LAYERED COMPOSITES WITH METAL MATRIX REINFORCED BY OXIDE FIBERS

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Abstract

To obtain layered heat-resistant composites with oxide fibers, a solid-phase method was used. The composite was a multilayer matrix of a viscous-plastic alloy Nb–C–Al and intermetallic compounds of niobium with aluminum, reinforced with Al_2O_3-oxide sapphire fibers. Fibers were obtained by the Stepanov method. Composites of the desired configuration were formed in the process of diffusion welding of multilayer packets assembled from U-shaped elements and the same aluminum elements with sapphire fibers inside. The microstructure of composites was investigated. The first results of mechanical tested.

Keywords: *layered composite, sapphire fibers, multilayer structure, intermetallic compound, diffusion welding, microstructure, bending strength*

1. INTRODUCTION

Operation of structural elements at elevated temperatures is limited by their specific strength. This is due to the fact that an increase in the operating temperature while simultaneously increasing the mechanical load leads to a rapid spending of the strength capabilities of the structural elements. Heat resistant composites with a metal matrix reinforced with durable fibers can solve this problem. If this is not even a complete solution, but the onset of a critical state, however, will be postponed for a long time. In composites, a matrix of an alloy with a high melting point and satisfactory crack resistance and, most importantly, oxide fibers with very high strength and creep resistance can be used [1].

An effective reinforcing agent for heat-resistant composites with a metal matrix can be single-crystal sapphire fibers obtained from the melt by the Stepanov method. Creating a composite with these fibers means getting answers to at least two questions. First, the interaction of the fiber and the matrix in the process of obtaining and operating the product and, secondly, the properties of the composite. For example, a large difference in the coefficients of thermal expansion of the matrix and fiber can lead to the fragmentation of fibers into lengths that do not allow their strength in the composite to be realized. The interaction between the fiber and the matrix forms the interface between them, which largely determines the strength and creep resistance of the composite [2–7].

The present work is devoted to the development and study of a composite with (Nb–Al)-matrix and sapphire fibers obtained by the solid-phase method. In the known composites of the method of internal crystallization [8], the matrix was formed from a melt of a certain composition. In this case, the melting point of the matrix alloy should be below the melting point of the fibers. But the melting point of the matrix can also be quite high, for example, as in this work, niobium alloys and, especially, molybdenum alloys. This presents significant problems for the compatibility of the melt of the matrix with the material of the crucible, as well as with reinforcing fibers. The solid phase method is free from these limitations, since it does not deal with the melting of the matrix. The consolidation of the constituent elements of the original package occurs at temperatures lower than the melting point and the matrix, and, especially, the fibers.

In this work, the microstructure of a composite with (Nb–C–Al)-matrix reinforced with sapphire fibers was studied using scanning electron microscopy and X-ray spectral analysis.

2. MATERIALS AND METHODS

2.1. Construction and assembly of NbC/Al/Al_2O_3-packages

Composites were obtained by diffusion welding of packages, artificially assembled from individual U-shaped elements and sapphire fibers with a diameter of ~ 0,25 mm, obtained by the modified Stepanov method. The elements were made of Nb–0,1 wt.%C alloy foils with a thickness of 50 μm and aluminum foils with a thickness of 10 μm. The foils were oriented so that the bend of the elements coincided with their directions of rolling (Fig. 1).

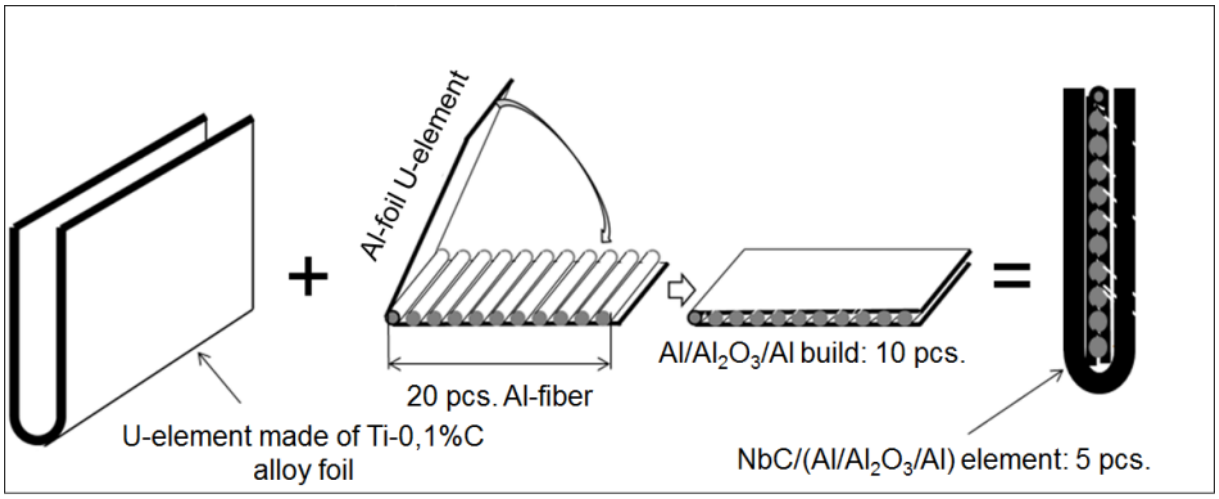


Fig. 1. Assembly of NbC/(Al/Al_2O_3/Al)-elements

Packages were assembled from five NbC/(Al/Al_2O_3/Al) elements, five Al/Al_2O_3/Al assemblies, and one (Nb–C)-alloy foil (Fig. 2). The number of fibers in the package – 200 pcs. Al_2O_3-fibers were laid on one of the inner surfaces of the Al-foil, on which strips of organic glue were applied, drying in air at room temperature. The fibers are oriented along the rolling direction of both aluminum foil and (Nb–C)-alloy foil. In the end, the package represented the alternation of (Nb–C)-alloy foil, aluminum, one row of 20 Al_2O_3 fibers and again aluminum, then everything repeated: NbC/Al/Al_2O_3/ Al ... NbC/Al/Al_2O_3/Al/NbC. The package contained 10 layers of fibers 35 mm long, equal to the width of the package. Then the length of all the fibers in the package was 7 m.

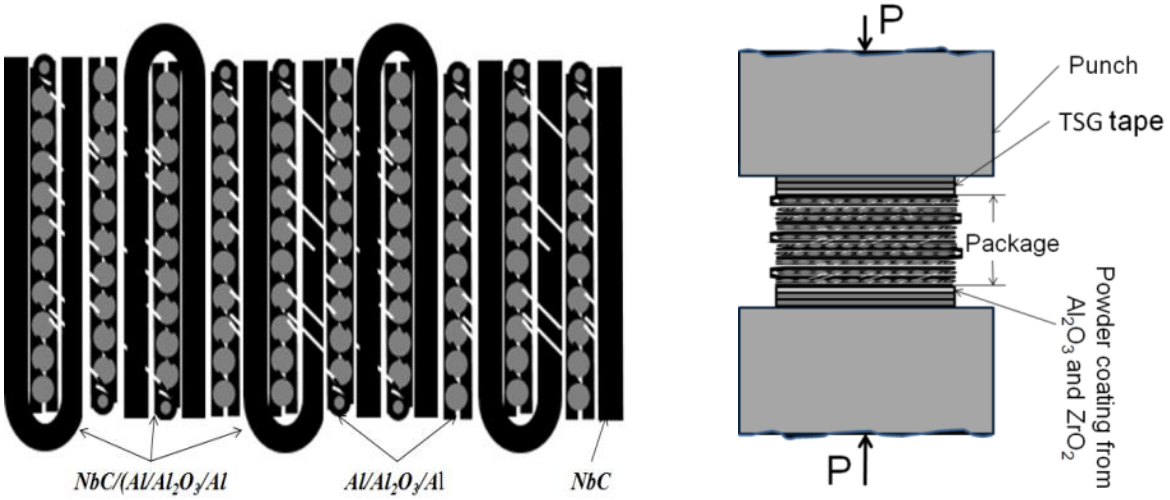


Fig. 2. Schematic representation of the package before diffusion welding

Fig. 3. The position of the package in the installation for diffusion welding in vacuum

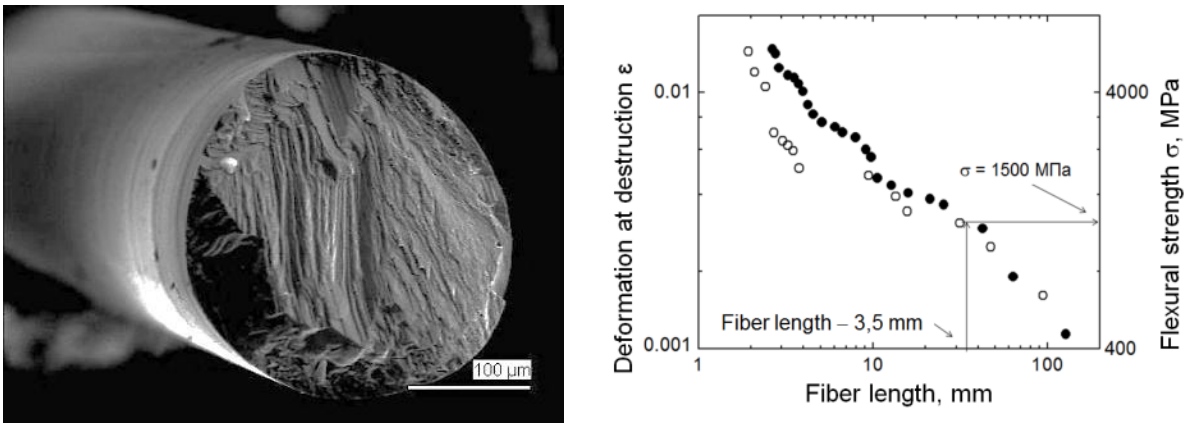
2.2. Diffusion welding packages

Diffusion welding (DW) of packages was carried out according to the mode: 600 °C, 3 h at a pressure of 5,6 MPa + 1400 °C for 30 min under a pressure of 10,5 MPa. Coatings of a mixture of Al_2O_3 and ZrO_2 powders were applied on both external surfaces of the packages. Between the punches and the package were placed gaskets of 2 tapes of thermally split graphite TSG (Fig. 3). After welding: the dimensions of the composite are 35 × 40 mm^2, the thickness is 1,6 mm, the calculated volume content of Al_2O_3-fibers in the composite is 15,5%.

3. RESULTS

3.1. Strength of Al_2O_3-fiber

The maximum deformation in the destruction of the fiber ε on the length of its fragment is determined by the ratio of the diameter of the fiber and the radius of the cylinder R, on which the fiber is "wound". Actually testing the strength of the fibers and produced by winding fibers on rigid cylinders of different diameters. The product of such tests is the dependence of the bending strength of the fiber on its length. Taking into account the brittle nature of the fracture (see Fig. 4, *a*), the fiber strength σ is equal to the product of the deformation ε by its Young's modulus equal to 400 GPa. From here σ fibers 35 mm long, incorporated in a package, are equal ~1500 MPa (fig. 4, *b*). For brittle fiber, this is great strength.



a *b*

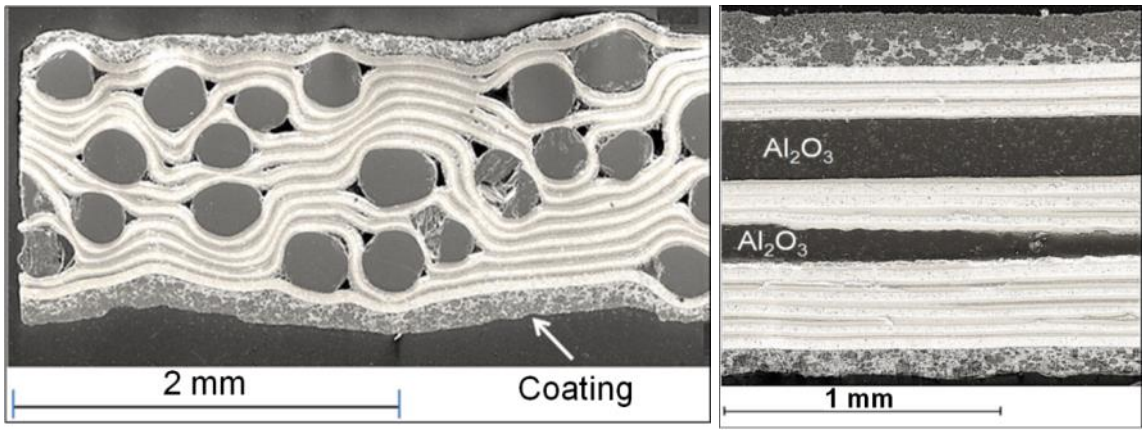
Fig. 4. The microstructure of fiber breakage after fracture when winding on a rigid cylinder (*a*) and the dependence of the strength of the fiber on its length (*b*)

3.2. Composite structure

The macrostructure of the package after diffusion welding is shown in Fig. 5. Both surfaces of the composite have protective coatings from a mixture of oxides Al_2O_3 and ZrO_2. In the cross section, triangular-shaped voids are clearly visible, located on both sides of each fiber. The appearance of such a defect was expected. There are well-known techniques to eliminate it, and they will be applied in the following experiments.

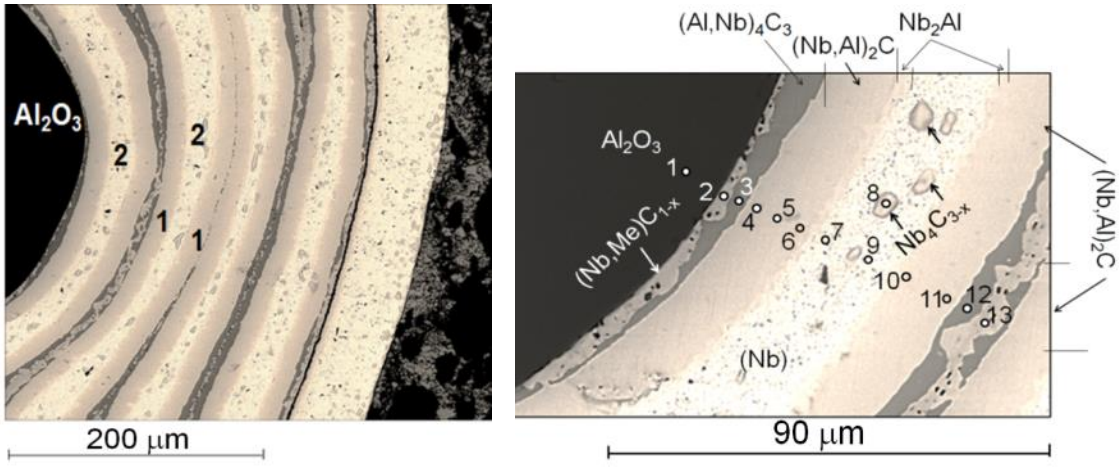
However, a more significant disadvantage of the layered structure of the composite is a complete violation of its laminar order. Since the fibers are not completely deformable, and their diameter significantly exceeds the combined thickness of the original aluminum and niobium alloy foils from carbon, during the welding process they are forced to bend around the fibers. Therefore, the fibers can also move in the volume of the composite, being subsequently in critical proximity to each other, which then will have a negative effect on the strength of the composite.

In fig. 6 presents almost all the characteristic structural components of the composite, which were manifested during solid-phase interaction of foils of the (Nb–0,1C)-alloy and aluminum in the DW process.



a *b*

Fig. 5. The structure of the cross (*a*) and longitudinal (*b*) section of the composite



a *b*

Fig. 6. The microstructure of the cross section of a composite of the matrix of the alloy Nb – 0.1C and aluminum reinforced with sapphire fibers

The microstructure of the layered matrix was studied using scanning electron microscopy and local X-ray spectral analysis. Layers inheriting foils of the (Nb–0,1C)-alloy have been reliably identified.

After the DW, they consisted of two sublayers 1 (see Fig. 6, *a*) of carbide $(Nb,Al)_2C$ = $(Nb_{1,35}Al_{0,74})_{2,09}C_{0,91}$ (see Fig. 6, *b*) and internal sublayer 2 from a Nb-solid solution with carbide precipitates of Nb_4C_{3-x} = $(Nb,Al)_{4,31}C_{2,69}$ (see analysis point 8). A more subtle analysis shows that sublayer 2 had a variable composition – from a Nb-solid solution of c 2 at.%Al in the central region to the hypereutectic composition $(Nb,Me)_{74,3}C_{25,7}$ (at.%), where Me is Al and Fe.

Between the sublayers 1 and 2 were relatively thin layers of the intermetallic compound of niobium with aluminum Nb_2Al.

A thin 2-phase layer 2,5–7,5 μm thick between the Al_2O_3-fiber and the $(Nb,Al)_2C$ carbide layer was the product of the interaction between Al-foils and (Nb–0,1C)-foils. Its light layer, facing the fiber, is a carbide $(Nb,Me)C_{1-x}$, where Me – Al and Fe (iron in the amount of several tenths of a percent is found in the spectra as an impurity in aluminum). The dark interlayer was carbide $(Al,Nb)_4C_3$ (see analysis points 3 and 12). The interaction of the matrix with the fiber is not marked.

3.3. Coating microstructure

Both surfaces of the composite had protective coatings from a mixture of oxides Al_2O_3 and ZrO_2 (see Fig. 5), obtained together with the formation of a layered structure of the composite. In fig. 7 shows its microstructure, consisting of dark and light "fields", the composition of which was determined using X-ray spectral analysis. It is highly likely that the dark “fields”, having the composition $Al_{31,4}O_{53,0}C_{15,6}$ (at.%), Were a mixture of Al_2O_3 and Al_4C_3. Light “fields” are represented by zirconium oxide $Zr_{1,09}O_{1,91}$ = ZrO_2 with small admixtures of carbon, niobium and aluminum. Carbon in the coating structure was present due to the atmosphere in the chamber for diffusion welding, rich in CO, since its heater was made of high-strength graphite.

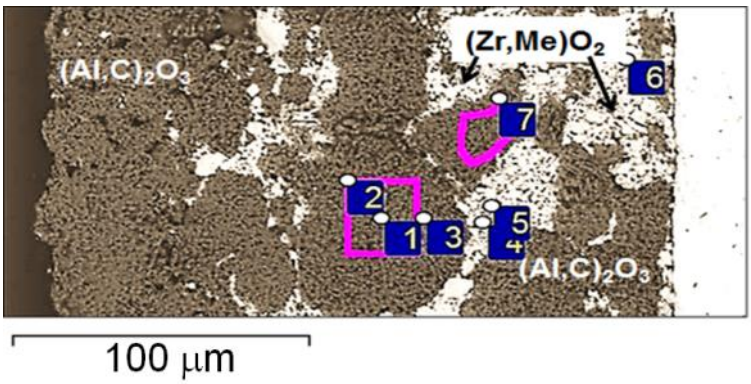
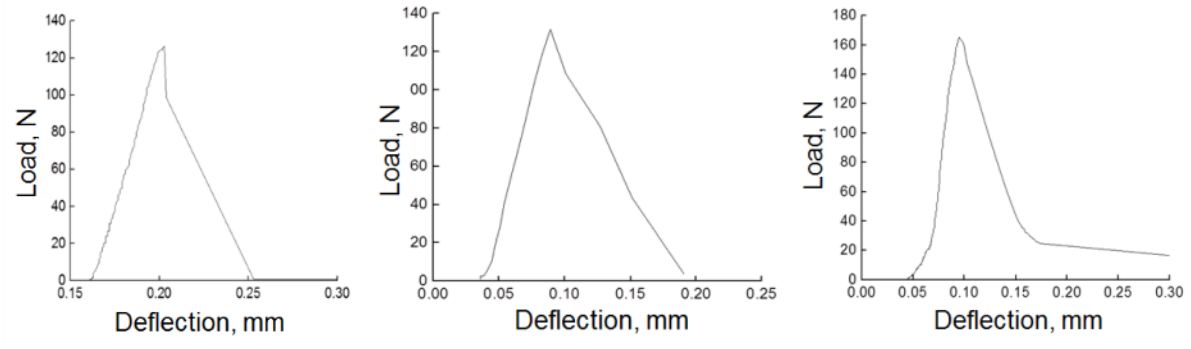


Fig. 7. The microstructure of the cross section of the coating on the surface of the composite

The results of local X-ray spectral analysis of the coating are as follows. Analysis points 1, 2, 3, 7: $(Al_{1,56}C_{0,78}Zr_{0,00}Nb_{0,00})_{2,35}O_{2,65}$ = $(Al,C)_2O_3$. Analysis points 4, 5, 6: $(Zr_{0,98}C_{0,07}Nb_{0,03}Al_{0,01})_{1.09}O_{1,91}$ = = $(Zr,Me)O_2$.

3.4. Mechanical testing

Samples of rectangular composites were tested for strength at room temperature for a 3-point bend. The fibers were located along the axis of the sample. Strength σ was calculated from experimental load-displacement diagrams of the point of application or deflection of the sample using known formulas of resistance of materials (Table 1). Since the layered structure is anisotropic, it made sense to make strength measurements by applying a load perpendicular to P ⊥ (ab) and parallel to P || (ab) to the plane of the composite (ab).Examples of diagrams are presented in fig. 8.



a *b* *c*

Fig. 8. Dependences of load-deflection when testing for three-point bending of composite samples of Nb0,1C/Al/Al_2O_3

Table 1. Strength in testing for 3-point bending σ and effective surface energy g of composite samples with sapphire fibers obtained by the Stepanov method, and a matrix based on Nb–0,1C alloy

Composite	P orientation relative to (ab)	σ, *MPa*	g, J/m^2
7NbC/AlO17	P ⊥ (ab)	167 ± 13	626 ± 195
6NbC/AlO17	P ⊥ (ab)	330 ± 26	
	P ‖ (ab)	350 ± 26	

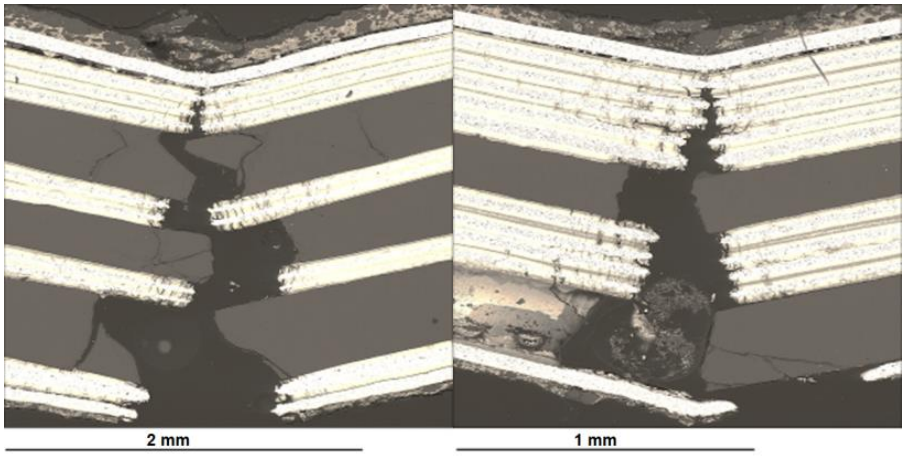
Along with the strength, the effective surface energy was determined, which characterizes the crack resistance of constructional materials, especially non-plastic materials, collapsing with the formation of cracks. The most well-known method for estimating the effective surface energy g, as the ratio of the external load operation to the size of the fracture surface, conducted by stretching a specimen to fracture, requires the preparation of special tooling and specimen, and work in many cases laborious for a number of ceramic, composite and other materials. In this paper, we present estimates "from above" of the g value using a simpler method, namely, testing samples in the form of rods on a 3-point bend. Shown in fig. 8 load-transfer diagrams allow us to make such an assessment. The effective surface energy of the material was determined according to the data recorded during the experiment, by calculating:

$$g = (1/2S)\int_y P(y)dy ,$$

where P is the load on the sample, y is the movement of the point of application of the load to the sample, S is the cross-sectional area of the sample [9].

The fibers used in the work for the preparation of composites have high, not less than 1500 *MPa*, strength [10]. However, the relatively low strength of samples of the composite material containing these fibers indicates that their strength has not been realized. Fracture diagrams (see Fig. 8) indicate that the material is destroyed in a largely fragile manner. But the falling branches of the load-deflection dependences indicate the presence in the samples also of a viscous-plastic structural component with a non-brittle fracture mechanism. In particular, this concerns the sample in fig. 8,*c*. Such a structural component in composite samples is – this is a sublayer 2 or the light middle of the layer inheriting the foil of the Nb–0,1C alloy (see Fig. 6). For the fibers themselves have a very high strength – not less than 1500 *MP*a.

Some "light" at the insufficiently high values of strength at room temperature shed micrographs of places of destruction, presented in Fig. 9.



a *b*

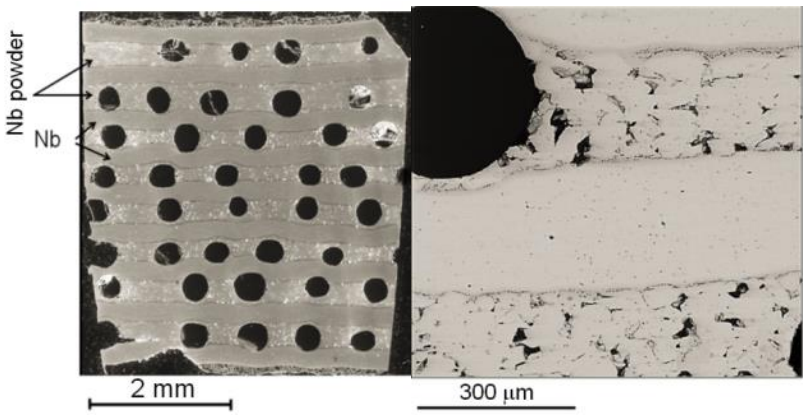
Fig. 9. Structure of composites with Al_2O_3 fibers in places of failure during bending tests P ⊥ (ab)

We see that the volume fraction of the fiber significantly exceeds the "critical". Breakage of one of them leads to additional loading of neighboring fibers through a relatively thin layer of the matrix so that it breaks them in the plane of the 1st fiber crack, forming a common crack that is longer than the critical length for a given load and for given sample sizes. The crack begins to spread non-stop, destroying the entire sample.

4. DISCUSSION

The conclusion on this composite is as follows. The low strength and rather brittle nature of the destruction of samples indicates the need to optimize the structure of the composite. Since, the high strength of single-crystal sapphire fibers is not fully realized. The situation can be improved by slightly reducing the average volume fraction of the fibers and eliminating the causes of zones of locally high volumetric fiber contents.

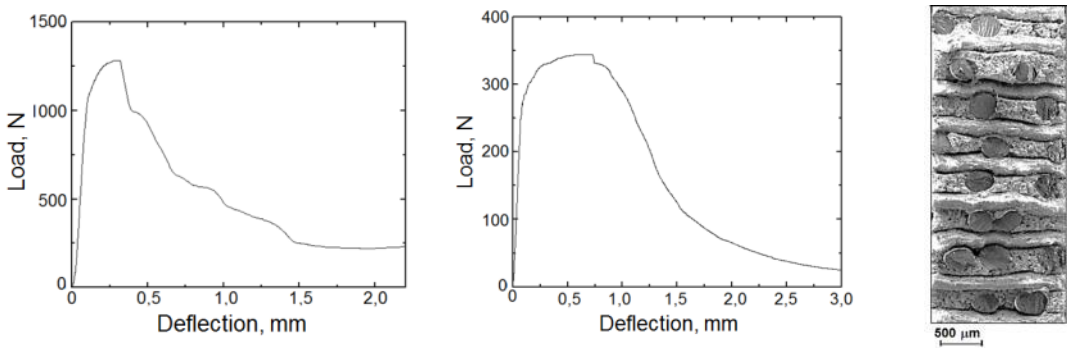
With these comments, such a composite was made. The structure of its cross section after diffusion welding is shown in fig. 10. In the layered structure of the composite, its laminar character is fully observed (1), there are no zones of critical proximity of the fibers (2), no voids diametrically located near the fibers (3) are detected.



a *b*

Fig. 10. Cross-section of the composite 8Nb/Al/Al_2O_3, made with consideration of the deficiencies in the first composites (see. Fig. 5, *a*): *a* – general view, *b* – part of the structure

The first tests for the new composite bending, carried out at room temperature (Fig. 11), showed higher values of strength equal to 789 MPa, if the load was applied perpendicularly, and 416 MPa, if – parallel to the plane of the composite. The type of experimental load-deflection curves (see Fig. 11, *a* and *b*) is characteristic of composites with a non-brittle fracture pattern.



a *b* *c*

Fig. 11. Dependences of load-deflection when testing for three-point bending of composite samples of $Nb/Al/Al_2O_3$ (*a* and *b*) and the fracture surface of the composite (*c*)

The new composite in its original form was composed of 4 U-shaped elements of niobium tape ~ 0.3 mm thick, eight U-elements of Al-tape 10 microns thick, inside which were one row of sapphire fibers covered with Nb-powder and one segment of Nb-tape. The diffusion welding mode of the package is similar to the previously studied composites.

The destruction surface (see Fig. 11, *c*) indicates that oxide fibers lie between the Nb-layers and are in close contact with the sintered Nb-powder.

5. CONCLUSIONS

- It is shown that it is possible to obtain a heat-resistant composite material with a high-temperature niobium-based matrix reinforced with reinforcing sapphire fibers grown by the modified Stepanov method using the solid-phase method.
- The first positive results have been obtained, indicating a real opportunity to manufacture composites with metal matrices reinforced with oxide fibers using the solid-phase diffusion method, bypassing any melting technologies. Confidence was obtained in the need for further research aimed at optimizing the structure of the composite by changing the volume fraction of fibers, the ratio of the initial components of the matrix and the modes of its formation.

ACKNOWLEDGMENTS

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