海外の話題

# Glass-Ceramics : Recent Advances and Trends

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Because they are formed by controlled internal nucleation and crystallization of glass, glass-ceramics are the most uniform and reproducible of ceramic materials. Nevertheless, they are restricted in composition to regions of glass-formation, normally silica based, and therefore do not possess the extreme hardness and stiffness of ceramics based on alumina, zirconia, carbides and nitrides. Nor do silicate materials possess the active electronic properties found in oxides with the perovskite structure (ferroelectrics, piezoelectrics, superconductors) or certain of the chalcogenides (semiconductors, electro-optics). Despite these shortcomings, glass-ceramic materials are entering a new growth phase based on improved mechanical properties, excellent electrical insulating (dielectric) characteristics, and a wide variety of aesthetic features, including textures, tints, and translucency ranging from opaque to completely transparent.

The improvement in mechanical properties of glass-ceramics has taken two forms: i) improved body strength and toughness in monolithic chain-silicate based materials, and ii) dramatic developments in fiber-reinforced glass-ceramics allowing graceful or non-catastrophic failure. Chain silicates are crystalline phases composed of a backbone of silica tetrahedra polymerized in one dimension. When crystallized from glass, these crystals form randomly-oriented needles or blades which interlock forming a microstructure reminiscent of natural jade. Good stength and unusual toughness result. In addition, some of these phases are susceptible to splintering or other cleavage phenomena associated with twinning which absorb energy, thus deflecting or blunting cracks and further increasing toughness. Glass-ceramics based upon acicular phases canasite (alkali-lime fluosilicate), richterite (alkali-Mg-fluosilicate), and enstatite ($MgSiO_3$) have all shown abraded flexural strengths and enstatite ($MgSiO_3$) have all shown abraded flexural strengths and fracture toughness in the range of 200 to 400 MPa and 3 to 6 MPa $m^{1/2}$, respectively, over double that of conventional glass-ceramics. Current applications include durable institutional tableware, and projected uses involve architectural materials and matrices for high temperature ceramic composites.

Glass-ceramic composites produced by incorporating state-of-the-art strong ceramic fibers in powdered crystallizable glass followed by hot pressing have demonstrated very high strenght and graceful failure. The key to this behavior lies in the very high strength and stiffness of new ceramic fibers like Nippon Carbon's silicon-oxycarbide (NICALON®), which can carry most of the load in a glass-ceramic composite. The glass-ceramic matrix can be tailored to bond in such a way that it holds the fiber composite firmly but does not allow fractures to propagate through the fibers. Such an intermediate bond produces a fiber pull-out failure mechanism absorbing great energy and achieving a gradual or pseudo-ductile flow before ultimate fracture. The crystalline glass-ceramic matrix will not flow at high temperature and also serves to protect the fibers from oxidation. Potential applications for such galss-ceramic composites include aircraft engine parts and space structures.

A large potential application for glass-ceramics developed in recent years at IBM and elsewhere involves the use of cordierite (Mg-Al-silicate) devitrifying frits in co-fired multilayer substrates for electronic packaging. A cordierite-based substrate has several advantages over currently widely-used alumina. A lower dielectric constant, 5-6, versus 7-8 for alumina, allows faster circuit response by minimizing capacitive effects. Also, cordierite frits can be fired below the melting point of copper, a far more ductile conductor than molybdenum, which must be used with the higher fired alumina-based system. In addition, recent developments in the area of microporous glass-ceramics have produced materials with dielectric constants below 3. The key advance here is the ability to nucleate very fine ($<1\mu m$) hydrogen bubbles uniformly in crystallizing glass.

Several recent applications for internally-nucleated glass-ceramics rely on the ability to control the crystal size in these materials, thereby developing a desired translucency or transparency with special aesthetic value. Haze-free, low-thermal-expansion, transparent glass-ceramics have found growing markets in versatile and attractive rangetop and microwave cookware (Corning VISION®) and as wood-stove windows. Translucent dental restorations, custom tinted to closely resemble natural teeth have been marketed in North America by Dentsply under the trade-name DICOR®. Translucent, tinted, and textured glass-ceramics are increasingly used in Japan and elsewhere in the form of architectural sheet (NEOPARIES®) produced by the Nippon Electric Glass Co. The ability to form unique and reproducable microstructures in glass-ceramics is the common thread to these successful developments.

〔筆者紹介〕
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1935年　カナダ生まれ
1962年　マサチューセッツ工科大学でPh.D.を取得
〃　コーニング・グラス社入社
感光性ガラス、結晶化ガラス等の研究に従事
多数の特許・論文を発表
1975年　Elected Fellow of American Ceramic Society
現　在　コーニング・グラス社Research Fellow

# Glass Ceramics：Recent Advances and Trends

## （要　約）

# 最近の結晶化ガラスあれこれ

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結晶化ガラスは、焼結セラミックス材料に比べ特性をコントロールしやすいという長所があるが、一方では、ガラスから出発する為に組成に制限があり、セラミックスのような機械的・電気的特性が得られないという短所をあわせもっていた。しかし最近この点が改善され、結晶化ガラスは新しい用途を見いだしつつある。

機械的性質の改善には１）結晶化ガラス自身の強度向上、および２）セラミックス繊維による強化の２つの方向が試みられている。
１）の方向では、互いにからみ合うような鎖状の結晶を析出させることにより従来の結晶化ガラスの倍以上の曲げ強度、破壊靱性をもつ材料が開発された。これは割れにくい食器や壁材、繊維強化セラミックスのマトリックス等の用途が考えられている。
２）の方向では、セラミックス繊維を結晶化ガラスマトリックスで結合した複合材が試みられている。繊維―マトリックス間の結合を強すぎも弱すぎもしない程度にすれば、強度、靱性は飛躍的に高まり、また破壊する際にも繊維が引き抜かれながら切れるので破断は金属のようにゆっくりと進行する。この材料は航空機エンジンや宇宙構造物等へ使われるであろう。

コージライト系の結晶化ガラス及びフリットは、低温焼成、低誘電率特性を生かして多層配線板に使われようとしている。

最近開発された発泡ガラスセラミックスでは誘電率が３以下のものも見出されている。低膨張透明結晶化ガラスは「中のみえる鍋」として急速に普及してきた。

その他の用途では、歯冠材料や壁材に新分野を開きつつある。

（訳：コーニングジャパン㈱営業本部開発部
小西　和之）