40 wt % carbon mixed with the same batch composition without WO₃ and carbon was melted.

The glass specimens and the amounts of WO₃ and carbon in the glass batches/cullet are listed in Table 1. Notably, the remelting process for Products A, B, C, G, H, and K was conducted under an oxidative atmosphere because the glass batches/cullet did not contain carbon.

### 3. Results and discussion

#### 3.1 Formation of CAS GC-H with relatively coarse microstructure by increasing the amounts of nucleation agent sources

In general, smaller nucleation agents require higher energy for crystallization, which retards crystal growth.4),5),14) That is, larger nucleation agents can lead to the formation of larger crystals. Meanwhile, an increase in the amount of nucleation agents promotes glass crystallization.4),5),14) The number of crystal particles in major crystalline phases is well known to be proportional to the amount of nucleation agents used.19) An increase in the number of nucleation agents generally results in smaller crystals because less raw material is used per one nucleation agent.4),5),14)
Based on the SEM images and particle size distributions for Products A and B [Figs. 2(a), 2(b), and 3], the average particle size increases from 9.3 µm for Product B to 49 µm for Products A. This increase is approximately fivefold and is consistent with the larger amounts of both WO₃ and carbon added to the glass batch (Table 1). The XRD patterns for Products A and B (Fig. 4) show reflections due to metastable CaAl₂Si₂O₈ but no reflections due to calcium tungstate. The lack of calcium tungstate is attributed to the relatively small amount of WO₃ in the glass batches (see experimental conditions). The (004) reflection observed in the patterns for Products A and B is due to the stacking direction of the aluminosilicate layers. Notably, layered crystals comprising stacked inorganic layers diversify the intensity of the reflection associated with the stacking direction relative to that associated with lateral atom arrangement because the crystallinity, stacking order, number, and lateral size of the inorganic layers vary depending on the type of layered crystals. Note also that the limitation of this study lies in the estimation of the change in the aspect ratio of the needle-like particles that is related to the growth mechanism, because diagonal cross-sections of the plate-like particles are observed in the SEM images of the house-of-cards structure.

Notably, the glass specimens containing metallic W particles as nucleation agents appeared black because of the presence of these particles. In addition, it is revealed that the colorless and transparent glass was obtained when glass batch without metallic particle sources was melted. Therefore, transmission spectra of black glass specimens are tentatively useful for the comparison in the amount of metallic W to be reduced by carbon. Meanwhile, in the

### Table 1. List of glass specimens and amounts of WO₃ and carbon in each melting process

<table>
<thead>
<tr>
<th>Product names</th>
<th>Additives in the melting process</th>
<th>Additives in the remelting process</th>
</tr>
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<tbody>
<tr>
<td>Product A</td>
<td>0.40 wt% WO₃, 2.0 wt% Carbon</td>
<td>---</td>
</tr>
<tr>
<td>Product B</td>
<td>0.080 wt% WO₃, 0.40 wt% Carbon</td>
<td>---</td>
</tr>
<tr>
<td>Product C</td>
<td>0.060 wt% WO₃</td>
<td>Glass batch containing 0.60 wt% Carbon</td>
</tr>
<tr>
<td>Product D</td>
<td>0.30 wt% WO₃</td>
<td>Glass batch containing 0.60 wt% Carbon</td>
</tr>
<tr>
<td>Product E</td>
<td>0.060 wt% WO₃</td>
<td>Glass batch containing 3.0 wt% Carbon</td>
</tr>
<tr>
<td>Product F</td>
<td>0.40 wt% WO₃, 0.40 wt% Carbon</td>
<td>---</td>
</tr>
<tr>
<td>Product G</td>
<td>0.080 wt% WO₃, 2.0 wt% Carbon</td>
<td>---</td>
</tr>
<tr>
<td>Product H</td>
<td>0.080 wt% WO₃, 0.40 wt% Carbon</td>
<td>Same compositional batch</td>
</tr>
<tr>
<td>Product I</td>
<td>0.080 wt% WO₃-P, 0.40 wt% Carbon</td>
<td>Same compositional batch</td>
</tr>
<tr>
<td>Product J</td>
<td>0.080 wt% WO₃, 0.060 wt% Carbon</td>
<td>---</td>
</tr>
<tr>
<td>Product K</td>
<td>0.080 wt% WO₃, 0.40 wt% Carbon</td>
<td>Same compositional batch without WO₃ and Carbon</td>
</tr>
</tbody>
</table>

Fig. 2. SEM images of Products A to I [from (a) to (i)]. Representative enlarged images in (a), (d), and (e) are shown in (‘a’), (‘d’), and (‘e’), respectively. The volume fractions (vol%) is indicated in the upper-right corners of the images.
It has been revealed that bright spots observed in the SEM images correspond to the relatively large metallic particles. In the present study, the SEM image of Product A contains bright spots within ca. 2\( \mu \)m that is larger than those observed in the SEM image of Product B [Figs. 2(a) and 2(b)]. Not all needle-like particles contain bright spots in this study, in agreement with the results of the previous studies.\(^{11,14,15}\) Thus, the detection of all metallic particles is the trials of not only this study but also studies of GCs prepared using metallic particles as nucleation agents,\(^{11,14,15}\) where the nucleation process that proceeds under heat treatment of the parent glass\(^ {16}\) could be required. This point will be conducted in another detailed study.

Collectively, the XRD patterns, SEM images, and particle size distributions (Figs. 2–4) reveal that the increase in the crystal size in the GAC-GC-Hs is proportional to the amount of both WO\(_3\) and carbon. Given the lack of a substantial difference in the volume fractions and an increase in the size of bright spots between Products A and B (Fig. 3) and the decrease in transparency of the parent glass products (Fig. 5), the addition of a nucleation agent sources likely promotes the growth of the metallic W particle nucleation agents. Notably, an increase in the nucleation agent size generally leads to an increase in crystal size.\(^{4,5,14}\)

To separately investigate the effects of increasing the amounts of WO\(_3\) and carbon on the crystal size, we melted WO\(_3\) in the glass prior to the reduction by carbon. The SEM images and particle size distributions for Products C to E [Figs. 2(c)–2(e) and 3] show that the average particle size in Product C increased from 9.0\( \mu \)m to 43 and 49\( \mu \)m in Products D and E, respectively. In addition, the volume fraction decreases in the order of Products C, D, and E. Notably, the crystal particles are clearly metastable CaAl\(_2\)Si\(_2\)O\(_8\) crystals based on the XRD patterns for Products C to E (Fig. 4). Given the decrease in transparency of the parent glasses in order of Products C to E (Fig. 5), an increase in the amount of either WO\(_3\) or carbon may likely lead to an increase in the particle size of the nucleation agent, accompanied by a decrease in the number of particles. A possible explanation for these results is proposed in the following subsection.
3.2 Feasible mechanism for increase in number of nucleation agents

Based on the glass compositions (see experimental section), the molar ratio of carbon to WO₃ (carbon/WO₃) in Product B, for example, is estimated to be 96.0. The nucleation process thus proceeds in the presence of an excess amount of carbon relative to the amount of WO₃. An increase in the carbon content leads to the generation or maintenance of a stronger reductive atmosphere. On the basis of the SEM images, volume fractions, and particle size distributions for Products C and E, as well as the transparency of the parent glass [Figs. 2(c), 2(e), 3, and 5], the metallic W particles likely grow under such a reductive atmosphere. Given the slight increase in the average size of crystal particles with decreasing volume fraction from Product D to E (Figs. 2 and 3), a decrease in the carbon content with increasing WO₃ content might slightly increase the number of nucleation particles, thereby enabling the growth of smaller crystals. Unfortunately, the parent glass of Product J is colorless and transparent, which is totally different from the representative color of the present glass (Fig. 6), suggesting that the oxidation of metallic W particles occurred. This transparency is attributed to the lower carbon content (carbon/WO₃ molar ratio of 14.4) in the glass batch for Product J than that for Products A and B (carbon/WO₃ molar ratio of 96.0). In addition, the glass cullet underwent remelting under an oxidative atmosphere because of the absence of carbon. Notably, after the first melting process, the glass specimens contained bubbles, likely resulting from the decarbonation of CaCO₃. Pre-heating of the glass batch could remove these bubbles. However, the remelting process is unavoidable for increasing the homogeneity of glass specimens. The limitation of this study lies in the melting process of glass batch with a lower carbon content under an oxidative atmosphere. Such the process will be required to control the melting atmosphere by inert gases, and the study is ongoing in our laboratory.

3.3 Brief investigation of the mechanical properties of CAS GC-H with a relatively coarse microstructure

On the basis of the aforementioned results, the co-addition of WO₃ and carbon is a feasible approach to
increasing the crystal size in CAS-GC-H. To demonstrate the advantage of the synthetic method proposed in the present study, we tentatively characterized the hardness of Product A using Vickers hardness test. Product H was also tested for comparison purpose. Figure 7 shows SEM images of Products A and H after Vickers indentation. All the crack-like defects observed in the images of Products A and H develop along crystal grains boundaries, as reported previously. In this previous study, the CAS GC-H exhibited a particle size similarly to that for Products B, C, F, and G. Given the relatively large crystal size of Products A and H, the smaller number of cracks propagating along grain boundaries than in previously reported products is understandable. In addition, the crack orientations in our previous report are feasible for CAS GC-H with relatively large crystals. Furthermore, the Vickers hardness of Product A (3.9 ± 0.3 GPa) is greater than that of Product H (4.5 ± 0.4 GPa) (Fig. 7). When the Vickers hardness in this study is compared with that reported previously, the value of Product A (3.9 ± 0.3 GPa) is greater than the Vickers hardness of CAS GC-H with relatively small crystals (4.2 ± 0.3 GPa). An increase in crystal size likely decreases the number of crystal-glass interfaces that release the impact energy. Interestsingly, the SEM images after Vickers indenterations, volume fraction, the number of particles for Products A and H (Figs. 2 and 7), show that the microstructure having large crystal size and volume fraction likely improve the mechanical property of CAS GC-H. This was strongly deduced because the crystals in CAS-GC-Hs with a parent glass having a single chemical composition were observed to increase in size. In our previous report, we discussed the increase in the number of particles and the degree of crystallinity with decreasing fracture toughness of CAS GC-Hs, however, the previous study compared glass specimens with different microstructures and compositions. Therefore, the present synthetic method provides new insights into the relationships between the crystal sizes and the mechanical properties of CAS GC-H. The detailed mechanical properties of CAS GC-H with relatively large crystals are worth further investigation. In addition, information about this microstructure might be useful for elucidating the fracture behavior of CAS-GC-H. Our group intends to undertake such studies in the future.

4. Conclusions

We have demonstrated microstructural control of CAS GC-Hs containing metallic W particle nucleation agents by increasing the amounts of both WO3 and carbon added as nucleation agent sources. An approximately fivefold increase in the average crystal particle size was observed, which is proportional to the amount of the nucleation agent sources. In addition, the obtained microstructure of the CAS GC-Hs exhibits improved mechanical property. Moreover, in our investigation of the effects of increasing the amounts of WO3 and carbon, we found that WO3/carbon should be appropriately added to glass batches/cullet during the nucleation process that proceed during the glass melting stage. In particular, the additives and their amounts, as well as the particle size/morphology strongly influence the remelting process. The present results therefore provide a method to precisely control the microstructures of CAS and other GCs.

Conceptualization Shingo Machida: conceptualization, data curation, writing—original draft, investigation, supervision. Nanami Murayama: data curation, investigation. Kei Maeda: writing-review and editing. Ken-ichi Katsumata: project administration. Atsuo Yasumori: project administration.

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Conflicts of Interest The authors declare no conflict of interest.

References


