

THE STRUCTURE, HEAT RESISTANCE, AND FRACTURE TOUGHNESS OF THE LAMINATE COMPOSITE BASED ON NIOBIUM WITH BORIDOSILICIDE STRENGTHENING

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Abstract

The technique of solid-state making of a laminate composite based on niobium with boride-silicide strengthening is presented. The technique consists in diffusion welding of a package of niobium foils covered with a suspension of silicon and boron powders in vacuum under pressure. The research of the micro-structure has determined that the composite represents the alternation of the layers of boron solid solution in niobium and the layers of intermetallic compounds. The strength testing in the temperature range 20–1500°C has shown quite acceptable strength under satisfactory fracture toughness at room temperature. The combination of ductile layers of solid solutions and high-strength brittle layers of intermetallic compounds assures the necessary mechanical characteristics.

Key words: laminate composite, multilayer package, diffusion welding, solid-phase interaction, niobium, boride, silicide, structure, strength, fracture toughness

1. INTRODUCTION

The operating temperatures of nickel-based super alloys commonly used today are not higher than 1150°C that is approximately 0.8 of melting temperature, i.e. they have reached the practical upper limit (Kolobov et al. 2008). One of the possible ways to increase the operating temperatures of heat-resistant materials is the production of composites (Kelly 2007, Mileiko 2007) based on refractory metals, in particular, niobium strengthened with intermetallic compounds (Svetlov 2010a, 2010b). The products made of heat-resistant materials are usually run in a wide range of temperatures. The presence of brittle intermetallic compounds in the composite structure puts a question on the increase of fracture toughness of such materials, especially at low temperatures (Korzhov & Kiiko 2015, Korzhov et al. 2015). As a rule, potentially high strength and creep resistance of intermetallic compounds may make a decisive contribution to high-temperature strength of such materials at the proper organization of a generic structure. A laminated structure with the alternation of layers of refractory metals, solid solutions and intermetallic layers allows one to ensure the solution of a triune task of high-temperature strength material development: security of the necessary balance of strength, fracture toughness and creep resistance. The use of solid-phase method for laminate composite production opens up the possibility to apply different alloys (Karpov et al. 2014) as the basis of initial materials keeping their positive characteristics during the technological process. In this respect the solid-state method is favorably compared with liquid-phase flow diagrams quite often applied for composite production, see, for instance, (Mileiko et al. 2002a, 2002b; Mileiko et al. 2009). The practical opportunity to form products from laminated materials in the process of composite production is also important in the long term.

2. LAMINATE COMPOSITE PRODUCTION

A laminate composite was produced in the form of flat plates obtained from a package of 60 µm thick niobium foils with covering. A Nb-foils was covered with a suspension of silicon and boron powders composition in the ratio 3:1 in polyethylene glycol. The covering was carried out by the method of coloration. The 35 mm wide and 40 mm long foil obtained by this method was collected to a multilayer package so that the rolling direction of the niobium foil coincided with the direction along the package length. Package bonding was carried out in a vacuum furnace (not higher than 10^{-4} mm Hg) with a

graphite heater. During the heating process polyethylene glycol evaporated at the temperature starting with $\sim 200^{\circ}\text{C}$. Diffusion welding was carried out at temperature 1500°C under the pressure of 14 MPa during 1 hour. As a result of bonding the package thickness was $\sim 1.7\text{ mm}$. From the obtained composite plate the specimens of approximately square cross-section were cut on an electrical-discharge machine for mechanical testing and study of a microstructure.

3. COMPOSITE STRUCTURE

The microstructure researches were carried out on the metallographic sections prepared by the appropriate method. The methods of scanning electron microscopy and X-ray spectrum analysis using digital scanning electron microscopes CamScan MV230 and Tescan VEGA-II XMU were employed. Since in the composite under study there was light element boron that was not determined under the evaluation of the chemical composition, the special technique was used. The originality of this technique consists in the laid in it algorithm of matrix correction PAP (Pouchou & Pichoir 1984) allowing one to calculate boron “by the difference”. In this case the reference niobium metallographic section located in one holder with the object under study was used to control the current magnitude of the probe. This fact has to be considered during the analysis of compositions with light elements. However, it can be used with high reliability at relative comparison of the elements concentrations in different phases.

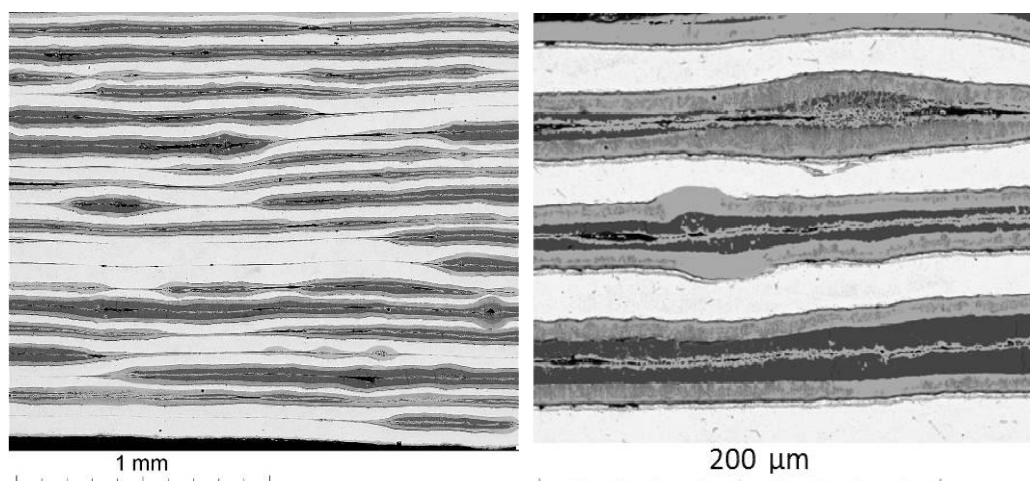


Figure 1. The structure of composite cross-section in the plain parallel to the rolling direction of Nb-foil

The structure of composite cross-section (Figure 1) seems to be regular enough. The layers of diffused zones (dark in the micrographs) formed in the place of (Si–B)-coatings interchanged with the layers (light in the micrographs) of boron solid solutions in niobium Nb(B) taking $\sim 40\%$ of the whole sectional area of the metallographic section. According to the data of X-ray spectrum analysis, between ~ 0 and $3.85\text{ at.}\%$ of boron was dissolved in niobium.

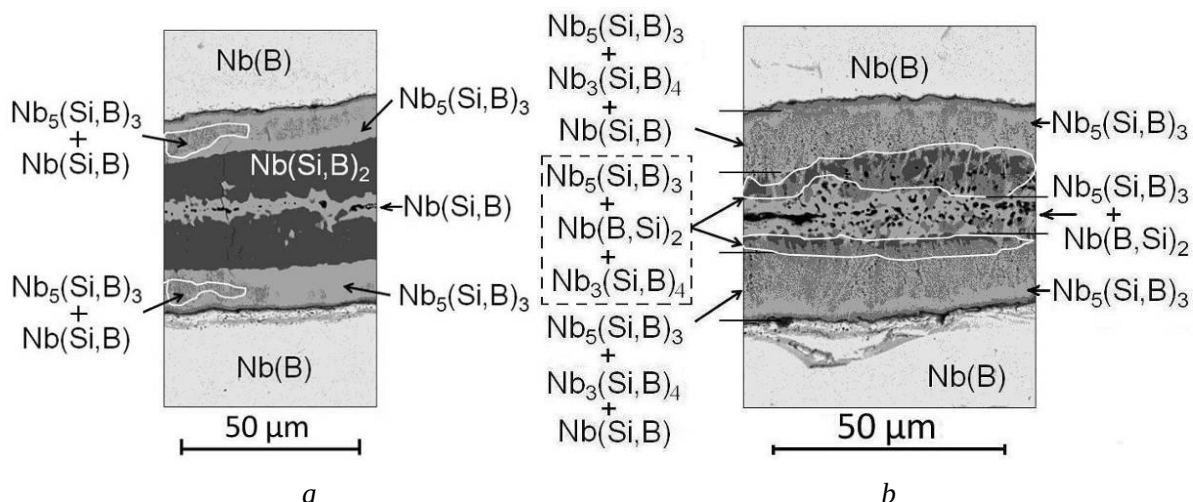


Figure 2. The structure of two segments of composite cross-section in the plain parallel to the rolling direction of Nb-foil

As a result of solid-phase interaction between Nb-foils and (Si–B)-coatings some variations of the microstructure of the formed diffusion layers were observed. The most typical variation is presented in Figure 2a with single-phase middle and intermediate zones. In the place of initial niobium foils boron solid solution in niobium Nb(B) was formed. In adjacent layers of the “matrix phase” Nb₅(Si,B)₃ the composition changed from Nb_{68.6}–Si_{31.4} (hereinafter at.%) $\equiv$ Nb_{5,49}(Si_{2,51}) to Nb_{65.5}–Si_{22.0}–B_{12.5} $\equiv$ Nb_{5,24}(Si_{1,76}B_{1,00})_{2,76}. That is, its composition could change from Nb₅Si₃ silicide not containing boron to the solid solution of boron in it – Nb_{5,24}(Si_{1,76}B_{1,00})_{2,76} with 12.5 at.%B. 2-phase regions marked in Figure 2a as Nb₅(Si,B)₃ + Nb(B,Si) (indicated by white contour lines) consisted of Nb₅(Si,B)₃ и Nb(B,Si): Nb_{51.5}–B_{36.9}–Si_{11.6} $\equiv$ Nb_{1,03}(B_{0,74}Si_{0,23})_{0,97}. Except 2-phase regions, the compound Nb₅(Si,B)₃ extensive fields free from inclusions of the second phase were observed in the external zones of a diffusion layer. A thin (central in the micrograph) interlayer and the adjacent layers of this zone were single-phase and consisted of triple intermetallic compounds Nb(Si,B): Nb_{1,01}(Si_{0,59}B_{0,40})_{0,99} and Nb(Si,B)₂ $\equiv$ Nb_{0,92}(Si_{1,59}B_{0,49})_{2,08} respectively. The latter phase with such a stoichiometric composition is present in the both constitution diagrams of Nb–Si (Lyakishev 1996) and Nb–B (Lyakishev 2001).

Except the described above structure, there were the regions with a structure the appearance and composition of which are presented in Figure 2b. Three-phase layers Nb₅(Si,B)₃ + Nb(B,Si)₄ + Nb(Si,B) adjoin the layers of boron solid solutions in niobium Nb(B). The parts of the three-phase layers are: “matrix” phase Nb₅(Si,B)₃, presented above in describing the same phase of Figure 2a; phase Nb(B,Si)₄ – intermetallic compound Nb₃(B,Si)₄ (silicon solid solution in boride Nb₃B₄) with the composition close to Nb_{42.8}–B_{54.7}–Si_{2.5} $\equiv$ Nb_{3,00}(B_{3,83}Si_{0,17})_{4,00} and also Nb(Si,B) with the composition Nb_{52.2}–B_{47.4}–Si_{0.4} $\equiv$ Nb_{1,04}(B_{0,95}Si_{0,01})_{0,96}. The layers containing Nb₃(B,Si)₄, Nb(Si,B)₂ and Nb₅(Si,B)₃ are indicated by white contour lines in the micrograph. These areas include: Nb₃(B,Si)₄ – triple intermetallic phase (grey color in the micrograph), its composition was described above, Nb(Si,B)₂ phase – boron solid solution in intermetallic compound NbSi₂ (dark color in the micrograph) with the composition Nb_{34.2}–Si_{54.5}–B_{11.3} $\equiv$ Nb_{1,03}(Si_{1,64}B_{0,33})_{1,97} and Nb₅(Si,B)₃ phase in a small amount (light contrast in the micrograph), its composition was described above. The central (in the micrograph) layer contained two phases: Nb₅(Si,B)₃ representing boron solid solution in silicide Nb₅Si₃ with averaged boron concentration 9.0 at.%, and Nb(B,Si)₂ – silicon solid solution in boride NbB₂. Silicon concentration in Nb(B,Si)₂ changed in a range between 0.5 and 18.9 at.%. Compound Nb₅(Si,B)₃ had the composition Nb_{55.0}–Si_{36.0}–B_{9.0} $\equiv$ Nb_{4,40}(Si_{2,88}B_{0,72})_{3,60}, and Nb(B,Si)₂ – the composition between Nb_{36.4}–B_{63.1}–Si_{0.5} $\equiv$ Nb_{1,09}(B_{1,89}Si_{0,02})_{1,91} and Nb_{33.7}–B_{47.4}–Si_{18.9} $\equiv$ Nb_{1,01}(B_{1,42}Si_{0,57})_{1,99}.

4. MECHANICAL PROPERTIES

The strength and fracture toughness were determined for the specimens with dimensions of $\sim 1.7 \times 1.7 \times 10 \text{ mm}^3$ at three-point bending under plane deformation conditions, as shown in Figure 3. At that, the strength testing were carried out in a temperature range 20–1500°C, and the fracture toughness testing were carried out at temperature 20°C. During the testing load and deflection (displacement) of the specimens were recorded. The latter allows one to judge on the character of behavior of the specimen material under loading.

4.1. Fracture toughness testing

The material under development is aimed at use in a wide range of temperatures. Fracture toughness, in particular at low temperatures, including room temperature 20°C, is the important characteristic of such materials.

The estimation of fracture toughness at room temperature was carried out for the edge-notched specimens of rectangular cross-section, as shown in Figure 3.

The critical stress intensity factor K^* was determined by maximum load by the formula (Broek 1974) using the source notations:

$$K^* = \frac{P^* S}{BW^{3/2}} [2.9(a/W)^{1/2} - 4.6(a/W)^{3/2} + 21.8(a/W)^{5/2} - 37.6(a/W)^{7/2} + 38.7(a/W)^{9/2}]$$

where P^* is maximum load, S is the distance between the extreme supports, B is the thickness of the sample, W is the height of the specimen, a is the depth of notch.

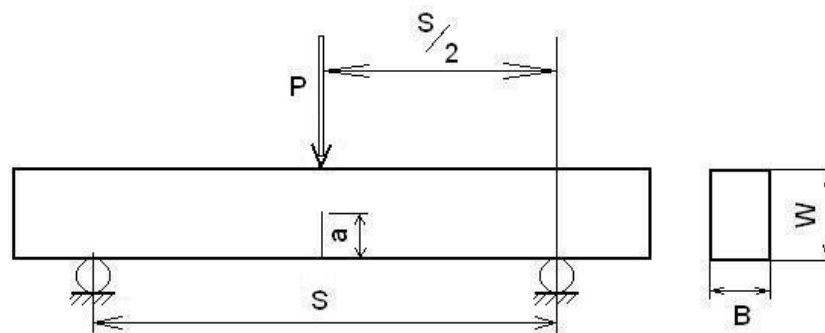


Figure 3. Diagram of specimen loading during the testing

As it has been pointed out, both current load and sample deflection value were recorded during the tests. It allows one not only to calculate the value of K^* , but also to evaluate the character of the destruction process of the sample material. After the tests the structure of the destroyed sample was studied.

Taking into account explicit anisotropy of the material structure, the testing of the specimens were carried out at load application in two orthogonally related directions: perpendicular and parallel to the layers plane.

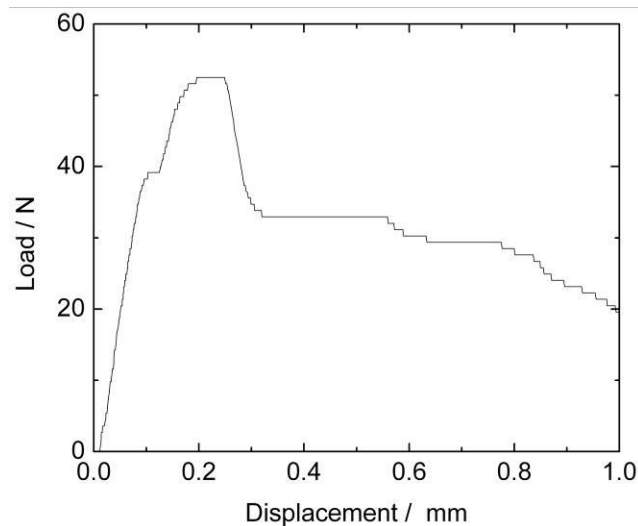


Figure 4. Load-specimen deflection dependence during fracture toughness test: load was applied to the sample in the direction perpendicular to the layers and the specimen structure is demonstrated in Figure 5

Figure 4 shows the result of the fracture toughness testing of one of the notched specimen at load application perpendicular to the layers plane. As the fracture advanced, different micro-destruction types demonstrated in Figure 5 occurred in the material. Under specimen fracture the debonding and displacement along the layers interface were observed. In strengthening layers formed on niobium-coating interface a large number of micro-fractures appeared. Viscous-plastic layers of niobium alloy prevented their propagation. Also in them there were necking in aggregate with the other types of micro-destruction leading to the sinuous trajectory of macro-crack and the increase of material fracture toughness. These processes reflect on the macroscopic level in the gradation of the load – sample deflection dependence (Figure 4).

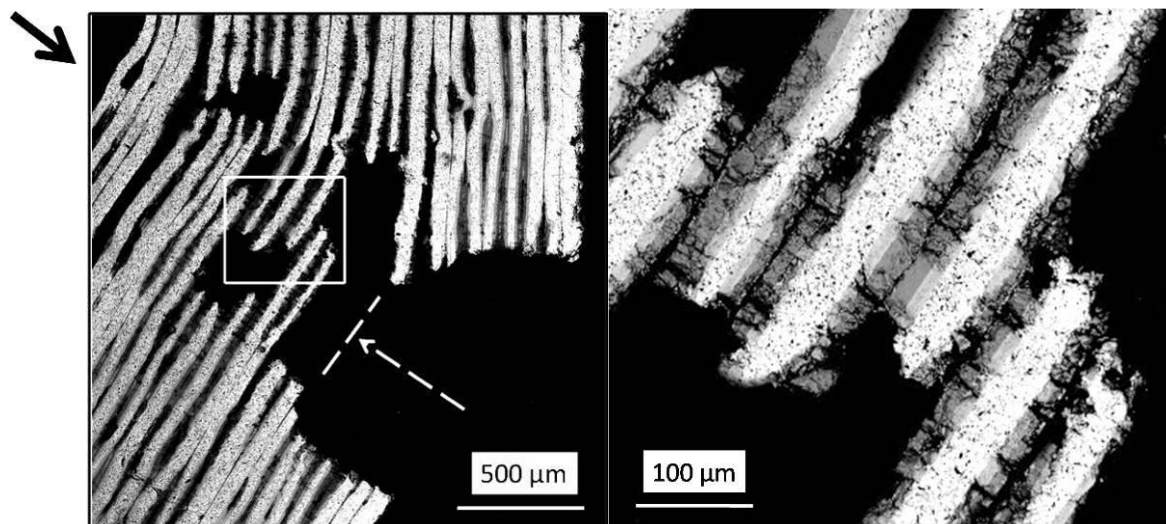


Figure 5. Specimen structure after the fracture toughness testing: the white arrow demonstrates the depth of edge notch and the black arrow shows loading of the specimen in the direction perpendicular to the layers; on the right there is the structure fragment in the destruction region at high magnification

Figure 6 presents the results of the specimen testing at load application in the direction parallel to the layers plain. The different character of the experimental load – specimen deflection dependences is obvious (the load is perpendicular or parallel to the plane of the layers). In the latter case the curve has a smooth form (Figure 6a). For the destruction of the specimen material in the notch tip region where stresses are concentrated (Figure 6b) multiple cracking and micro-fractures in brittle boride-silicide layers are typical. The layer of Nb-alloy is characterized by viscous-plastic destruction.

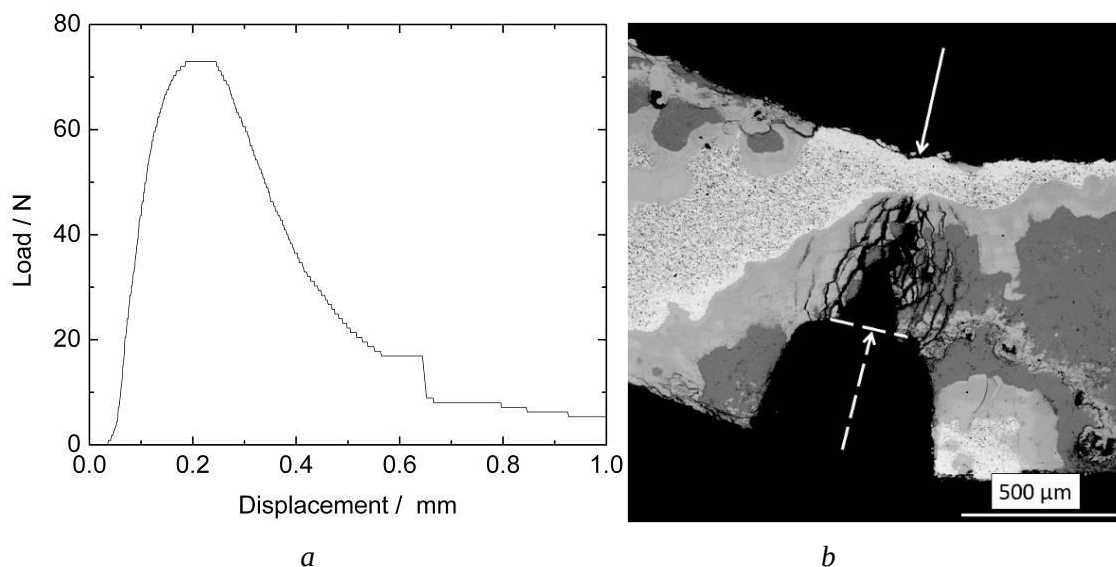


Figure 6. Experimental load-specimen deflection: *a* – dependence during the testing; *b* – specimen structure after the fracture toughness testing, where the dotted arrow shows the depth of edge notch and the solid arrow demonstrates loading of the specimen in the direction parallel to the layers

As a result of processing load-notched specimen deflection dependences, the fracture toughness values for two batches of specimens were obtained: at load application in the direction perpendicular to the layers plain $K_{\perp}^* = (13.0 \pm 1.3) \text{ MPa} \cdot \text{m}^{1/2}$; at load application in the direction parallel to the layers plain $K_{\parallel}^* = (12.0 \pm 0.5) \text{ MPa} \cdot \text{m}^{1/2}$. The peculiarities of destruction on account of the anisotropy of material structure led to the difference of the values of the quantities K^* proper as well as the dispersion of their values. The tests results show that the value of material fracture toughness in the direction perpendicular to the layers plain is higher than in the direction parallel to the layers plain.

The values of the fracture toughness quantities K^* indicate that the tested material is between typical ceramics and high-strength structural metal alloys for fracture toughness.

4.2. Strength testing

The estimation of strength was carried out for the specimens of rectangular cross-section by the testing at three-point bending similarly to the fracture toughness testing, as shown in Figure 3. In this case the specimens did not have notches. Samples strength was determined by maximum load by the formula $\sigma = (3P \cdot S) / (2BW^2)$ (Ruditsin, Artemov & Ljuboshits 1970).

4.2.1. Strength testing at room temperature

During the testing both load and specimen deflection was recorded as well as during the fracture toughness testing.

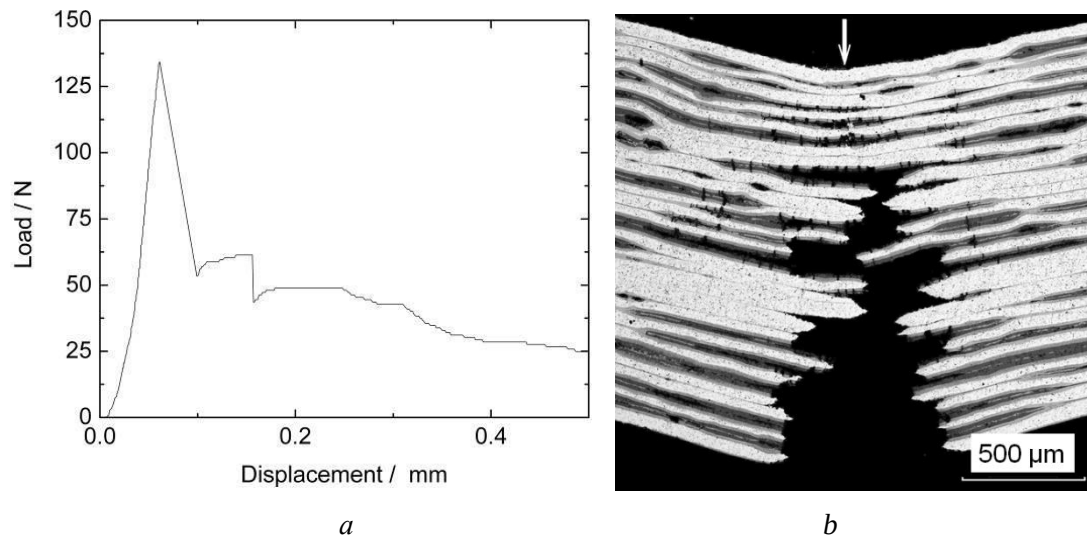


Figure 7. Experimental load-deflection dependence: *a* – specimen structure after the strength testing; *b* – the direction of load application is perpendicular to the layers (it is demonstrated by the arrow)

In Figure 7a the load-deflection dependence has a stepped form that sequentially reflects the process of specimen structure destruction (Figure 7b). The destruction occurs as the macro-crack propagation and it is accompanied by different types of micro-destruction similar to those occurring at the fracture toughness tests of the notched specimens.

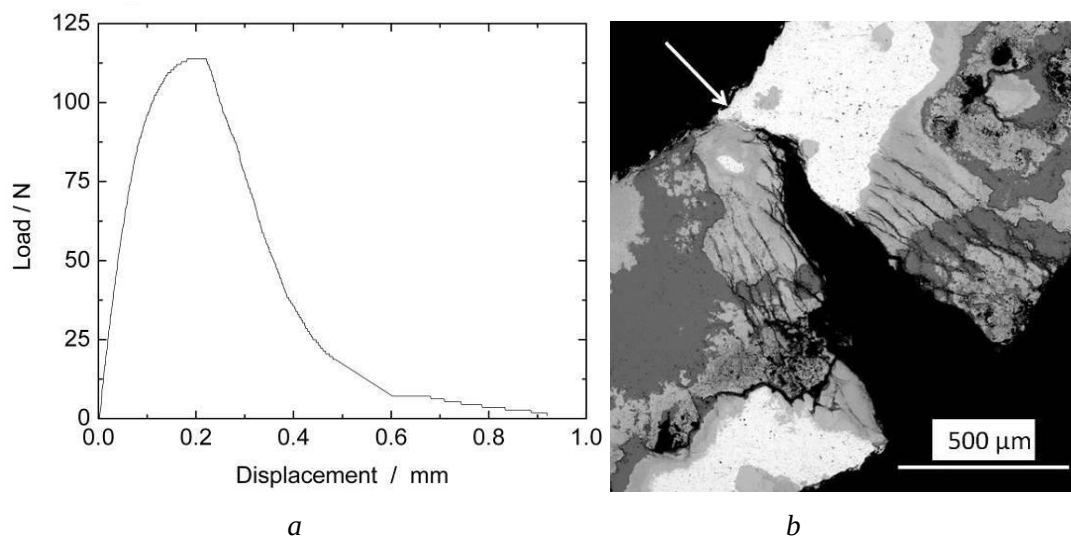


Figure 8. Experimental load-deflection dependence: *a* – specimen structure after the strength testing; *b* – loading of the specimen in the direction parallel to the layers (it is shown by the arrow)

Figure 8a presents rather a smooth (unlike the previous one) load – specimen deflection curve during the test of the specimen with load application along the layers. In such a specimen under loading along the macro-crack in brittle boride-silicide layers micro-fractures almost parallel to it are formed, and the layer of a solid solution is plastically deformed (Figure 8b).

At load application in the directions perpendicular and parallel to the layers plain strength $\sigma_{\perp} = (600 \pm 180) \text{ MPa}$, $\sigma_{\parallel} = (790 \pm 48) \text{ MPa}$, respectively. Higher strength of the specimens at load application parallel to the structure layers may be explained by higher section modulus at bending of high-modular

high-strength boride-silicide layers in comparison with the layers located perpendicularly to loading direction.

4.2.2. Strength testing at high temperatures

The testing at high temperatures was performed in a water-cooled chamber in argon atmosphere with the registration of load-specimens deflection as well as during the testing at room temperature. Load was applied to the specimens in the direction perpendicular to the layers of the composite structure.

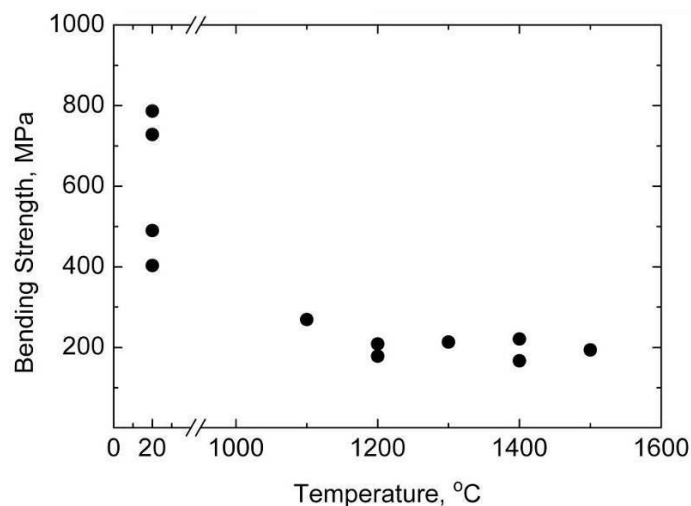


Figure 9. Dependence of the strength of composite specimens on temperature as a result of bending testing

The testing results at high temperatures are presented in Figure 9. The data on the specimens testing at room temperature with the same direction of load application also are shown in this figure for comparison.

5. CONCLUSION

1. The opportunity to obtain a laminate composite representing alternation of the layers of a solid solution of silicon and boron in niobium and the boride-silicide layers as strengthening components from a package of niobium foils coated on one side with a suspension of silicon and boron powders composition by hot pressing under pressure in vacuum by the method of solid-state interaction has been shown for the first time. The layers are formed as a result of inter-diffusion of the initial components with almost lacking material porosity caused by the Kirkendall effect at a specified production mode.
2. The testing at room temperature with load application perpendicularly to and along the layers plain have demonstrated the high strength of the composite with fracture toughness being between typical ceramics and high-temperature strength alloys. The testing at temperatures 1100–1500°C has also shown satisfactory strength.
3. The analysis of the structure of the composite specimens after fracture has demonstrated that the destruction is of complicated and essentially anisotropic character. The micro-destruction structure includes the formation of micro-cracks being stopped on the interfaces of boride-silicide layers and solid solution layers, displacement along the layers interface, as well as plastic deformation of solid solution layers with the formation of necks. These processes assure sufficient resistance to the structure destruction of the material containing brittle components.

4. The presented work is of the pilot character: the material has reserves in increase of fracture toughness. The researches on resistance to creep at high temperatures as well as on optimization of the initial composition and production modes determining the direction of further investigations are also necessary.

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