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ZrO$_2$-SiO$_2$-Al$_2$O$_3$

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RAPID QUENCHING OF MELTS IN THE SYSTEM ZrO$_2$-SiO$_2$-Al$_2$O$_3$

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Abstract - The formation region of amorphous phases has been determined by the rapid quenching of melts in the system ZrO$_2$-SiO$_2$-Al$_2$O$_3$ using arc-imaging furnaces and twin-rollers. Re-heating of the amorphous phase brought about the crystallization mainly of t-ZrO$_2$, 210 nm in size, and/or mullite, up to 2 ~ 5 μm in size above 970°C.

I- INTRODUCTION

In the recent years, noble processes have been developed to prepare advanced materials. Rapid quenching of melts is interesting as a new technique for providing amorphous or metastable phases. We have applied this technique to the samples in the system ZrO$_2$-SiO$_2$-Al$_2$O$_3$ which is important in the science and the technology of alkali-resistant glass, refractory and advanced ceramics, because this system contains corundum (α-Al$_2$O$_3$), Zirconia (ZrO$_2$), Zircon (ZrSiO$_4$) and Mullite (3Al$_2$O$_3$·2SiO$_2$ as representative composition). This paper deals with the formation of amorphous phases by rapid quenching of melts and the crystallization from the amorphous phases upon re-heating.

II- EXPERIMENTAL

Starting materials were high purity Zirconia (ZrO$_2$: 99.9%, Soekawa Chemical Co. Ltd., Tokyo, Japan), Silica (SiO$_2$: Guaranteed reagent, Kanto Chemical Inc., Tokyo, Japan) and Alumina (α-Al$_2$O$_3$: 99.9%, Iwatani Chemical Industry Co. Ltd., Tokyo, Japan) powders. The required proportions were weighed and mixed thoroughly in an agate mortar using ethanol for 2 hours. The mixtures were melted on the water-cooled copper plate with a xenon arc-imaging furnace /1/ (UF-10001, USHIO Inc., Tokyo, Japan) applying from 6 to 8 kw power in air. The molten samples became spherical globules with the diameter of ~2 mm by surface tension in a few seconds on radiation. According to measurement of weight loss after melting, the compositional change by evaporation was negligible in this procedure.

For rapid quenching, the brobule was molten again on a graphite stage and then dropped in a steel twin-roller 30 mm in diameter as shown in Fig. 1 (a) /2/.

Another technique used another arc-imaging furnace /3,4/ (SC-5D, Nichiden Machinary Inc., Shiga, Japan) for floating-zone crystal growth, where molten droplet 3~4 mm in diameter at the end of a sintered bar specimen (4 x 4 x 40 mm$^3$) fell into a steel twin-roller 50 mm in diameter as shown in Fig. 1 (b).

The cooling rate of the molten samples quenched by the twin-rollers rotating at ~4000 rpm were estimated to be 10$^5$ K/sec based upon the relation by Ota et al. /4/ between the critical cooling rate and the composition of the samples for glass formation in the system Li$_2$O-SiO$_2$. 

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The rapidly quenched samples were studied with TG-DTA (Thermoflex, Rigaku Electric Inc., Tokyo, Japan) up to 1100°C at 10°C/min in air, or re-heated at 1200°C for various hours for crystallization. The products were examined by an X-ray diffractometer (RU-200, Rigaku Electric Inc., Tokyo, Japan) optical microscope (Vanox, Olympus, Tokyo, Japan), SEM (T-200, JEOL, Tokyo, Japan) and TEM (H-700, Hitachi, Tokyo, Japan). The phase analysis, lattice parameter and crystallite-

Fig. 1
Schematic illustration of rapid quenching of melts using arc-imaging furnace and twin-roller
(a) with multi-purpose 10 kw Xe arc-imaging furnace /1, 2/.
(b) with arc-imaging floating-zone furnace /3, 4/.

size determination were carried out by step-scanning technique using Cr2O3 as an internal standard. Calibration curves had been determined previously by adding known amounts of Cr2O3 to each phase.

III - RESULTS AND DISCUSSION
III. 1 Amorphous Formation in the System
ZrO2-SiO2-Al2O3
The rapid quenching using the twin-rollers resulted in the formation of amorphous materials as shown in Fig. 2, /2/. The products with wide compositional region were transparent flakes with few tens μm in thickness and showed no crystallinity under X-ray diffraction (Fig. 3). SiO2-rich compositions gave almost transparent products but t-ZrO2 phase partially crystallized at the thicker rims of the flakes. This suggests that SiO2-rich melts have high viscosity which reduces the cooling rate owing to increasing the thickness of the sample between rollers. In the ZrO2-rich samples, t-ZrO2 phase mainly crystallized all over the flakes. Al2O3-rich samples produced a slight amount of α-Al2O3 phase as well as ZrO2 phase under X-ray diffraction. Mullite phase was observed, only for compositions of mullite and 60 wt% Al2O3 - 40 wt% SiO2 in the samples studied.

Fig. 2
Formation region of amorphous phase by rapid quenching of melts using arc-imaging furnace and twin-roller.
- - - - present work, ○:Am only, ●:Am + tr. crystalline phase, □:Am +crystalline phase(s) indicated.
- - - - Amorphous region by flame fusion (Thorne, 1965)
- - - - Amorphous region by hydrolysis of alkoxides (Makishima et al., 1980)
The formation region of complete amorphous phase was different from that by chemical polymerization of metal alkoxides /5/, but in good agreement with Thorne's /6/ results. He also rapidly quenched the melts using a flame spherulization technique where a dispersion of samples was injected into an oxy-hydrogen flame spraying in distilled water. The amorphous region obtained from rapidly quenched melts extends toward Al₂O₃ side rather than ZrO₂ side. The liquidus surface of Al₂O₃ is lower temperature than ZrO₂ side in the system ZrO₂-SiO₂-Al₂O₃ /7/. Sarjeant and Roy /8/ described that critical quenching rate below which detectable crystalline phases are obtained from melt were proportional to a square of the melting temperature. Therefore in the system ZrO₂-SiO₂-Al₂O₃, amorphous materials tended to form in the high Al₂O₃ compositions rather than in the high ZrO₂ compositions seen in the case of Makishima.

The crystallization of t-ZrO₂ in the amorphous region near the SiO₂-ZrO₂ join seemed to be caused by the phase separation due to the two-liquid region in the system SiO₂-ZrO₂. The crystalline phase of the quenched samples was mainly metastable t-ZrO₂ phase of which crystallite size became larger with the distances from the amorphous formation region as indicated in Fig. 4. Monoclinic ZrO₂ was observed in the products of the outer region in this diagram. This is consistent with the argument /9/ that t-ZrO₂ can crystallize from amorphous phases then transform into m-ZrO₂ but m-ZrO₂ cannot crystallize directly from the amorphous phases. This is further supported by the crystallization of the amorphous phases upon reheating described below.

Fig. 3
X-ray diffraction patterns of various samples rapidly quenched.
30S30A40Z means 30 wt% SiO₂-30 wt% Al₂O₃-40 wt% ZrO₂ as a starting composition.

Fig. 4
Crystallite size of t-ZrO₂ precipitated in the rapidly quenched samples.

III. 2 Crystallization from the Amorphous Phase by Heating
Re-heating of the amorphous phases brought about crystallization. According to DTA, a small endothermic peak was observed at = 920°C corresponding to glass-transition temperature, and an extreme exothermic peak at 950°-1000°C of crystallization as shown in Fig. 5. The starting temperature of crystallization of t-ZrO₂ in the amorphous region near the SiO₂-ZrO₂ join seemed to be caused by the phase separation due to the two-liquid region in the system SiO₂-ZrO₂. The crystalline phase of the quenched samples was mainly metastable t-ZrO₂ phase of which crystallite size became larger with the distances from the amorphous formation region as indicated in Fig. 4. Monoclinic ZrO₂ was observed in the products of the outer region in this diagram. This is consistent with the argument /9/ that t-ZrO₂ can crystallize from amorphous phases then transform into m-ZrO₂ but m-ZrO₂ cannot crystallize directly from the amorphous phases. This is further supported by the crystallization of the amorphous phases upon reheating described below.

Fig. 5
DTA curve of the amorphous phase by rapid quenching of melt. Sample : 20 wt% ZrO₂-80 wt% 3Al₂O₃·2SiO₂ heating rate : 10°C/min.
zation peak in DTA with heating rate of 10°C/min was higher in the samples located inner of the amorphous region (Fig. 6). No distinct exothermic peak was observed in the samples crystallized already during quenching and in the SiO₂-ZrO₂ rich samples probably due to slow crystallization kinetics. Figure 7 shows the phase assemblages of various samples after reheating up to 1100°C in air indicating the crystallization of t-ZrO₂ in ZrO₂-rich region, mullite in mullite-rich region and t-ZrO₂ + mullite in intermediate region. The phase analysis (Table 1) demonstrated the increase of t-ZrO₂ and mullite by the crystallization. The content of m-ZrO₂, however, remained constant within the experimental errors (+5 wt%) upon reheating.

These results revealed that mullite and t-ZrO₂ were crystallized from the amorphous phase at 950°C - 1000°C. The exothermic reaction observed in DTA corresponds to the crystallization of mullite, because no significant peaks were observed in DTA of the samples in which only the contents of t-ZrO₂ increased upon re-heating as indicated in Fig. 6. The crystallite size of t-ZrO₂ crystallized from the amorphous phase was about 10 nm similar to the critical crystallite size at the boundary of the amorphous region as shown in Fig. 4.

The re-heating of the amorphous phase up to 1100°C yielded t-ZrO₂ and mullite but still left a considerable amounts of the amorphous phase as indicated in Table 1. The heat treatment at 1200°C, on the other hand, brought about almost complete crystallization /10/. For

![Fig. 6](image)

Beginning temperature (°C) of the crystallization from the amorphous phase by DTA with 10°C/min.

![Fig. 7](image)

Crystallization of t-ZrO₂ and/or mullite from the amorphous phase by re-heating up to 1100°C with 10°C/min. Filled symbols mean the crystallization before re-heating.

<table>
<thead>
<tr>
<th>Sample composition*</th>
<th>Crystalline phase (wt%)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before heating</td>
</tr>
<tr>
<td></td>
<td>m-ZrO₂</td>
</tr>
<tr>
<td>302705 OA</td>
<td>12</td>
</tr>
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<td>35240525A</td>
<td>--</td>
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<tr>
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<td>19</td>
</tr>
<tr>
<td>10240550A</td>
<td>--</td>
</tr>
<tr>
<td>10290(3.2M)</td>
<td>--</td>
</tr>
<tr>
<td>20280(3.2M)</td>
<td>--</td>
</tr>
<tr>
<td>40Z10550A</td>
<td>--</td>
</tr>
<tr>
<td>40Z30530A</td>
<td>--</td>
</tr>
</tbody>
</table>

* Z:ZrO₂ S:SiO₂ A:Al₂O₃ 3.2M:3Al₂O₃·2SiO₂

** The remains are amorphous phases
example, the amorphous phase with 20 wt% ZrO₂ + 80 wt% 3Al₂O₃.

2SiO₂ composition crystallized into 83.8 wt% mullite + 11.3 wt% t-ZrO₂ + 2.4 wt% m-ZrO₂ within a half hour. The TEM observation revealed that the product consist of mullite grains 3–5 μm in size which contained tiny ZrO₂ crystals 10–20 nm in size, Fig. 8 (a). These mullite grains were single crystals as indicated in Fig. 8 (b). The characteristic radial arrangements of ZrO₂ crystals in the mullite grains, Fig. 8 (c), suggest that these ZrO₂ crystals were precipitated by the exolution upon crystallization of mullite from the amorphous matrix. These microstructures also suggest that the crystallization of mullite rather than ZrO₂ is dominant upon heating of these materials.

According to the lattice parameters, the composition of mullite would change from Al₂O₃-excess (77 wt% Al₂O₃) toward stoichiometric (72 wt% Al₂O₃ for 3Al₂O₃·2SiO₂) by prolonged heat treatment at 1200°C. The details of the crystallization process in these materials are reported in another paper /10/.

REFERENCES

/10/ Yoshimura, M. Kaneko, M. and Sōmiya, S., Yogyo Kyokai Shi, to be published.

Fig. 8 (a): Transmission electron micrograph of sample (20 wt% ZrO₂-80 wt% 3Al₂O₃·2SiO₂) after re-heating at 1200°C for 12 h.
(b): Electron diffraction of (a). [Mullite]
(c): Array of t-ZrO₂ particles in the mullite grain.