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Corrosion behaviour and mechanism of basalt fibres in acidic and alkaline environments

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ABSTRACT

In this study, the corrosion behaviour and mechanism of basalt fibres immersed in H_2SO_4 and NaOH solutions with a series of concentrations were investigated, and the effects of the H_2SO_4 concentration on the stress corrosion were also studied. The corrosion is highly concentration-dependent, and the reaction rate directly determines the corrosion level. For H_2SO_4-corroded basalt fibre, the cracks between the outer layer and the inner core are primarily inclined to form when the ion depletion depth is small, whereas spiral and axial cracks are successively formed when the ion depletion depth is high.

1. Introduction

As a type of high performance natural fibre, basalt fibre has gained increasing attention from both academia and industry and is considered a serious alternative to glass fibre for use as reinforcement in composites with polymer, metallic and concrete matrices [1–5]. In addition to compatibility with the matrices, good chemical resistance, which determines fibre applications in different environments, is also required for reinforcement fibres [6–8]. Most fibres are affected by acid and alkali solutions; corrosion causes strength degradation of the fibre and causes composite failure because the reinforcement handles the external load when composites are in service. Aiming to evaluate the durability of basalt fibre in acid/alkaline environments, studies were conducted, and the results were compared with glass fibre [9–13]. The alkaline resistance of basalt fibre was superior to that of E-glass fibre, whereas the acid resistance was similar to that of E-glass fibre [6]. The differences in the corrosion resistances of basalt and E-glass fibres are a result of the different components, although the main components, SiO_2 and Al_2O_3, are the same for the two types of fibres. The E-glass fibre has a much higher contribution of CaO and B_2O_3, whereas Fe_2O_3 and FeO are only found in the basalt fibre [13]. For the basalt fibre, Wu et al. [11] and Wei et al. [12] concluded that the acid resistance was much better than the alkali resistance, whereas the opposite conclusion was obtained by Ramachandran et al. [6] and Wang et al. [14]. This conflict may be due to the different origins, which lead to unconformity of the basalt components [15–17], and it is widely accepted that in addition to the constitution of fibres and the composition of the aging solution, the corrosion rate is also affected by numerous parameters, such as temperature, aging time, and fibre sizing [18].

For inorganic fibres, in addition to chemical corrosion, the environmental stress corrosion cracking should also be considered [19–21]. To date, spiral and axial cracks have been observed on the surface of both glass and basalt fibres in acidic environments, and two known models were employed to describe the crack formation [22–25]. Stress corrosion is considered as the reason in both models. Metcalfe et al. [22] concluded that the shrinkage stress caused by the corrosion-induced volume mismatch between the surface and core of the fibre is the main cause of the cracks. However, for the axial cracks, this model does not provide a reasonable explanation. In contrast, the ion-depletion-depth model, which was proposed by Qiu et al. and was applied to basalt fibre by Nasir et al. [23,24], can explain the formation of spiral and axial cracks. Qiu et al. [23] showed that the internal stress state, which leads to the surface crack morphology, is determined by the balance of the shrinkage stress and residual stress, which is introduced during fibre fabrication. In contrast to aging in an acidic environment, no cracks were observed when basalt fibre or glass fibre was soaked in alkaline solution [6,9,12] because the corrosion in alkaline media is mainly controlled by the dissolving of the SiO_2- network and not by diffusion of non-siliceous ions, as occurs under acid attack [26].

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Table 1
XRF result of the desized CBF.

Composition	SiO_2	Al_2O_3	TFe_2O_3	CaO	Na_2O	TiO_2	MnO	MgO	K_2O	P_2O_5
Content (wt.%)	52.95	15.80	9.72	8.30	3.37	1.38	0.12	6.46	0.71	0.24

Table 2
The basic parameters and tensile properties of the desized CBF cord.

Parameter	Desized CBF cord
Breaking force (N)	319.4 (±10.0)
Breaking elongation (%)	3.3 (±0.1)
Yarn fineness (tex)	600 (200 tex/3)
Density (g/cm^3)	2.64

In general, understanding the strength degradation resulting from chemical and stress corrosion and the composition-dependent mechanism is important for the application of basalt fibre as a reinforcement of polymer-based composites. To the best of our knowledge, the chemical corrosion behaviour of basalt fibre in acid/alkaline media with different concentrations has not been systematically studied, and the effects of the acid concentration on the stress corrosion of basalt fibre, especially the relationship between the different ion depletion depths caused by the acid concentration and the crack formation, have not been studied. In this research, the effects of the concentration of the immersing solution on the mass loss and the tensile properties of degraded continuous basalt fibre (CBF) cords were studied. Scanning electron microscopy (SEM) was employed to observe the surface morphologies of basalt fibres after immersing in H_2SO_4 and NaOH solutions with a series of concentrations, and energy dispersive X-ray spectrometry (EDS) was applied to qualitatively study the ion transfer between basalt fibre and H_2SO_4/NaOH solutions. The ion depletion depth and the crack formation in the basalt fibres in H_2SO_4 solutions with concentrations ranging from 0.25 mol/L to 2.5 mol/L were also observed and analysed by SEM, and the mechanism was discussed.

2. Experimental procedure

2.1. Materials

CBF (BC11-200) was provided by Sichuan Aerospace Tuoxin Industrial Co., Ltd. The filament diameter is 11 μm ± 2 μm and the yarn fineness is 200 tex. The CBF cord (200 tex/3) was fabricated by twisting 3 ply CBF yarns together (250 twists per meter) by Shandong Tianheng Fibre Co., Ltd.

2.2. Fibre treatment

To remove the sizing and any dirt on the surface, CBF cords were first desized by soaking in acetone for 50 min, washed with distilled water 5 times, and dried in vacuo at 105 °C for 30 min before further treatment [27]. The chemical compositions of the desized CBF are listed in Table 1, and the basic properties of desized cords are shown in Table 2.

The desized CBF cords were first weighed (M_1) and then stored in a H_2SO_4 or NaOH solution at 25 °C ± 1 °C with a series of concentrations for different times. The fibre: H_2SO_4/NaOH solution mass ratio was 1:50, and the beakers were sealed with para film. Then, the cords were taken out and washed with distilled water 3 times and were dried in vacuo at 105 °C for 30 min. The treated CBF cords were weighed again to obtain M_2. The samples immersed in H_2SO_4 solutions at concentrations of 0.25 mol/L, 0.75 mol/L and 2.5 mol/L were named as BH 0.25, BH 0.75 and BH 2.5, respectively, whereas the samples immersed in NaOH solutions at concentrations of 0.5 mol/L, 1.5 mol/L and 5.0 mol/L were named as BN 0.5, BN 1.5 and BN 5.0, respectively.

2.3. Measurement

The composition of CBF was examined by AXIOS Minerals X-ray fluorescence (XRF) from PANalytical, Netherlands. The mass of the CBF cords before and after treatment was measured with an electronic analytical balance (JA 1003, Jinghai Instruments, Shanghai) with a precision of 0.001 g, and the mass retention was calculated according to Eq. (1):

$$Mass\ retention(\%) = (1 - \frac{M1 - M2}{M1}) \times 100 \quad (1)$$

The tensile properties of the CBF cords were tested with a GOTECH AI-7000-M universal testing machine at a drawing rate of 200 mm/min, and the gauge length of the tested cord was 250 mm. The mean values were calculated based on 5 specimens. The surface morphologies of the CBF cords before and after treatment were characterized by a JEOL JSM-7500F scanning electron microscope (SEM). The elemental composition of the specified areas on the surface of treated CBF cords was tested with a JEOL JSM-7400F SEM equipped with an Inca X-Max energy dispersive X-ray spectrometer (EDS) manufactured by Oxford Instruments, UK.

3. Results and discussion

3.1. Mass retention and tensile behaviour of the CBF cord

The mass retention ratios of the CBF cord versus immersion time and concentration of the immersion solution are illustrated in Fig. 1**(a)** and **(b)**, respectively. The mass retention of the CBF cord was significantly affected by the immersion solution type (acid or alkali), immersion time and concentration. With increasing treatment time, the mass of the cords immersed in acid and alkali solutions decreased, and the result indicated that the investigated basalt fibre showed better mass retention when immersed in an alkali rather than an acidic solution. Furthermore, as depicted in Fig. 1**(b)**, when the concentration of H_2SO_4 increased, the mass retention of degraded CBF cord rapidly decreased initially then increased with the concentration when it was higher than 0.75 mol/L. For example, the mass retention ratios were 92.4% and 97.4% when the concentrations of the H_2SO_4 solution were 0.25 mol/L and 2.5 mol/L, respectively, revealing that the latter is much higher than the former. However, the mass retention variation of CBF cords immersed in NaOH solution was different, decreasing with increasing concentration up to 4.0 mol/L and remaining relatively stable or slightly increasing from 4.0 to 5.0 mol/L.

The remaining breaking force and elongation at break of the degraded CBF cords treated with H_2SO_4 and NaOH were normalised relative to the properties of the desized CBF cord (Table 2), and the retention ratios versus immersion time and concentration are presented in Figs. 2 and 3, respectively. The variation trend of the tensile properties is similar to that of the mass retention. According to the results, the corrosion is concentration-dependent for the H_2SO_4 and NaOH solutions, and the increase in the concentration affects the corrosion in two different ways: (1) the rate of reaction and (2) the activity or the mobility of the ions. An increase in the concentration leads to an acceleration in the rate of reaction for