Ceramics International 42 (2016) 13601–13604

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Crystallization and microstructure formation of glass with $Y_2Si_2O_7$-mullite eutectic composition

Shunkichi Ueno [a,*], Tomoe Tada [a], Yohei Suzuki [a], Junko Nozawa [a], Byung-Koog Jang [b], Tohru Sekino [c]

[a] College of Engineering, Nihon University, Koriyama, Fukushima 963-8642, Japan
[b] National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
[c] The Institute of Science and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

ARTICLE INFO

Article history:
Received 26 March 2016
Received in revised form
24 May 2016
Accepted 24 May 2016
Available online 24 May 2016

Keywords:
$Y_2Si_2O_7$-mullite eutectic
Crystallization
Phase separation
Eutectic structure

ABSTRACT

The crystallization and microstructure formation of glass with a $Y_2Si_2O_7$-mullite eutectic composition were examined. A crystallization of $Y_2Si_2O_7$ and the mullite phase due to phase separation occurred at 1174 °C, and a well-developed $Y_2Si_2O_7$ facet crystal was formed. This sample was melted down and solidified via heat treatment at 1250 °C and 1300 °C, temperatures below the melting point of a $Y_2Si_2O_7$-mullite eutectic. As a result of this solidification, a directional eutectic microstructure was formed.

1. Introduction

A recent silicon carbide (SiC) ceramic and its composites have high reliability of mechanical properties at elevated temperatures, and these materials are promising for use as gas turbine hot section components [1]. However, the surface of silicon carbide ceramics is oxidized under gas turbine conditions, and the formed silica layer is corroded by water vapor, promoting recession of the SiC substrate. Yuri and Hisamatsu estimated the recession rates for some ceramics [2]. In their report, SiC ceramics were recessed about 3 mm under gas turbine conditions at 1523 K for 10,000 h [2]. Hence, for the application of SiC ceramics and their composites to gas turbine hot section components, an oxidation- and corrosion-resistance environmental barrier coating (EBC) layer is required. In our previous reports, the water vapor corrosion resistance for some oxides was examined, and some oxides, such as ZrO_2, HfO_2, and $Ln_2Si_2O_7$ (Ln=rare earth), show excellent water vapor corrosion resistance under gas turbine conditions at elevated temperatures [3]. However, when the EBC layer is composed of a polycrystalline solid, the boundary glassy phase is corroded selectively by water vapor under gas turbine conditions. Additionally, a porous structure is formed through the EBC layer, even if the crystalline phase of the oxide EBC material shows excellent water vapor corrosion resistance [4,5]. The corrosive gases pass through the porous channel of the EBC layer, and the non-oxide ceramic substrate is oxidized. Hence, a microstructure without a boundary glassy phase is desired for the development of future EBCs.

Commonly, upon solidification of the oxide eutectic system, excess impurities will be removed from the solidified bulk by segregation, and a microstructure without a boundary glassy phase is formed [6]. Hence, the oxide eutectic composites, especially the eutectic composites with a ZrO_2, HfO_2, or $Ln_2Si_2O_7$ (Ln=rare earth) phase as an edge member, are promising materials for EBCs.

Since the EBC layer must coat the Si buffer layer, a low-temperature coating process for a eutectic EBC layer is required. One idea is to use the crystallization or phase separation of the glass or the amorphous phase with eutectic composition by heat treatment at low temperatures.

Murakami and Yamamoto examined the phase equilibria of the Al_2O_3-Y_2O_3-SiO_2 ternary system in 1991 [7]. In their report, the lowest solid line appears in the $Y_2Si_2O_7$-$Al_6Si_2O_{13}$ quasi-binary system, and its temperature is 1340–1345 °C [7,8]. Since the melting point of Si is 1414 °C, it is possible to melt and solidify the $Y_2Si_2O_7$-$Al_6Si_2O_{13}$ eutectic layer on the Si buffer layer using a furnace.

In our previous report [9], the crystallization mechanism of the glass with $Y_2Si_2O_7$-$Al_6Si_2O_{13}$ eutectic composition was discussed. In this system, $Y_2Si_2O_7$ phase with low symmetry phase first grew

* Corresponding author.
E-mail address: ueno@chem.ce.nihon-u.ac.jp (S. Ueno).

http://dx.doi.org/10.1016/j.ceramint.2016.05.154
0272-8842/

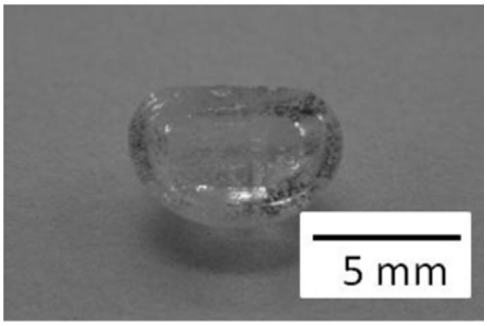

Fig. 1. Glass sample prepared by quenching the melt.

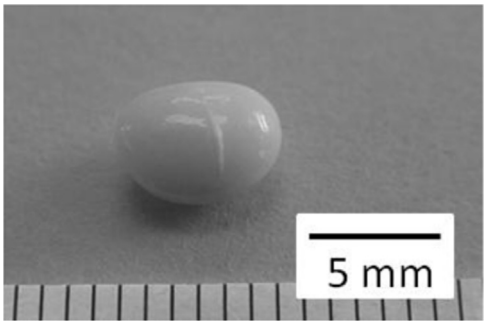

Fig. 3. External view of the sample after heat treatment at 1250 °C.

from the bulk surface at 1029 °C (T_a) and stable $Y_2Si_2O_7$ phase and mullite phase crystallized together at a time at 1157 °C (T_c) where, the value of T_a and T_c were measured using DTA data which heating rate was 40 °C/min [9]. The activation energy for the crystallization at 1157 °C (T_c) can be estimated to 329 kJ/mol which is extremely low compared with that of mullite from glass state [9].

In this paper, the microstructure formation mechanism of the glass with a $Y_2Si_2O_7$-mullite eutectic composition is discussed.

2. Experiments

Y_2O_3 powder (99.9% purity, Kojundo Chemical Laboratory Co., Ltd.), Al_2O_3 powder (99.9% purity, Kojundo Chemical Laboratory Co., Ltd.), and SiO_2 powder (99.9% purity, Kojundo Chemical Laboratory Co., Ltd.) were used as starting materials. The powders were mixed in a molar ratio of Y_2O_3:Al_2O_3:SiO_2=12.2:22.0:65.8 according to the reference [7,10] and pressed into a rod shape 5 mm in diameter and 100 mm in length by a cold isostatic press. The sample was calcined at 1473 K for 7.2 ks in air, and the feed rod was prepared.

The glass with a $Y_2Si_2O_7$-mullite eutectic composition was prepared by quenching the molten phase using an optical floating zone furnace in an Ar atmosphere. A xenon lamp was used as an optical source. The xenon lamp and sample placed on the focus in the elliptical mirror that has two different focus in the optical floating zone furnace. The feed rod was hooked onto the upper shaft. This melting system was set up in a quartz tube. The environmental gas was introduced into the quartz tube. The molten phase was dropped onto a copper plate. The distance between the melting position and the copper plate was fixed at 0.23 m.

The sample was crushed into powder, and the powdered glass was used for the X-ray diffraction (XRD) measurement and differential thermal analysis (DTA). The powder XRD measurement was performed using the X-ray diffraction apparatus D2-PHASER (Bruker AXS K.K.). The DTA measurement was performed using the TG-DTA apparatus TG-DTA2020SA-NF23 (NETZSCH Japan Co.). DTA measurement was performed in an Ar flow with a 30 °C/min heating and cooling rate. A bulk glass sample was used for the heat treatment.

3. Results and discussion

Fig. 1 shows the external view of the glass with a $Y_2Si_2O_7$-mullite eutectic composition. The sample appears clear and colorless. No diffraction peaks were observed for this sample in the XRD pattern, as described in our previous report [10].

Fig. 2(a and b) shows the DTA curve for the powdered glass in the heating and cooling steps, respectively. Since the curves for the heating and cooling steps cross in the figure, to avoid any confusion, the curve for each step was drawn in a separate chart. The glass transition temperature appears at 913 °C, marked as T_g. The glass begins to crystallize at 1010 °C, marked as T_a, and an exothermal peak marked as T_c appears at 1174 °C. Then the sample melts down once at 1330 °C, marked as T_m. However, this sample recrystallized at 1359 °C and 1395 °C, marked as T_{rc}. From the thermal analysis, it can be understood that (1) a kind of crystallization begins at T_a; (2) another kind of crystallization occurs at T_c; and then (3) the sample melts down under the present heating rate condition. Furthermore, (4) recrystallization from the melt occurs. In our previous report, the crystallization mechanisms at T_a and T_c were examined [9]. At T_a, a dendritic $Y_2Si_2O_7$ crystal grows from the bulk surface to the inner part of glass, and the $Y_2Si_2O_7$ phase and mullite phase crystallized due to phase separation of the glass at T_c as reported in our previous report [9]. Since no exothermic or endothermic peaks were observed in the cooling step, as shown in Fig. 2(b), a stable phase and microstructure are formed by recrystallization, namely, solidification at T_{rc}.

To clear the microstructure formation by the phase separation at T_c, a heat treatment for the bulk sample was performed for 10 h at 1250 °C, which temperature was higher than T_c. Fig. 3 shows the external view of the sample after the heat treatment. The glass

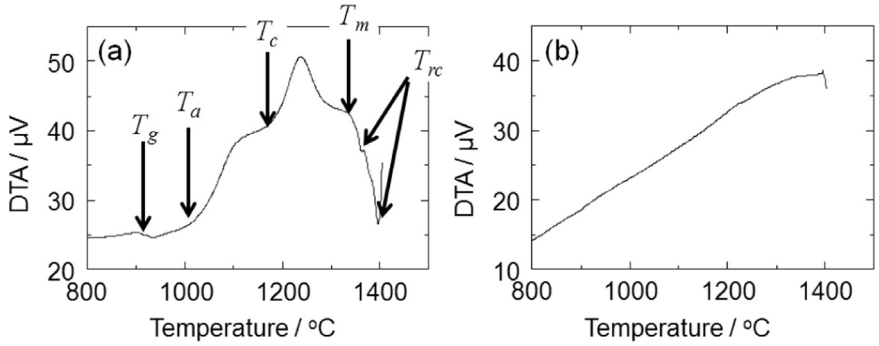

Fig. 2. DTA curve for the glass (a) heating step and (b) cooling step.