Materials and Design 73 (2015) 60–66

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

High alkali-resistant basalt fiber for reinforcing concrete

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ARTICLE INFO

Article history:
Received 13 November 2014
Accepted 21 February 2015
Available online 26 February 2015

Keywords:
Basalt fiber
Alkali resistance
AR-glass fiber
Zirconia doping
Fiber reinforced concrete

ABSTRACT

Basalt glasses and fibers with zirconia content in the range from 0 to 7 wt% were obtained using $ZrSiO_4$ as a zirconium source. Weight loss and tensile strength loss of fibers after refluxing in alkali solution were determined. Basalt fiber with 5.7 wt% ZrO_2 had the best alkali resistance properties. Alkali treatment results in formation of protective surface layer on fibers. Morphology and chemical composition of surface layer were investigated. It was shown that alkali resistance of zirconia doped basalt fibers is caused by insoluble compounds of Zr^{4+}, Fe^{3+} and Mg^{2+} in corrosion layer. Mechanical properties of initial and leached fibers were evaluated by a Weibull distribution. The properties of basalt fibers with $ZrSiO_4$ were compared with AR-glass fibers. The performance of concrete with obtained fibers was investigated.

1. Introduction

Alkali-resistant glass (AR-glass) fiber was preferably designed to reinforce cementitious matrices which are widely used in construction industry. AR-glass fiber is applied in glass fiber reinforced concrete (GFRC) and textile reinforced concrete (TRC) production. Usually short AR-glass fibers are added to GFRC in order to prevent drying shrinkage of concretes at early ages and to increase the fracture toughness of the brittle matrix [1]. TRC consists of a fine-grained cement matrix and high-performance textile: fabrics, meshes, yarns. This composite material is notable for high strength properties and pseudo-ductile behavior, which is characterized by large deformations due to its tolerance to multiple cracking [2]. TRC and GFRC can be used both in the creation of slender architectural constructions and in the strengthening of reinforced concrete structures. Most of these applications require that high tensile strength and toughness of TRC do not degrade significantly with time [3].

A significant alkalinity of Portland cement leads to corrosion of glass fiber reinforced materials. Alkaline medium of cement remains not only at the hardening stage, but also hereafter due to the presence of pore solution in the concrete. To evaluate the alkali resistance of glass fibers, the following solutions are mainly used: NaOH, saturated $Ca(OH)_2$, cement solution and mixtures of NaOH and Na_2CO_3 [4]. The major factors, affecting the corrosion rate of glass in alkaline solutions, are as follows: the surface of area exposed, the volume of the leaching solution, the nature of the leaching solution, its replenishing frequency, and the temperature of leaching [5].

There are several stages in the reaction of glass with alkaline solution. Initially OH^- is adsorbed on the glass surface. Then the following reactions occur:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\ldots-\overset{|}{\underset{|}{\mathrm{Si}}}-+\mathrm{OH}^- + m\mathrm{H_2O} \rightarrow n\mathrm{SiO_2}\cdot m\mathrm{H_2O}+\mathrm{OH}^- \quad (1)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OR}+\mathrm{H_2O} \Leftrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH}+\mathrm{R}^+ + \mathrm{OH}^- \quad (2)$$

$$n\mathrm{SiO_2}\cdot m\mathrm{H_2O} + 2q\mathrm{NaOH} \rightarrow q\mathrm{Na_2O}\cdot n\mathrm{SiO_2}\cdot p\mathrm{H_2O} + n\mathrm{H_2O} \quad (3)$$

At the final stage, the reaction products are removed from the glass surface. Since the number of active adsorption centers on the glass surface is limited, the corrosion process is stabilized at a certain phase. The following glass destruction depends only on dissolution rate of the reaction products [6].

There are several approaches to increase alkali resistance of fibers:

- to improve glass composition [5,7];
- to apply new sizings and coatings [8–11];
- to use cement and concrete additives [12,13].

To realize the first approach, zirconia addition is most widely used. Improvement of alkali resistance properties is caused by the formation of a thin stable hydrated, zirconium-rich layer on the glass surface. The layer, formed after the beginning of alkaline attack on the glass network, slows down the diffusion of OH^- ions

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http://dx.doi.org/10.1016/j.matdes.2015.02.022
0261-3069/

into the bulk glass. Thus, further network breakdown can be significantly reduced [3]. The alkali resistance of glass fibers rises with increasing zirconia content [14]. Most of AR-glass fibers contain large amount of zirconia (16–20 wt%) providing therefore higher alkali resistance as compared to other glass fibers [5,7]. The main disadvantage of AR-glass fiber is a high cost.

In recent years basalt continuous fiber (BCF) is increasingly used in GFRC and TRC along with the AR-glass fiber. BCF is notable for its low cost, high mechanical properties [15] and good resistance to alkaline attack both at room temperature and at elevated temperatures [16,17]. Application of basalt fiber results in an increase of GFRC mechanical properties [18]. Studies indicate the feasibility of using BCF as reinforcement material in TRC composites [19]. Moreover, basalt fiber is cheaper than AR-glass fiber. However, alkali resistance properties of basalt fiber are inferior to AR-glass fibers [6].

The present work is a continuation of previously published study [20] devoted to effect of ZrO_2 addition on the alkali resistance and mechanical properties of basalt continuous fiber. In this paper, to increase the alkali resistance of basalt fiber, zircon ($ZrSiO_4$) was used as a zirconium source.

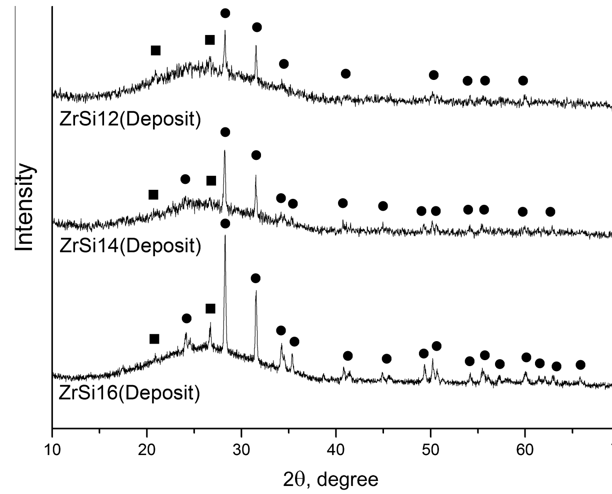

Fig. 1. XRD patterns of deposits obtained on the bottom of the platinum crucible in the glass preparation process (■ – quartz SiO_2, ● – zirconia ZrO_2).

2. Experimental

2.1. Sample preparation

Basalt fibers with various zirconia contents were produced in two stages. The first stage included obtaining of basalt bulk glasses. Basalt rock from the Sil'tsevskoe deposit (Carpathians, Ukraine) was used as a raw material. Zirconia doped basalt glasses were prepared by adding of $ZrSiO_4$ to milled basalt batch. The batch mixture was heated in platinum crucible in a high-temperature furnace at a rate of 250 °C/h up to 1000 °C and at 30 °C/h in the range of 1000–1600 °C, then homogenized at 1600 °C for 24 h. The molten glass was quenched in water from 1550–1590 °C. The chemical composition of glasses is presented in Table 1. Total iron content is expressed as Fe_2O_3 in the paper. In the case of ZrSi6–ZrSi16 glasses, a white deposit was observed on the bottom of platinum crucible after the molten glass had been poured out. XRD patterns of deposits are presented in Fig. 1.

In the second stage, basalt fibers with various zirconia contents were produced from obtained glasses on a laboratory scale system [21]. The deposit formed during the preparation of glasses ZrSi6–ZrSi16 was not used. The fibers had filament diameters of 10–12 μm. Sizing was not applied in the fiber production.

Basalt fiber properties were compared with commercial AR-glass fiber (manufacturer – Owens Corning) characteristics. It has the following chemical composition: 9.8% Na_2O, 65.1% SiO_2, 6.3% CaO, 18.8% ZrO_2. AR-glass fiber was preliminarily annealed at 500 °C to completely remove sizing, then it was placed in platinum crucible and was heated up to 1600 °C. Glass quenching and the fiber production were carried out according to the method described above.

The materials used in concrete preparation include cement CEM I 32.5N, mortar sand with particle size 0–1.6 mm and chopped fibers with 12 mm in length. Chopped fibers were prepared by cutting of continuous fibers obtained on a laboratory scale system. The density of basalt, ZrSi10 and AR-glass fibers were equal to 2.65 g/cm^3, 2.69 g/cm^3 and 2.57 g/cm^3 respectively. The mixture proportions of concrete are presented in Table 2. Dry mixture of components was mixed for 2 min and then water was added slowly. The amount of water was chosen so that the slump was 105–115 mm. The fresh concrete was mixed for 3 min to ensure even dispersion of fibers in the concrete and was cast in molds. Concrete in molds was vibrated for 3 min with frequency 50 Hz. Specimens were cured in a chamber at 20 ± 3 °C and 95 ± 5% relative humidity and were de-molded after 24 h. Hardened concrete was tested at 28 days.

2.2. Testing methods

X-ray fluorescence (XRF) analysis of the glasses was performed on a PANalytical Axios Advanced spectrometer. Characteristic X-rays were excited by an Rh-anode X-ray tube (current capacity up to 4 kW, maximal current 160 mA). For the XRF analysis, powdered glasses were pressed in pellets with polystyrol as a binder.

X-ray diffraction (XRD) measurements were performed on a THERMO ARL X'TRA powder diffractometer with a semiconducting Peltier-cooled detector (Cu Kα1 radiation, λ = 1.54060 Å, Cu Kα2 radiation, λ = 1.54443 Å). XRD patterns were collected in the range

Table 1
XRF analysis of basalt glasses.

Sample	Added to the basalt batch		Chemical composition (wt%)								
	$ZrSiO_4$ (wt%)	In terms of ZrO_2 (wt%)	ZrO_2	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
ZrSi0	0	0	–	2.1(2)	3.4(2)	15.2(5)	55.3(4)	1.5(2)	9.0(5)	1.10(8)	11.9(3)
ZrSi2	2	1.3	1.3(1)	2.1(2)	3.3(2)	14.9(5)	54.9(4)	1.5(2)	8.8(4)	1.08(8)	11.7(3)
ZrSi4	4	2.7	2.7(1)	2.0(2)	3.3(2)	14.6(5)	54.4(4)	1.4(1)	8.6(4)	1.06(7)	11.4(2)
ZrSi6	6	4.0	3.6(1)	2.0(2)	3.2(2)	14.4(5)	54.1(4)	1.4(1)	8.5(4)	1.04(7)	11.3(2)
ZrSi8	8	5.4	4.9(1)	2.0(2)	3.2(2)	14.1(5)	53.6(4)	1.4(1)	8.3(4)	1.02(7)	11.0(2)
ZrSi10	10	6.7	5.4(1)	1.9(2)	3.1(2)	14.0(5)	53.5(4)	1.4(1)	8.3(4)	1.01(7)	10.9(2)
ZrSi12	12	8.1	6.3(1)	1.9(2)	3.1(2)	13.8(5)	53.2(4)	1.4(1)	8.2(4)	1.00(7)	10.8(2)
ZrSi14	14	9.4	6.9(1)	1.9(2)	3.1(2)	13.6(5)	53.0(4)	1.4(1)	8.1(4)	0.99(7)	10.7(2)
ZrSi16	16	10.8	7.0(1)	1.9(2)	3.1(2)	13.6(5)	53.0(4)	1.3(1)	8.1(4)	0.99(7)	10.7(2)