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Corrosion of uncoated and oxide-coated basalt fibre in different alkaline media

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ABSTRACT

The corrosion behaviour of the zirconium dioxide and titanium dioxide coated basalt fibre in sodium and calcium hydroxide solutions was studied. The morphology, elemental, phase composition of fibre before and after exposure to alkaline media was examined by different analytical techniques. It was shown that the oxide coatings slow down corrosion, and zirconium dioxide slows down corrosion of basalt fibre to a higher extent than titanium dioxide. The morphology and composition of solid corrosion products depend on a type of alkaline medium. The schemes of corrosion for the uncoated and coated basalt fibres in alkaline media were proposed.

1. Introduction

Basalt fibres show several advantages that make them an alternative to glass fibre as reinforcing material in composites with polymer, metal and cement matrices [1]. Despite higher density of basalt fibre compared with glass fibre (2.8 vs. 2.56 g/cm3), its mechanical properties are superior to the mechanical properties of glass fibres. For example, specific elastic modulus (E) and specific tensile strength of basalt fibre are higher than those for glass fibre (e.g. compare E = 31.78 GPa/g/cm3 for basalt fibre vs. 30 GPa/g/cm3 for glass fibre) [2]. Further, basalt fibre has better thermal stability, elastic behaviour, stability in salt water, alkaline and acidic media [3,4]. The manufacturing process of basalt fibre is less energy consuming and needs no additives, which makes it cheaper than the glass fibre process [5]. Due to valuable properties and low cost, basalt fibre has been proposed as reinforcement of cement matrices, which are widely used in construction industry. It was shown that the addition of basalt fibres results in improved flexural strength, fracture energy and toughness of cement matrix composites [1,6]. Moreover, the addition of basalt fibres reduces noticeably the dry shrinkage of cement mortar at the early stages of hardening. However, it should be emphasised that the high alkalinity of cement matrix can lead to corrosion of basalt fibres, especially at the earlier stages of hardening. Because of alkaline etching, degradation of the mechanical properties of basalt fibres and basalt fibre reinforced concrete occurs.

Several serious works deal with the development of approaches to improve the alkali resistance of glass and basalt fibres in cement matrices [7–13]. The approaches include (i) modification of the fibres composition by adding an alkali-resistant component, e.g. ZrO2, to raw material; (ii) application of alkali-resistant coatings on fibres; (iii) the cement matrix modification through special additives [9]. Among these approaches, the application of the alkali-resistant coatings on reinforcing fibres seems to be the most promising one. Indeed, in this case alkali-resistant coating is applied directly on the most sensitive area, namely, the surface of reinforcing basalt fibre exposed to aggressive medium and, therefore, can restrict the access of aggressive alkaline medium to the reinforcement and thus prevents dissolution and destruction of the fibre. Another important advantage of this approach is that a great number of materials can serve as alkali barrier coatings for basalt fibre. Hence, the most appropriate material can be chosen in terms of its alkali resistance, cost and deposition methods.

Earlier, zirconium dioxide was studied as alkali-resistant coating for basalt fibre [10,11]. Jung and Subramanian [11] showed that alkali resistance of basalt fibres can be enhanced by hydrated zirconium dioxide films formed by the sol–gel process. One can note that expensive and air-sensitive organometallic precursor was used to prepare hydrated zirconia sols. Rybin et al. [10] proposed simple and readily controlled sol–gel method for the preparation of stable hydrated zirconium dioxide sol, and showed that the ZrO2

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coating slows down the corrosion of basalt fibre in NaOH solution, with higher extent by applying dense zirconia coating than the porous coating on fibre surface. Titanium dioxide can be considered as alternative because of its relative stability in alkali media and cheapness.

The aim of the present work is to compare the corrosion behaviour of the zirconia and titania coated basalt fibres in two alkali media, namely, 2 M NaOH solution and saturated Ca(OH) 2 solution. A choice of 2 M NaOH solution was related to the fact that this is a highly aggressive media (pH 14) and could be used for accelerated etching of fibre. The saturated Ca(OH) 2 solution (pH 12,4) is similar to the medium of hydrated cement matrix and could be used for modelling of a real-time corrosion of basalt fibre [14]. As a reference, the data on the behaviour of uncoated basalt in the same alkali media were involved.

2. Experimental

2.1. Coating deposition

As-received basalt fibres (RB 13–2400) were of commercial grade (Vulcan LLC RPE, Russia). According to manufacturer's EDS data, as-received basalt fibres have the following percentage (wt.) composition: Na2O: 2.77; MgO: 4.12; Al2O3: 17.73; SiO2: 55.63; K2O: 1.59; CaO: 8.06; TiO2: 1.12; FeO + Fe2O3: 8.97. For ZrO2 sol preparation, zirconyl chloride octahydrate ZrOCl2·8H2O (CG, Hf content not more than 1%, Khimsnab, Russia) was used as precursor. The coating solution was prepared by dissolving ZrOCl2·8H2O at a concentration of 0.4 M in the ethanol–water (volume ratio 9:1) solution. Before coating procedure, the ZrO2 sol was aged for 3 days.

To prepare TiO2 sol titanium tetrachloride (TiCl4, CG, Reachem, Russia) was used as precursor. Titanium tetrachloride was added dropwise to a calculated amount of frozen distilled water (mole ratio H2O/TiCl4 = 10:1) to form aqueous titanium chloride solution, which was used for the synthesis of corresponding hydrosol by electrochemical sol–gel method [15]. Aqueous TiO2 sol of 0.8 M concentration was used immediately after preparation.

The coating stage involved the immersion of basalt fibre into sols for 1 min. The specimens were dried in the air at ambient temperature and then placed in the furnace heated preliminarily to 550 °C. Such heating scheme was used to minimise the effect of crystallization of the fibre and to prevent the degradation of mechanical properties of fibre. The specimens were kept for 0.5 h in argon flow at atmospheric pressure and cooled in the air.

2.2. Chemical attack

Two different alkali media, namely, 2 M NaOH solution (pH 14) and saturated (0.02 M) Ca(OH) 2 solution were used to test as-received and coated basalt fibres. To prepare saturated Ca(OH) 2 solution, calcium oxide (CG, Reachim, Russia) was preliminary calcined at 1000 °C for 2 h, cooled in desiccator and then dissolved in deionised water. The oxide-coated and as-received fibres were divided into parts of ~7 cm in length, each part was placed into individual plastic bag for testing in 2 M NaOH and saturated Ca(OH) 2 solutions during a definite period of time (16 and 64 days) at ambient temperature. The fibre: alkali solution mass ratio was 1:100. The zip-locked plastic bags 1 L in volume were used as containers for etching. To minimise the pH change of Ca(OH) 2 solution due to CO2 penetration in plastic bags, the latter were placed in hermetic box. After exposure to alkaline media, the samples were taken out, gently washed twice with distilled water in order to remove chemicals, and dried in air at ambient temperature till constant weight.

2.3. Specimen characterization

The morphology of uncoated and oxide coated fibres was studied by scanning electron microscopy (SEM) using the TM-1000 and 3400 S instruments (Hitachi Ltd., Japan). SEM accelerating voltages were 15 kV and 30 kV, respectively. The changes in surface elemental compositions were examined by means of energy-dispersive X-ray analysis (EDS) SwiftED-TM (Oxford Instruments Ltd.). All samples were preliminary coated by gold layer of a thickness of 5–7 nm. The probes were taken from different areas of the same filament and from different filaments of the same batch. As a rule, a mean arithmetic value calculated from 5 to 6 measurements for the same type fibre was used for consideration. For correct comparison of elemental composition, the elemental data were normalised to four main elements (Si, Al, Ca, Fe); the oxygen content was not measured. The X-ray powder diffraction (XRD) patterns of the samples were recorded using the D8 Advance diffractometer (Cu-Kα irradiation, Bruker, Germany) at room temperature. The qualitative phase analysis was performed using the ICDD PDF-4 database.

3. Results and discussion

3.1. Etching of the as-received basalt fibre in NaOH and Ca(OH) 2 solutions

Earlier, Rybin et al. [10] studied etching of basalt fibre in 2 M NaOH solution in details. One can summarise the previous results as follows. The surface of the as-received basalt fibre (Fig. 1a) is greatly affected by NaOH solution, so that corrosion layer is formed on the surface of fibre (Fig. 1b). After exposure of basalt fibre in NaOH solution for 16 days, one can observe the formation of corrosion layer consisting of two clearly distinguishable sublayers. Based on the data of EDS, XRD and IR analysis, it was stated that the layer adjoining the fibre is composed of plate-like hexagonal crystals of iron

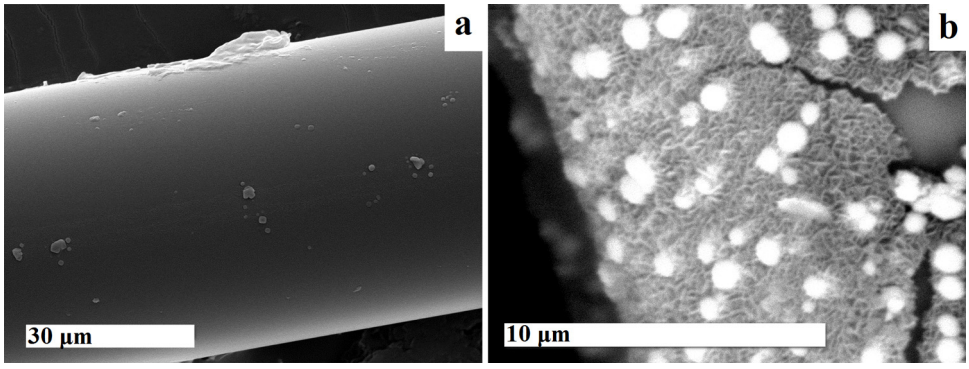

Fig. 1. SEM images of as-received basalt fibre (a) and basalt fibre etched in 2 M NaOH solution for 16 days (b).