

**STRUKTURE EVOLUTION OF MULTILAYER MATERIALS OF HEAT-RESISTANT
INTERMETALLIC COMPOUNDS UNDER THE INFLUENCE OF TEMPERATURE IN
THE PROCESS OF DIFFUSION WELDING UNDER PRESSURE
AND THEIR MECHANICAL PROPERTIES**

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Abstract

Multilayer materials of high-resistant intermetallic compounds of some transition metals with aluminum and silicon were obtained by diffusion welding of packages, collected from a large number of the respective foils, such as niobium and aluminum. Materials of intermetallics with silicon were obtained by the welding of packages built from metal foils with Si-coating. The change in the structure according to the temperature of the welding was studied, and the high-temperature bending strength was determined.

Key words: *multilayer composite, high-resistant material, intermetallic compound, diffusion welding, package rolling, layered structure, bending strength.*

1. INTRODUCTION

This work is devoted to the formation of high-temperature synthetic composites with a multilayer structure consisting of alternating layers of strong, but brittle by a nature, intermetallic compounds of refractory metals and relatively ductile solid solutions based on the same refractory metals. Intermetallics are designed to provide the strength at high temperatures for the material, and solid solutions – a crack resistance under normal conditions. After detailed analysis, it was concluded that the basis for such materials can serve refractory transition metals Nb, Mo and Ti and its alloys with vanadium, chromium, tungsten, zirconium, and hafnium. As a high-temperature component in the composites are most acceptable intermetallic compounds of refractory metals with silicon and aluminium.

Active development of the research in this area due to the fact that modern super alloys based on the system Ni-Al, because of its relatively low melting point, reached the limit of operating temperature, 1150°C. This topic has been recently published review of the expert in the area of creation of high-temperature materials for an aircraft engines, Professor I. L. Svetlov [1, 2]. Important benefits of high-temperature materials on the basis of the aforementioned refractory metals, compared to complexly doped alloys Ni-Al, are lower by ~ 20% density and a higher melting point [3, 4]. And achieved for Nb-Mo-Ti-Si in-situ composites, melted by directional solidification, the strength values $\sigma_{0.2}$, equal to 650 MPa at 1500°C [5], let us hope that the products made from them, will be able to operate at temperatures of ~200°C higher than the similar products of alloy Ni-Al.

Ingots of refractory metal alloys with a specified chemical composition and purity of gases and nonmetallic impurities melted by vacuum arc melting in water-cooled copper mold with a consumable

electrode or non-consumable W-electrode. To make the structural directionality for the alloy an ingot after arc melting was subjected to hot isostatic extrusion.

A promising method is a method of precision casting according to lost wax [5]. But for high-temperature alloys, a using of this method is hampered because of the problem of inertia and deformation resistance of ceramic tooling for casting temperatures above 1700°C. It "pulls" behind itself the necessity of developing new inert and refractory ceramics.

In addition to melting methods for the obtaining of high-temperature alloys of refractory metals and the method of powder metallurgy is reviewed. To increase the plasticity of alloys and to create of barriers against the spread of cracks use, so-called the mechanochemical synthesis for a development of a nano-crystalline structure of the alloy [6, 7]. By mechanical alloying with following hot pressing were obtained niobium composite materials reinforced with silicides, two compositions – Nb-Ti-Si and Nb-Ti-Si-Hf-Cr-Al [8]. After the compaction by dint of one-way cold pressing and subsequent sintering in vacuum at 1500°C, the absolute values of the density and hardness were 6.85 g/cm³ and 78 HRA for 3-component material and 7 g/cm³ and 82 HRA for multicomponent material.

Another species of powder metallurgy for an obtainment of prospective high-temperature materials, in particular on the basis of Nb-Si, is a granular metallurgy [9]. It is a way of powders (granules) of alloys, including solidification of the melt in the form of pellets with a high (103-104 °C/s) cooling rate, and the subsequent consolidation of the granules. During plasma spraying of a rotating electrode melt drops solidify in an inert gas atmosphere, and have a perfect spherical shape.

Common to all of the aforementioned materials microstructure is the presence of two mandatory structural components. This – the intermetallic phase, strong at high temperatures, and plasticizing phase, the role of which performs the relatively ductile solid solution of Al and Si in the alloy forming refractory metal, such as niobium or molybdenum. Solid solution is present in the form of interlayers between the intermetallic structural elements and, thus, is "extinguish" the spread of cracks occurring in the brittle intermetallic phase.

In the high-temperature alloys, obtained melting means and method of powder metallurgy, such structures are formed naturally. In the present paper embodies the idea of artificially creating a strict layered microstructure using diffusion welding under pressure of multilayer packages collected from foils of, such as aluminum and niobium or niobium alloys. This is – if you create a high-temperature material on the basis of Nb-Al, in which both components are well-deformed metal. If you need a material on the basis of Nb-Si, then the source package is built from Nb-foils with a one-sided or double-sided Si-coated. Based material doped alloy of Nb-Si should be obtained from foils of doped niobium alloy with silicon coating. The desired structure is formed during welding package by mutual diffusion of the components. Advantages of the developed method:

- initially set the directionality of the structure;
- strict observance of the alternation of strong but brittle intermetallic phases, and relatively ductile solid solution;
- Possibility fairly simply to regulate scale (from micro-to nano-) parameters of the layered structure;
- no need for precision casting according to lost wax and development for it inert and refractory ceramics;
- Opportunity initially to set desired product shape by diffusion welding of packages using curly mold of high strong graphite.

Despite the ease and availability of diffusion welding we did not find work, which would take similar attempts to obtain high-temperature materials based systems of refractory metal-silicon (aluminum). The proposed method has been tested by us on the system Ni-Al [10-12]. Depending on the ratio of Ni:Al were obtained multilayer composite materials of Ni_3Al - and NiAl-intermetallics, as well as a solid solution of Al in niobium.

The aim of this work is a study of the effect of the heating temperature at the welding on the formation of the diffusion structure of multilayer composites of Nb with aluminum and silicon, having limited sources of both components. In the studying of structure of multilayer composites low limit of temperature range determined by the melting point of aluminum. The upper limit of the interval must be greater than the expected operating temperature of the developed materials. If for such composites as Nb/Al and Nb/Si, the last taken as 1350-1400°C, the upper limit of the temperature range should be at least not less than 1700°C.

2. SYSTEM Nb-Al

2.1. Producing of multilayer composites of Nb/Al

In the first stage the multilayered composite Nb/Al-plates with a certain ratio Nb:Al were produced by diffusion welding (DW) under pressure of the packages containing several tens of Nb-foils, alternate with aluminum foil. For example, if Nb:Al = 4, on the state Nb-Al diagram this is consistent with single- phase region $\beta\text{-Nb}_3\text{Al}$ assuming that the Nb and Al during of the mutual diffusion spent completely.

To obtain Nb/Al-composites with layers thicknesses of the two components is less than 1 μm the DW was combined with the previously developed method of package rolling (PR) [13, 14]. In the technology "PR + DW" at the construction of packages did not use pure aluminum and its alloy with 2 wt.%Si. This is undertaken with the purpose of giving strength to aluminum to improve its joint deformation with niobium. In the 1-st cycle by a rolling on the vacuum rolling mill and subsequent rolling at room temperature for packages built from the Nb- and AlSi-foils multilayered Nb/AlSi-tape was prepared. And already in the 2-nd or even 3-rd cycle the package for diffusion bonding was manufactured from foils of this tape.

For example, for composite Nb/AlSi, presented in this paper, in the 1-st cycle of the package is built from 16 Nb-foils with a thickness of 0.3 mm and 15 foils of an alloy of Al-Si with a thickness of 0.05 mm. Welding of the package took place in the process of rolling mill at the vacuum with heating at 450°C and rolling at room temperature up to 0.3 mm. Of the segments of this tape was built the 2-nd pack, and the cycle repeated. And only in the 3-rd cycle the package from already multilayered foils has been by the DW. Calculated ratio Nb/AlSi = 3. This corresponded to a two-phase, $\beta\text{-Nb}_3\text{Al} + \sigma\text{-Nb}_2\text{Al}$, area of the (Nb-Al)-diagram.

After DW Nb/Al-composites, made only the DW and "PR + DW", and other composites are massive plates of up to $\sim 35 \times 40 \text{ mm}^2$ and a thickness of 2.5-3.5 mm. Outer Nb-foil consciously undertook thicker than the inner, for example, 0.1 – for Nb/Al and 0.2 mm – for Nb/Si. Therefore, at the DW, they "did not germinate by intermetallics through" and served as a kind of consolidating armatures for produced plates of material.

2.2. Diffusion welding method (DW)

2.2.1. Technique to study the microstructure

The microstructure was studied by scanning electron microscopy using a scanning electron microscope CamScan MV2300 and Vega 2, equipped with detectors of secondary and reflected

electrons and X-ray microanalysis. The content of elements in the layers of intermetallic phases was determined by the local analysis. Local probe on the surface of the sample is $2\ \mu\text{m}$. The error in determining the concentration of elements in layers $1\text{--}2\ \mu\text{m}$ was 10%, in layers thicker than $2\ \mu\text{m}$ – 3–5%.

2.2.2. Effect of temperature on the microstructure of the diffusion zone between the niobium and aluminum

DW of multilayer package built from niobium and aluminum foils were carried out in a vacuum chamber. The package was placed between two strips, made of high-strength graphite. The pressure created by hydraulic press with 50 tons maximum force and transmitted via punches from the same graphite. The heating was carried out in two stages. At the 1-st stage, the temperature is not higher than the melting point of aluminum ($\sim 680^\circ\text{C}$) to prevent it from leaking at higher temperatures, but it was enough to tie all the aluminum in the intermetallic compound NbAl_3 , a melting point of which equal to 1680°C and which, according to the state diagram of Nb-Al formed at 1590°C eutectic with Nb_2Al – other intermetallic compound.

In confirmation of this in Fig. 1 shows a portion of the layered structure of multilayer packet after DW at 500°C under a pressure of 20 MPa. The package was assembled from 19 Nb-foil with thickness of $40\ \mu\text{m}$, 20 Al-foils ($10\ \mu\text{m}$) and two Nb-foils ($95\ \mu\text{m}$), located on the outside. Shows that between Nb-layers, ie, in the place where the aluminum was, a layer of dark color and $14\text{--}17.5\ \mu\text{m}$ thick was formed. According to the local X-ray spectral analysis (LXRSA) in the layer contained $\sim 75\ \text{at.}\%\text{Al}$. This corresponded to a compound NbAl_3 . At the border $\text{NbAl}_3\text{--Nb}$ (Fig. 1a, points 2 and 3) an interlayer with thickness of about $1.2\ \mu\text{m}$ was visible, which was different for light contrast. Noteworthy (Fig. 1c, point 1) that the layer is enriched with copper ($\sim 9\ \text{at.}\%$) and iron ($\sim 1\ \text{at.}\%$) – with impurities concomitant aluminum. It is known that copper is slightly soluble in niobium and, apparently, does not dissolve in NbAl_3 . Therefore, it is pushed to the periphery of its layer at diffusion interaction of the Nb with Al.

In real experiments on the DW of multilayer Nb/Al-packages immediately after the first stage should further increase in temperature. And already then, depending on the temperature of the 2-nd stage the change in the structure of the diffusion zone was monitored. In Fig. 2 shows a fragment of the cross-sectional microstructure of the packet with size of $50\times 40\ \text{mm}^2$ with a temperature of the second stage in the range of $850\text{--}950^\circ\text{C}$ for 1 h under the force of the press 6 T. The package consisted of 12 Nb-and 11 Al-foil with thickness of 130 and $45\ \mu\text{m}$, respectively.

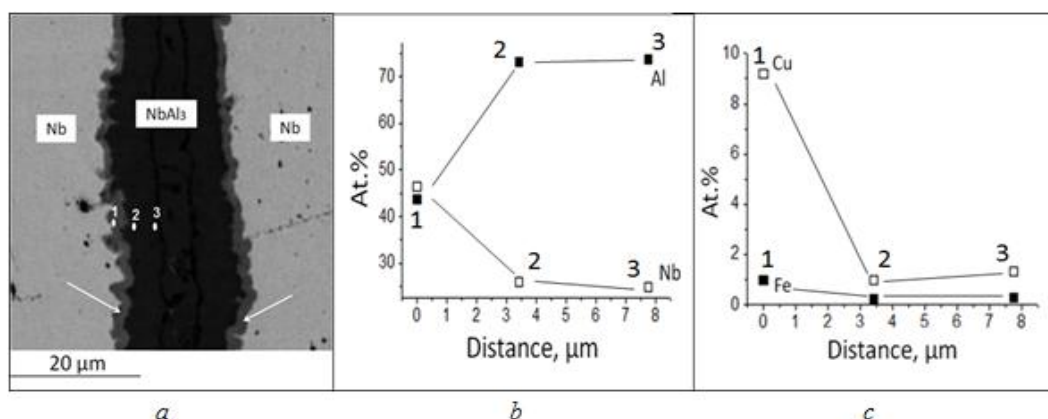


Fig. 1. The microstructure of the diffusion zone (a) and results LXRSA (b, c) of Nb/Al-package with dimensions of $75\times 40\ \text{mm}^2$ and a thickness of 1.15 mm after DW at 500°C for 2 h under pressure of 20 MPa (6 T). The ratio of the thickness $t(\text{Nb}):t(\text{Al}) = 4$

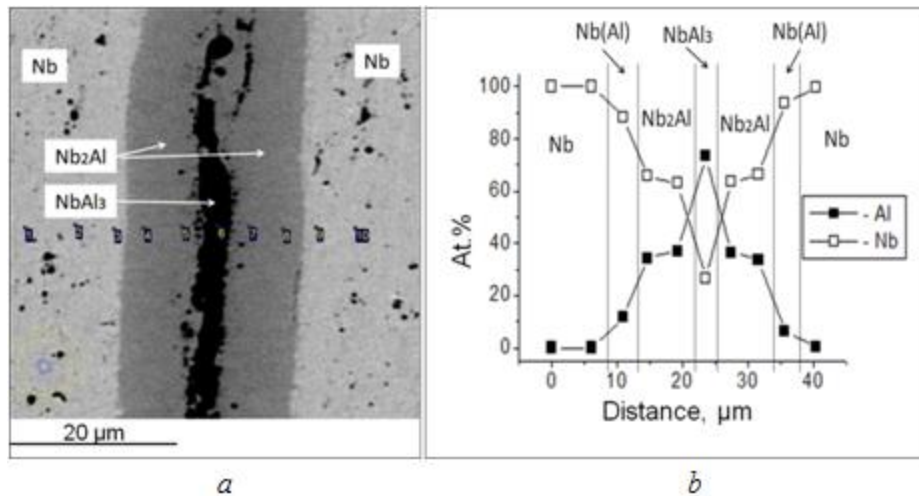


Fig. 2. The microstructure of the diffusion zone (a) and its concentration dependences of Nb and Al (b) multilayer Nb/Al-package after DW by regime: 500°C, 2 h + 850-950°C, 1 h at a pressure of 30 MPa.

The ratio of $t(\text{Nb}):t(\text{Al}) \approx 2.9$

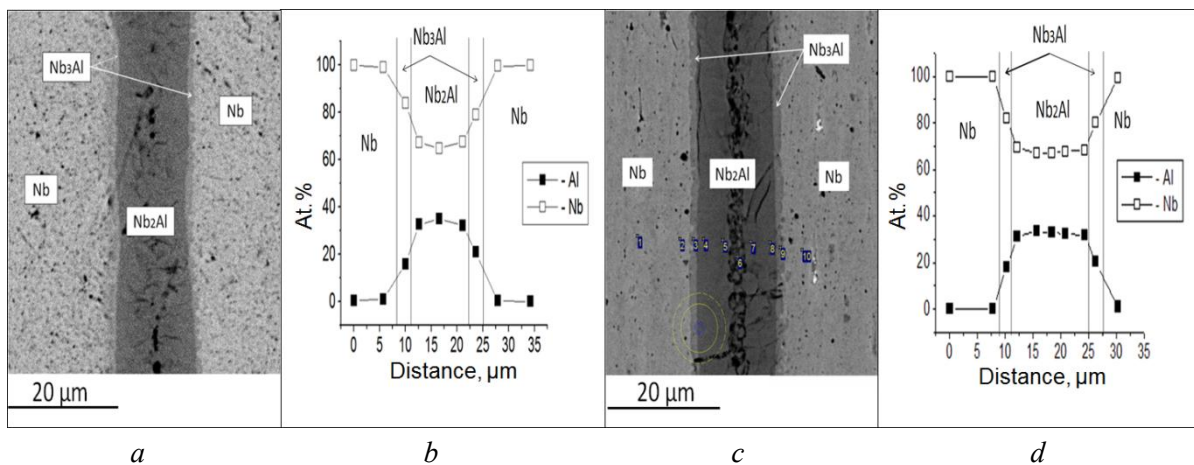


Fig. 3. Microstructure of diffusion zones (a and c) and the results of LXRSA (b and d) of two Nb/Al-packages after DW by the regime 500°C, 2 h + 1300°C, 1 h: a and b – 21 Nb-foil of 40 μm + 20 Al-foils of 10 μm, the size of 75×40 mm², 5 MPa, $t(\text{Nb}):t(\text{Al}) = 4$; c and d – 11 Nb-foils of 130 μm + 10 Al-foils of 20 μm, the size of 50×40 mm², 7.5 MPa, $t(\text{Nb}):t(\text{Al}) = 6.5$

According LXRSA diffusion zone after the DW by that regime consisted of two layers with thickness of ~8 μm from the intermetallic compound Nb₂Al, containing about 33 at.%Al, and intermittent NbAl₃-layer with thickness from 4 μm to zero with the concentration of aluminum is equal to 75 at.%. In areas where the layer NbAl₃ interrupted, Nb₂Al thickness was ~18 μm. The diffusion of aluminum in niobium and formation of solid solution based on niobium at that temperatures and exposure time was not observed.

The next two multilayer Nb/Al-packages were DW by the same regimes (500°C, 2 h + 1300°C, 1 h; 1.5 T), but due to the fact that they were different sizes, at different pressures. Besides the thickness ratio Nb- and Al-foils were also different. The first (Fig. 3a and b) had to do t(Nb):t(Al), equal to 4, corresponding to single-phase region of β -Nb₃Al on state diagram of Nb-Al, and the second package (Fig. 3c and d) – t(Nb):t(Al) = 6.5, corresponding to the two-phase region of the diagram: β -Nb₃Al + solid solution of Al in niobium Nb(Al).

But these differences do not affect the phase composition of the diffusion zone and the relationship of the phases present in it. In both packages, it consisted of Nb₂Al-layer with thickness of about 13 μ m, and two thin (~1 μ m) layers of another compound of the niobium-aluminum – Nb₃Al, located on the boundary Nb₂Al-Nb. Was noted only external difference between Nb₂Al-layers in the two resulting flat composites. In the composite with the ratio t(Nb):t(Al), equal to 6.5 (Fig. 3c), within the intermetallic layer Nb₂Al noted the presence of unbroken area of small voids. It is assumed that they are formed during the process of preparation of the polished specimen in places where residual intermetallic phase of NbAl₃ was local been. It is considered the weakest of the three intermetallic compounds found in the system of Nb-Al. If we assume that the voids were due to Kirkendall effect, they would have to be present and in the composite with a smaller ratio of t(Nb):t(Al). One might think that an increase in temperature or even the time of the DW at 1300°C should lead to a complete transformation of NbAl₃-compound to the following on the content of aluminum intermetallic compound – Nb₂Al and, therefore, exclude the presence of voids in its diffusion layer.

As in the previous case, at the selected parameters of the DW has not detected the formation of a solid solution.

The microstructure of multilayer packages after the DW at temperatures of 1500°C and above is qualitatively different. The rise in temperature from 550°C to a temperature of the second stage was performed in about 1 h. After a holding for 30 min at 1500°C (Fig. 4) the microstructure of composite was alternating layers of compound Nb₂Al (~35 at.%Al) with thickness of 20-25 μ m and layers already a solid solution based on niobium Nb(Al) ~10 μ m thick, containing ~10 at.%Al, both sides of which were located intermetallic compound layers Nb₃Al (20-22 at.%Al) with thickness of ~5 μ m.

Even more significant changes in the microstructure of the composite were caused an increase in temperature of the second stage of the DW to 1700°C (Fig. 5). A larger sample volume was occupied compound of Nb₃Al in the form of layers of thick ~40 μ m, which according to local X-ray spectral analysis contained from 20 to 22 at.%Al and alternated with layers of the solid solutions based on niobium Nb(Al) with the thickness of ~6 μ m, containing ~17 at.%Al. Remains of Nb₂Al-phase were observed only in the form of elongated islands within the layers Nb₃Al (see Fig. 5a).

The following composite (see Fig. 5c and d) was differed from the previous one only by the pressure of the DW, which is ~6 MPa. Almost the entire volume of the composite was became busy compound of Nb₃Al-layers, having contained 21-23 at.%Al. Besides these, in the structure a visible presence of thin (~4 μ m) layers, which at this stage of the study can be attributed to the Nb-solid solution Nb(Al), was noted. The aluminum content in them varied from 17 to 20-21 at.%, overlapping with the data of the LXRSA for the layers of Nb₃Al.

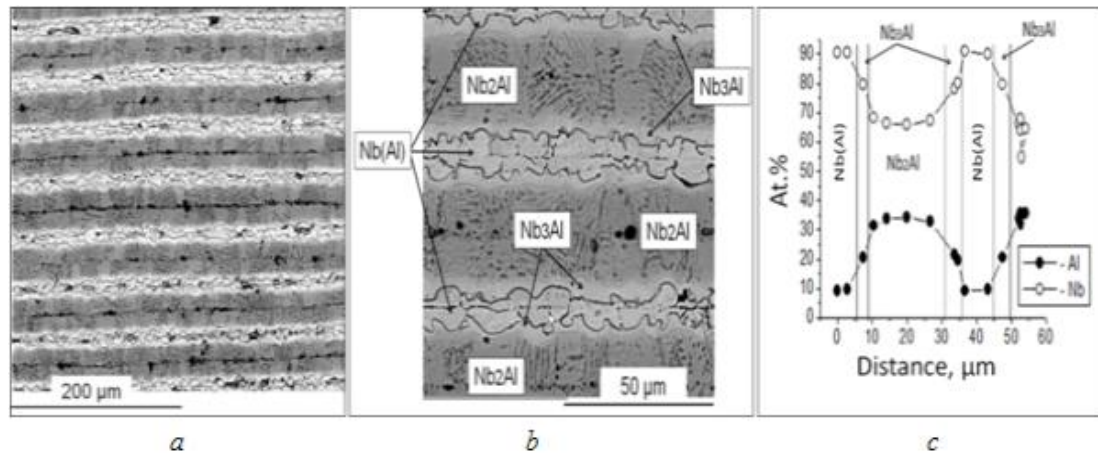


Fig. 4. The microstructure of the cross-section (*a* and *b*) and the concentration dependences of niobium and aluminum (*c*) for a multilayer package of Nb/Al after the DW by the regime: 550°C, 1 h + 1500°C, 30 min under the pressure of 6.25 MPa: 32×40 mm², t(Nb):t(Al) = 4. Package of Nb/Al contained 46 Nb-foils with thickness of 40 μm, 47 Al-foils (10 μm) and 2 outer Nb-foils with thickness of 0.2 mm

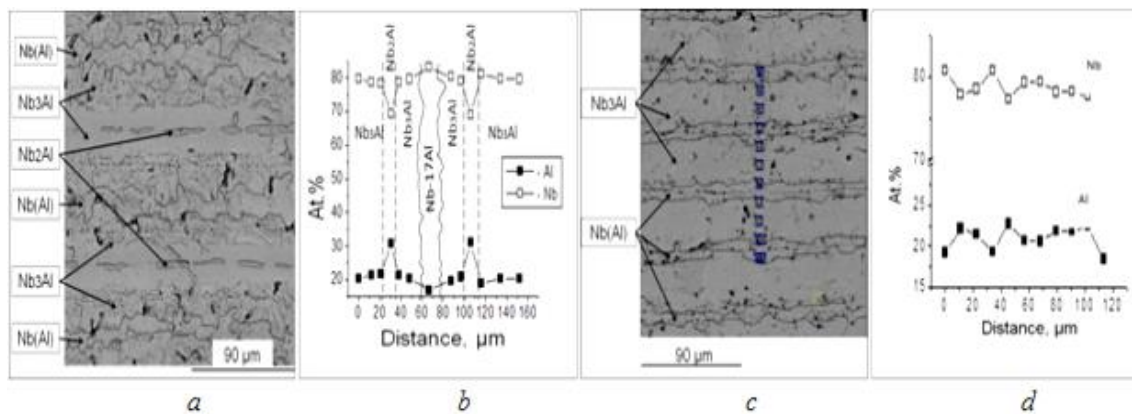


Fig. 5. The microstructure of the cross section (*a* and *c*) and the concentration dependences of niobium and aluminum (*b* and *d*) for two (*a* and *b*, *c* and *d*) multilayer Nb/Al-packages after the DW by the regime: 550°C, 1 h + 1700°C, 30 min under the pressure of 12.25 and 6.25 MPa, respectively, with t(Nb):t(Al) = 4:

a and *b* – 33 Nb-foils with the thickness of 40 μm + 34 Al-foils (10 μm) + 2 external Nb-foils (0.13 mm), the size of 32×20 mm²;

c and *d* – 42 Nb-foils (40 μm) + 43 Al-foils (10 μm) + 2 external Nb-foils with thickness of 95 μm, the size of 32×40 mm²

Noticeable change in the layered structure with decreasing pressure 2 times can be explained as follows. It was observed at the DW aluminum partially was squeezed out of the package. This caused a deviation of Nb:Al ratio of the design in the direction of Nb(Al). Therefore, the lower the pressure,

the less the solid solution of Al in niobium is presented in the structure and the closer it is to the content of aluminum Nb₃Al-phase.

In Fig. 6a shows a multilayer structure of latest composite plate with a small magnification. Our attention was drawn to a transverse crack, crossing all the inner layers of the composite and "quenching" in its outer layer of Nb-solid solution. Since the thin section was prepared with the sample has passed the bend test (fragment structure is removed near the place of destruction), we assume that it was formed under the mechanical testing.

This fact prompted the construction of the composite, obstructing free passage of the crack through the entire volume of the material. In Fig. 6b shows the multilayered structure of the four Nb₃Al-multilayers separated artificially paved interlayers of almost pure niobium. In that composite fracture that occurred in one of the heat-resistant but brittle, multilayers, should not be extended to the entire cross section of the material. Each multilayer in the composite is made up of 10 Nb- and 9 Al-foils with thickness of 40 and 10 μm respectively, the thickness of Nb-layers – 90 μm . Assembly and the DW such a package was done at one time.

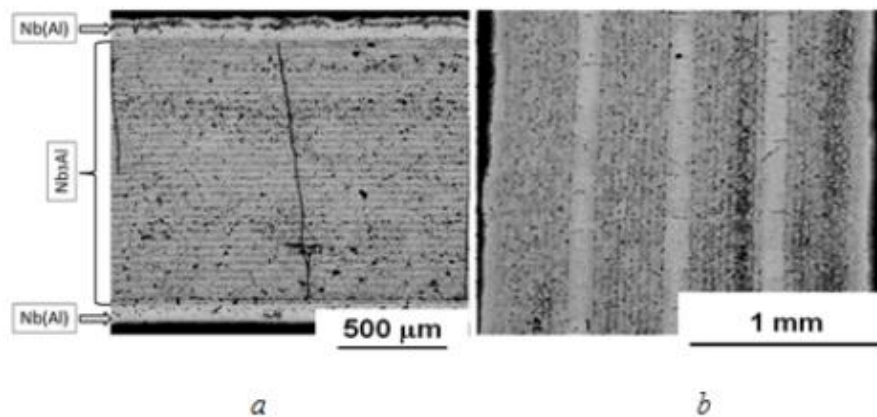


Fig. 6. The structure of the cross-section of multilayer Nb/Al-composites of two constructions after diffusion welding at 1700°C for 30 min at a pressure of 6 MPa

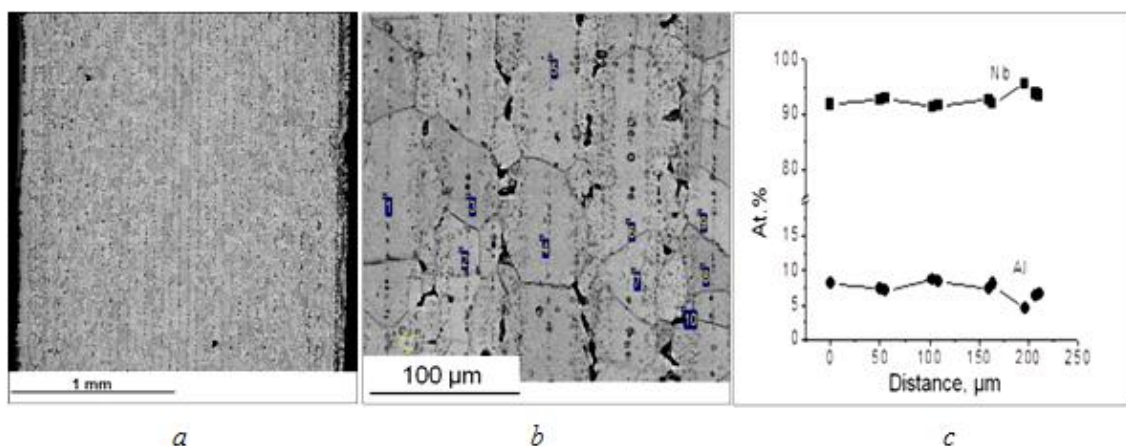


Fig. 7. Macro- (a), microstructure (b) and the results of local X-ray analysis (c) of multilayer Nb/Al-package with ratio $t(\text{Nb}):t(\text{Al}) = 6$ after the DW under pressure of 6.25 MPa on the treatment of 550°C, 1 h + 1700°C, 30 min

And, finally – a multilayer Nb/Al-composite containing 36 Nb- layers with thickness of 60 μm , 37 Al-layers (10 μm) and 2 outer Nb-layers of 90 μm . It had $t(\text{Nb}):t(\text{Al}) = 6$. This was consistent with the fact that if niobium and aluminum fully spent, the final structure should be a structure consisting only of layers of a solid solution of Al in Nb.

The structure of this composite after the DW at 1700°C (Fig. 7) had a well-defined layered structure, each layer of which was Nb-solid solutions containing from 5 to 9 at.%Al.

2.2.3. Comments on the results of microstructural studies

According to the classic rules of mutual diffusion the formation of intermetallic phases in the Nb-Al should occur in the sequence from the intermetallic compound with a greater content of Al to intermetallic compound with less its contents and then to a solid solution of Al in niobium – $\text{NbAl}_3 \rightarrow \text{Nb}_2\text{Al} \rightarrow \text{Nb}_3\text{Al} \rightarrow \text{Nb}(\text{Al})$. In the case of limited sources of Nb and Al [at that source of Al, limited to a greater extent – $t(\text{Nb}):t(\text{Al}) = 4$] a complete picture of diffusion will be the structure with intermetallic compounds containing less aluminum and Nb(Al). Established [15], which NbAl_3 easily and quickly was formed at temperatures below 1000°C and at 1500°C and above was completely was consumed with the formation of intermetallic compounds with a lower concentration of aluminum. The process of inter-diffusion is the more complete, the more exposure time, and goes faster, the higher the temperature. Therefore, at an increasing of temperatures at the DW from 500 to 1700°C and at relatively low exposures the evolution of the multilayer structure from $\text{NbAl}_3 + \text{Nb}$ to $\text{Nb}_3\text{Al} + \text{Nb}(\text{Al})$ or only to Nb(Al) is a law.

2.3. Method of “PR + DW”

2.3.1. Production of multilayer packages

As reported above, was used for packaging is not pure aluminum and aluminum alloy with 2 wt.%Si.

In the 1st cycle the package is built from 16 Nb-foils with a thickness of 0.3 mm and 15 foils of an alloy of Al-Si with thickness of 50 μm . The ratio of $t(\text{Nb}):t(\text{AlSi})$ was equaled 6. The welding of the package took place in the process of rolling at mill in the vacuum with heating up to 450°C and reduction per pass ~30% and subsequent rolling at room temperature up to 0.3 mm. After the 1st cycle the design thickness of Nb-layers was 2.16 μm , the thick of AlSi-layers – 2.7 μm .

2nd cycle. Of the 16 segments of the tape after the 1st cycle and 15-foils of an alloy of Al-2%Si thickness of 50 μm was formed about the second package and the cycle was repeated. The ratio of $t(\text{Nb}):t(\text{AlSi})$ became equal to 3.0.

And in the 3rd cycle of the package of 3.5 mm thick, collected from 12-foils with thickness of 0.29 mm after 2nd cycle with the dimensions $22 \times 35 \text{ mm}^2$ was subjected to the DS by the regime: 600°C, 2 h, 10.5 MPa + 1700°C, 15 min, 5.5 MPa. The ratio of $t(\text{Nb}):t(\text{AlSi})$, equal to 3, it was close to the calculated ratio for Nb_3Al of stoichiometric concentration [$t(\text{Nb}):t(\text{AlSi}) = 3.25$]. Prior to the DW in welded multilayer Nb/Al-package 3072 Nb-layer with the design thickness of 876 nm, 2880 AlSi-layer of 146 nm thick and 180 AlSi-layer of 2.7 μm thick were contained.

2.3.2. Microstructural studies

The typical microstructure of the material in the cross section parallel to the direction of rolling, is shown in Fig. 8a. For relatively a small increase the alternating light and dark layers with very different thicknesses in length were clearly visible. Bright layers – this is what happened to the niobium, dark - that before the DS was alloy of Al-Si. Both layers are sometimes flat-out so that exploded and turned into elongated islands, leading to the fact that the individual layers of niobium or an alloy of Al-Si were connected with layers their own kind. This process took place at all stages of

deformation. This explains the discrepancy between the calculated thickness of layers and thickness, measured experimentally.

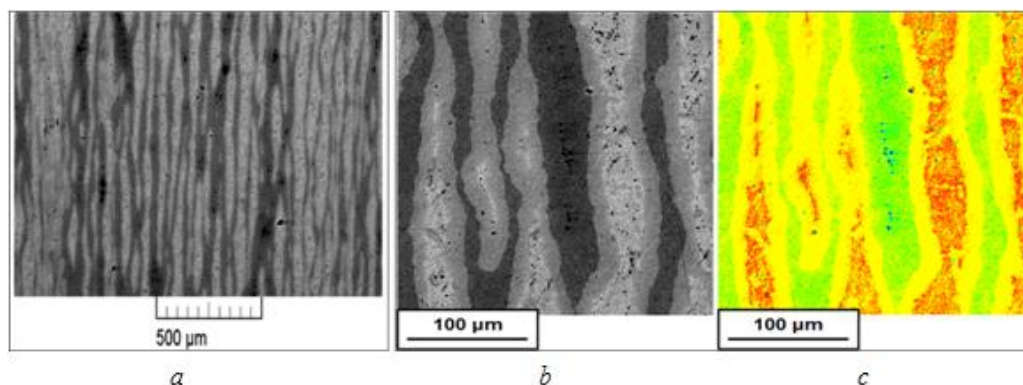


Fig. 8. The microstructure of the multilayer Nb/AlSi-composite after two cycles of PR and DW with differing light contrasts different phases

At higher magnification (Fig. 8b and c) in light contrast can distinguish three phases. According LXRSA they were identified as a solid solution based on niobium Nb(Al) – the lightest phase (on a color picture – red), Nb₂Al – phase dark (or green) and Nb₃Al – phase gray (or yellow). The presence of a large number of intermetallic Nb₂Al compound was due to small time of high-temperature aging. The aluminum content in the Nb₂Al- and Nb₃Al-layers – respectively 29-31 and 20-22.5 at.%, in layer of Nb(Al) – about 14 at.% (Fig. 9).

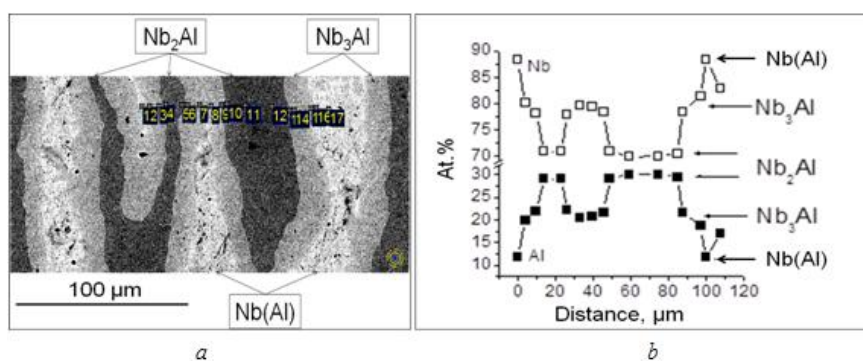


Fig. 9. Microstructure of the composite in a section parallel to the rolling direction, with points of LXRSA (a) and the results of LXRSA as the concentration curves (b)

Silicon, initially localized in the layers of Al-Si-alloy, during the DW was distributed throughout the volume of the laminate. However, according to LXRSA its concentration values were at background levels. But even the background concentration of silicon in Nb₃Al-phase [0.10-0.15 wt.% (0.32-0.51 at.%)] was greater than in Nb₂Al and Nb(Al) [~0.06 wt.% (0.18 at.%)]. In such silicon content in the test object reliable detection limit its concentration of 0.16 wt.%.

2.4. The strength of the bending test

Short-term strength was calculated when in tests on the 3-point bending on the basis of 28 mm in the temperature range 1150-1350°C. Heating and tests were made in a vacuum. The samples were cut from the plates so that their length corresponded to the rolling direction of foils that make up the package. The direction of load application was parallel to the layers (Fig. 10). Results are shown in Fig. 11.

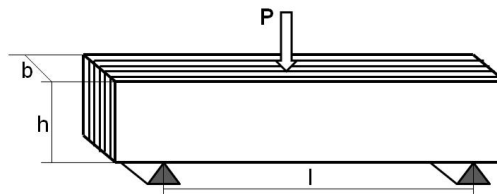


Fig. 10. Scheme for sample load, applied parallel to the layers: b, h and l – width, height and base, respectively, P – load

Regardless of the method of producing a laminate reinforced with layers of intermetallic compound of Nb_3Al , the numerical values of its short-term strength at temperatures from 1200 to 1350°C were varied in the range of 200-360 MPa. At room temperature, it was equal to ~430 MPa. High temperature-strength of laminated composite with layers of solid solutions based on niobium, shown in Fig. 7, in the same temperature range was dropped to ~120 MPa.

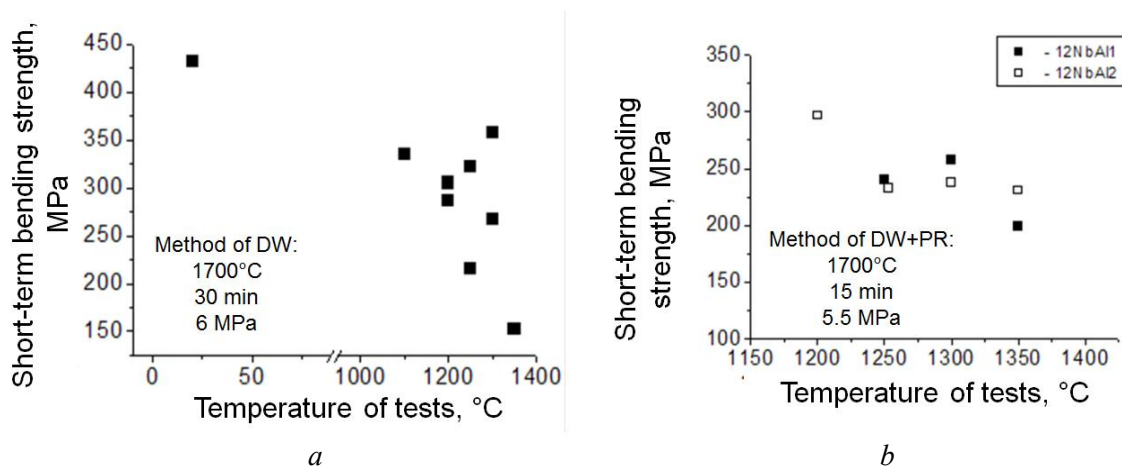


Fig. 11. Depending short-term bending strength of the temperature of the test: a – a composite of see Fig. 5b and 6a, the DW method; b – method of “PR + DW” (12NbAl1 and 12NbAl2 – two multi-plate, obtained under identical conditions of PR and DW)

3. SYSTEM Nb-Si

3.1. Assembly and DW of multilayer packages

To obtain multilayer composites of Nb/Si package was made up of Nb-foils with a thickness of 20 μm and more with an one- or two-side Si-coating. By method similar to the method of screen printing, on the surface of foil the suspension of Si-powder with size of 1-3 μm in polyethylene glycol first was applied. Polyethylene glycol then was easily evaporated at $\sim 250^\circ\text{C}$ in the air and firmly hold on the surface the Si-coating was remained. Coating thickness depended on the consistency of the suspension and the number of acts of its application. In the studied here flat Nb/Si-composite the thickness of single coating ranged from 35 to 50 μm .

The DW under pressure could be held in two stages – at $850\text{--}900^\circ\text{C}$ for several hours, followed by heating to 1700°C and a short (15-30 min) exposure. But DW performed and without low-temperature shutdown, and with the gradual heating from room temperature to 1700°C and ~ 30 minutes of exposure.

3.2. The microstructure of multilayer composites

In contrast to the Nb/Al-packages in the system Nb-Si is not the problem of the low melting point of one of the components. Silicon melts at 1414°C , and the eutectic reaction of his with the compound of NbSi_2 is at 1400°C . Besides NbSi_2 , niobium with silicon else forms two chemical compounds – Nb_5Si_3 and Nb_3Si (Fig. 12). But at room temperature, there are only the first two compounds. Nb_3Si at 1770°C decomposes by peritectic reaction to almost pure niobium and $\alpha\text{-Nb}_5\text{Si}_3$. In view of this, the strengthening of intermetallic phase in the system of Nb-Si can be viewed only compound Nb_5Si_3 .

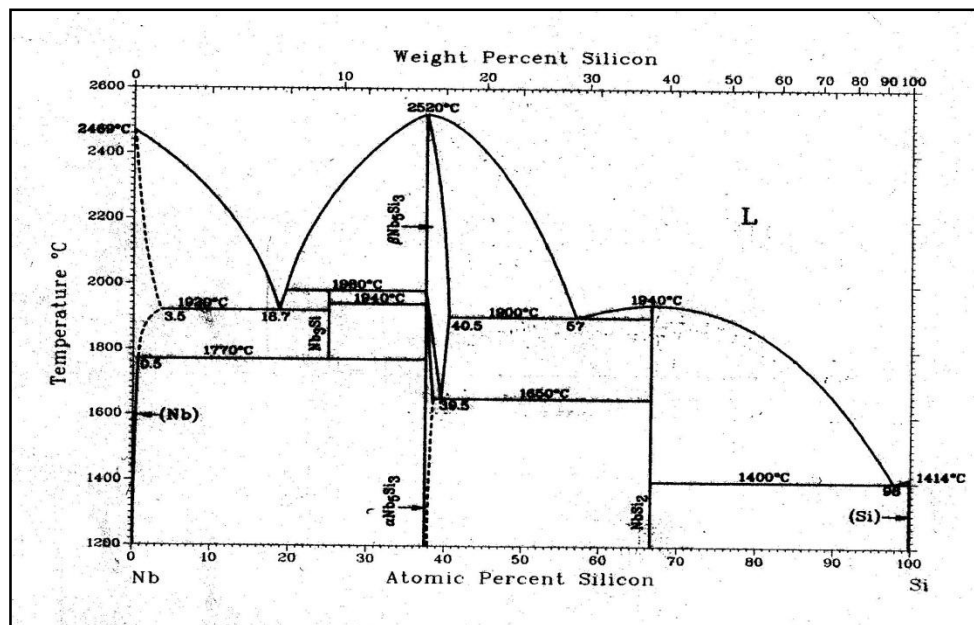


Fig. 12. State diagram of Nb-Si

Composite of 1Nb/Si. Multilayer package Nb/Si with size of $32 \times 40 \text{ mm}^2$ consisting of the 40 Nb-foils with a thickness of 20 μm with one-side Si-coating and two outer Nb-foils with a thickness of 0.2 mm was subjected to DW at 1300°C for 2 hours under a pressure of 6.45 MPa.

The cross section of the package after the DW had a pronounced layered structure (Fig. 13) with layers of intermetallic compound of NbSi_2 of ~40 microns thick, separated by very thin layers of silicon. And, if closer to the surface Si-interlayers were clearly visible, in the middle of the composite were vanishingly small or nonexistent. Within the layers the structure of approximately equiaxial grains was observed, one of the size of which was equaled to the thickness of the layer. Data on the local X-ray spectral analysis were summarized in Fig. 14 and in Tabl. 1. The X-ray spectra were showed for points 1 and 2 (see Fig. 14c and d).

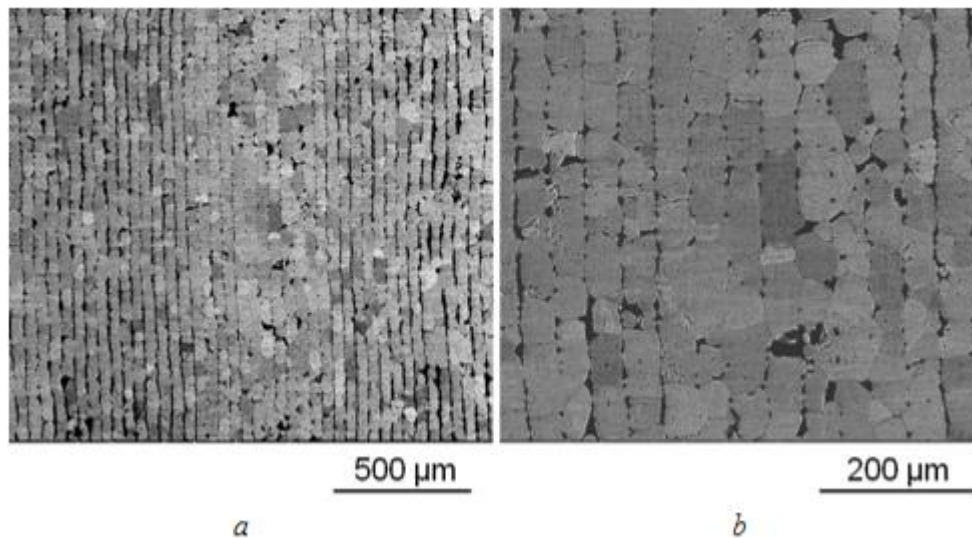


Fig. 13. Macro- (a) and microstructure (b) of the Nb/Si-package made of foils with one-side Si-coating after the DW at 1300°C

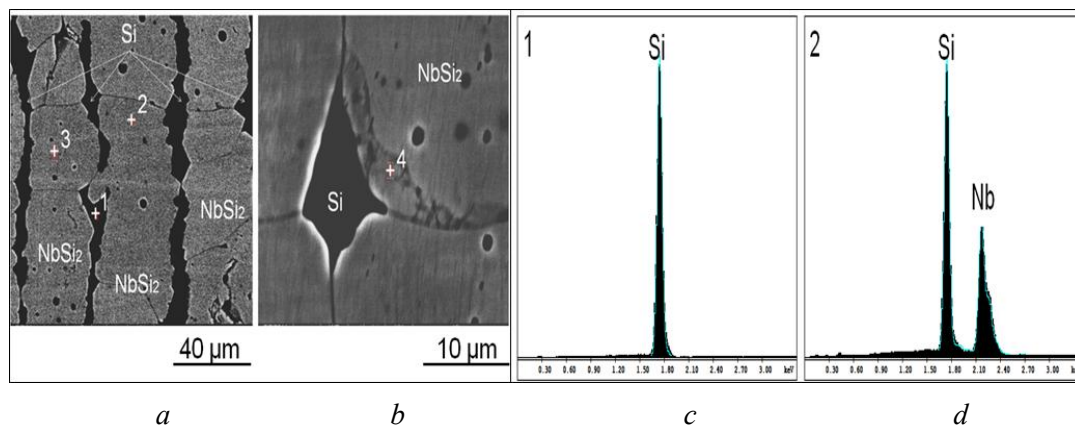


Fig. 14. The microstructure of the fragment cross-section of 1Nb/Si-composite indicating the detected phases (a and b) and the X-ray spectra at points 1 and 2 (c and d)

Table 1. The results of LXRSA for the 1Nb/Si-composite

Number of spectrum	Element concentration, wt.% \ at. %		Phase
	Nb	Si	
1	0	100	Si
2	61.8/32,9	38.2/67.1	NbSi ₂
3	61.5/32.5	38.5/67.5	NbSi ₂
4	60.4/31.6	39.6/68.4	NbSi ₂
5	58.3/29.7	41.7/70.3	NbSi ₂
(300×300 μm)			

Composite of 12Nb/Si3. Package with size of 12×51 mm² was assembled from 47 Nb-foils of 30 μm thick with one-side Si-coating of average 52 μm thick and two Nb-foils of 0.18 mm thick as the outer facings, one of which also had a Si-coating. The ratio of the thickness of the Nb-film to the thickness of Si-coating t(Nb)/t(Si) = 0.58. The DW was carried out at a pressure of 11.76 MPa at 1550°C for 30 min.

Large pores and heterogeneities were absent at the macrostructure of the composite (Fig. 15a). Intermittent bright thin bands were a solid solution based on niobium with a concentration of silicon in the range of 0.6-0.85 at.%. The concentration of silicon in the outer Nb-plates on the part of Nb₅Si₃ could reach ~1.1 at.%. The remaining volume of the material was submitted by the compound of Nb₅Si₃ with an average concentration of silicon and niobium, respectively equaled to 36.1 and 63.9 at.%. However, at the high magnification in the structure of the layers were found interlayers (Fig. 15b), differing by the contrast of light from Nb₅Si₃. According LXRSA they identified as a compound of Nb₃Si with ~23.85 at.% Si.

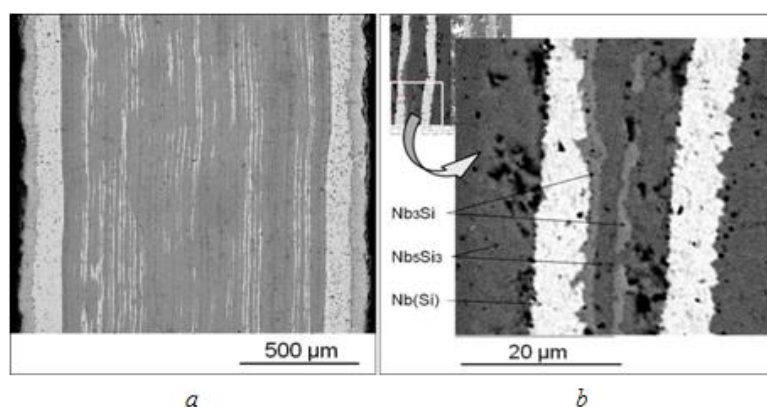


Fig. 15. Macro- (a) and microstructure (b) of cross-section of 12Nb/Si3-composite after the DW at 1550°C for 30 min under pressure 11.76 MPa

Composite of 12Nb/Si1: 20 Nb-foils with a thickness of 0.1 mm with Si-coating of 65 μm thick + 1 Nb-foil with a thickness of 0.1 mm as the outer facing. The ratio of t(Nb)/t(Si) = 1.54. The DW was under pressure of 7.1 MPa at 1700°C for 30 min.

Composite structure was consisted of intermetallic compounds layers of Nb_5Si_3 of 35.4-36.1 *at. %* Si and 63.9-64.6 *at. %* Nb, alternating with layers of solid solution of silicon in Nb in an amount of 0.2 to 1.2 *at. %* (Fig. 16).

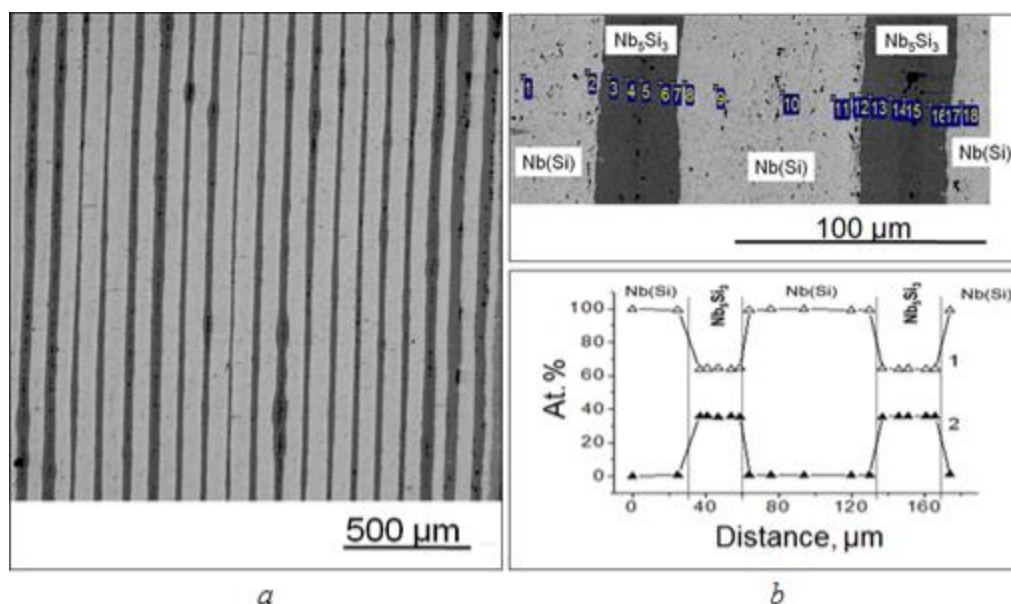


Fig. 16. Macrostructure of 12Nb/Si1-composite with thickness of 2.2 mm with 21 layers of niobium and 20 layers of silicon after the DW at 1700°C for 30 min under pressure of 7.1 MPa (a) and an illustration of LXRSA data (b)

But even after such a relatively high temperature in the layers of the Nb_5Si_3 -compound were found remnants of NbSi_2 -phase as inclusions in black (Fig. 17). Point 1 had composition, *at. %*: 64.9Si and 35.1Nb.

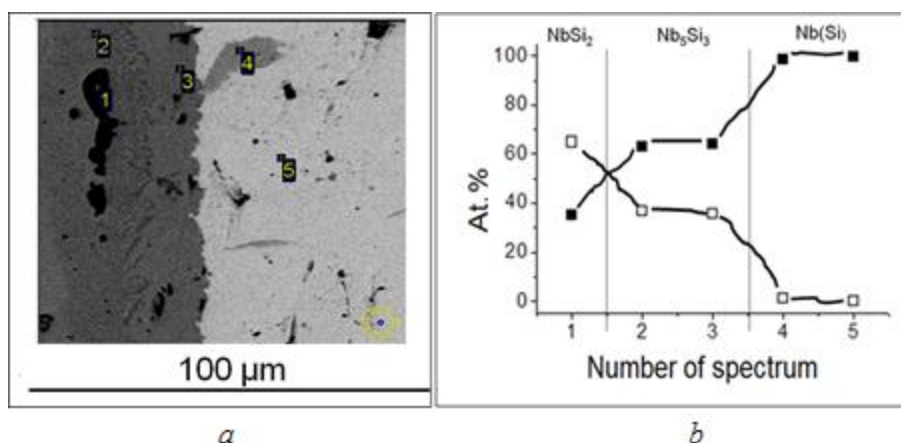


Fig. 17. Fragment of intermetallic layer microstructure with the inclusion of NbSi_2 (a) and the change in concentration of Nb and Si on the border of Nb_5Si_3 -Nb(Si) (b)

It is known that the thinner layers in a multilayer composite, the higher the strength characteristics. For example, in [16] for laminated composite Cu/Nb, resulting gradual rolling batch, that contained more than 32000 nanoscale layers of copper and niobium was obtained hardness of 350 HB. This high hardness of a material consisting of very ductile metals are corresponded HB of medium carbon steel.

For heat-resistant material of (Nb-Si)-system with a layered structure is important to keep a optimal ratio between plasticizing layers of Nb-solid solution and strong layers of the intermetallic compound. If in the case of (Nb-Al)-system for thinning layers before the DW is used method of PR, for Nb-Si it was unacceptable. Of course, of the foils of nanometer thickness speech can not be. In reality, for the assembly of multilayer packages of Nb/Si Nb-foils with a thickness of 20 and 30 μm were used. To build another group of packages foils with thickness of 0.1 and 0.2 mm were used. Averaged for each packet thicknesses of Si-coatings on foils of niobium were ranged from 36 to 69 μm . Their average value was equaled to $54 \pm 15 \mu\text{m}$.

However, the microstructure of the composites with Nb-foils of 20 and 30 μm thick forming after the DW at a maximum temperature of 1700°C required by technology was not quite satisfactory (Fig. 18a and b and Table 2, composites of 12Nb/Si4 and 12Nb/Si2). Bright layers in these photos is Nb(Si), the layers of gray – Nb₅Si₃. "Stitches" of dark inside Nb₅Si₃-layers were pores and voids. One of the assumptions that they were formed in that place where there were intermetallic compound NbSi₂, silicon-rich, and which, because of their weakness, were crumbled out during the preparation of the micro section. Local areas where it has been preserved were found at high magnification. In areas where there were no layers of the solid solution (see Fig. 19) interlayer's of NbSi₂-phase were between layers of Nb₅Si₃, and sometimes in large quantities. Then it is clear that it is necessary to exclude the existence of NbSi₂ in composites after the DW at 1700°C, for what the ratio of Nb:Si is necessary to support on the entire surface of Nb-foils so as to conform to the state diagram in region of eutectoid of Nb₅Si₃ + Nb(Si), and not eutectoid region Nb₅Si₃ + NbSi₂.

Another reason is Kirkendall effect. Prevent or minimize the formation of pores due to this effect may increase pressure at the DW. But it is also possible that the formation of structures affect both of the aforementioned factors.

Composites, welded from packages of Nb/Si with foils of 100 and 200 μm thick, were different from the previous composites with defect-free and dense structure (Fig. 18c and d). But the ratio of the volume of layers of Nb₅Si₃-compound (gray bars with thicknesses of $\leq 30 \mu\text{m}$), and the volume occupied by the layers of the solid solution (light strips with thickness of $\geq 120 \mu\text{m}$) must be reversed.

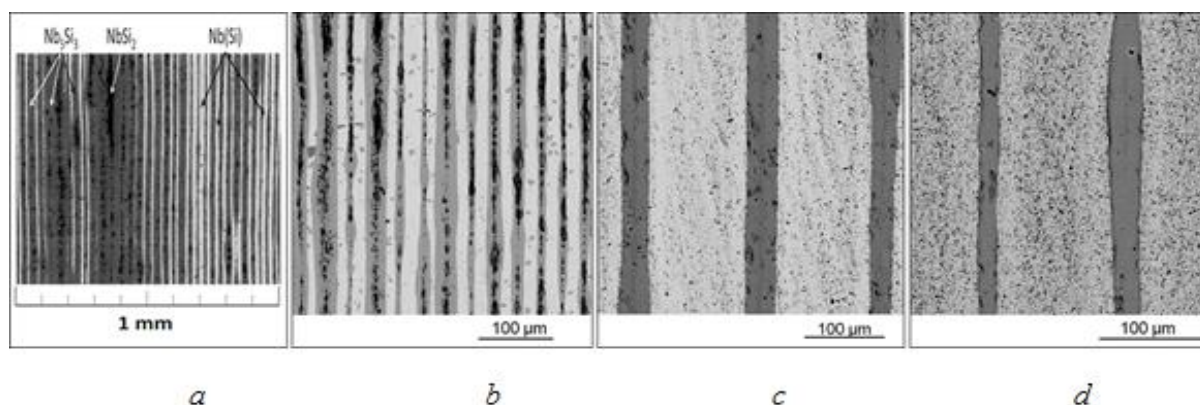


Fig. 18. The microstructure of the composites of 12Nb/Si2 (a), 12Nb/Si4 (b), 12Nb/Si6 (c) and 12Nb/Si7 (d) after the DW at 1700°C for 30 min

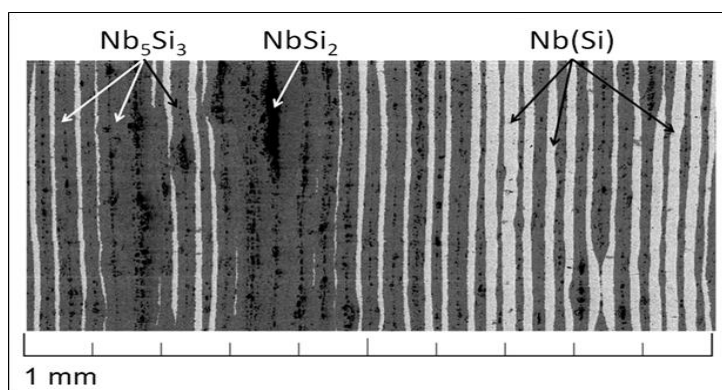


Fig. 19. The microstructure of the 12Nb/Si2-composite with thickness of 1.95 mm of intermetallic compounds of niobium and silicon (Nb_5Si_3 and NbSi_2) and a solid solution of silicon in niobium [Nb(Si)] after the DW at 1700°C

Table 2. Structural parameters and the pressure at the DW of Nb/Si-composites. DS temperature, °C: for 12Nb/Si1, 12Nb/Si2, 12Nb/Si4, 12Nb/Si6 and 12Nb/Si7 – 1700; for 12Nb/Si3 – 1550

Designation	Thickness of Nb-foils, μm	Averaged thickness of coating, μm	Ration $t(\text{Nb})/t(\text{Si})$	Pressure at DW, MPa	Note on the structure
12Nb/Si4	20	46	0.43	11.4	Defective
12Nb/Si2	30	52	0.58	6.3	Defective
12Nb/Si1	100	65	1.54	7.1	No defects
12Nb/Si6	200	69	2.90	13.3	No defects
12Nb/Si7	200	36	5.56	21.4	No defects
12Nb/Si3	30	52	0.58	11.8	No defects

From the comparison of the results of scanning electron microscopy, the design parameters of packages and magnitudes of the pressure at the DW the following conclusions can be done.

1. On the structure formation of composites in the process of diffusion welding at 1700°C in the most affected ratio of the thickness of the Nb-foil to thickness of Si-coating $t(\text{Nb})/t(\text{Si})$. In Table 2 composites, welded at this temperature, are placed in ascending relations $t(\text{Nb})/t(\text{Si})$ from 0.43 to 5.56. The data show that the effect of the ratio $t(\text{Nb})/t(\text{Si})$ prevails over the effect of pressure at the DW. Both composite – 12Nb/Si4 and 12Nb/Si2 – have $t(\text{Nb})/t(\text{Si})$ is twice less than 1 and both have defective structures, although the pressure in the DW from the first composite was almost two times higher.

2. In composites with defect less structures ratio $t(\text{Nb}_5\text{Si}_3)/t[\text{Nb}(\text{Al})] \approx 0.25$. But for the mechanical properties the optimal condition are structures with a volume content of the layers of intermetallic phases in excess of the volume of layers of Nb(Al), or at least comparable to them.

3. Paragraphs 1 and 2 of the following recommendations: reduce the thickness of Si-coating in Nb/Si-packages, consisting of Nb-foils of 20 and 30 μm thick to the relationship $t(\text{Nb})/t(\text{Si}) = 1.5\text{-}3$.

3.3. Results of the strength of bending test

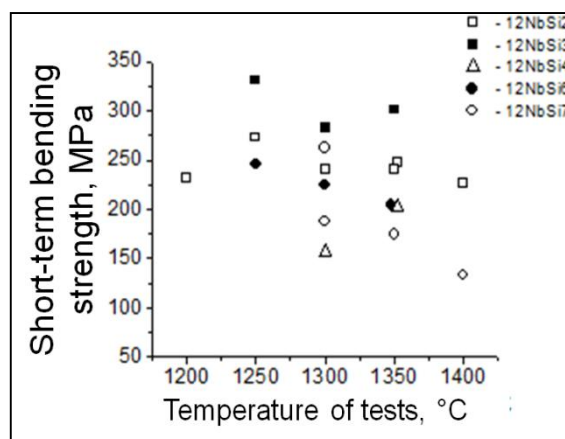


Fig. 20. Depending on strength of 3-point bending tests on temperature for composites of 12NbSi2, 12NbSi3, 12NbSi4, 12NbSi6 and 12NbSi7 after the DW at 1700°C

Short-term strength (Fig. 20) in the temperature range 1350-1400°C was equaled 175-300 MPa. At 1400°C value of 230 MPa was obtained. Load was applied parallel to the layers.

4. CONCLUSIONS

1. By diffusion welding under the pressure massive samples of 2-4 mm thick, consisting mainly of a large number of layers of solid intermetallic compounds of Nb_3Al or Nb_5Si_3 were produced. As a relatively ductile composite component, capable of providing the material fracture toughness at room temperature, were the outer Nb-layers of the solid solution with the thickness of 100-200 μm , and the inner interlayers of micron-thick, alternating with multilayers of intermetallic compounds.

2. The first bending tests at temperatures up to 1400°C were showed that the material with such a structure can have the strength 200-300 MPa. The proposed technology approach provides promising prospects for the production of heat-resistant material on the basis of niobium alloys with Al and Si, can operate at 1300°C and higher.

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