Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials

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Edited by

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A Collection of Papers Presented at the 38th International Conference on Advanced Ceramics and Composites
January 27–31, 2014
Daytona Beach, Florida

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Preface

This CESP issue contains papers that were presented during two symposia held during the 38th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, Florida, January 26-31, 2014:

- Symposium 7: 8th International Symposium on Nanostructured Materials and Nanocomposites
- Symposium 8: 8th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

Over 170 contributions (invited talks, oral presentations, and posters) were presented by participants from universities, research institutions, and industry, which offered interdisciplinary discussions indicating strong scientific and technological interest in the field of nanostructured systems. This issue contains 23 peer-reviewed papers that cover various aspects and the latest developments related to nanoscaled materials and functional ceramics.

The 8th International Symposium on AMPT also honored Professor Stuart Hampshire, University of Limerick, Ireland, recognizing his outstanding contributions to science and technology of advanced structural and multifunctional ceramics and his tireless efforts in promoting their wide scale industrial applications.

The editors wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their valuable comments and suggestions. Financial support from the Engineering Ceramics Division of The American Ceramic Society (ACerS) and industry sponsors is gratefully acknowledged. The invaluable assistance of the ACerS staff of the meetings and publication departments, instrumental in the success of the symposium, is gratefully acknowledged.

We believe that this issue will serve as a useful reference for the researchers and technologists interested in science and technology of multifunctional or nanostructured materials and devices.

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Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of seven issues published from manuscripts submitted and approved for the proceedings of the 38th International Conference on Advanced Ceramics and Composites (ICACC), held January 26-31, 2014 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 38th ICACC hosted more than 1,000 attendees from 40 countries and approximately 800 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following 19 symposia and sessions.

Symposium 1	Mechanical Behavior and Performance of Ceramics and Composites
Symposium 2	Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
Symposium 3	11th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
Symposium 4	Armor Ceramics
Symposium 5	Next Generation Bioceramics and Biocomposites
Symposium 6	Advanced Materials and Technologies for Energy Generation and Rechargeable Energy Storage
Symposium 7	8th International Symposium on Nanostructured Materials and Nanocomposites
Symposium 8	8th International Symposium on Advanced Processing & Manufacturing Technologies for Structural & Multifunctional Materials and Systems (APMT), In Honor of Prof. Stuart Hampshire

Symposium 9	Porous Ceramics: Novel Developments and Applications
Symposium 10	Virtual Materials (Computational) Design and Ceramic Genome
Symposium 11	Advanced Materials and Innovative Processing ideas for the Industrial Root Technology
Symposium 12	Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases)
Symposium 13	Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy
Focused Session 1	Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials
Focused Session 2	Advanced Ceramic Materials and Processing for Photonics and Energy
Focused Session 3	Rare Earth Oxides for Energy, Optics and Biomedical Applications
Focused Session 4	Ion-Transport Membranes
Special Session	2nd Pacific Rim Engineering Ceramics Summit
Special Session	3rd Global Young Investigators Forum

The proceedings papers from this conference are published in the below seven issues of the 2014 CESP; Volume 35, Issues 2-8, as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites IX, CESP Volume 35, Issue 2 (includes papers from Symposium 1)
- Advances in Solid Oxide Fuel Cells X, CESP Volume 35, Issue 3 (includes papers from Symposium 3)
- Advances in Ceramic Armor X, CESP Volume 35, Issue 4 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics VII, CESP Volume 35, Issue 5 (includes papers from Symposia 5 and 9)
- Advanced Processing and Manufacturing Technologies for Nanostructured and Multifunctional Materials, CESP Volume 35, Issue 6 (includes papers from Symposia 7 and 8)
- Ceramic Materials for Energy Applications IV, CESP Volume 35, Issue 7 (includes papers from Symposia 6 and 13)
- Developments in Strategic Materials and Computational Design V, CESP Volume 35, Issue 8 (includes papers from Symposia 2, 10, 11, and 12 and from Focused Sessions 1, 2, 3, and 4); the 3rd Global Pacific Rim Engineering Ceramics Summit; and the 3rd Annual Global Young Investigator Forum

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 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 39th International Conference on Advanced Ceramics and Composites (http://www.ceramics.org/daytona2015) January 25-30, 2015 in Daytona Beach, Florida.

To purchase additional CESP issues as well as other ceramic publications, visit the ACerS-Wiley Publications home page at www.wiley.com/go/ceramics.

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Volume Editors
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Multifunctional Materials

OXYNITRIDE GLASSES AS GRAIN BOUNDARY PHASES IN SILICON NITRIDE: CORRELATIONS OF CHEMISTRY AND PROPERTIES

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ABSTRACT

Silicon nitride is recognized as a high performance material for both wear resistant and high temperature structural applications. Oxide sintering additives, such as yttrium or rare earth oxides plus alumina or magnesia, are used in processing the ceramic to provide conditions for liquid phase sintering. The oxynitride liquid promotes densification and on cooling remains as an oxynitride glass at triple point junctions and also as intergranular films between the elongated hexagonal β-Si_3N_4 grains. The properties of silicon nitride, especially fracture behavior and creep resistance at high temperatures are influenced by the glass chemistry, particularly the concentration of modifier, and the volume fraction within the ceramic.

This paper provides an overview of liquid phase sintering of silicon nitride ceramics, grain boundary oxynitride glasses and the effects of chemistry and structure on properties. As nitrogen substitutes for oxygen in bulk oxynitride glasses, increases are observed in glass transition and softening temperatures, viscosities, elastic moduli and thermal expansion coefficient. These property changes are compared with known effects of grain boundary glass chemistry on properties of silicon nitride ceramics.

INTRODUCTION – SINTERING AND MICROSTRUCTURAL DEVELOPMENT IN SILICON NITRIDE CERAMICS

Silicon nitride has been the subject of major programmes of research for the last four decades, principally in response to the challenge to develop a suitable ceramic for high temperature structural applications in gas turbine engines[1,2]. The search for improved materials has led to a better understanding of the role of sintering additives in the densification and microstructural development of silicon nitride-based ceramics and the consequences for final properties[2,3]. Improvements in powder manufacture and ceramic forming techniques and the development of alternative firing processes has led to a complete "family" of silicon nitride materials[1,2] including Reaction-bonded Silicon Nitride RBSN, Hot-pressed Silicon Nitride HPSN, Sintered Silicon Nitride (SSN), Gas-pressure Sintered Silicon Nitride (GPSSN), Sintered Reaction-bonded Silicon Nitride (SRBSN), Hot-Isostatically-Pressed Silicon Nitride (HIPSN) and solid solutions known as SiAlONs, after their major elemental components[4].

Oxynitride glasses were first discovered in silicon nitride based ceramics as intergranular phases which are formed because the sintering additives, usually mixed oxides such as yttria plus alumina, promote liquid phase densification during high temperature processing[1-6]. At ~1750-1900°C, the additives react with silicon nitride and silica present on the nitride particle surfaces to form a Y-Si-Al-O-N liquid phase which promotes densification and transformation of α- to β-Si_3N_4 through a solution-diffusion-precipitation process, according to the following reaction[2]:

$$\alpha\text{-}Si_3N_4 + SiO_2 + M_xO_y + Al_2O_3 \rightarrow \beta\text{-}Si_3N_4 + \text{Y-Si-Al-O-N phase} \quad (1)$$

M = Y or RE (other rare earths) the oxides of which may be used in place of yttria[7,8] and some silicon nitrides are sintered with RE (incl. Y) oxides plus MgO[9,10] in place of alumina. Growth of elongated prismatic hexagonal β-Si_3N_4 crystals occurs along their c-axes to form an interlocking microstructure and, following sintering, the liquid cools as an intergranular glass, at triple points or as vitreous films between grains with film thickness in the range 0.5–1.5 nm, depending strongly on chemical composition[7].

Figure 1 shows a scanning electron micrograph of silicon nitride densified with 6 wt.% yttria and 2 wt.% alumina[11]. The microstructure consists of β-Si_3N_4 grains, with high aspect (length to diameter) ratios, surrounded by a Y-Si-Al-O-N glass phase (white). Figure 2 shows a high resolution transmission electron microscope (HRTEM) image of two β-Si_3N_4 grains separated by an amorphous intergranular film (IGF) leading to an oxynitride glass triple pocket (TP)[11]. The grain boundary chemistry (RE, Al or Mg content and O:N ratio) and volume fraction of these glass phases control the microstructural development which determines the overall properties of the ceramic, especially fracture resistance, ambient and high temperature strengths, creep resistance and oxidation resistance[2,5,6,8]. Essentially, the elongated grains canfunction as reinforcements similar to whiskers or fibers in reinforced ceramics. As an example, with Y_2O_3/Al_2O_3 additives, as the Y:Al ratio of the intergranular glass increases, fracture toughness of the ceramic also increases which is indicative of easier debonding at the silicon nitride grain interfaces[6], favouring the activation of toughening mechanisms such as crack-deflection and crack-bridging[6,8,10]. The evolution of β-Si_3N_4 microstructures during sintering is influenced by the adsorption of RE cations at silicon nitride grain surfaces and by the viscosity of the intergranular liquid. Theoretical and scanning transmission electron microscopy show[12] that RE atoms exhibit different tendencies to segregate from the liquid to grain surfaces and have different binding strengths at these surfaces.

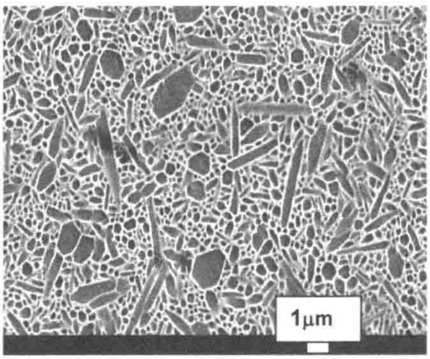

Figure 1. Scanning electron micrograph of silicon nitride (6 wt.% Y_2O_3 + 2 wt.% Al_2O_3) showing dark β-Si_3N_4 grains and bright YSiAlON glass[11].

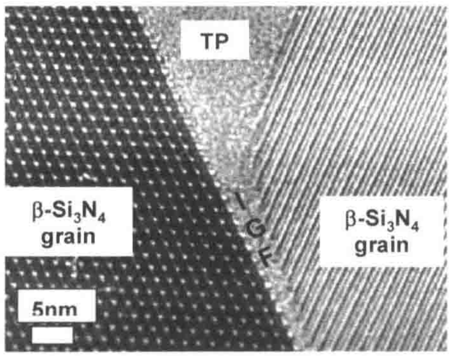

Figure 2. TEM micrograph of silicon nitride showing two β-Si_3N_4 grains, a triple point (TP) glass pocket and intergranular film (IGF)[11].

The desire to understand more fully the nature of these grain boundary phases resulted in many further investigations of oxynitride glass formation and properties[13-28]. In the following sections, an overview is given of oxynitride glass synthesis and the effects of composition on properties.

With a knowledge of silicon nitride additive compositions and quantities and also properties of the bulk glasses, the residual stresses in the interfacial glasses can be calculated. This allows correlations of mechanical behaviour of the ceramic with grain boundary glass chemistry.

SYNTHESIS OF OXYNITRIDE GLASSES AND REPRESENTATION OF SYSTEMS

Oxynitride glasses can be formed when a nitrogen containing compound, such as Si_3N_4 (or AlN), dissolves at high temperatures in either a silicate or alumino-silicate liquid 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, RE] cation). The extent of the glass forming regions in various M-Si-Al-O-N systems has been studied previously and represented using the Jänecke prism[14,18,19] with compositions expressed in equivalent percent (eq.%) of cations and anions 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, M1, M2 and M3 with valencies of v_{M1}, v_{M2}, and v_{M3}, respectively, then:

$$\text{Equivalent \% of M1} = (v_{M1}\,[M1])\times 100/(v_{M1}\,[M1] + v_{M2}[M2] + v_{M3}[M3]) \qquad (2)$$

where [M1], [M2] and [M3] are, respectively, the atomic concentrations of M1, M2 and M3, in this case, Si^{IV}, Al^{III} and, for example Y^{III}, with its normal valency of 3.

If the system also contains two types of anions, X1 and X2 with valencies v_{X1} and v_{X2}, respectively, then:

$$\text{Equivalent concentration of X1} = (v_{X1}\,[X1])\times 100/(v_{X1}\,[X1] + v_{X2}[X2]) \qquad (3)$$

where [X1] and [X2] are, respectively, the atomic concentrations of X1 and X2, i.e. O^{II} and N^{III}.

Figure 3 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 greater than ~10 eq.% N is incorporated until the solubility limit for nitrogen is exceeded at approximately 28 eq.% N.

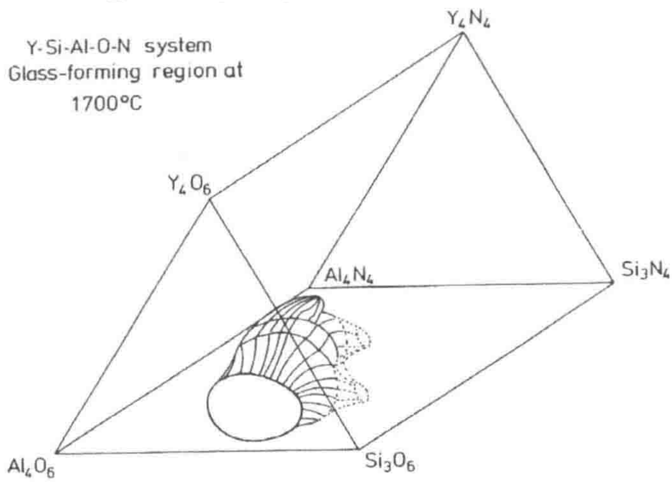

Figure 3. Glass forming region of the Y-Si-Al-O-N system on cooling from 1700°C[19]

Preparation of glasses involves weighing the appropriate quantities of silica, alumina, the modifying oxide and silicon nitride powders and ball milling in isopropanol for 24 hours, using sialon milling media, followed by evaporation of the alcohol before pressing into pellets.