Developments in Strategic Materials

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The American Ceramic Society

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A Collection of Papers Presented at the
32nd International Conference on Advanced
Ceramics and Composites
January 27–February 1, 2008
Daytona Beach, Florida

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Developments in Strategic Materials

Preface

This proceedings issue, *Developments in Strategic Materials,* contains a collection of 28 papers presented during the 32nd International Conference on Advanced Ceramics and Composites, Daytona Beach, FL, January 27-February 1, 2008. Papers are included from five symposia as listed below

- Geopolymers
- Basic Science of Multifunctional Materials
- Science of Ceramic Interfaces
- Materials for Solid State Lighting

The first paper provides an overview on developments in oxynitride glasses. This paper was presented by Stuart Hampshire, University of Limerick, during the plenary session of the conference.

The editors thank the assistance of all the organizers and session chairs and to the authors and reviewers for their contribution and hard work. The successful international gathering of geopolymer researchers was directly due to the generous financial support for speakers, provided by the US Air Force Office of Scientific Research (AFOSR) through Dr. Joan Fuller, Program Director of Ceramic and Non-Metallic Materials, Directorate of Aerospace and Materials Science.

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Introduction

Organized by the Engineering Ceramics Division (ECD) in conjunction with the Basic Science Division (BSD) of The American Ceramic Society (ACerS), the 32nd International Conference on Advanced Ceramics and Composites (ICACC) was held on January 27 to February 1, 2008, in Daytona Beach, Florida. 2008 was the second year that the meeting venue changed from Cocoa Beach, where ICACC was originated in January 1977 and was fostered to establish a meeting that is today the most preeminent international conference on advanced ceramics and composites

The 32nd ICACC hosted 1,247 attendees from 40 countries and 724 presentations on topics ranging from ceramic nanomaterials to structural reliability of ceramic components, demonstrating the linkage between materials science developments at the atomic level and macro level structural applications. The conference was organized into the following symposia and focused sessions:

Symposium 1	Mechanical Behavior and Structural Design of Monolithic and Composite Ceramics
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	5th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Ceramic Armor
Symposium 5	Next Generation Bioceramics
Symposium 6	2nd International Symposium on Thermoelectric Materials for Power Conversion Applications
Symposium 7	2nd International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications
Symposium 8	Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT): An International Symposium in Honor of Prof. Yoshinari Miyamoto
Symposium 9	Porous Ceramics: Novel Developments and Applications

Symposium 10	Basic Science of Multifunctional Ceramics
Symposium 11	Science of Ceramic Interfaces: An International Symposium Memorializing Dr. Rowland M. Cannon
Focused Session 1	Geopolymers
Focused Session 2	Materials for Solid State Lighting

Peer reviewed papers were divided into nine issues of the 2008 Ceramic Engineering & Science Proceedings (CESP); Volume 29, Issues 2-10, as outlined below:

- Mechanical Properties and Processing of Ceramic Binary, Ternary and Composite Systems, Vol. 29, Is 2 (includes papers from symposium 1)
- Corrosion, Wear, Fatigue, and Reliability of Ceramics, Vol. 29, Is 3 (includes papers from symposium 1)
- Advanced Ceramic Coatings and Interfaces III, Vol. 29, Is 4 (includes papers from symposium 2)
- Advances in Solid Oxide Fuel Cells IV, Vol. 29, Is 5 (includes papers from symposium 3)
- Advances in Ceramic Armor IV, Vol. 29, Is 6 (includes papers from symposium 4)
- Advances in Bioceramics and Porous Ceramics, Vol. 29, Is 7 (includes papers from symposia 5 and 9)
- Nanostructured Materials and Nanotechnology II, Vol. 29, Is 8 (includes papers from symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials II, Vol. 29, Is 9 (includes papers from symposium 8)
- Developments in Strategic Materials, Vol. 29, Is 10 (includes papers from symposia 6, 10, and 11, and focused sessions 1 and 2)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD and BSD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 33rd International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2009) January 18–23, 2009 in Daytona Beach, Florida.

TATSUKI OHJI and ANDREW A. WERESZCZAK, Volume Editors
July 2008

Contents

OXYNITRIDE GLASSES

THERMOELECTRIC MATERIALS FOR POWER CONVERSION APPLICATIONS

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*This paper was presented at the 31st International Conference on Advanced Ceramics and Composites, held January 21-26, 2007 and was mistakenly excluded from the proceedings. It is being included in this 2008 proceedings.

GEOPOLYMERS

MULTIFUNCTIONAL CERAMICS

SCIENCE OF CERAMIC INTERFACES

MATERIALS FOR SOLID STATE LIGHTING

Oxynitride Glasses

DEVELOPMENTS IN OXYNITRIDE GLASSES: FORMATION, PROPERTIES AND CRYSTALLIZATION

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University of Limerick, Limerick, Ireland

ABSTRACT

Oxynitride glasses are effectively alumino-silicates in which nitrogen substitutes for oxygen in the glass network. They are found at triple point junctions and as intergranular films in silicon nitride based ceramics. The properties of silicon nitride, especially fracture behaviour and creep resistance at high temperatures are influenced by the glass chemistry, particularly the concentrations of modifyer, usually Y or a rare earth (RE) ion, and Al, and their volume fractions within the ceramic. This paper provides an overview of the preparation of M-Si-Al-O-N glasses and outlines the effects of composition on properties. As nitrogen substitutes for oxygen, increases are observed in glass transition (T_g) and dilatometric softening (T_{ds}) temperatures, viscosities, elastic moduli and microhardness. If changes are made to the cation ratios or different rare earth elements are substituted, properties can be modified. The effects of these changes on mechanical properties of silicon nitride based ceramics are discussed.

This paper also outlines new research on M-Si-Al-O-N-F glasses. It was found that fluorine expands the glass forming region in the Ca-Sialon system and facilitates the solution of nitrogen into glass melts. T_g and T_{ds} decreased with increasing fluorine substitution levels, whilst increasing nitrogen substitution resulted in increases in values for these thermal properties. Nitrogen substitution for oxygen caused increases in Young's modulus and microhardness whereas these two properties were virtually unaffected by fluorine substitution for oxygen.

Oxynitride glasses may be crystallized to form glass-ceramics containing oxynitride phases and a brief outline is presented.

INTRODUCTION

Oxynitride glasses were first discovered as intergranular phases in silicon nitride based ceramics[1,2] in which the composition, particularly Al content as well as N content, and volume fraction of such glass phases determine the properties of the silicon nitride. Oxynitride glasses can be formed when a nitrogen containing compound, such as Si_3N_4 (or AlN), dissolves in either a silicate or alumino-silicate liquid at ~1600-1700°C which then cools to form a M-Si-O-N or M-Si-Al-O-N glass (M is usually a di-valent [Mg, Ca] or tri-valent [Y, Ln] cation). In particular, the chemistry of these oxynitride glasses has been shown to control high temperature mechanical properties and ambient fracture behaviour of silicon nitride based ceramics[1-4]. The desire to understand the nature of these grain boundary phases has resulted in a number of investigations on oxynitride glass formation and properties[5-12].

EXPERIMENTAL PROCEDURE

The extent of the glass forming regions in various M-Si-Al-O-N systems (M = Mg, Y, Ca, etc.) has been studied previously[5,7,8] and represented using the Jänecke prism with compositions expressed in equivalent percent (e/o) of cations and anions[5,7] instead of atoms or gram-atoms. One equivalent of any element always reacts with one equivalent of any other element or species. For a system containing three types of cations, A, B and C with valencies of v_A, v_B, and v_C, respectively, then:

Equivalent concentration of A = (v_A [A])/(v_A [A] + v_B[B] + v_C[C]), where [A], [B] and [C] are, respectively, the atomic concentrations of A, B and C, in this case, Si^{IV}, Al^{III} and the metal cation, M, with its normal valency.

If the system also contains two types of anions, C and D with valencies v_C and v_D, respectively, then:

Equivalent concentration of C = (v_C [C])/(v_C [C] + v_D[D]), where [C] and [D] are, respectively, the atomic concentrations of C and D, i.e. O^{II} and N^{III}.

Fig. 1 shows the glass forming region in the Y-Si-Al-O-N system which was studied by exploring glass formation as a function of Y:Si:Al ratio on vertical planes in the Jänecke prism representing different O:N ratios. The region is seen to expand initially as nitrogen is introduced and then diminishes when more than 10 e/o N is incorporated until the solubility limit for nitrogen is exceeded at ~28 e/o N.

Preparation of glasses involves mixing appropriate quantities of silica, alumina, the modifying oxide and silicon nitride powders by wet ball milling in isopropanol for 24 hours, using sialon milling media, followed by evaporation of the alcohol before pressing into pellets. Batches of 50-60g are melted in boron nitride lined graphite crucibles at 1700-1725°C for 1h under 0.1MPa nitrogen pressure in a vertical tube furnace, after which the melt is poured into a preheated graphite mould. The glass is annealed at a temperature close to the glass transition temperature (T_g) for one hour to remove stresses and slowly cooled.

Bulk densities were measured by the Archimedes principle using distilled water as the working fluid. X-ray analysis was used to confirm that the glasses were totally amorphous. Scanning electron microscopy allowed confirmation of this and assessment of homogeneity.

Differential thermal analysis (DTA) was carried out in order to measure the glass transition temperature, T_g, which is observed as the onset point of the endothermic drift on the DTA curve, corresponding to the beginning of the transition range.

The viscosity results presented were obtained from a high temperature "deformation-under-load" (compressive creep) test on cylinders of 10 mm diameter in air between 750 and 1000°C. These have also been compared with results from three point bending tests (bars of dimensions: 25mm x 4mm (width) x 3mm (height) with a span of 21 mm. Viscosity, η, is derived from the relationships between (i) the stress/strain relations in an elastic solid and

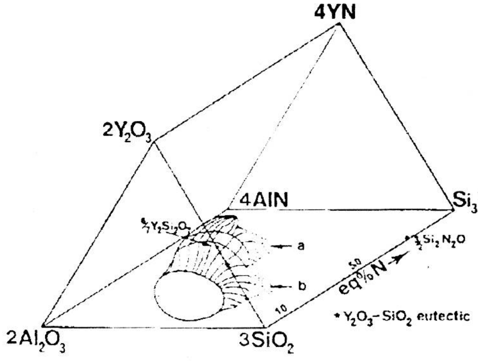

Fig. 1 Glass forming region of the Y-Si-Al-O-N system on cooling from 1700°C[5,7]

(ii) those that relate to a viscous fluid:

$$\eta = \sigma / [2(1+\upsilon)\dot{\varepsilon}] \qquad (1)$$

where σ and $\dot{\varepsilon}$ are the applied stress and the creep rate on the outer tensile fibre and υ is Poisson's ratio (taken as 0.5). The results from both types of test show good agreement[5,7,12].

RESULTS AND DISCUSSION

EFFECTS OF NITROGEN ON PROPERTIES

The first systematic studies on the effect of replacing oxygen by nitrogen on properties of oxynitride glasses with fixed cation compositions were reported by Drew, Hampshire and Jack[5,7]. Fig. 2 shows that for all Ca-, Mg-, Nd- and Y- Si-Al-O-N glasses with a fixed cation composition (in e/o) of 28Y: 56Si: 16Al (standard cation composition), incorporation of nitrogen resulted in increases in glass transition temperature (T_g). They also reported that nitrogen increases microhardness, viscosity, resistance to devitrification, refractive index, dielectric constant and a.c. conductivity. In a more extensive study of the Y-Si-Al-O-N system[8], it was confirmed that glass transition temperature (T_g), viscosity, microhardness and elastic moduli all increase systematically while coefficient of thermal expansion (CTE) decreases with increasing nitrogen:oxygen ratio for different series of glasses.

As shown in Fig. 3, values of Young's modulus increase by 15 to 25% as ~17-20 e/o N is substituted for oxygen at fixed cation ratios[8,9]. The coefficient of thermal expansion (α) was found to decrease as N content increased[8] at fixed Y:Si:Al ratios.

Fig. 4 shows the effects of nitrogen content on viscosity for a series of glasses[13] with composition (in e/o) of 28Y:56Si:16Al:(100-x)O:xN (x=0, 5, 10, 18). It can be seen that viscosity increases by much more than 2 orders of magnitude as 18 e/o oxygen is replaced by nitrogen. Similar trends have been reported for other Y-Si-Al-O-N glasses with different cation ratios[12].

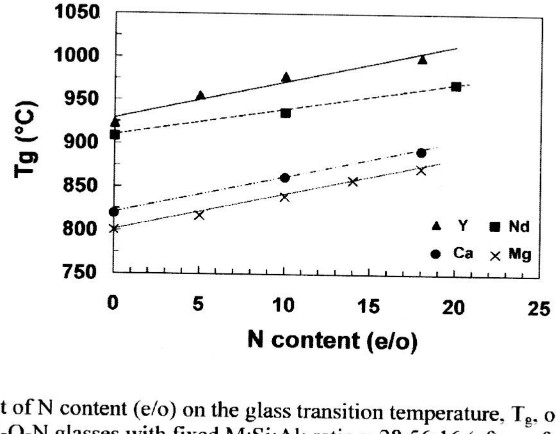

Fig. 2. Effect of N content (e/o) on the glass transition temperature, T_g, of Mg-, Ca-, Nd- and Y-Si-Al-O-N glasses with fixed M:Si:Al: ratio = 28:56:16 (after ref. 5).

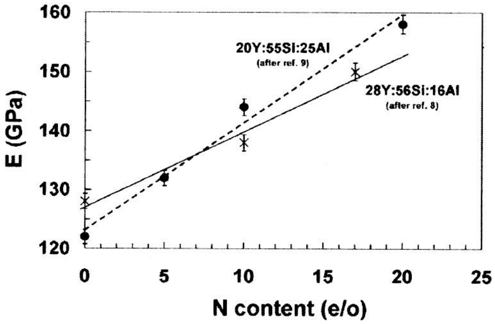

Fig. 3. Effect of N (e/o) on Young's modulus (E) for glasses with fixed Y:Si:Al ratios (data from refs. 8 and 9).

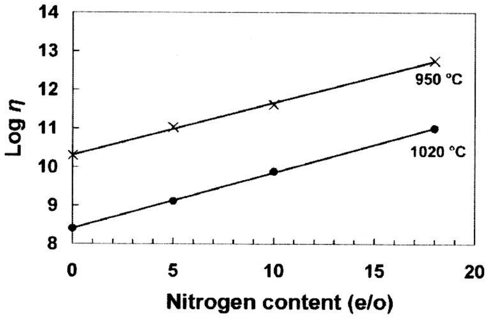

Fig. 4 Effect of N (e/o) on viscosity for glass with fixed Y:Si:Al ratio = 28:56:16 at 950 and 1020 °C (data from ref. 13).

All of these increases in properties are known to be due to the increased cross-linking within the glass structure as 2-coordinated bridging oxygen atoms are replaced by 3-coordinated nitrogen atoms[5-9]. In certain cases, some nitrogen atoms may be bonded to less than three Si atoms, as in:

(i) $\equiv Si - N^{-} - Si \equiv$

or

(ii) $\equiv Si - N^{2-}$

The local charge on the so-called "non-bridging" nitrogen ions is balanced by the presence of interstitial modifying cations (Y, etc.) in their local environment. In the case of silicate glasses, non-bridging oxygen atoms replace bridging oxygen atoms at high modifier contents. In (i) above, while the N atom links two silicon atoms rather than three, it still effectively "bridges" the network ions.