Study of the fracture surface of concretes reinforced with basalt fiber coated with titanium and zirconium dioxides. Fiber-reinforced concrete composites

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Abstract. It is impossible to imagine the development of modern technologies without the use of efficient and affordable fibrous materials based on minerals, glass, and other fibers. The intensive development of the production of fibers and materials based on them worldwide determines the formulation of significant scientific and technical problems of obtaining them with a given set of properties and high-quality indicators, optimization of processing, and rational use. However, the possibility of modifying the composition of the rock with other components that could significantly improve the physical and chemical properties of the fibers is not always taken into account. For the first time, a study was conducted to research the coating of basalt fibers, such as TiO₂, ZrO₂ and their effect on the physical and chemical characteristics of aluminosilicate melts made from rocks, fiber formation processes, structure, and physical and chemical properties of fibers. Studies have shown that fibers modified with oxides of TiO₂ and ZrO₂ have higher chemical resistance in aggressive environments compared with unmodified fibers obtained from melts of similar component groups.

1. Introduction

The study of the basalt fiber surface morphology and its elemental composition before and after interaction with the alkaline medium allows us to determine the details of the etching of basalt fiber in an aggressive environment and the impact on this process when coating its surface. Several different methods are used to determine the effect of an alkaline environment on glass fibers. The etching kinetics of basalt fiber with zirconium dioxide coatings has a more complex dependency. In the first two weeks from the beginning of etching, the coating performs its protective function. But in the next two weeks, the etching of the coated fiber accelerates. According to the references [1], due to the weak connection with the surface, the formed corrosion layer, after reaching a defined thickness, begins to peel off, opening access to the alkaline surface of the basalt fiber, and the process of corrosion layer formation starts from the beginning.

2. Materials and methods of the research

2.1. Study of the fracture surface of concretes reinforced with basalt fiber

Two problems hinder the widespread use of basalt fiber for reinforcing composites with aggressive matrices, primarily the cement ones. The first problem is the degradation of the properties of basalt fiber in the alkaline environment of hardening concrete due to the slow alkaline etching of basalt fiber, followed by a decrease in the fiber mechanical strength [2,3]. The second problem is to ensure the isotropic distribution of the fiber over the volume of the concrete. The solution of both problems has [4,5,6] the prospect of solving by surface modification of basalt fibers.

Research of alkali resistance of basalt fibers, including those modified with titanium and zirconium dioxides in an alkaline environment of hardening concrete was performed. The Figure 1 shows the
research results of the concrete density change depending on the water-cement ratio for the cement brand used in the experiment.

![Figure 1](image.jpg)

**Figure 1.** Effect of water-cement ratio on the density of fiber-reinforced concrete before adding basalt fibers.

At a low water-cement ratio (0.075), the amount of water was insufficient to prepare a homogeneous concrete mixture. The samples prepared from this mixture had a highly porous structure, and the removal from the mold resulted in mechanical damages to the samples. At a ratio of 0.1, the water amount was already sufficient to form strong bonds, but the mixture mobility was low. With a further increase of the water-cement ratio, there was a decrease in the concrete density, which was associated with an increase in pores filled with water. During hardening and storing water-filled pores convert into pores filled with air. Another reason may be the mobility reduction of the concrete mixture due to the introduction of the fiber. Electron microscope (EM) images of concretes reinforced with basalt fibers with and without coatings show that the fiber distribution is homogeneous enough over the volume of the concrete matrix, with individual fibers isolated from each other by a layer of the concrete matrix.

The Figures 2 a and b show the electron microscope images of the destruction of concrete reinforced with basalt fiber (uncoated) after two years of exposure. The figure shows a thick layer with an uneven surface, areas of peeling, deep depressions on the surface of the basalt fiber. These morphological features indicate the process of fiber etching in a strongly alkaline medium of hardening concrete (pH = 13).

It has previously been shown [7,8,9] that the process of etching of the basalt fiber in an alkaline medium involves the partial dissolution of the aluminosilicate composition of the fiber and the formation of a corrosion layer consisting of iron and calcium compounds. Severe changes in morphology, elemental, and phase composition, which occur to basalt fiber in an alkaline environment, lead to a loss of mechanical strength, which, in turn, significantly reduces the positive effect of its addition. Notably, the main changes in fiberglass occur in the first month of hardening, so when storing samples in the laboratory air atmosphere, the difference in morphology of the fracture surface of the samples, which lasted for three months and two years, is almost invisible.
Figure 2. Electron microscope images of concrete reinforced with uncoated basalt fiber: examples of fiber degradation.

A comparative analysis of the concrete matrix morphology and the reinforcing fiber surface shows a significant amount of needle crystals in the concrete matrix. However, needle crystals are not observed on the surface of the fiber. It can be assumed that the thick surface layer consists mainly of corrosion products, but we cannot exclude hydrated components of a cement. Note that there is a strong enough connection between the basalt fiber and the concrete matrix (Figure 2, a).

2.2. Study of the fracture surface of concretes reinforced with basalt fiber

The Figure 3 shows the cross-section of the destruction of concrete reinforced with basalt fiber with one- and two-layer ZrO₂ coating after two years of aging. Electron microscopic examination of the morphology of the basalt fiber with ZrO₂ coating showed that there are "bridges" on its surface.

The analysis of Figure 3 a, shows that the aging of basalt fibers coated with zirconium dioxide in a concrete matrix does not lead to significant morphology changes, as compared to basalt fibers without protective coating. The coating retains its integrity, although there is peeling observed in some areas. Such observation is especially true for areas with "bridges" of a width up to 1.5-2 μm (Figure 3 c). In places of exfoliation, a juvenile unprotected surface of basalt fiber forms and can become subject to further alkaline etching.
Figure 3. Electron microscope images of the fracture surface of the concrete reinforced with the zirconium dioxide $\text{ZrO}_2$ coated fiber.

The analysis of electron microscope images also shows that there is no strong adhesion between the basalt fiber with $\text{ZrO}_2$ coating (1 layer) and the concrete matrix. Notably, the zirconium dioxide coating preserves the integrity, relative inertness, and relief uniformity of hardening concrete in the alkaline environment, which prevents the adhesion of concrete matrix components to the fiber and provides poor adhesion at the boundary "coated fiber - concrete matrix". Accretion of zirconium dioxide coating layers, which leads to an even higher amount of surface defects, and increases the roughness of the fiber relief, contributes to the adhesion of the concrete matrix, the formation of large units of concrete matrix components, and needle crystals on the surface. As a result, the bonding between the surface-modified fiber and the concrete matrix becomes stronger (Figure 3, d). Notably, the electron microscope images did not reveal traces of friction of cement or coated sand particles on the fiber during the preparation of fiber concrete samples. There were smaller exfoliation areas near the stress concentrates (and, accordingly, cracks) in the coating. These areas may occur due to the weakening of the connection with the basalt base resulting from alkaline etching, and coatings weekly bound with the area surface peel off after destruction of the sample.

Cut analysis of the fracture surface of the concrete reinforced with titanium dioxide coated basalt fiber indicates the traces of deeper interaction of the alkaline medium of hardening concrete on the fiber surface than of basalt fiber coated with zirconium dioxide (Figure 3). A large number of areas with exfoliation of a corrosion layer confirm this research. Comparison of the behavior of the basalt fiber with and without $\text{TiO}_2$ coating in the concrete matrix allows us to conclude that $\text{TiO}_2$ coating can protect the fiber from the interaction of alkali to some extent.
Figure 4. Electron microscope images of the fracture surface of the concrete reinforced with titanium dioxide coated fiber.

Thus, according to electron microscopy data, the basalt fiber coated with titanium dioxide occupies an intermediate position between the uncoated fiber and the zirconium dioxide-coated fiber when compared by the corrosion resistance in the concrete matrix. These data correspond with the reference data on alkali resistance of metal oxides [10]. Analysis of electron microscopy data also shows a noticeable bond between the concrete matrix and the surface modified with titanium dioxide fiber (Figure 4 a, b).

It should be noted that the main purpose of these studies was to identify changes in the fiber after its durable stay in the concrete matrix. At this stage of research, achieving maximum strength was not a priority. To see the full picture of the research, it was decided to abandon the addition of a third component, which could improve the strength characteristics of fiber concrete, for example, SiO\textsubscript{2} [11].

The introduction of basalt fiber resulted in a concrete compressive strength decrease due to the growing number of voids. The compressive strength of concrete reinforced with basalt fiber with a single layer of zirconium dioxide after two years is 26 ± 4 MPa. Samples reinforced with basalt fiber with TiO\textsubscript{2} coating showed higher compressive strength (33 ± 8 MPa) compared with concrete samples reinforced with ZrO\textsubscript{2} coated fiber. At the same time, the compressive strength of non-reinforced concrete brand M200 after two years of etching should be ~ 40 MPa [12]. The strength decrease of concrete reinforced with titanium dioxide coated fiber is due to the weaker interaction between the fiber and the cement matrix, like electron microscope images of the cross-sectional fiber concrete surface show (Figure 3). Assumably, sufficient adhesion between the fiber and the concrete matrix, in this case, contributes to good load transfer and, as a result, to higher strength, compared with those of concrete reinforced with ZrO\textsubscript{2} coated basalt fiber.

Thus, it was shown that the preliminary modification of the surface of basalt fiber by applying oxide coatings increases the stability of the fibers in the alkaline environment of the concrete matrix. Among the “uncoated fiber - titanium dioxide-coated fiber - zirconium dioxide-coated fiber” unprotected fiber is subject to the highest corrosion in the concrete matrix.

3. Summary
During the studies, techniques for alkaline etching of ZrO\textsubscript{2} and TiO\textsubscript{2} coated basalt fiber were developed. These techniques allow increasing the strength of basalt fiber in an alkaline environment. Complex physical and chemical studies of the original basalt fiber before and after etching in an alkaline environment were also performed. It was shown that during the etching of the basalt fiber in a solution of sodium hydroxide, the aluminosilicate framework dissolves, and a layer of hexagonal plates forms. Signs of fiber etching in a calcium hydroxide solution appear much later than in a sodium hydroxide solution. It is shown that a small amount of CO\textsubscript{2} in both alkaline solutions leads to the formation of calcium carbonate particles on the fiber surface. Application of the ZrO\textsubscript{2} and TiO\textsubscript{2}
coatings slows down the process of the basalt fiber etching in both alkaline solutions and the ZrO₂ coating provides more reliable resistance to alkali than the TiO₂ coating. Also, studies have shown that the previous surface modification of basalt fibers by applying oxide coatings increases the stability of the fibers in the alkaline environment of the concrete matrix. Among the "uncoated fiber - coated fiber from titanium dioxide-coated fiber from zirconium dioxide" unprotected fiber is subject to the highest corrosion in the environment of the concrete matrix.

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