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Composite oxide fibers and brittle matrix composites based on them

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Abstract. Composite oxide fibers were obtained on the basis of various initial mixtures of oxides of aluminium, calcium, barium and yttrium. The fibers contain components that provide the necessary strength and fracture toughness. High strength is provided by alumina. Fracture toughness is mainly determined by the formation of layered components of calcium hexaaluminate or barium hexaaluminate in the fiber structure. Relatively weak planes in the structure of the hexaaluminates play the role of brakes of cracks in composites consisting of non-plastic components. Composites with brittle matrices were made on the basis of these fibers, tests of which showed their “quasiplastic” behavior under load. The strength values in the temperature range of 20–1400 °C and fracture toughness correspond to the requirements for structural materials.

1. Introduction

The growing requirements for structural materials, in particular, heat-resistant composite materials developed for work in a wide range of temperatures, lead to the need to include in the structure of chemical compounds that were not previously used, which can provide work in new conditions. They can be strength and exhibit significant creep resistance at high temperatures. But many of them are brittle. This raises the problem of ensuring the overall non-brittle behavior of a material containing brittle components. It is known that fibrous composites with brittle components can exhibit quasi-plastic behavior. This is usually achieved by organizing relatively weak interfaces between the fibers and the matrix, which inhibit the propagation of cracks in the composite structure [1]. Such an opportunity, as a rule, is realized due to special coatings on the fiber, which provide the necessary characteristics of the fiber – matrix interface. As coatings, for example, lanthanum orthophosphate, which is capable of plastically deforming at sufficiently low temperatures or calcium hexaaluminate, which can exfoliate [2, 3]. As a rule, these coatings are performed on polycrystalline oxide fibers with limited creep resistance at high temperatures, and, in addition, the technological procedure for applying coatings leads to complication of composites manufacture and an increase in their cost. To obtain the fibers required for the reinforcement of brittle matrices, it is proposed to use composite fibers that include, for example, high-strength Al_2O_3 sapphire and calcium hexaaluminate $\text{CaAl}_{12}\text{O}_{19}$, the presence of weak planes in the crystal structure of which can provide the “quasi-plastic” behavior of the composite as a whole. The barium hexaaluminate $\text{BaAl}_{12}\text{O}_{19}$ can perform a similar role. The “weak” planes in these layered compounds in the destruction of the composite structure play the role of crack brakes. In addition, the proposed fibers are aimed at using them at high temperatures. Therefore, the creep resistance of such fibers is an important parameter. The possibility of a higher



creep resistance at high temperatures of $Y_3Al_5O_{12}$ yttrium aluminum garnet based fibers, than sapphire-based Al_2O_3 fibers, is known, that is, such fibers can be of use for high-temperature composites [4]. Therefore, yttrium oxide Y_2O_3 as an additional initial component of the initial compositions of the mixtures of oxides of some batches of fibers was used in this work. The use of the internal crystallization method [5] to obtain fibers allows us to significantly solve the tasks. The internal crystallization method in brief is that a molybdenum carcass with straight hollow coaxial channels is made. A mixture of the necessary oxides is made also. In a high-temperature furnace, the mixture of oxides is melted in a crucible, the end of the molybdenum carcass is immersed in the melt, and the melt fills the channels due to capillary forces. Then the specimen with the channels rises into the cold zone, the melt crystallizes in the channels and forms composite oxide fibers. As a result of the technological procedure of the internal crystallization method associated with heating the specimen with a molybdenum carcass to about 2000 °C, followed by cooling to room temperature, molybdenum recrystallizes and becomes embrittled. Specimens with brittle molybdenum matrix and oxide fibers are obtained. As a result, a hierarchically organized composite system with composite oxide fibers (for example, $Al_2O_3 - CaAl_{12}O_{19}$) and with a brittle molybdenum matrix (Mo) are automatically formed using the initial mixtures of two oxides $Al_2O_3 - CaO$ of a selected composition. The specimens of composites can be tested for strength and fracture toughness and studied their structure. The molybdenum carcass can also be removed by etching with a mixture of nitric and hydrochloric acids, and the fibers thus extracted are placed in another matrix (for example, the intermetallic NiAl). Using constitution diagrams of $Al_2O_3 - CaO$, $Al_2O_3 - BaO$ and $Al_2O_3 - Y_2O_3$ systems as the basis, the choice of initial compositions of mixtures of oxides and technological regimes can be used to obtain various composite oxide fibers intended for use as a reinforcing component, first of all, brittle matrices.

2. Experimental procedures

The characteristics of the composite oxide fibers obtained by the internal crystallization method are determined, firstly, by the initial composition of the mixtures of oxides and, secondly, by the technological regimes, an important parameter of which is the pulling rate V of specimens into the cold zone during the crystallization of the fibers. These two parameters will later be indicated when presenting fibers (for example, $Al_2O_3 - 4.2$ wt.% CaO fibers, $V = 50$ mm/min were made from a charge of the initial mixtures of two oxides $Al_2O_3 - CaO$ of the indicated weight composition and crystallized when the molybdenum carcass containing the fibers was drawn into cold zone at a rate of 50 mm / min). The fabrication of fibers based on the internal crystallization method presented in this work was based on the preparation of powders mixtures of various initial weight compositions of $Al_2O_3 - CaO$ oxides, aimed primarily at obtaining composite fibers of the composition $Al_2O_3 - CaAl_{12}O_{19}$. Experimental variations of mixtures of oxides $Al_2O_3 - CaO$ included from 0 wt.% CaO to 8.0 wt.% CaO. The composition of $Al_2O_3 - 8.0$ wt.% CaO corresponds nominally to calcium hexaaluminate $CaAl_{12}O_{19}$. The composition of $Al_2O_3 - 20.0$ wt.% BaO corresponds nominally to calcium hexaaluminate $BaAl_{12}O_{19}$. The initial composition of the mixtures of oxides $Al_2O_3 - 39.0$ wt.% $Y_2O_3 - 2.8$ wt.% CaO is aimed at obtaining fibers of the composition $Al_2O_3 - Y_3Al_5O_{12} - CaAl_{12}O_{19}$, and other set of oxides $Al_2O_3 - 24.0$ wt.% $Y_2O_3 - 2.4$ wt.% CaO is aimed at obtaining fibers of the composition $(Al_2O_3 - Y_3Al_5O_{12}) - CaAl_{12}O_{19}$, – the eutectic is indicated in parentheses. Taking into account the complex conditions of crystallization of melts of mixtures of oxides in the channels of the molybdenum carcass, the actual final composition of the fibers could differ from that mentioned and contain other compounds, for example, $CaAl_4O_7$, $YAlO_3$ [6, 7]. It should be noted that the issues of the formation of the structure of oxide fibers in molybdenum carcasses require separate special studies. In any case, the composite structure of the fibers obtained contains high strong components and less strong components with relatively weak planes, which provide an increase in the fracture toughness of the whole composite material. The presented work is aimed at solving the problems of providing the necessary balance of strength and fracture toughness.

Composites with composite fibers and brittle matrix of recrystallized molybdenum, and fibers for their use in composites with other matrices were made by the internal crystallization method. The obtained fibers were tested for strength, and composite specimens for strength and fracture toughness. As an example of a composite with a different matrix, pilot specimens with an NiAl intermetallic matrix were made. Specimens were made by hot pressing in vacuum in graphite molds. The molds were filled with a powder of the matrix material with unidirectional fibers distributed in the powder. The resulting specimen preparation was pressed in a vacuum chamber in the regime of 1420 °C – 30 min – 20 MPa.

The fibers obtained in different regimes and with different compositions were tested for strength at room temperature using a technique specially developed for fibers of this type [8]. Briefly, it is as follows. The fiber is fixed on a metal foil substrate with natural rubber glue. The fiber with foil substrate are wound sequentially step by step on a series of rigid cylinders of decreasing diameters. After each step, breaks appear in the fiber due to bending. Then, the average distance between breaks at each step is measured (“fiber length”) and the “ultimate strain” ε is determined at which these breaks occurred: $\varepsilon = d / 2R$, where d is the fiber “diameter” and R is the cylinder radius. Considering the brittle nature of the fracture of the fibers and the linear of strain curve of the fiber material, the bending strength of the fiber can be determined by multiplying the magnitude of the ultimate strain by the Young's modulus of the fiber material (up to 400 GPa).

The strength and fracture toughness of composites was determined under three-point bending testing by known methods on specimens in the form of rods of rectangular cross section. Moreover, the specimens for determining fracture toughness had side notch, and the values of fracture toughness, as critical stress intensity factors, were calculated using the formulas given in [9]. Testing of composite specimens was carried out at room temperature as well as at high temperatures (the latter is specifically indicated). At high temperatures, strength tests were carried out in a vacuum chamber.

Studies of the microstructure of fibres and composites were carried out in the digital scanning electron microscopes Tescan VEGA-II and CamScan MV230. Both microscopes have W-cathodes and are equipped with detectors of secondary and reflected electrons and energy dispersive X-ray microanalyzer.

3. Results and discussions

The side surface and fracture surface of the fibers (Figure 1) clearly demonstrate the layered structures of the calcium hexaaluminate CaAl_2O_9 and barium hexaaluminate BaAl_2O_9 fibers, the purpose of which is to inhibit cracks by the “weak” planes. Exfoliating in front of the crack tip, these materials blunt it, reducing the stress concentration, and inhibit its propagation, increasing the fracture toughness of the entire composite structure.

Figure 2 shows as an example the results of testing one of the batches of composite fibers made from the initial mixture of oxides $\text{Al}_2\text{O}_3 - \text{CaO}$. It can be seen that, over a fiber length of 1 mm, the strength may exceed more than 1000 MPa (Figure 2a), which is quite enough for their use in composite materials. Falling regression dependence is characteristic of brittle objects of this kind and is determined by the distribution of relatively weak “defects” in the bulk and on the surface of the fibers. The fiber fracture surface (Figure 2b) has a “non-brittle appearance”, and surface fractures pass through calcium containing areas (of light color). The structure and composition of fibers in cross section (Figure 2c) has a completely composite appearance.

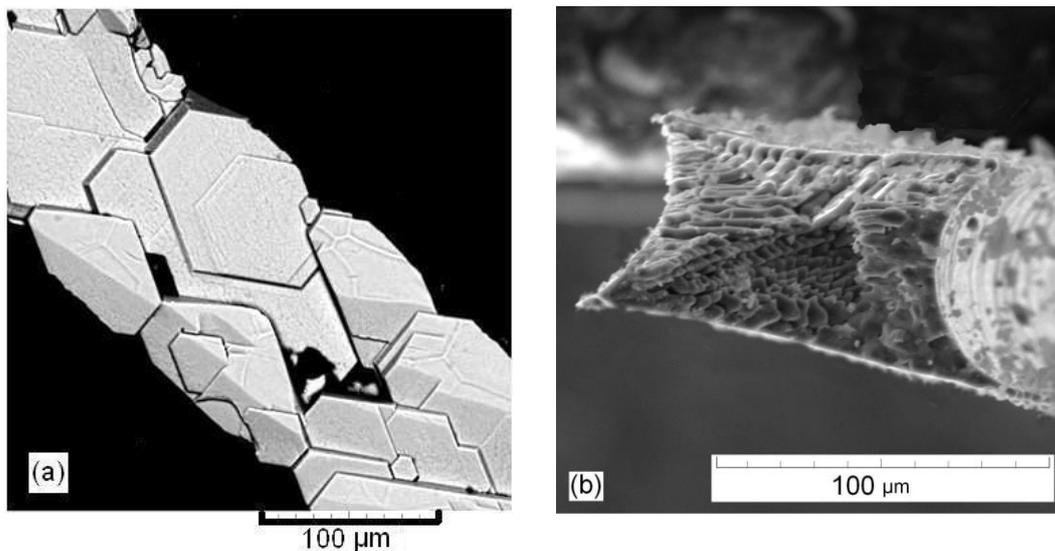


Figure 1. The side surface of calcium hexaaluminate fiber $\text{CaAl}_{12}\text{O}_{19}$, $V = 50$ mm/min (a), the fracture surface of the tested fiber of barium hexaaluminate $\text{BaAl}_{12}\text{O}_{19}$, $V = 800$ mm/min (b).

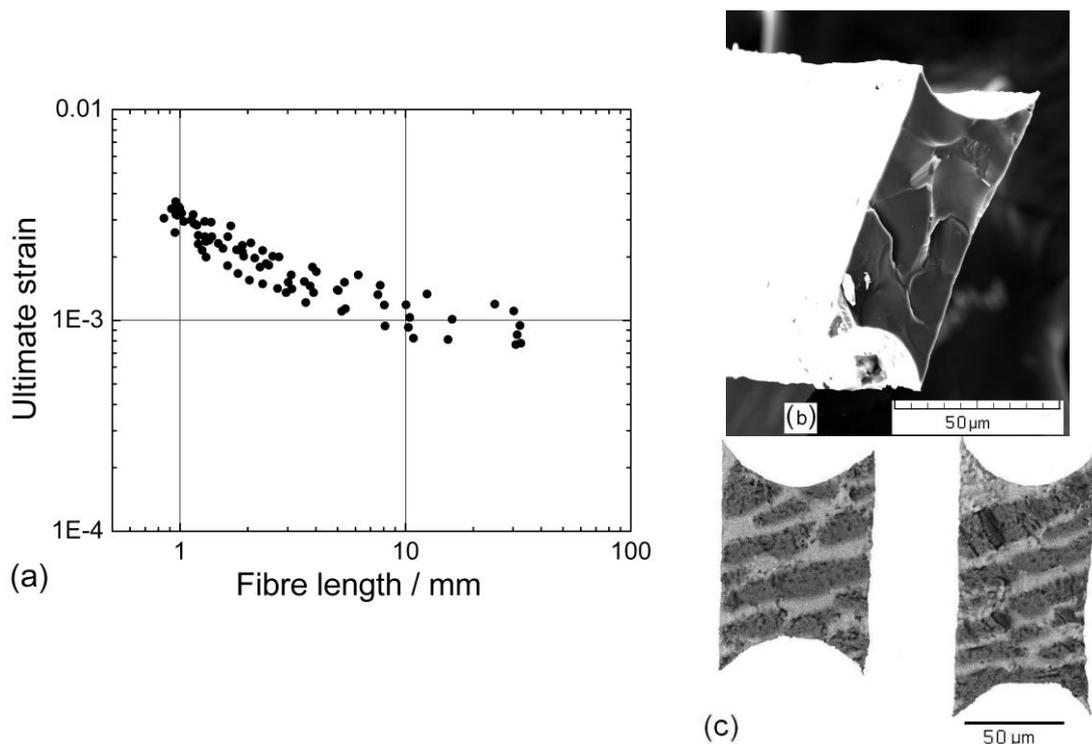


Figure 2. The dependence of the ultimate strain on the length of the fibers of the batch of initial composition $\text{Al}_2\text{O}_3 - 4.2$ wt.% CaO , $V = 50$ mm/min (a); the fracture surface of the tested fiber (b); fibers in cross section: dark areas – Al_2O_3 , light areas – calcium containing compounds (c).

When tested, composite specimens with oxide composite fibers and brittle molybdenum matrix exhibit "quasi-plastic" deformation curves, as shown for one of the specimens in Figure 3a. The specimen was tested for fracture toughness, the test scheme is presented in the inset of the figure. The

value of the critical stress intensity factor for this specimen was $22 \text{ MPa}\cdot\text{m}^{1/2}$, which is quite acceptable for construction materials of this type. The dependence of the values of the critical stress intensity factor of similar specimens with fibers of the same initial composition ($\text{Al}_2\text{O}_3 - 3.2 \text{ wt.}\% \text{ CaO}$) on the pulling rate of them into the cold zone during crystallization of the fibers (Figure 3b) was also obtained. Dependence has a maximum, which opens up the possibility of optimizing the parameters of technological regimes. It is also seen that the fracture toughness of all composite specimens substantially exceeds the fracture toughness of the specimen from the matrix material without fibers (Mo carcass).

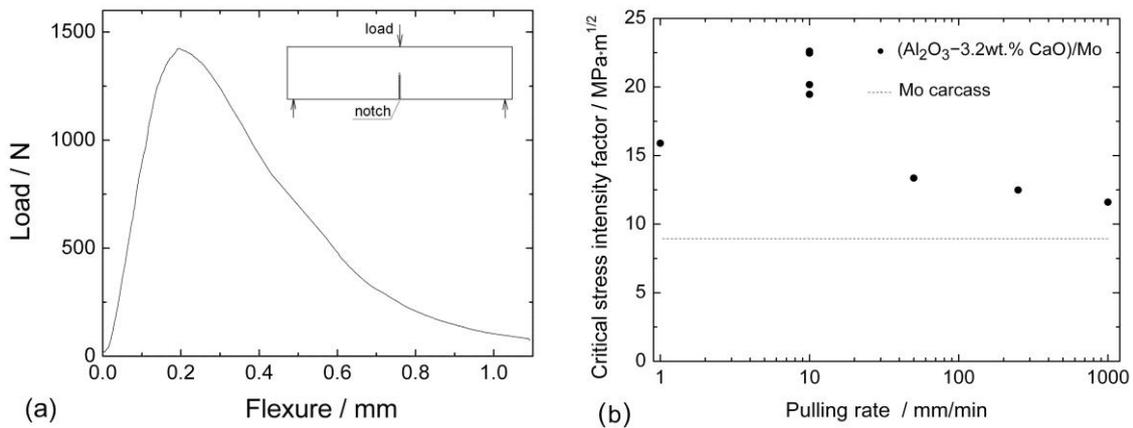


Figure 3. Test results of composite ($\text{Al}_2\text{O}_3 - 3.2 \text{ wt.}\% \text{ CaO}$) / Mo, $V = 10 \text{ mm/min}$ of specimens with a notch for fracture toughness (specimen sizes $\approx 5 \times 15 \times 60 \text{ mm}$): the flexure dependence on the load of one of the specimens when tested, the arrows indicate the direction of load application (a); the dependence of the critical intensity factor of the specimens on the pulling rate them into the cold zone during the crystallization of the fibers; the dotted line is the value of the critical intensity factor of the molybdenum carcass without fibers (b).

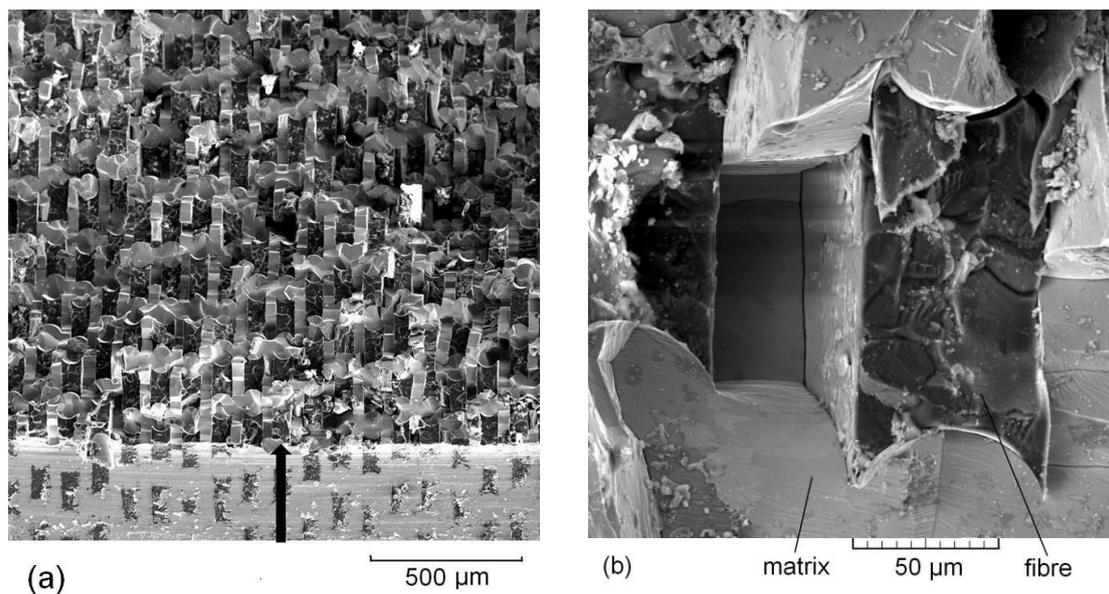


Figure 4. Fracture surface of the composite specimen ($\text{Al}_2\text{O}_3 - 4.2 \text{ wt.}\% \text{ CaO}$) / Mo, $V = 50 \text{ mm/min}$ with a notch after tests for fracture toughness: the area of the fracture surface, the arrow shows the depth of the initial notch (a); one of the composite fibers in the molybdenum matrix after fracture (b).

The “non-brittle” of fracture is also confirmed by observations of the fracture surfaces of composite specimens. In Figure 4 one can clearly see delaminations and shifts along the fiber–matrix interfaces, pulling out the fibers from the matrix, the fibers crushing, the uneven relief of the fracture surface of the composite fibers themselves, which makes a significant contribution to the overall fracture toughness of the composite.

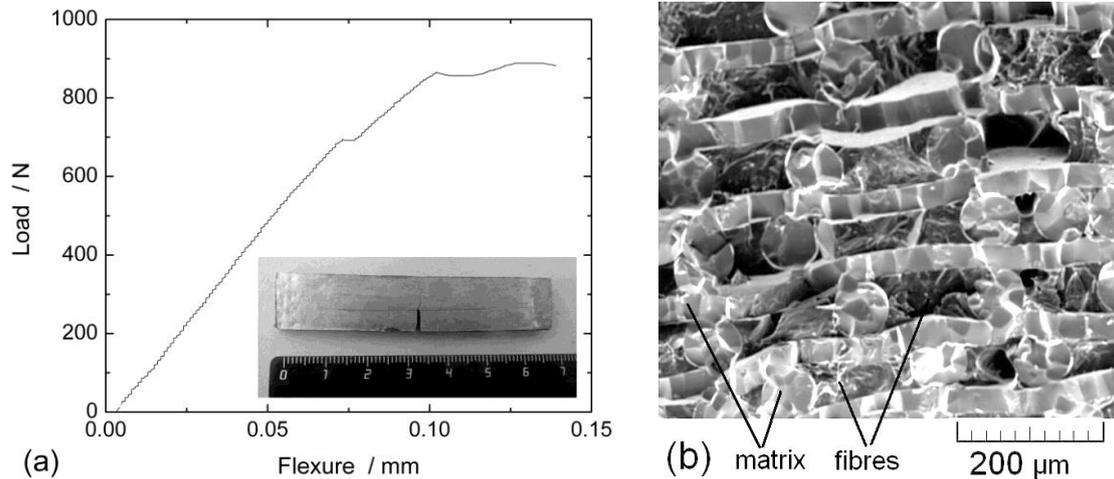


Figure 5. View of the curve of deformation of a composite specimen with a notch ($\text{Al}_2\text{O}_3 - 39.0 \text{ wt.}\% \text{ Y}_2\text{O}_3 - 2.8 \text{ wt.}\% \text{ CaO} / \text{Mo}$, $V = 50 \text{ mm/min}$ during fracture toughness test, inset view of the specimen after test (a); the surface area of the fracture of the specimen (b).

In addition to composites with molybdenum matrix and fibers obtained from various mixtures of the initial oxides $\text{Al}_2\text{O}_3 - \text{CaO}$, composites with a molybdenum matrix and fibers from mixtures of the initial oxides $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3 - \text{CaO}$ were obtained, tested and investigated. The results for one of such composite specimens are shown in Figure 5. The fracture toughness (critical stress intensity factor) of the specimen shown in the figure is an acceptable value of $19 \text{ MPa}\cdot\text{m}^{1/2}$. The strain curve is non-linear, the macrocracks path in the specimen is also non-linear (Figure 5a). The fracture surface has a non-brittle appearance (Figure 5b) with a set of microfractures (fiber splitting, delamination and shifts along the fiber–matrix boundaries), increasing the overall fracture toughness.

Fibers and composites are designed to work in a wide range of temperatures. Therefore, tests on the strength of composites with brittle molybdenum matrix and composite fibers of different composition were carried out in the temperature range of $20\div 1400 \text{ }^\circ\text{C}$. The results are shown in Figure 6. The strength over the entire temperature range is quite satisfactory for structural materials of this kind.

In addition to composites with composite fibers and brittle molybdenum matrix, the structure of which was formed in a single technological cycle, composite specimens were made with an intermetallic matrix with fibers extracted from the auxiliary molybdenum matrix. Specimens, as already mentioned, were made by hot pressing in a vacuum. Figure 7a shows a bunch of fibers prepared to be placed in a mold with a powder of matrix material (NiAl intermetallic compound). Figure 7b shows the fracture surface of one of the composite specimens with the specified fibers and matrix tested for strength. The strength of the presented composite specimen was 320 MPa . The surface of fracture has a “non-brittle” character: an uneven relief of the fibers and the composite as a whole are seen, traces of shifts along the fiber-matrix boundaries are observed, as well as crushing of the fibers.

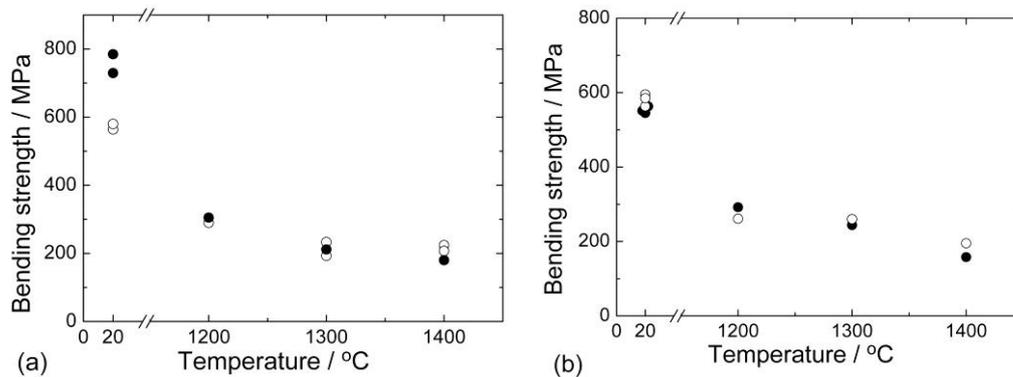


Figure 6. Dependence of the strength of composite specimen on the test temperature of various compositions and conditions of fiber crystallization: composites ($\text{Al}_2\text{O}_3 - 3.2 \text{ wt.}\% \text{ CaO}$) / Mo, $V = 50 \text{ mm/min}$ (black dots on the graph) and ($\text{Al}_2\text{O}_3 - 4.2 \text{ wt.}\% \text{ CaO}$) / Mo, $V = 250 \text{ mm/min}$ (a); composites ($\text{Al}_2\text{O}_3 - 39.0 \text{ wt.}\% \text{ wt. Y}_2\text{O}_3 - 2.8 \text{ wt.}\% \text{ CaO}$) / Mo, $V = 50 \text{ mm/min}$ (black dots) and ($\text{Al}_2\text{O}_3 - 24.0 \text{ wt.}\% \text{ Y}_2\text{O}_3 - 2.4 \text{ wt.}\% \text{ CaO}$) / Mo, $V = 50 \text{ mm/min}$ (b).

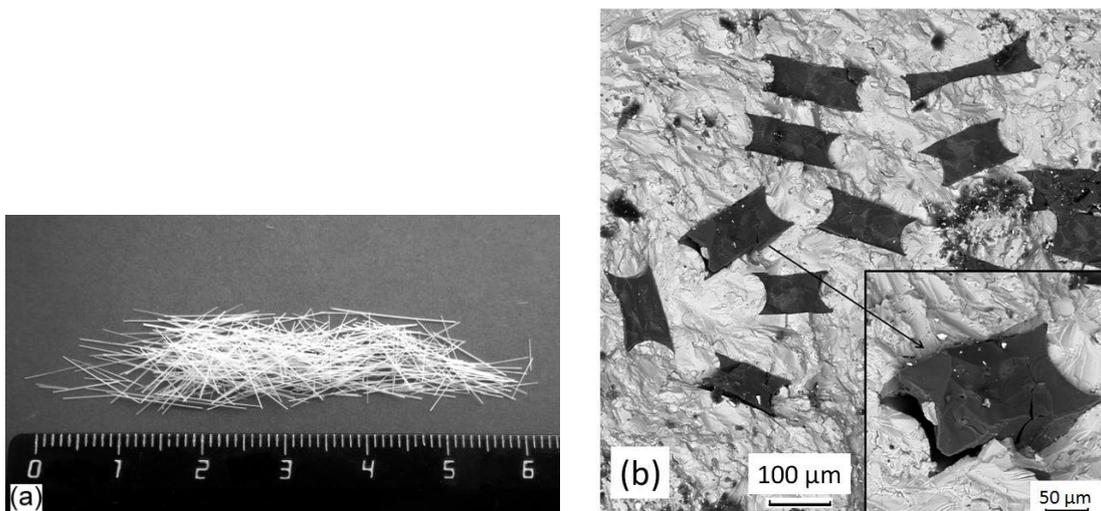


Figure 7. A bunch of composite fibers of a batch ($\text{Al}_2\text{O}_3 - 4.2 \text{ wt.}\% \text{ CaO}$), $V = 50 \text{ mm/min}$ (a); a fracture surface of the composite with the indicated fibers and intermetallic matrix ($\text{Al}_2\text{O}_3 - 4.2 \text{ wt.}\% \text{ CaO}$) / NiAl after the strength test (b).

4. Conclusion

Composite oxide fibers based on initial mixtures of aluminium and calcium or barium oxides, as well as yttrium, were obtained by the internal crystallization method. Composites with brittle matrices of recrystallized molybdenum and nickel-aluminium intermetallic and with these fibers were also made. Studies of the structure showed that the composite fibers contain both high-strength compounds and relatively weak ones with a specific layered structure braking cracks that provides acceptable fracture toughness in the whole of composites with non-plastic components. Thus, fibrous composites with “quasi-plastic” behavior were obtained from brittle components. Tests of composite specimens showed that the strength values in a wide range of temperatures and fracture toughness correspond to the conditions of use of materials of this kind.

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