Crystallization of glass with $Y_2Si_2O_7$-mullite eutectic composition

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In this paper, the crystallization of the glass with $Y_2Si_2O_7$-mullite eutectic composition was examined. A dendrite $Y_2Si_2O_7$ crystalline grows from the surface of the glass bulk at 1302 K. A competitive growth of $Y_2Si_2O_7$ phase and mullite phase occurs at 1430 K. The activation energy for the competitive growth can be estimated to 329 kJ/mol. The activation energy for the crystallization of hypoeutectic and hypereutectic composition increases with increasing the amount of the primary phase.

Key-words : $Y_2Si_2O_7$-mullite eutectic, Crystallization, Competitive growth, Activation energy

1. Introduction

Since silicon carbide (SiC) ceramic and its composites show high oxidation resistance and have high reliability at elevated temperatures, these materials are promised to be used as gas turbine hot section components.¹ However, under high speed exhaust gas, the surface of silicon carbide ceramics is oxidized and the formed silica layer is easily corroded by water vapor promoting the recession of the SiC substrate. For example, Yuri and Hisamatsu suggested that SiC ceramics will be recessed about 3 mm under gas turbine conditions at 1523 K for 10,000 h.² Hence on the application of SiC ceramics and its composites for gas turbine hot sections component, an oxidation-corrosion resistance environmental barrier coating (EBC) layer is required. Some oxides, such as ZrO₂, HfO₂ and Ln₂Si₂O₇ (Ln = rare earth) show excellent water vapor corrosion resistance under gas turbine conditions at elevated temperatures.³,⁴ On the development of EBC for non-oxides ceramics, commonly, oxides EBC layers were prepared by plasma spraying.⁵ Since the EBC layer is composed of polycrystalline solid, a small amount of glassy phase exist at the grain boundary and the boundary glassy phase can be easily corroded by water vapor under gas turbine condition then, a porous structure is formed through the EBC layer, even if the crystalline phase of oxide EBC material shows an excellent water vapor corrosion resistance.⁶,⁷ The corrosive gases easily pass through the porous channel of the EBC layer and the non-oxides ceramics substrate will be oxidized. Hence, an EBC layer without boundary glassy phase is required for the development of future EBC.

On the solidification of oxides eutectic, the excess impurities will be removed from the bulk by segregation.⁸ Hence, the eutectic composites, especially the eutectic with ZrO₂, HfO₂ or Ln₂Si₂O₇ (Ln = rare earth) phase are promising materials for EBC.

In our previous report, an Al₂O₃-HfO₂ eutectic EBC without boundary glassy phase and its preparation method using optical focusing process are proposed.⁹ However, the EBC layer must coat on Si or MCrAlY buffer layer. Hence, a low temperature coating process for eutectic EBC layer is desired. One idea is to use the phase separation of amorphous phase.

The phase equilibria of Al₂O₃-Y₂O₃-SiO₂ ternary system were examined by Murakami and Yamamoto in 1991.¹⁰ In their report, the lowest solid line appears in Y₂Si₂O₇-Al₂Si₂O₅ quasi-binary system and its temperature is 1613 K.¹⁰ They pointed out that two kinds of activation energy for the crystallization of the glass in Al₂O₃-Y₂O₃-SiO₂ ternary system exist.

In this paper, the crystallization mechanism of the glass with $Y_2Si_2O_7$-mullite eutectic composition will be discussed.

2. Experiments

$Y_2O_3$ powder (99.9% purity, Kojundo Chemical Laboratory Co., Ltd.), Al₂O₃ powder (99.9% purity, Kojundo Chemical Laboratory Co., Ltd.) and SiO₂ powder (99.9% purity, Kojundo Chemical Laboratory Co., Ltd.) were used as starting materials. The powders were mixed in molar ratio of $Y_2O_3$:Al₂O₃:SiO₂ = 12.2:22.0:65.8 according to the reference¹⁰ in ethanol. After drying at 353 K in air, the mixed powder was pressed into rod shape with 5 mm diameter and 100 mm in length. The calcination was performed at 1473 K for 7.2 ks in air and the feed rod was prepared.

The glass with $Y_2Si_2O_7$-mullite eutectic composition was prepared by quenching of liquid phase using optical floating zone furnace in Ar atmosphere. The pressure was controlled to 0.2 MPa. Xenon lamp was used as an optical source. The Xenon lamp and sample put on the focus in the elliptical mirror. The feed rod was hooked on upper shaft. This melting system was set up in a quartz tube. The environmental gas was introduced into the quartz tube. The molten phase drops on a copper plate. The distance between the melting position and the copper plate was fixed to 0.23 m.

The sample was crushed into powder and the powder glass was used for the X-ray diffraction (XRD) measurement and differential thermal analysis (DTA). The powder X-ray diffraction measurement was performed using X-ray diffraction apparatus of D2-PHASE (Bruker AXS K.K.). The differential thermal analysis was performed using TG-DTA apparatus of TG-DTA200SA-NF23 (NETZSCH Japan Co.). The measurement of the thermal analysis was performed in Ar flow with 0.08, 0.17, 0.33 and 0.67 K/s in heating rate. Bulk glass sample was used for...
the heat treatment.

3. Results and discussion

Figures 1(a) and 1(b) show the external view and powder X-ray diffraction pattern of the glass with Y2Si2O7–mullite eutectic composition. The sample shows clear and colorless and no diffraction peaks can be detected. Two kinds of halo patterns around 2θ = 27 and 45° can be confirmed. In this glass, Y3+ ion, Al3+ ion, Si4+ ion and O2− ion exist. In the glass of Al2O3–Y2O3–SiO2 system, Y3+ ion acts as modifying ion.11) Hence it is considered that the former halo pattern shows (Si and Al based, Y)−O radial distribution and the latter halo pattern shows (Y-based, Si or Al)−O radial distribution. No detailed structural analysis for this glass was performed in this study.

Figure 2 shows DTA curve for the powder glass. The heating rate for this data is 0.67 K/s. The glass transition temperature $T_g$ was 1168 K. The glass begins to crystallize at 1302 K marked as $T_a$ and a large exothermal peak marked as $T_c$ appears at 1430 K. Then the sample melts down at 1600 K marked as $T_m$. To examine the crystallization mechanism of this glass at $T_a$, a heat treatment for the glass bulk was performed at 1273 K for 72 ks in air. Figures 3(a) and 3(b) show the external views of the sample before and after the heat treatment. The glass devitrified after the heat treatment.

Figure 4 shows the cross section view of the glass after the heat treatment. Dendrite crystals grow from the bulk surface. Some cavities are formed around the dendrite crystal due to the loss of density due to the crystallization. Since the amount of the dendrite crystal in glass bulk is small, no diffraction peaks for the crystalline can be detected in the powder X-ray diffraction pattern of this sample. Hence a heat treatment at 1373 K which is also lower than the temperature of $T_c$ for 7.2 ks was performed.

Figure 5 shows the powder X-ray diffraction pattern of the sample after the heat treatment at 1373 K. Two weak peaks appear on the strong halo pattern. These peaks can be indexed as monoclinic Y2Si2O7 phase with space group C2/m (JCPDS Card No. 38-0440). This crystal structure is unstable for Y2Si2O7. Hence, it can be seen that the phase crystallized at $T_a$ is Y2Si2O7 phase.

To examine the crystallization at exothermal peak of $T_c$, a heat treatment at 1523 K which is higher than the temperature of $T_c$ for 7.2 ks was performed. Figure 6 shows the powder X-ray diffraction pattern of the sample after the heat treatment. Y2Si2O7 phases and a mullite phase can be detected. For Y2Si2O7 phase, a stable monoclinic phase (JCPDS Card No. 38-0223) and triclinic phase (JCPDS Card No. 21-1454) co-exist in this sample. In the phase diagram, the Ln2Si2O7 (Ln = rare earth) phases show seven different kinds of crystal structure.12) In the case of Y2Si2O7 phase, four types of stable crystal structure are known.12) The phase transition from triclinic phase to monoclinic phase of Y2Si2O7 occurs at 1498 K.12) Parmentier et al. examined the crystallization of Y2Si2O7 from amorphous phase which prepared by sol–gel method.13) In their report, triclinic phase, monoclinic phase and a small amount of silica defect type apatite phase appears after heat treatment at 1573 K for 86.4 ks.13) However, in this experiment, no trace for the apatite type phase was detected.
Since the number of exothermal peak for the crystallization is one, $Y_2Si_2O_7$ phase and mullite phase grow competitively at $T_c$.

The activation energy for the crystallization from the glass or amorphous phase can be determined by Kissinger plot using the temperature of exothermal peak height and heating rate according to Eq. (1).14),15)

$$\ln\left(\frac{\alpha^n}{T^n}\right) = \frac{mE}{RT} + \text{const}$$  \hspace{1cm} (1)

Where, $\alpha$, $E$, $R$ and $T$ denotes the heating rate, activation energy, gas constant and temperature of the peak height, respectively.15) The values of $m$ and $n$ are numerical factors depending on the crystallization mechanism. In this experiment, since the $Y_2Si_2O_7$ phase nucleates at bulk surface and grows from the surface to center of the bulk, the values of $m$ and $n$ were fixed to 1 according to the reference.15)

Figure 7 shows the Kissinger plot for crystallization at exothermal peak. From the slope of Fig. 7, the activation energy for the crystallization of this glass sample can be estimated to $329 \text{kJ/mol}$. Luo et al. examined the phase separation of $Y_2Si_2O_7$ phase and cristobalite phase from the glass state and reported that the activation energy for the phase separation can be estimated to $347 \text{kJ/mol}$.16) That experimental value of activation energy is very close to that of our experimental data. When the composition of the glass deviates from eutectic composition, the competitive growth of $Y_2Si_2O_7$ and mullite phase must be occurred after the crystallization of the primary phase enough. Hence, it is considered that the activation energy for the crystallization of the glass with eutectic composition is lower than that of the glass with hypo- and hyper-eutectic composition.

### 4. Conclusion

In this paper, the crystallization of the glass with $Y_2Si_2O_7$-mullite eutectic composition was discussed. In this case, $Y_2Si_2O_7$ dendrite grows from the surface of the glass bulk at $1302 \text{K}$. And a competitive growth of $Y_2Si_2O_7$ phase and mullite phase occurs at $1430 \text{K}$. The activation energy for the competitive growth of $Y_2Si_2O_7$ phase and mullite phase is estimated to $329 \text{kJ/mol}$, which is lower than that of the activation energy for the crystallization of mullite. The amount of the primary phase strongly affects to the activation energy for the crystallization of glass. The activation energy for the crystallization increases with increasing the amount of primary phase.

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