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Compositional effects on mechanical properties, viscosity, and crystallization of (Li_2O, B_2O_3, MgO)-Al_2O_3-SiO_2 glasses

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ABSTRACT

Compositional effects on mechanical properties, viscosity, crystallization and crystallization kinetics of MgO-Al_2O_3-SiO_2 based high-strength (HS) glass and glass fibers were examined in detail by varying ($Li_2O + B_2O_3$)/MgO ratio (LB/M). A set of complementary techniques was applied to the crystallization studies, including differential scanning calorimetry (DSC), powder x-ray diffraction (XRD), scanning electron microscopy equipped with energy dispersive spectrometer (SEM/EDS). Phase identification and crystal morphology survey were made. Crystallization kinetics of the HS glass fibers under various thermal conditions was studied in detail to elucidate plausible crystallization mechanisms in relationships to LB/M. Our study showed that the combined, high concentration of Li_2O and B_2O_3, at the expense of MgO, i.e., higher LB/M, suppressed crystal growth in glass. From the DSC studies, exothermic peaks came from formation of β-quartz (s.s.) below 900°Cand subsequent transformation into cordierite greater than 1000 °C according to XRD analysis of the heat-treated samples. For crystallization under the non-isothermal conditions, Kissinger and Matusita & Sakka methods were applied to elucidate glass crystallization mechanism(s). In addition, the HS glass fibers were shown to have 29% higher tensile strength and 15% higher modulus than E-Glass fibers commercially used for a wide range of composite applications.

1. Introduction

High-strength and high-modulus glass fibers, under categories of S-Glass and R-Glass,_ENREF_1 respectively, have been commercially utilized as reinforcements in advanced composites for more than forty years [1–6]_ENREF_2, including energy-storage flywheels, ballistic armors, helicopter blades, glare plates for fuselages, rods for fiber optic overhead cables, etc. Under the S-Glass category, fibers of S-2 Glass® (AGY, US), T-Glass (Nittobo, Japan), and HS™ Glass (Sinoma, China) contain primarily SiO_2, Al_2O_3, and MgO without CaO, whereas E-Glass containing significant amount of CaO, but little or lower MgO [7]. On the other hand, R-Glass contains almost the same molar concentration of CaO as MgO. In turn, S-Glass fibers offer significantly improved mechanical properties over E-Glass fibers and additional improvements over R-Glass fibers. However, penalties associated with making S-Glass fibers are significantly higher viscosity, or higher melting temperature, and higher fiber forming temperature due to its significantly higher liquids temperature relative to E-Glass and R-Glass manufacturing processes. As a result, a standard, large scale furnace technology of E-Glass (30,000–120,000 MT/y/furnace) or R-Glass fibers (30,000–50,000 MT/y/furnace) cannot be applied to produce S-Glass fibers. A typical S-Glass fiber production line with multiple stand-alone production platforms can only produce S-fibers at a capacity one order of magnitude lower at least.

In glass and fiber glass industry, glass melting and fining temperature ($T_{log\eta=2}$) is defined at the melt viscosity of 10^2 dPa s and fiber forming temperature ($T_{log\eta=3}$) at the melt viscosity of 10^3 dPa s or higher to maintain ΔT ($T_{log\eta=3}$ - T_{liq}) no less than 55 °C [8] as a general practice of E-Glass fiber drawing process. However, for S-Glass fibers that has very high liquidus temperature (T_{liq}) and fast crystallization rate, by the ΔT definition, the drawing process is impossible because its $T_{log\eta=3}$ is either close to T_{liq} or lower, i.e., $\Delta T \leq 0$. Under this circumstance, the fibers are drawn at much higher temperature to ensure sufficiently wide ΔT. From experience, the practical $T_{fiberization}$ should be kept above T_{liq} at 70 °C or greater to avoid crystal formation in a bushing well, which can lead

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to crystal beading or fiber breakage. Higher operating temperature accelerates refractory corrosion in Forehearth and creep and volatile losses of bushings made of rhodium/platinum alloy. As a result refractory inclusions and bushing sagging can also lead to fiber breakages and a shorter bushing service life, respectively.

High-strength HS™ glass fibers reported in this study belong to the family of S-Glass fiber, which are primarily composed of MgO, Al_2O_3, and SiO_2 (MAS for short). The MAS glass compositions are known to have significantly higher liquidus temperature according to the phase diagram as compared with E-Glass, primarily composed of CaO, Al_2O_3, and SiO_2 (CAS for short) [8], which explains why MAS glasses, or S-Glass, has negative or much lower positive ΔT than CAS glasses.

To reduce temperatures of glass melting and fiber drawing of S-Glass, we performed a feasibility study examining any potential processing benefits that could be gained by using Li_2O and B_2O_3 without a significant impact on the mechanical properties of the modified HS™ fibers. Two compositions of the HS glass fibers (HS-A and HS-B) were investigated, which were formulated with different ($Li_2O + B_2O_3$)/MgO ratios (LB/M for short) without changing SiO_2 and Al_2O_3. As will be discussed later, the use of Li_2O and B_2O_3 was proven to be effective in enhancing batch-to-glass melting by reducing melt viscosity [7,9]. In addition, the modified glasses were shown to exhibit different crystallization kinetics. The HS-B glass with lower LB/M ratio had higher tendency towards crystallization than the HS-A glass, while both had similar process characteristics in terms of glass melting and fiber forming temperatures. Furthermore, the modified HS fibers were shown to have significantly higher mechanical properties over E-Glass fibers.

Structures of the MAS glasses have been studied by other researchers using neutron scattering and X-ray diffraction techniques and Reverse Monte Carlo simulations [10], ^{17}O MAS NMR (magic angle spinning nuclear magnetic resonance) and 3Q MAS and ^{27}Al MAS NMR [11], and ^{27}Al MAS NMR and Raman spectroscopy [12]. For the MAS glass system, MgO provides free oxygens for Al_2O_3 to form four-fold $[AlO_{4/2}]^-$ tetrahedron units as well as some polyhedron units of five-fold $[AlO_{5/2}]^{2-}$ and six-fold $[AlO_{6/2}]^{3-}$ [13]. MgO functions as a charge compensator to maintain a local charge neutrality of the aluminate groups. The resulting local structures enhance the degree of the glass network polymerization, especially for the MAS glass with $MgO/Al_2O_3 = 1$. Excessive MgO (i.e., MgO - $Al_2O_3 > 0$), however, can also depolymerize the glass network; "free MgO" functions as the network breaker, creating non-bridging oxygen. Different glass property responses depend on the MgO/Al_2O_3 ratio [10,14]. Compositional, catalytic effects of ZrO_2, TiO_2, and CeO_2 (as dopants) on nucleation and crystallization in MgO-Al_2O_3-SiO_2 [15], phase separation and crystallization in MgO-Al_2O_3-SiO_2-TiO_2 glass with and without Ga_2O_3 [16], solid solution formation of (Li_2O, MgO)-Al_2O_3-nSiO_2 [17], and ion field strength effects on the activation energy of crystal growth of RO-Al_2O_3-SiO_2-(3-5) B_2O_3 (R = Mg, Ca, Ba) and effects of TiO_2, ZrO_2, Cr_2O_3 and NiO on the activation energy of crystal growth of MgO-Al_2O_3-SiO_2 glass [18] have been studied by others. The common methods used in the studies were differential thermal analysis (DTA) and x-ray diffraction analysis (XRD), plus small-angle X-ray scattering measurement was performed to study phase separation in glass [16]. No information was provided in the literature, detailing mechanisms of crystal growth for all cases. To our best knowledge, the effect of LB/M ratio on S-Glass crystallization behavior has not been well characterized; a detail study was considered important to gain scientific understanding of the MAS system property response to other metal cation modifications. In turn, it allows us to explore composition design options to mitigate S-Glass fiber processing challenges. Our study reported here covers the effects of Li_2O, B_2O_3 and MgO on the HS glass fiber mechanical properties, characteristic processing temperatures, phase formation, crystallization kinetics, and its associated plausible mechanisms of crystal growth under non-isothermal conditions.

2. Experimental

2.1. Sample preparation

Glass compositions formulated in our study were named HS-A and HS-B, respectively. Both designed and measured compositions are summarized in Table 1 along with their corresponding LB/M ratios calculated by their designed concentrations. For both glasses, the concentrations of SiO_2, Al_2O_3, and minor constituents under 'Others' were kept constant, whereas the concentrations of B_2O_3 and Li_2O varied simultaneously, exchanging with MgO.

Batches of HS-A and HS-B glass were prepared by using technical grade materials containing SiO_2, Al_2O_3, MgO, B_2O_3 and Li_2O (actual materials are business confidential information). The batches were homogenized by using a pneumatic blender. The two batches were pre-heated at 1100 °C for 2 h and then melted and refined at approximately 1560 °C and 1450 °C, respectively, in an electric batch melting furnace. Fibers of each glass type were subsequently drawn above 1400 °C from a 400-tip Pt/Rh bushing, which was directly connected to the glass melting furnace. Fiber strands made by the above process had a filament diameter range of 7–11 μm.

2.2. Thermal analysis

Crystallization kinetics of the HS glasses was studied by using differential scanning calorimetry (DSC). The measurements were carried out using Netzsch STA 449 F3 with operating parameters: <1 μW of data processing installation, ±0.1 μg for the microbalance accuracy, ±0.01 K for temperature sensor accuracy. The DSC scans were ran in air between room temperature and 1450 °C at four different heating rates (β), 5, 10, 15, and 20 K/min. Prior to the tests the apparatus was calibrated according to the International Standard ISO 11357-1 (2009). The glass samples were separately pulverized using an agate mortar and pestle to control sample size between 200 and 240 meshes. For the DSC tests, 10 ± 0.5 mg of each sample was used, while an empty platinum crucible was used as reference. By the DSC method, glass transition temperatures (T_g) were determined according to the International Standers ISO 11357-2: 2009.

2.3. Melt property characterizations

Viscosities of the HS-A and HS-B glass, including E-Glass, were measured over the temperature range between 1200 °C and 1550 °C, using a high-temperature viscometer (Orton RSV-1600, US; B-type thermocouple; 1600 °C maximum temperature). The viscometer assembly was calibrated twice by using a standard glass, NIST SRM717A, prior to the measurements. Experimental errors of the measurements were within 2% in a logarithmic scale. The reference standard for the experiment was ISO 7884-2 (1998).

Experimental viscosity (η) data of the glasses were fitted to

Table 1
Designed and measured compositions of the HS glasses.

ID	mol%	SiO_2	Al_2O_3	MgO	B_2O_3	Li_2O	Others	LB/M
HS-A	Designed	58.8	15.1	19.5	3.6	2.4	0.60	0.308
	Measured	58.84	15.19	19.32	3.61	2.45	0.59	0.314
HS-B	Designed	58.8	15.1	22.7	1.8	1.0	0.60	0.123
	Measured	58.62	15.17	22.86	1.82	1.02	0.51	0.124