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Novel glass compositions for fiber drawing

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Abstract

Strengthening concrete by fiber reinforcement is a new trend nowadays. Glass is one of the materials that have the highest chemical durability in concrete. Chemically durable glass compositions in alkaline environment have been studied for 25 years by our group. SMZS (SrO–MgO–ZrO_2–SiO_2) system glass compositions possess high chemical durability in alkaline solutions. Further investigations show that recently discovered SMFMZS (SrO–MgO–FeO–MnO–ZrO_2–SiO_2) glasses exhibit better chemical durability when compared to the former one containing more SrO in the composition as a modifying oxide.

The main purpose of the present study was to produce glass fibers made of our own SMZS and SMFMZS glass systems compositions inhibiting better alkali durability compared to the commercial E-glass fiber. Further study on the SMFMZS glass samples in terms of fiber drawing revealed that magnesia-silicate related many crystalline phases were formed during the process. Determining possible crystallization temperatures of SMFMZS system glasses were carried out by the gradient furnace. Additionally, those formed crystals were fully characterized by SEM and EDX. To prevent surface and bulk crystallization during fiber drawing, the composition changes were made. Consequently, successful composition was achieved.

Keywords: B. Electron microscopy; B. Fibers; B. Microstructure-final; D. Glass

1. Introduction

Although most glasses are known as inert materials having high corrosion resistance, all the glass products are chemically reactive up to a certain degree. It is important to have a good knowledge about how a glass alters a solution with which it is in contact or how the glass product is altered by the solution. The prediction of such effects, even when the conditions are well specified, is an inexact process; there are no neat formulas to calculate the effect of the numerous variables involved. There is no absolute or explicit measure of chemical durability as well. Glasses are usually graded relative to one another after being subjected to similar experimental conditions [1]. Chemical attacks on glass occur either by an ion exchange process or by a network disruption process. The former is considered as an attack on non-bridging oxygen atoms (or ions) by reagents with an electron deficiency, and the latter as an attack on bridging oxygen atoms by reagents with an electron excess, such as seen in an alkaline solution where unlimited numbers of OH^- ions are available. This is an irreversible process resulting in permanent damage to the glass network [2]. The chemical durability of silicate glasses is critically dependent upon pH and the nature of the attacking solution.

Silicate glasses are among the most chemically inert commercially available materials. The rate of alkali extraction from glass by aqueous solutions is largely determined by the glass composition. Generally, the rate decreases with declining alkali content of the glass, with decreasing alkali ion radius or when part of the SiO_2 is replaced by almost any other divalent oxide; Ca and Mg oxides are the ones most often used commercially [1]. Addition of CaO makes the starting batch

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cheaper and the desired properties of final glass easier to be obtained, also gives better alkali durability. Of all the oxides, ZrO_2 is known as the most effective oxide improving the chemical durability of silicate glasses [3]. The extreme durability of ZrO_2-containing glasses in an aqueous solution is attributed to the fact of the predominance of ionic species like $(ZrO)^{2+}$, Zr^{4+} and $(HZrO_3)^-$ occurrence at very low and high pH values, respectively. Thus, a hydrated ZrO_2 surface is stable at all conceivable pH values of the solution.

Karasu et al. [4] studied high chemical and corrosion resistant SrO–MgO–ZrO_2–SiO_2 (SMZS) glass system. They have reported that when the glass was exposed to the NaOH solution, Sr ions passed into the solution and glass endurance was reduced. Under the light of the data achieved, suitable oxides were added into the glass structure and the amount of SrO ion was diminished in their studies. Then, this glass was named as SrO–Mn_2O_3–Fe_2O_3–MgO–ZrO_2–SiO_2 (SMFMZS) system glass. Furthermore, SrO is the most expensive component in the system, therefore, its replacement by any other suitable component would decrease the cost.

The obtained overall results indicate that SMFMZS system glasses have very high alkali resistance [3,5] and are required to produce fiber glasses for the evolution of reinforced concrete structures. In the relevant study [5], Fe and Mn containing compounds were reported to possess higher alkali resistance than that of E-glass. In the light of these previously done studies, especially Fe11, Mn5.5Fe5.5 compositions revealed significantly more alkali resistance.

Glass fibers exhibiting high alkali endurance are perfect candidates for concrete reinforcement. The nature and chemical structure of glass fibers used in glass fiber reinforced composite (GFRC) materials are the key factors for designing and controlling the final desired properties of the composite structure [6]. Accordingly, it is clearly stated that the proper choice of the glass fiber before starting to produce GFRC is the most significant parameter.

The main purpose of the present work was to produce an alternative glass composition which shows alkali durability as good as commercial E-glass fiber one's. Here, considered as a first novelty of the present study, a standard material and commercially available E-glass fiber were tested to compare with our novel compositions. Then, taking SMZS glass group into an account, it was tried to produce glass fiber named as Fe11 composition. The crystallization of Fe11 glass being a modified composition of SMFMZS group was investigated. However, the results clearly showed that it was not convenient for fiber drawing, and it was decided that the composition should be further improved. So, the new glass composition named as Zrn1 was generated for the fiber production. It must be pointed out that this one includes certain amount of soda-lime-silica (SLS) glass to form a glass with no bulk crystallization. Results revealed that addition of sodium (Na^+) cation through soda-lime-silica (SLS) glass to the structure suppresses the formation of magnesia silicate related crystal phases. Only small amount of surface crystallization was observed. Additionally, a successful glass drawing was carried out from the relevant melt.

2. Experimental procedure

Raw materials of the starting batch and commercial glass fiber which is known as E-glass were analyzed with XRF (Rigaku ZSX Primux model) instrument. This instrument was used to determine the mineral content of raw materials and also to clarify the amorphous degree of the commercial fiber product which was considered as a standard glass fiber. The X-ray diffraction (XRD) patterns were collected under a Cu tube with K_α radiation at 1.5405 Å, scanning in between the 10–70°, 2θ degree. To collect the necessary data in 0.5 h range, increments of 1° and a swept time of 0.5 s were used. The applied voltage and current were 40 kV and 30 mA, respectively.

To know the combustion temperature of polymer layer on the surface of commercial glass fiber and also the weight loss Netzch STA 409 PG thermal analyzer was used. The glass fibers were chopped into 2–3 mm size which is suitable for DTA characterization. The DTA curves were measured from 20 to 1400 °C with Netzsch STA 409PC apparatus using α-alumina as reference. The samples were heated in air at heating rates of 10 °C/min. Then, characteristics of heat treated fiber surfaces and polymeric material coated fiber surfaces with no treatment were performed by FTIR (FTS 165 FTIR-transmittance mode) analysis to investigate the type of the polymer coating. FTIR spectra for all the glasses were obtained by using Tensor 27 model Bruker Optic GMBH FTIR Spectrometer. KBr disk technique was employed: 1% (0.8 mg) glass fiber powder (<45 mm) was mixed with 99% KBr. Scans were performed between 3000–500 cm^{-1}, at a resolution of 4 cm^{-1} and 30 scans per sample. The background was subtracted from all the spectra before the normalization.

In order to determine the chemical resistance of glass fibers in the basic environment, 40 g NaOH was added into 1 l of pure water, and hence 1 M NaOH solution was obtained. Afterwards, this was put into 250 ml plastic containers. Then, the glass fibers being approximately cut in 5 mm length were suspended in the solution to perform the chemical resistance test at 75 °C. One has be very careful about the use of suitable material resistant to the erosive effects of alkali environment in terms of keeping the fiber test samples inside it. Furthermore, XRD was performed to the samples after chemical resistance test to observe any possible phase formation as a result of interactions between glass fiber and attacking chemical solution.

The surface textures of the heat treated and as-received fibers after chemical resistance test, and the elemental constituents of newly occurred phases were identified with the combination of ZEISS SUPRA 50 VP SEM instrument and OXFORD brand EDX detector.

Carbolite BLF 17 glass melting furnace was employed to produce Fe11 and Zrn1 glasses. Experimental procedure for both can be described with the conventional route; batch preparation, pre-calcination and glass melting. The prepared batch was firstly placed into a platinum crucible, and then calcination was conducted for carbonate bearing compounds. Finally, to melt the batches, homogeneously mixed batches