Oxide composite fibers with quasiplastic components and composites with brittle matrices on their basis

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Abstract. By the internal crystallization method oxide composite fibers containing high-strength sapphire and hexaaluminates of calcium, lanthanum or barium are obtained. The presence of “weak” planes in the layered structure of hexaaluminates provides cracks inhibition. The dependences of the ultimate strain (strength) of the fibers of these compositions on the length are obtained. The positive effect of such fibers was evaluated on composites with brittle matrices of recrystallized molybdenum and nickel-aluminum intermetallic. The fracture toughness of composite materials with such fibers significantly exceeds the fracture toughness of composites with sapphire fibers. The composites were tested in the temperature range of 20–1400 °C and showed non-brittle behavior under load, and their strength and fracture toughness correspond to the requirements for structural materials of this kind. The structure of fibers and composites was also studied by electron microscopy.

1. Introduction
This work is a continuation and development of researches on the fabrication of non-brittle fibrous composite materials from brittle components, some examples of which are from different years [1–6]. These works are based on the idea, apparently, first clearly articulated in [7]. It consists in the organization of an inhomogeneous non-plastic medium containing relatively weak interfaces on the crack propagation path. Under the influence of the stress concentration arising in the zone of the tip of the crack and before it, the material delaminates along “weak” interfaces. These delaminations lead to a blunting of the crack, a decrease in stress concentration, and ultimately to a braking of the crack that destroys the material. The problem of obtaining non-brittle materials from brittle components is particularly acute due to the need to develop high-temperature materials, where sufficiently ductile metals can no longer be used due to high operating temperatures, and more refractory but brittle compounds (intermetallic compounds and various ceramics) begin to be used. In the case of fibrous composites this idea is usually realized through special coatings on fibers that provide a relatively weak fiber – matrix interface [1–4]. As a rule, these coatings have low creep resistance, complicate and increase the cost of fabrication composite materials. The basis of the present work is composite fibers [5, 6], which contain both high-strength components and layered components containing relatively weak planes in their structure, which provide the necessary fracture toughness according to the mechanism described above. Their high strength combined with the ability to provide sufficient crack resistance of high-temperature composite materials has led to the need to expand the range of compositions of such fibers, obtaining and researching composites based on them. This paper gives examples of the results of the fabrication and testing of fibers of three different compositions containing sapphire Al₂O₃ and hexaaluminates of calcium CaAl₁₂O₁₉, lanthanum LaAl₁₇O₁₈, and
barium BaAl$_2$O$_3$. Fibers and composites with a recrystallized brittle molybdenum matrix were obtained by the internal crystallization method [8]. The difficult crystallization conditions for the melts of mixtures of the initial oxides in complex molybdenum channels determined by the method not only complicate the task of controlling the process of obtaining fibers of the required composition, but also make the fibers even more composite in composition, expanding the set of their characteristics, including useful ones. The fibers extracted from the molybdenum matrix were tested for strength and also used as a reinforcing component in a composite with an intermetallic nickel-aluminum matrix. Such composites were obtained by hot pressings a prepregs containing unidirectionally arranged fibers and nickel-aluminum powder.

All fibers are united by the presence of high-strength components: aluminum oxide (sapphire) and hexaaluminates, which are designed to provide, respectively, sufficient strength and non-brittle, “quasiplastic” behavior of composite structures that do not contain plastic deformable components.

2. Methods of fabrication and research

In the work mainly two technological methods were used. To obtain composites with oxide composite fibers and a molybdenum matrix, as well as to obtain fibers for use in matrices other than molybdenum, as already mentioned, the internal crystallization method was used [8]. The method in brief consists in the fabrication of a molybdenum carcass with hollow axial channels, the volume fraction of which in the carcass of the present work was approximately 0.4 of the total volume. The channels serve as shapers for the fibers, a characteristic cross-sections of which are shown in Figures 1b, 2b, 3b, 4b, 5b. In addition, a batch is prepared from a given mixture of oxide powders. The powders are weighed, mixed in ethanol, dried and pressed into tablets. Then the tablets are melted in a molybdenum crucible in a special high-temperature vacuum installation. In the work we used, as already mentioned, mixtures of oxides Al$_2$O$_3$ and CaO, Al$_2$O$_3$ and La$_2$O$_3$, Al$_2$O$_3$ and BaO. Then the molybdenum carcass, in which the longitudinal axis of the channels occupy a vertical position, is lowered endwise into the oxide melt. The melt fills the channels due to capillary forces. Further, the carcass with filled channels rises at a certain speed into the cold zone, during which the fibers crystallize. The resulting fiber composite specimen can be used for further researches, or fibers can be extracted from it for use, for example, in other matrices. In the process of obtaining such composite specimens they are heated to a temperature of about 2000 °C and then cooled. As a result, molybdenum recrystallization occurs, it is embrittled at the same time, and composite specimens with a brittle matrix and oxide fibers are obtained. Naturally, the structure and properties of the fibers are determined by both the initial composition of the oxides and technological regimes, the essential parameter of which is the crystallization rate of the fibers, which is determined by the rate of drawing of the specimen into the cold zone. The initial weight composition of the oxides to obtain the fibers and the drawing rate V of the specimen during crystallization of the fibers are given in the captions to Figures. The fibers were separated from the molybdenum matrix by etching it with a mixture of acids. To obtain fiber composites with the fibers and matrices from powders the hot pressing method was used. Powder of matrix material was poured into a graphite mold interspersed with layer-by-layer laying with a given step of unidirectionally arranged fibers. Thus obtained preform was subjected to hot pressing in vacuum at high temperature. The flat a specimen was then cut into rods of rectangular cross section with a longitudinal axis along the fibers suitable for mechanical testing.

Composite specimens were tested under three-point bending of rectangular cross-section rods; moreover, in the case of fracture toughness tests, specimens with a side notch were used to determine the critical stress intensity factor $K^*$ [9]. Strength values were calculated using well-known strength of materials formulas. The values of the effective surface fracture energy were determined as $g^* = (1/2S) \int P(x) dx$, where $P$ is the load on the specimen, $x$ is the displacement of the point of application of the load to the specimen (flexure of the specimen), $S$ is the cross-sectional area of the specimen. Specimens were tested in the range of $20 \pm 1400$ °C; testing at high temperatures were carried out in a vacuum chamber.
Single fibers were tested at room temperature according to the procedure [10], which briefly consists in the following. The fiber is fixed to the metal foil substrate with rubber glue and wound sequentially on a series of rigid cylinders of decreasing diameters. At each step the number of breaks is calculated and the average fiber length between them is determined, the ultimate (maximum) deformation in the fiber is also calculated at the same time and the correspondence is established: ultimate strain – fiber length. Since the materials of the oxide fibers have an almost linear strain curve, fracture strength can be determined by multiplying the Young's modulus by the ultimate stress value.

The microstructure of composites and fibers was studied using the digital scanning electron microscopes CamScan MV230 and Tescan VEGA-II equipped with W-cathodes and detectors of secondary and reflected electrons and energy dispersive X-ray microanalyzer. This allowed not only to observe the features of structures, but also to determine their composition by chemical compounds. Analysis by chemical elements and constitution diagrams of the corresponding oxide systems allow us to do this in the first approximation.

3. Results and discussions
The results of fabrication and testing of fibers based on sapphire – calcium hexaaluminate, sapphire – hexaaluminate lanthanum, sapphire – hexaaluminate barium are given as examples. Figures 1a, 2a, 3a show the dependences of ultimate strain (fracture strain) on the length of fibers of various batches. The decreasing dependences in semilogarithmic coordinates have a linear shape, which indicates their power dependence, which is typical for objects of this type. Considering that the elastic modulus of fiber materials can be estimated at 300–400 GPa, the strength of fibers over a length of about 1 mm can be more than 1000 MPa, which is quite sufficient for using these fibers as reinforcing components of structural materials.

![Figure 1.](image)

**Figure 1.** The dependence of the ultimate strain on the length of the fibers of the batch of initial composition \( \text{Al}_2\text{O}_3 - 4.2 \text{ wt.\% CaO}, V = 250 \text{ mm/min} \) (a); the fracture surface of the tested fiber (b): black areas – \( \text{Al}_2\text{O}_3 \), light areas – calcium containing compounds including CaAl_{12}O_{19}.

In addition to these compounds, the fibers can also contain other complex oxides containing aluminum, calcium [5], lanthanum, barium presented in the corresponding constitution diagrams of the oxide systems. The appearance of these compounds is primarily caused by the difficult crystallization conditions of the initial melts in the channels of the molybdenum carcass. However, the analysis of this multifaceted process is beyond the scope of this work and should be the object of future research.
Figure 2. The dependence of the ultimate strain on the length of the fibers of the batch of initial composition equivalent to LaAl$_{11}$O$_{18}$, $V = 50$ mm/min (a); the fracture surface of the tested fiber (b): black areas – Al$_2$O$_3$, light areas – lanthanum containing compounds including LaAl$_{11}$O$_{18}$.

Figure 3. The dependence of the ultimate strain on the length of the fibers of the batch of initial composition equivalent to BaAl$_{12}$O$_{19}$, $V = 800$ mm/min (a); the fracture surface of the tested fiber (b): black areas – Al$_2$O$_3$, light areas – barium containing compounds including BaAl$_{12}$O$_{19}$.

Thus, with the initial compositions of oxide mixtures equivalent to lanthanum or barium hexaaluminates, ordered composite structures with other components are also formed as a result of crystallization. Fibers contain a high-strength component sapphire (black in images of fiber fracture surfaces) and complex oxides (gray) containing hexaaluminates, which should provide the necessary fracture toughness of composite structures, Figures 1b, 2b, 3b. Complex fracture surfaces of fibers and composites (Figures 1b, 2b, 3b, 4b, 5b) confirm this.
Figure 4. The flexure dependence on the load of one of the composite specimen (Al₂O₃ – LaAl₁₁O₁₈) / Mo, V = 250 mm/min with a notch for fracture toughness testing, specimen size ≈ 5×15×60 mm (a); the fracture surface of the tested specimen (b): Mo–matrix has white colour, fibres have black-gray colour.

Figure 4 shows the testing results of one of the specimens obtained by internal crystallization with composite oxide fibers containing sapphire and lanthanum hexaaluminate and a brittle molybdenum matrix from recrystallized molybdenum. “Quasiplasticity” at the macroscopic level is manifested in the nonlinearity of the deformation curve of the specimen during bending testing (Figure 4a). Debondings and shifts along the fiber-matrix interfaces, pulling out the fibers from the matrix, fracture of the fibers along weak layers are visible on the relief of the fracture surface of the specimen (Figure 4b). These microfracture processes lead to non-brittle fracture of the composite material as a whole.

Figure 5. The flexure dependence on the load of one of the composite specimen (Al₂O₃ – LaAl₁₁O₁₈) / NiAl tested on strength, specimen size ≈ 4×4×20 mm (a); the area of a fracture surface of the tested specimen (b): (Al₂O₃ – LaAl₁₁O₁₈)-fibre in NiAl-matrix.

Similar results were obtained on a composite material with the same fibers and a brittle intermetallic nickel-aluminum matrix (Figure 5) made by hot pressing in the regime of 1400 °C – 30 min – 30 MPa.
Figure 6. Correlations between critical stress intensity factors $K^*$ and effective fracture surface energy $g^*$ of composite specimens with a brittle molybdenum matrix and oxide fibers of different composition of the Al$_2$O$_3$ – CaO system (a) and the sensitivity of the specimens to notches $\sigma_n^*/\sigma_0^*$ (b), $\sigma_n^*$ is the strength of the specimens with a notch, $\sigma_0^*$ is the strength of the specimens without a notch.

Figure 7. The temperature dependences of the strength of composite specimens with oxide fibers and a molybdenum or nickel-aluminium matrix (a), the compositions of specimens are indicated in the graph field (details in the text); a specimen with a molybdenum matrix after testing at a temperature of 1400 °C (b); fibers used for the making of specimens with a nickel-aluminium matrix (c). The numbers on the ruler scale indicate centimeters.

For composites with composite oxide fibers with initial variations of mixtures of oxides Al$_2$O$_3$ – CaO included from 100% Al$_2$O$_3$ to Al$_2$O$_3$ – 8.0 wt.% CaO containing sapphire and calcium hexaaluminate, and a brittle molybdenum matrix from recrystallized molybdenum, a series of testings were carried out to determine the critical stress intensity factor $K^*$, effective surface energy $g^*$ and notch strength sensitivity $\sigma_n^*/\sigma_0^*$ (Figure 6). In addition, a specimen of molybdenum carcass without fibres was tested, which showed $K^* = 8$ MPa$\cdot$m$^{1/2}$. And for the specimen with sapphire fibers the value $K^* = 13$ MPa$\cdot$m$^{1/2}$ was obtained. An almost linear correlation was established between the $K^*$ and $g^*$ values (Figure 6a), which indicates the reliability of the results and the correctness of approaches to their estimations. Strength values $\sigma_0^*$ were obtained on specimens without notches. And the values of $\sigma_n^*$ were obtained on specimens with a side notch reaching the middle of the cross section of the specimen, while calculating the strength value the remaining half of the section was taken into account. The values of $\sigma_n^*/\sigma_0^*$ can reach values close to unity, which indicates the almost complete
insensitivity of the specimens to notches. And the values $K^*$ and $\frac{\sigma^*_n}{\sigma_0^*}$ correlate quite naturally with each other (Figure 6b).

In addition, tests were conducted on composite specimens over a wide temperature range. Specimens with a molybdenum and nickel-aluminum matrix were tested. The specimens used fibers with initial composition equivalent to LaAl$_{11}$O$_{18}$, and crystallized at different drawing rates $V = 50$ mm/min (designation “1” on the graph), $V = 250$ mm/min (designation “2” on the graph), Figure 7a. Figure 7b shows one of the specimens with molybdenum matrix after the testing, visible trajectory of the crack is nonlinear, which indicates the non-brittle nature of the fracture of the composite material. Figure 7c shows fibers of type “2” used for the manufacture of specimens with a nickel-aluminum matrix.

Thus, the test results of specimens of composite materials showed that their characteristics fully satisfy the requirements for structural materials.

4. Conclusion

Using the internal crystallization method from the initial oxides of aluminum, calcium, lanthanum and barium, fibers of three different compositions containing sapphire and hexaaluminates of calcium, lanthanum or barium were obtained. As a result of testing, the dependences of the ultimate strain (strength) of the fibers on the length were obtained. The strength of the fibers was quite sufficient to use them as a reinforcing component of composite materials.

Composites with the mentioned fibers and brittle matrices of recrystallized molybdenum and nickel-aluminum intermetallic were made and tested in the temperature range of $20 \div 1400$ °C. The results of testing for strength and fracture toughness showed that the level of the obtained values fully corresponds to the requirements for structural materials of this kind.

The shapes of the deformation curves during testing and observations of the fracture structure of specimens of composite materials containing non-plastic components are showing the non-brittle "quasiplastic" nature of their fracture.

These results on composite materials were achieved mainly due to the presence of oxide composite fibers containing components of sapphire and hexaaluminates which provide the necessary strength and fracture toughness respectively.

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