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Crystallization of Inviscid Melt Spun (IMS) Calcia–Alumina (CA) Eutectic Fibers

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Abstract: Crystallization behavior of vitreous calcia–alumina (CA) fibers of eutectic composition (46·5 wt% CaO–53·5 wt% Al_2O_3) was studied by differential thermal analysis (DTA), scanning electron microscopy (SEM) and X-ray diffraction (XRD). From DTA results, crystallization temperature of the CA fibers ranges from 948 to 1034°C according to DTA heating rates. The activation energy value for crystallization of the CA fibers was determined as 490 kJ/mol and 477 kJ/mol via Kissinger and Augis–Bennett methods, respectively. SEM for crystallized CA fibers showed surface roughness, whereas that for vitreous CA fibers showed typical glassy fracture. Wide angle X-ray diffractometer analysis on CA fibers which were crystallized by the DTA scans showed $Ca_{12}Al_{14}O_{33}$ formation as a major phase and $CaAl_2O_4$ formation as a minor phase.

1 INTRODUCTION

Vitreous CaO–Al_2O_3 (CA) fibers have been successfully produced by inviscid melt-spinning (IMS). Cunningham *et al.*[1] first reported the production of vitreous CA fibers using the IMS process. Dunn and Paquette[2] made fine filaments using the vitreous CA fibers by using a 'redrawing' technique. They observed small amounts of crystallinity by heating the eutectic CA fibers to their softening temperature (1200°C) and attenuating the fibers. Wallenberger and co-workers[3–14] showed that the CA fibers were vitreous as produced by IMS up to approximately 82 wt% of Al_2O_3 whereas the fibers are crystalline as produced above 82 wt% of Al_2O_3.

It is of importance to study the crystallization behavior of these CA fibers as reinforcements for glass-ceramic or metal matrix composites since the mechanical properties of these systems degrade rapidly once they crystallize.[15] Wallenberger *et al.*[11] studied crystallization of CA fibers of 39·0 wt% CaO–61·0 wt% Al_2O_3 with heat treatment of 1200°C for 1 h. Their results indicate almost complete crystallization of $Ca_{12}Al_{14}O_{33}$ and $CaAl_2O_4$ as major phases. Dunn and Paquette[2] report that the redrawn CA fibers of 53·5 wt% Al_2O_3 and 46·5 wt.% CaO show small amounts (5–15%) of an unidentified crystalline phase after exposure to 1200°C for less than 1 s during the redrawing process.

Mitchell *et al.*[16] heat treated vitreous CA fibers of eutectic composition (46·5 wt% CaO–53·5 wt% Al_2O_3) at 900, 1000, and 1100°C for 6–6000 s to characterize the crystallization process. The results show $Ca_{12}Al_{14}O_{33}$, $Ca_3Al_{10}O_{18}$, and $CaAl_4O_7$ formation with different amounts in all crystallized fibers.

The purpose of the present study is to measure the exact crystallization temperature of the CA fibers of eutectic composition with different heating rates and to determine the activation energy value for crystallization of the IMS CA fibers using differential thermal analysis (DTA).

2 EXPERIMENTAL

The procedures of CA fiber fabrication are described in detail in previous works.[16,17] To confirm that the as-produced CA fibers were non-crystalline, the powdered CA fibers were investigated

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using an X-ray diffractometer (XRD: Nicolet Stoe Transmission/Bragg-Brentano, Stoe Co., Germany) with a Cu-Kα source, a 5-s time constant, a 10–70° scan, and 0·05° step size.

The DTA (Perkin-Elmer DTA 1700, Norwalk, CT) measurements were performed using 100 mg of the CA fibers (~250 μm diameter and ~10 mm length) in an alumina crucible in an air atmosphere with heating rates of 3, 5, 10, 20, 40 and 80°C min from 600 to 1200°C. The temperatures of the DTA were calibrated using pure aluminum and copper.

The microstructure of the fractured surface of vitreous and crystallized (during DTA scan) CA fibers were examined by scanning electron microscopy (SEM: Jeol SEM 35-C, Japan).

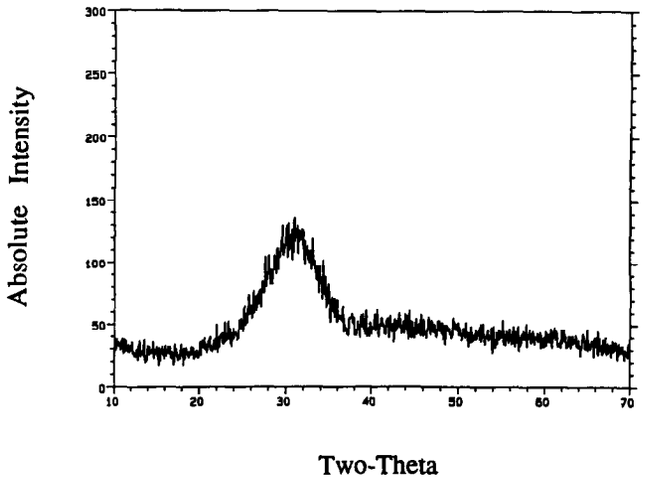

Fig. 1. XRD pattern for vitreous IMS CA fibers.

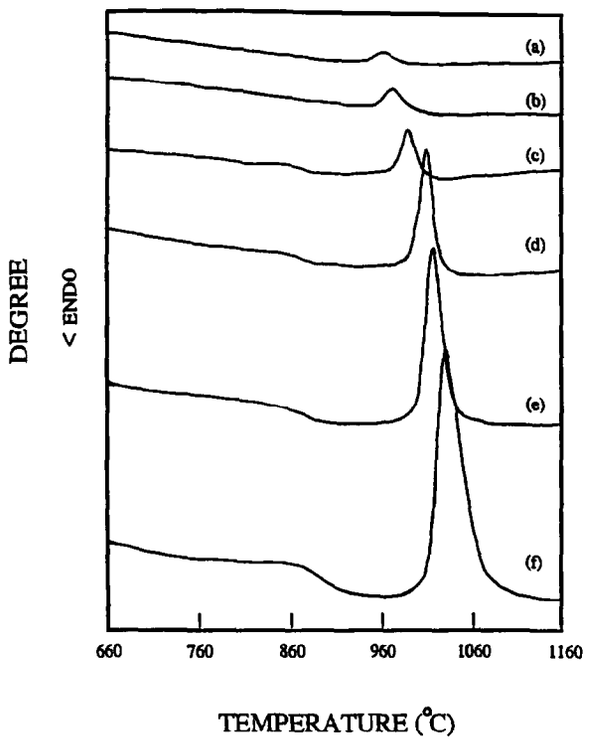

Fig. 2. DTA curves for IMS CA fibers with heating rates of (a) 3, (b) 5, (c) 10, (d) 20, (e) 40 and (f) 80°C/min.

The crystallized CA fibers which were used for DTA measurements were ground and checked for phase formation by XRD.

3 RESULTS AND DISCUSSION

The XRD result for the vitreous IMS CA fiber which was a ground powder form is shown in Fig. 1. Clear non-crystallinity is observed for this sample. DTA results for the CA fibers with various heating rates (3, 5, 10, 20, 40 and 8°C/min) appear in Fig. 2. Crystallization peak temperatures (T_p) for the CA fibers with different heating rates are listed in Table 1. The faster the scan speed, the higher T_p becomes because the whole sample can not follow the rapid temperature increase of the DTA due to heat transfer problems. Thus, the sample will crystallize at a higher temperature with rapid heating.

The DTA results were analyzed primarily using the Kissinger equation:[18]

$$\ln (\phi/T_p^2) = -E_{ck}/RT_p + \text{const.} \quad (1)$$

where ϕ is the DTA heating rate; T_p is crystallization peak temperature; E_{ck} is the activation energy

Table 1. Crystallization peak temperatures (T_p) of IMS CA Fibers (°C)

DTA heating rates (°C/min)					
3	5	10	20	40	80
948	968	983	995	1021	1034

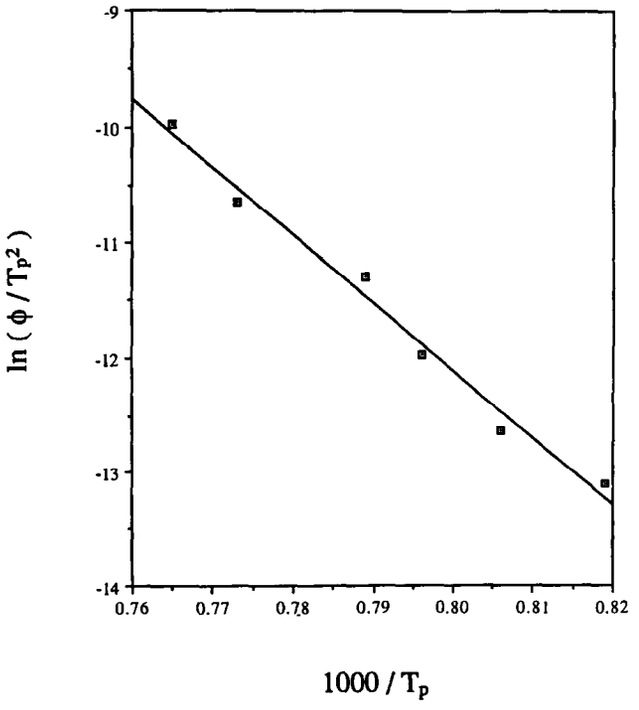

Fig. 3. Kissinger plot for IMS CA fibers.

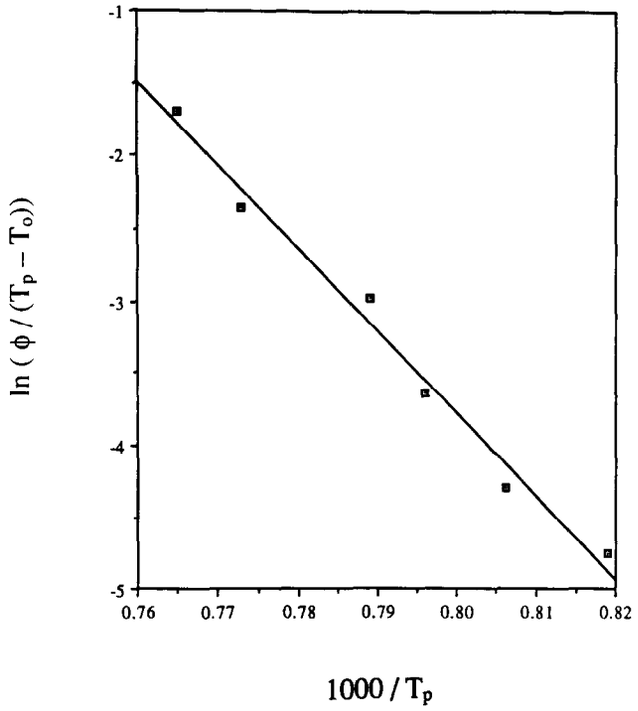

Fig. 4. Augis–Bennett plot for IMS CA fibers.

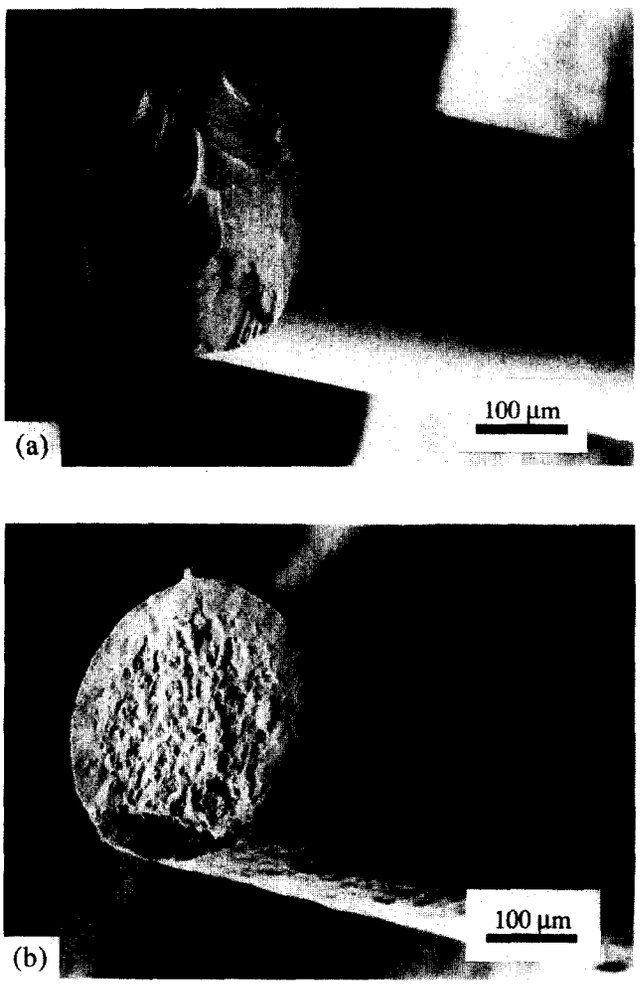

Fig. 5. SEM of fractured surface of (a) vitreous (b) crystallized (during DTA scan: 40°C/min from 600 to 1200°C) IMS CA fibers.

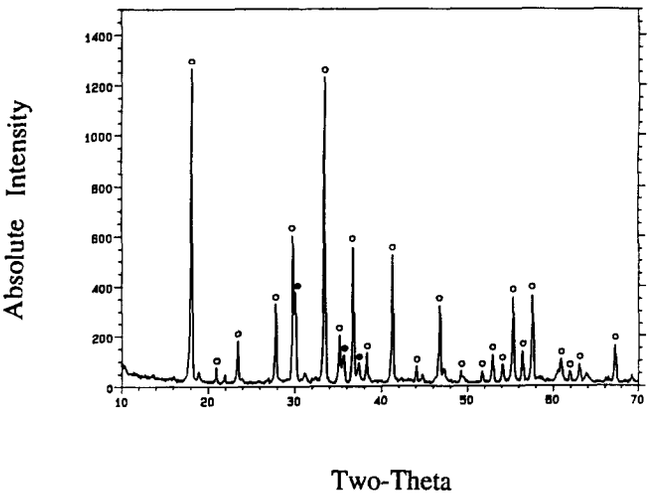

Fig. 6. XRD pattern showing $Ca_{12}Al_{14}O_{33}$ (○) and $CaAl_2O_4$ (●) formation for the IMS CA fibers crystallized during DTA scan (40°C/min from 600 to 1200°C).

for crystallization estimated by the Kissinger method; and R is the gas constant. Figure 3 represents the plot of ln (ϕ/T_p^2) vs $1/T_p$. From the slope of the plot E_{ck} value could be determined as 490 kJ/mol for the CA fibers. To confirm the accuracy of this activation energy value the following Augis–Bennett[19] equation can be applied:

$$\ln (\phi/(T_p - T_o)) = -E_{cab}/RT_p + \text{const.} \qquad (2)$$

where T_o is the temperature from which the DTA scan starts (here, 600°C) and E_{cab} is the activation energy for crystallization via the Augis–Bennett method. The E_{cab} value can also be calculated from the slope of ln $(\phi/(T_p - T_o))$ vs $1/T$ plot as shown in Fig. 4. The E_{cab} value for the CA fiber was determined as 477 kJ/mol.

Figure 5 shows the SEM photographs of fractured (a) vitreous as-spun and (b) crystallized CA fibers. A clear glassy fractured surface is shown for the as-spun CA fiber. Surface roughness which represents crystallinity is shown for the crystallized CA fibers.

The XRD results for the crystallized CA fibers are shown in Fig. 6. The peaks represent formation of $Ca_{12}Al_{14}O_{33}$ as a major phase and $CaAl_2O_4$ as a minor phase in the crystallized CA fibers as expected from the phase diagram of $CaO–Al_2O_3$.

4 CONCLUSIONS

From DTA measurements the crystallization temperature range for the IMS CA fibers was determined as 948–1034°C according to DTA heating rates. The activation energy values for crystallization of the CA fibers from DTA results were determined as 490 and 477 kJ/mol via Kissinger and

Augis–Bennett methods, respectively. SEM for the vitreous CA fibers showed glassy fracture, whereas that for crystallized CA fibers showed surface roughness. The XRD result from the crystallized CA fibers showed $Ca_{12}Al_{14}O_{33}$ formation as a primary phase and $CaAl_2O_4$ formation as a minor phase.

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REFERENCES

1. CUNNINGHAM, R. E., RAKESTRW, L. F. & DUNN, S. A., Inviscid melt spinning of filaments via chemical jet stabilization. In *AIChE Symposium Series, Vol. 180, Spinning Wire From Molten Metal*, ed. J. W. Moltern & W. J. Privott. American Institute of Chemical Engineers, New York, NY, 1978.
2. DUNN, S. A. & PAQUETTE, E. G., Redrawn inviscid melt-spun fibers–potential low-cost composite reinforcements. *Adv. Ceram. Mater.*, **2** (1987) 804–8.
3. WALLENBERGER, F. T., WESTON, N. E. & BROWN, S. D., Calcium aluminate glass fibers: Drawing from supercooled melts versus inviscid melt spinning. *Mater. Lett.*, **11** (1991) 229–35.
4. WALLENBERGER, F. T., WESTON, N. E. & BROWN, S. D., Melt processed calcium aluminate fibers: Structural and optical properties. In *SPIE Proc., Vol. 1484, Growth and Characterization of Materials for Infrared Detectors.* Society of Photo-Optical Instrumentation Engineers, Bellingham, WA, 1991.
5. WALLENBERGER, F. T., WESTON, N. E. & MOTZFELDT, K., Inviscid melt spinning of alumina fibers: Jet stabilization mechanism. *Ceram. Engng Sci. Proc.*, **12** (1991) 1039–47.
6. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Inviscid melt-spinning: strength of amorphous alumina fibers, In *Advanced Structural Inorganic Composites*, ed. P. Vincenzini. Elsevier Press, Amsterdam, North-Holland, 1991.
7. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Melt spun calcium aluminate IR fibers: Product value. In *Proc. 2nd Int. Conf. on Electronic Materials*, ed. R. P. H. Chang *et al.* Mater. Res. Soc., Pittsburgh, PA, 1991.
8. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Inviscid melt spinning: As-spun crystalline alumina fibers *J. Mater. Res.*, **5** (1990) 2682–6.
9. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Inviscid melt spinning of alumina fibers: Jet stabilization dynamics. *SAMPE Quart.*, **22** (1990) 15–22.
10. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Melt spun calcium aluminate fibers: Infrared transmission. *J. Non-Cryst. Solids*, **124** (1990) 116–9.
11. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Inviscid melt spinning—IMS Crystallization of amorphous alumina fibers. *SAMPE Quart.*, **21** (1990) 30–4.
12. WALLENBERGER, F. T., WESTON, N. E. & DUNN, S. A., Inviscid melt spinning (IMS): As-spun amorphous alumina fibers. *Mater. Lett.*, **9** (1990) 121–7.
13. WALLENBERGER, F. T., Melt spinning of amorphous alumina fibers, *Am. Soc. Bull.*, **69** (1990) 1646–8.
14. WALLENBERGER, F. T., WESTON, N. E., MOTZFELDT, K. & SWARTFAGER, D. G., Inviscid melt-spinning of alumina fibers: chemical jet stabilization. *J. Am. Ceram. Soc.*, **75**(3) (1992) 629–36.
15. MITCHELL, B. S., PhD Thesis, University of Wisconsin-Madison, 1991.
16. MITCHELL, B. S., YON, K.-Y., DUNN, S. A. & KOUTSKY, J. A., Phase identification in calcia–alumina fibers crystallized from amorphous precursors. *J. Non-Cryst. Sol.*, **152** (1993) 143–9.
17. SUNG, Y.-M., DUNN, S. A. & KOUTSKY, J. A., Inviscid melt spinning (IMS) and phase identification of CaO–Al_2O_3–MgO (CAM) fibers. *Ceram. Int.*, **20**(5) (1994) 337–41.
18. KISSINGER, H. E., Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand.* (U.S.), **57** (1956) 217–21.
19. AUGIS, J. A. & BENNETT, J. E., Calculation of the Avrami parameter for heterogeneous solid-state reactions using a modification of the Kissinger method. *J. Therm. Anal.*, **13** (1978) 283–92.