Lawrence Berkeley National Laboratory

Recent Work

Title

THE CRYSTALLIZATION BEHAVIOUR OF A Mg-Si-O-N GLASS

Permalink

<https://escholarship.org/uc/item/1wv4435d>

Authors

Shaw, T.M.
Thomas, G.

Publication Date

1983-03-01

UC-25
LBL-17271
c.1

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 20 1984

LIBRARY AND
DOCUMENTS SECTION

Published as a chapter in Progress in Nitrogen
Ceramics, F.L. Riley, Ed., Martinus Nijhoff Publishers,
The Netherlands, 1983

THE CRYSTALLIZATION BEHAVIOUR OF A Mg-Si-O-N GLASS

T.M. Shaw and G. Thomas

March 1983

For Reference

Not to be taken from this room

LBL-17271
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE CRYSTALLIZATION BEHAVIOUR OF A Mg-Si-O-N GLASS

T. M. Shaw and G. Thomas

Department of Materials Science and Mineral Engineering
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

This research was supported by the National Science Foundation grant DMR-77-24022. Technical staff and facilities were provided by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

ABSTRACT

The crystallization behaviour of a glass of composition 59 wt.% SiO_2 , 32 wt.% MgO and 9 wt.% Si_3N_4 has been investigated. The as-cooled glass was found to have separated into a magnesia rich and a silica rich phase on cooling. The magnesia rich phase in the glass could be readily crystallized to enstatite by heating to temperatures above 1000°C . In contrast the silica rich phase was highly resistant to crystallization at all temperatures. The microstructure developed during crystallization of the magnesia rich phase consisted of fan-like arrangements of lath shaped enstatite crystals and showed many of the features common to spherulitic crystal growth. A large volume change associated with crystallization of the magnesia rich phase resulted in the formation of porosity in crystallized glass samples. At temperatures above about 1300°C the spherulitic microstructure recrystallized to faceted grains of enstatite in regions close to the silica rich phase, the reaction apparently being initiated by softening of the silica rich phase. Also at higher temperatures silicon oxynitride crystallized out from the magnesia rich phase, appearing as small crystals situated between the lath shaped enstatite grains.

INTRODUCTION

Oxynitride glasses, present as thin intergranular films in hot-pressed or sintered silicon nitride materials, are now widely recognized as being responsible for the deterioration in properties of these materials at high temperatures. Several investigators have reported preparing bulk samples of oxynitride glasses¹⁻⁵ but so far there have been few investigations of their properties⁴. In particular there have been no systematic studies of the crystallization behaviour of oxynitride glasses. The present paper reports the results of a detailed study of crystallization in a Mg-Si-O-N glass. Emphasis is placed on identification of temperature ranges where crystallization occurs and characterization of the resulting microstructures.

EXPERIMENTAL

The glass used in the investigation was prepared by melting weighed amounts of SiO_2 , MgO and Si_3N_4 powders in a molybdenum crucible in an atmosphere of nitrogen. The melting schedule consisted of heating the powder mixture to 1700°C , holding at this temperature for four hours, then cooling to room temperature by turning off the power to the graphite heating elements. Cooling was sufficiently rapid for the temperature of the melt to fall below 1000° in about three minutes. The powder mixture was made up to give a melt with a composition of 59 wt.% SiO_2 , 32 wt.% MgO and 9 wt.% Si_3N_4 .

Small samples of the glass were given isothermal heat treatments in the temperature range 800° - 1350°C . Polished sections of the heat treated glass samples were examined using reflected light microscopy. Thin sections of the samples were used for transmitted polarized light microscopy and also to prepare specimens for transmission electron microscopy. Final thinning of T.E.M. specimens was carried out by ion

beam milling. Thinned specimens of both the as-cooled glass and heat treated glass were examined using Philips 301 and 400 microscopes operating at 100 kV. Energy dispersive and energy loss spectrometer attachments to the Philips 400 were used for composition analysis of the phases formed in the glass.

RESULTS AND DISCUSSION

Characterization of the glass.

On cooling the melt produced a light gray opaque glass. Examination of the microstructure of the glass using TEM revealed that the opaqueness was caused by separation of the glass into two distinct phases. A typical view of the microstructure, which consists of groups of droplets of a minor phase dispersed in a continuous glass matrix, is shown in fig. (1). Contrast between the two phases arises largely from preferential thinning of the minor phase during specimen preparation. Compositional analysis of the two phases, to be presented in detail elsewhere,⁶ showed that the minor phase contained both SiO_2 and Si_3N_4 but virtually no MgO , whereas the matrix phase contained SiO_2 , MgO and Si_3N_4 . From quantification of the analysis it was found that the silica-rich minor phase had a composition close to the SiO_2 - Si_3N_4 binary in the MgO - SiO_2 - Si_3N_4 system and contained about 4-5 wt.% Si_3N_4 . The matrix phase had a composition which lay close to the MgSiO_3 - $\text{Si}_2\text{N}_2\text{O}$ tie line in the MgO - SiO_2 - Si_3N_4 system and contained about 8-9 wt.% Si_3N_4 .

Crystallization.

Heat treatments at temperatures below 1000°C had little effect on the microstructure of the as-cooled glass. Some small crystals were observed after heating for long times at temperatures close to 1000°C but growth of the crystals was very slow. Once temperatures above 1000°C were reached the rate of crystallization rapidly increased and after heating for two hours at 1020°C crystallization had occurred throughout the glass. The crystalline phase formed during crystallization was identified as enstatite (MgSiO_3) by X-ray diffraction. Fig. (2)(a) shows a transmitted polarized light micrograph of the crystallized glass. Dark cross-like features are visible in several regions suggesting a spherulitic morphology in which fibrous crystals grow radially from a central nucleation site. Another feature of the microstructure was coarse porosity that formed throughout the glass as it crystallized (see Fig. 2(b). Comparison of the bulk density of the glass (2.68 grams/cc measured using sink float technique) with the density of enstatite (3.21 grams/cc) indicated that on the order of a 15% change in volume should accompany crystallization of the glass to enstatite. About 5% of this volume change could be accounted for by shrinkage of the sample during crystallization. The remaining 10% could be adequately accounted for by the formation of porosity in the sample, indicating that porosity in the sample results from the large volume change that accompanies crystallization of the glass.

Examination of the crystallized glass using TEM revealed that only the magnesia-rich matrix phase crystallized during heat treatment; the

silica-rich minor phase was unaffected and preserved its globular shape. The microstructure developed in the magnesia-rich phase (fig. (3)) consisted of lath shaped enstatite crystals several microns long and about $0.1\text{ }\mu\text{m}$ across arranged in fan-like arrays. Although the spherical clusters of crystals that are typical of a spherulitic morphology were not observed, the microstructure exhibited many of the features characteristic of spherulitic growth, i.e., diverging arrangements of fibrous crystals and noncrystallographic branching of the fibers. Similar microstructures were observed after the glass was given two hour heat treatments at 1050°C , 1100°C and 1200°C . Holding at higher temperatures produced changes in the crystallized microstructure subsequent to the crystallization of enstatite from the magnesia-rich glassy phase.

Fig. (4) shows the appearance of one of the silica-rich droplets present in the as-cooled glass after a heat treatment of two hours at 1350°C . The silica-rich phase, light gray areas in the dark field image shown in fig. (4), although uncrystallized is no longer confined to well defined droplets and has partly penetrated between the enstatite laths crystallized from the surrounding magnesia-rich glass. In addition, faceted grains of enstatite, dark regions in fig. (4), have developed in and around the glassy pocket. The appearance of the microstructure suggests that softening of the silica-rich phase has initiated recrystallization of the surrounding enstatite spherulites to a more equilibrium microstructure of faceted enstatite grains dispersed in a silica-rich glass.

A second difference observed in the microstructure after heating at temperature about 1300°C was the presence of a large number of small crystals in regions between individual enstatite laths that made up the spherulites. The crystals gave rise to extra reflections in electron diffraction pattern, as arrowed in fig. (5)(a), and could be clearly seen when imaged using one of these reflections, fig. (5)(b). From careful analysis of the diffraction patterns the crystals were identified as crystals of silicon oxynitride growing with a definite orientation relationship with respect to the enstatite laths. A possible explanation for this behavior is that during crystallization of enstatite from the magnesia-rich phase, nitrogen in the glass is rejected to regions between the enstatite laths. The nitrogen may then crystallize out as silicon oxynitride during high temperature heat treatments, the silicon oxynitride crystals nucleating heterogeneously on enstatite grains.

ACKNOWLEDGEMENTS

This work was supported by a grant from the National Science Foundation grant DMR-77-24022 and by the U. S. Department of Energy under Contract Number DE-ACO3-76SF00098. We are grateful to Dr. R. E. Loehman for supplying the material for the investigation.

REFERENCES

1. Mulfinger, H. O. J. Amer. Ceram. Soc. 49 (1966) 462-467.
2. Elmer, T. H. and M. E. Nordberg. J. Amer. Soc. 50 (1967) 275-279.
3. Dancy, E. A. and D. Janssen. Canadian Met. Quarterly 15 (1976) 103-110.
4. Jack, K. H. in Nitrogen Ceramics, Proc. NATO Advanced Study Institute, ed. F.L. Riley 257-261. Noordhoff (1977).
5. Loehman, R. E. J. Amer. Ceram. Soc. 62 (1979) 491-494.
6. Shaw, T. M. and R. E. Loehman and G. Thomas to be published.

FIGURE CAPTIONS

Figure 1. Bright field image of phase separation in the as-cooled glass.

Figure 2. Optical micrographs of a glass sample crystallized at 1020°C. (a) transmitted polarized light micrograph showing "spherulitic" contrast. (b) reflected light micrograph showing pores formed in the sample during crystallization.

Figure 3. Bright field electron micrograph of enstatite crystals grown from the glass during a heat treatment of two hours at 1020°C.

Figure 4. Dark field image showing the appearance of one of the silica droplets found in the as-cooled glass after heating for two hours at 1350°C.

Figure 5. (a) SAD from a glass sample crystallized at 1350°. The arrowed reflections indicate the presence of silicon oxynitride in the microstructure, (b) Dark field image of the silicon oxynitride crystals.

Fig. 1

XBB 802-1977

XBB 806-7155

Fig. 2a

XBB 809-10371

Fig. 2b

XBB 809-10374

Fig. 3

Fig. 4

XBB 809-10379

Fig. 5a

XBB 809-10375

Fig. 5b

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720