

**MICROSTRUCTURE AND FUNCTIONAL PROPERTIES OF MICRO- AND
NANOSTRUCTURE METAL COMPOSITES OBTAINED BY DIFFUSION WELDING
AND ROLLING OF MULTILAYER PACKAGES**

Valery P. Korzhov, Michael I. Karpov

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka,
Moscow Region, Russia. E-mail: korzhov@issp.ac.ru

Abstract

Multilayered nanostructure composites of Cu/Fe, Cu/Nb, and Cu/(Nb/NbTi) with an ≤ 10 nm the average thickness of individual layers mechanical and superconducting properties which are implemented immediately after rolling, and micro- and nanostructure composites of Ni/Al, Ti/Ni, and (Cu/Nb)/Cu₁₂Sn functional properties which, in contrast to the first, are manifested after rolling and heat treatment were investigated. Composites of (Cu/Nb)/Cu₁₂Sn in final form were a multilayer tape of superconducting compound Nb₃Sn. Welding of stacks carried by heat treatment under pressure and rolling mill in a vacuum with heating to 900-950 °C and large (~30%) compression in a single pass. The microstructure was investigated by scanning electron microscopy and X-ray analysis. For superconducting composites critical current density and upper critical magnetic field were measured. Shown that the pinning of superconducting vortices in alloys of NbTi are occurred at interlayer Nb-NbTi boundaries. Change in hardness and strength of multilayer composites under rolling deformation is described by the expression of the Hall-Petch relationship, in which instead of the grain size appeared thick of layers.

Key words: multilayered composite, micro- and nanostructure, NbTi alloy, superconducting compound, rolling, heat treatment, the superconducting properties, hardness, strength, superconducting vortices, the Hall-Petch expression.

1. INTRODUCTION

Using the methods of intense plastic deformation (IPD) allows to obtain metals and alloys of ultra fine-grained structure with grain sizes in sub microcrystalline (0.1-1 μ m) range and of a nanocrystalline structure with the dimensions of the structural elements <100 nm.

Kind of IPD is a multiple rolling of multilayer packages [1, 2]. In the first cycle a package can be assembled from the foils of one, two or more dissimilar metals, in the second cycle – from multilayer foils after first cycle, in the third cycle – from even more multilayered foils after the second cycle, etc. (Fig. 1). By this technique, each individual foil experienced at the rolling a huge total strain. In practice, to deform a separate foil of the thickness of 0.3-0.4 mm to a thickness of 10 nm will last three cycles. If in the nanocrystalline materials, obtained by methods of the SPD, the structural nanometer-sized elements were grains, then in the nanostructure composites such elements were separate layers.

The condition for a success in the multiple rolling of packages were a strong connection of foils, caused by a phenomenon of “a grasping”, which occurs as the result of a formation in a process of the rolling metallic bonds between atoms of contacting physically clean, so-called juvenile, surfaces when they approach each other at a distance of the interatomic forces. The ability of metals to the grasping is a physical property of the juvenile surfaces and depends on their nature. In ideal conditions, the grasping is a thermodynamically favorable process and should be done spontaneously. Under the ideal

conditions implied a convergence of the atomically smooth surfaces, free of oxide and adsorbed films, at a distance equal to the sum of radii of neighboring metals. In the package rolling is just the deformation of metal foils, providing the appearance of juvenile surfaces, their approach and increase the actual area of the clutch.

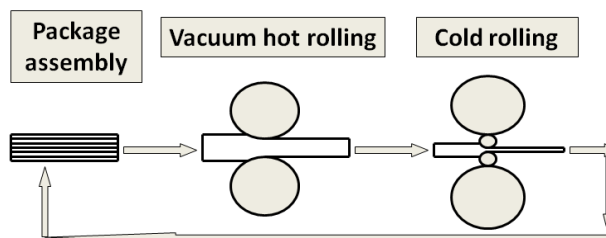


Fig. 1. The scheme of one production cycle in the technology of multilayer composites

An essential role for the setting plays a preparation of the contacting surfaces, which consisted of carefully removing from them oil and grease films. This was achieved by the chemical etching followed by a lengthy "rinsing" in running water. Washing was used as in an alcohol, less in an acetone. Useful procedure before building of the package was the vacuum annealing of foils at moderate temperatures, if along with the cleaning of the surface improved and their plasticity. For the grasping of the foils was positive to machine of their surfaces with wire brush, metal brushes, and then roughen the surface. Moreover, the training of surfaces, it is recommended not to do beforehand, and just before the vacuum rolling.

By the reusable multiple rolling got the multilayer nanostructure composites with an average thickness of individual layers of $t \leq 10$ nm. In these materials, t is a parameter that determines the mechanical properties of the material, since it affects on the path length of dislocations in the active slip systems. In addition, the thickness of the layer affects on the ratio of the interface surface to the volume of the phases, which plays a crucial role in the restructuring process during a heating. In this sense the rolling of multilayer packages is fairly simple method of controlled preparation of the artificial nanostructure objects for a scientific research.

A work with nanostructure composites pursued the following goals. First, the composites were of interest already in that form of what they were got. Thus, in [3] the film laminated composite Mo/W 50 μm thick, consisting of Mo- and W-layers are the thickness of 4 nm, obtained by CVD-method has the hardness and the tensile strength 15 times higher than similar characteristics of the monolithic alloy. In [4], multi-layered composite of Cu/Nb with ~32 000 layers of copper and niobium thickness of 11 nm, obtained by rolling over three cycles, had a Brinell hardness equal 350HB. High hardness of the material consisting of the plastic metals in line the hardness of average-carbon steel.

Secondly, the nanostructure composites consisting of two or more metals are interested as a starting material for obtaining the alloys with predictable functional properties through controlled a heat treatment. Diffusion processes between the layers, contacting the juvenile surfaces have very different the temperature and time regimes than the interdiffusion that takes place in normal conditions. Grain boundaries and interfaces in materials with submicro- and nanocrystalline structures so full of dislocations, that the coefficient of grain boundary diffusion is many orders of magnitude greater than the coefficient of bulk diffusion. In such artificial nanostructure elements can expect unexpected results. An example of such composites can be laminated composites of Ti/Ni and Ti/Nb with different

volume content of components, of which, after an appropriate treatment can be obtained alloys of different composition.

The third possibility to use of nanostructure multilayer composites was to obtain pseudo alloys representing plastic matrix reinforced with intermetallic layers. These structures can be obtained by the annealing of the composites consisting of layers of metals capable of the forming one with another chemical compound. Examples of such systems are the systems of nickel and niobium with aluminum. Such has been realized in our earlier work to obtain the superconducting compound Nb_3Al in multilayer tapes Nb/Al [5].

And finally, the fourth – is to get a multi-layer micro- and nanostructure composites from a single metal or alloy.

Diffusion welding under pressure gave a rise to the method of producing such multilayer composite materials, which are not required to deform by the rolling or when they could not be deformed. These materials can be flat and fairly thick, but at the same time, consist of multiple layers of dissimilar metals of micro- and nanoscale thickness. Moreover, if the metals can form among themselves, with appropriate heat treatment of alloys and chemical compounds, then, as the multilayer tape composites of thin sections, you can get the laminates composed of alternating layers of relatively ductile alloy and strong intermetallic component. Such possibilities of the diffusion welding under the pressure are exemplified by the composites consisting of Ni- and Al-layers of micron thick.

2. MULTILAYERED COMPOSITE TAPES WITH SUPERCONDUCTING ALLOYS NbTi

2.1. Theoretical background

Mixed state of the 2-nd kind superconductors is characterized by a partial penetration of an external magnetic field H in the sample in the form of quantum vortex filaments. Each such thread has a normal core of the radius of the order of the coherence length ξ , extending along direction of H , around which undeviating superconducting current flows oriented so that it produced a magnetic field was directed along the normal core and the same direction as the external field. The eddy current excite a field of the radius of the order of the penetration depth of the magnetic field λ , which can significantly exceed ξ .

If in this state through the superconductor perpendicular to the superconducting vortex filaments pass an electric current, and then the thread will start to operate the Lorentz force. In the superconductors without structural defects at arbitrarily small Lorentz force vortex lines would start to move, which would generate heat and superconductivity would collapse. But in the real world the superconductors, like any other metal, contain various structural defects, in which threads can pin. Now for the start of their movement is required is a finite current, which creates a Lorentz force, which will be sufficient for the separation of the vortex filaments from defects. This current is called the critical current I_c , and its density – the critical current density j_c . It can greatly vary as a result of thermal and mechanical processing. Please be aware that not all defects are able to effectively interact with the vortex filaments. Jobs, single impurity atoms, and similar "minor" defects are ineffective, as their typical size is much smaller than the characteristic size of the thread – the coherence length ξ . On the contrary, the structural defects with dimensions of order and more ξ are very effective centers of engagement (pinning) of the vortex filaments and can provide the large critical current density in the superconductor j_c [6]. Defects in the normal state are more efficient than the superconducting defects. [7].

V. V. Schmidt [6] theoretically examined the interaction of vortex filaments with the flat surface of the 2-nd kind superconductor and showed that even a defect-free wafer of the superconductor of thickness $d \gg \lambda$ in the mixed state can carry substantial superconducting current of about 10^5 A/cm^2 . Imagine

that a massive thick superconducting plate is replaced by a set of thin superconducting plates, artificially separated by a dielectric layer or a normal metal. Now the current can flow through each of these plates (each time in a layer $\sim \lambda$ around the edges of the plates), and in general over the section of the composite superconductor will go a lot of current.

A similar situation has been realized in multilayer composites of Cu/Nb in which layers of niobium being the 2-nd kind superconductor, separated by the non-superconducting layers copper. It was found that the ratio of j_c in the case when the magnetic field was parallel to the plane of the tape to j_c for the perpendicular orientation of the field and the plane of the tape in fields of 0.5-0.6 T was equal to 410 [4]. Such the large anisotropy of the critical current density was indicative of vortex pinning by extended planar boundaries of the copper-niobium.

2.2. Preparation and characterization of nanostructure composite tapes based on superconducting NbTi alloys

Next objects of study are multilayered tapes, in which the superconducting layers were made of wrought alloys Nb-30, 31 and 50%Ti (wt.%), but as a normal layers – layers of niobium [8]. What niobium itself is a superconductor of 2-nd kind, did not prevent him to perform the role of a normal metal, and since the critical current measurements performed in magnetic fields is many times greater than its second critical field. Composites contained from ~ 1200 to ~ 29000 layers of niobium and alloy NbTi. When the thickness of the ribbon equaled 0.3 mm thickness of the layers varied from ~ 140 to ~ 10 nm respectively.

In the composites of Cu/Nb/Nb50Ti through equal number of layers of an alloy and of niobium arranged layers of copper. Their number, counting the two outer layers, is 16. The thickness of the Cu-layers is ~ 9.7 microns (Table 1). A thickness of the layers of niobium and the alloy were the same. Composites of Cu(Nb/Nb31Ti) distinguished by the fact that there were only two outer Cu-layer of the thickness of $\sim 9 \mu\text{m}$ and thickness of layers of niobium, as compared with the layers of the alloy, was 1.5 times less than the thickness of the alloy. Was produced by five variants of the composites with an alloy of 50 and 31% titanium, characterized by the quantity and, consequently, thick of niobium and NbTi layers. The table shows the calculated thickness of the layers. According to the data transmission electron microscopy (TEM), it is well consistent with the average values of measured thicknesses (Fig. 2). Samples for TEM were prepared by an original technique. With the end of the bundle of several the tape strips was placed a slice of thickness of ~ 1 mm, which was subjected to thinning.

Table 1. The number and the thickness of the Nb- and NbTi-layers in the multilayered composite tapes

Variant number	Number of layers, pieces			Estimated layer thickness, nm			FC*
	niobium	alloy	copper	niobium	alloy	copper	
A series of composites with layers of Nb-50%Ti alloy							
1	675	540	16	119,5	119,5	9680	0,215
2	990	825	16	80,0	80,0	9680	0,220
3	1800	1575	16	57,3	57,3	9680	0,223
4	2850	2565	16	26,8	26,8	9680	0,229
5	7440	6975	16	10,1	10,1	9680	0,234
A series of composites with layers of Nb-31%Ti alloy							

1	1395	1116	2	90.9	137.6	9100	0.473
2	2046	1705	2	61.2	91.8	9100	0.523
3	2730	2340	2	43.8	67.2	9400	0.523
4	5700	5130	2	20.9	31.2	9400	0.533
5	14880	13950	2	7.9	11.8	9400	0.550

*Coefficient of filling

Composite tapes were prepared by the three-cycle rolling [1, 2]. Each cycle includes the assembly of multilayer package, hot rolling of the package and rolling it at room temperature. In the first cycle a package was assembled from the foils of niobium and the alloy. To obtain a set of the composite tapes with different thickness of individual layers, for each of the variants of the original tape, amounts of the foils of niobium and the alloy were varied. For example, for a composite of Cu/Nb/Nb50Ti with the minimum number of layers (Nb – 675, alloy – 540), and, therefore, with their maximum thickness, the number of Nb-foils was 5, the number of foils of the alloy – 4. For the tape with a maximum number of layers (Nb – 7440, alloy – 6975) and a minimum their thickness, the initial amount of Nb-foils is 16, the number of foils of an alloy – 15. In the second cycle of the package consisted of 9 (for the first variant) and 31 (for the latest variant) is already multi-layered foil thickness 0.3 mm, obtained after the first cycle and in the third cycle – from 15 more multilayered foils after the second cycle and 16 Cu foil. Copper was introduced as a stabilizer, by analogy with the traditional multi-core superconducting cables. Composite of Cu(Nb/Nb31Ti) with the maximum number of layers additionally rolled to a thickness of 0.15 and 0.075 mm, and then the thickness of the layers of niobium and the alloy becomes equal ~5 and ~2.5 nm respectively.

2.3. The microstructure of composite tapes

Fig. 3a shows the microstructure of the cross-section of one of the above composites Cu(Nb/Nb31Ti), which contained 2730 Nb-layers and 2340 layers of Nb-31%Ti alloy (see Table 1). The investigated section is located along the rolling direction. According to scanning electron microscopy, the layers of niobium looked bright stripes, layers of alloy – dark. It also shows the microstructure of the cross section of composite Cu/Nb/Nb50Ti tape with inner Cu-layers after a 2-nd and 3-rd cycles of rolling, respectively. This composite is specially made to study the effect of heat treatment for an interdiffusion between the layers. In the 1-st cycle of the package was contained the six foils of niobium and 5 the foils of the Nb-50%Ti alloy. The thickness of them was different. In the 2-nd cycle 11 such multilayer foils is left up foils of copper (Fig. 3b). The layers of alloy look dark stripes. Light relief to the allocated bandwidth – it's the layers of copper, niobium layers looked thin light strips. After the third cycle of rolling the microstructure of the multilayer tape is shown in Fig. 3c. In total it contains 605 layers of alloy, 726 layers of niobium and 121 layer of copper, of which 11 layers were thicker than all other copper layers.

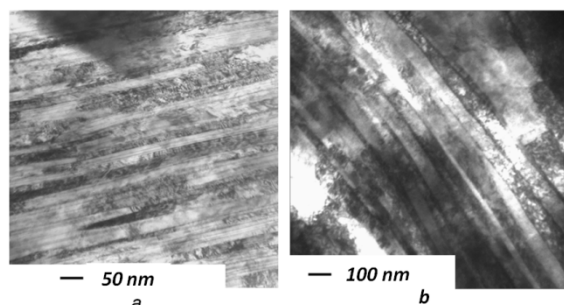


Fig. 2. Data of transmission electron microscopy. The microstructure of composite Cu(Nb/Nb31Ti) tape of 5-th variant (see Table 1) (a) and Cu(Nb/Nb30Ti) tape contained ~29700 Nb- and NbTi-layers (b), of thickness of 0.3 mm

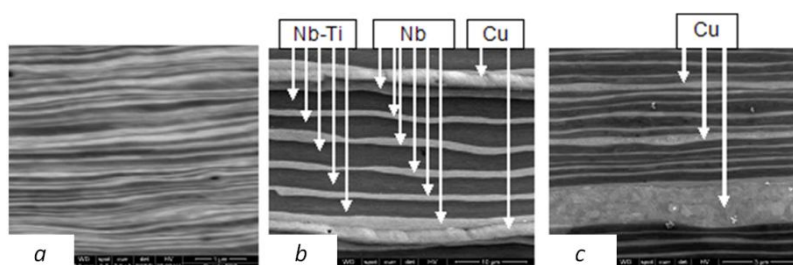


Fig. 3. The microstructure of the cross-section of composite tapes: a – Cu(Nb/Nb31Ti), variant 3 (see Table 1); b and c – a composite of Cu/Nb/Nb50Ti with internal layers of copper after a 2-nd and 3-rd cycles of the rolling respectively

In the composites with internal Cu-layers the layers of niobium, except that they formed interlayer boundaries of Nb-NbTi, sang the role of diffusion barriers to prevent the diffusion of copper to titanium in the alloy and the diffusion of titanium from the alloy to copper. True, this applies only to the Nb-layers, which are in contact with layers of copper.

2.4. The critical current density

Measurements of the critical current I_c was carried out at liquid helium temperature of 4.2 K in external magnetic field H up to 7 T by a superconducting solenoid. I_c values were determined from current-voltage characteristics (CVC), each of which was filmed at a fixed value of H (Fig. 4). For the value of I_c was assumed current at which the voltage drop was equal to 0.5 $\mu\text{V}/\text{mm}$. The critical current density j_c was calculated for all section of the sample. The plane rolled composite tape was oriented parallel (Fig. 5a) and perpendicular (Fig. 5b) the direction of H , and the flow of transport current in both cases it was perpendicular to H .

In magnetic fields above 1-1.5 T Nb-layers, because of the small second critical magnetic field of niobium H_{c2} , must become no superconducting. As stated above, inside a 2-nd kind superconductor, in the mixed state, magnetic field H penetrates in the form of vortex filaments. When passing through the conductor transport current I on the vortices begins to act, the Lorentz force L . This force would move the vortices and superconductivity would collapse, but in the case of parallel orientation of the magnetic field and the rolling plane of the composite (Fig. 5c), they have the opportunity to pin on the boundaries of Nb-NbTi. The figure shows in the form of vertical rods, the boundary of Nb-NbTi are gray in color. For the perpendicular orientation (Fig. 5d) the vortices are not able to pin in the

interlayer boundaries. In real situation in the explorer there are always other structural defects, for which the vortices can pin, so that the critical current and the second case does not equal zero. The question is how much is effectively pinning.

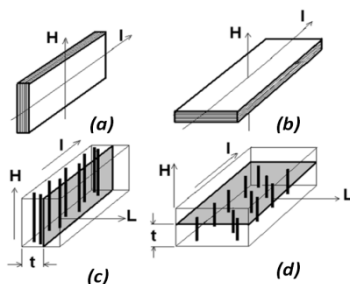
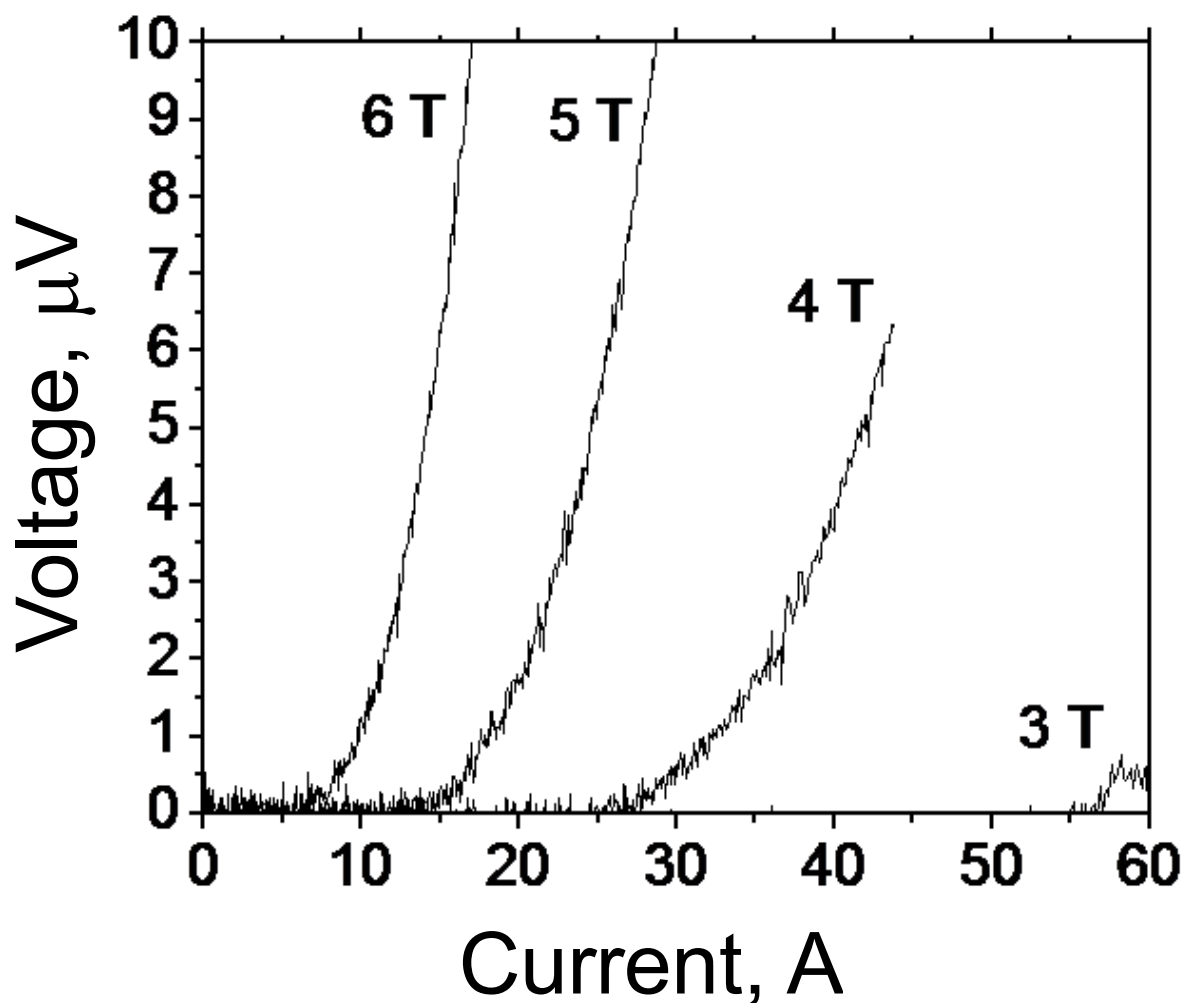


Fig. 4. CVC of Cu/Nb/Nb50Ti-tapes with 14 internal and 2 external Cu-layers in fields 3, 4, 5 and 6 T. The number of Nb- and NbTi-layers – 990 and 825, respectively. The thickness of layers – 80 nm

Fig. 5. Schematic representation of the orientation of the composite sample in a superconducting solenoid with respect to the magnetic field H and the location of the vortex filaments in the NbTi-layer thickness t : a and b – H is parallel to, c and d – H perpendicular to the plane of the composite

Fig. 6 shows the typical dependence of the critical current density j_c of the magnetic field H for samples of laminated Cu(Nb/Nb30Ti)-composite thickness of 0.15 mm, subjected to different thermo mechanical processing. Composite contained ~15300 Nb-layers of ~3.5 nm thick and ~14400 alloy layers of ~5.5 nm thick. The upper group of curves $j_c(H)$ refers to a sample in which the critical current was measured when the plane of the composite and the direction of the magnetic field were parallel and belonged to the perpendicular orientation of the magnetic field to the plane of the composite.

It is seen that the values of j_c in each of these groups differ on the order of in the fields 5-6.5 T and more than an order of magnitude – in the field 7 T. This is indicative of the pinning of superconducting vortices in the interlayer boundaries of Nb-NbTi.

More convincing evidence of effective pinning of the vortices at the boundaries between layers of niobium and alloy is the anisotropy of the critical current density. It is the ratio of the critical current density measured at the parallel orientation of rolling plane of the composite to the field $j_{c\parallel}$, to the current density measured on the same sample, but at the perpendicular orientation $j_{c\perp}$: $j_{c\parallel}/j_{c\perp}$. Anisotropy as a function of the thickness of the NbTi-layer t for two sets of composites, each of which contained five composites of Cu/Nb/Nb50Ti and Cu(Nb/Nb31Ti), respectively (see Table 1), is shown in Fig. 7. When the thickness of the NbTi-layer was fallen anisotropy increased c 3-5 for composites with t , equal to 138 nm, up to 11-20 for the ribbons, rolled to 0.15 mm, with t of about 5.5 nm. The largest anisotropy for this family of composites, which is equal to 235, was achieved in the ribbons thickness of 0.075 mm with $t \sim 3$ nm.

Qualitative change in the efficiency of the pinning of superconducting vortices on the interlayer boundaries of Nb-NbTi occurred at the layer thickness equal ~10 nm.

The anisotropy is strongly dependent on the magnetic field strength. It's easy to see, if we again turn to Fig. 6. Its value varies from 7-17 at 5-6 T to 100-450 at 7 T.

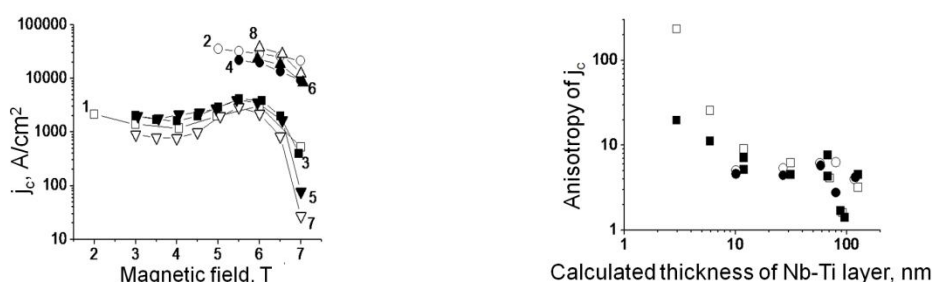


Fig. 6. Dependence of j_c on H for the composite of Cu(Nb/Nb30Ti): 1 and 2 – after the cold deformation (c. d.); 3 and 4 – c. d. + annealing at 600°C for 5 h; 5 and 6 – c. d. + 600°C for 5 h + 250°C for 295 h; 7 and 8 – c. d. + 250°C for 295 h. For the upper group of curves H is parallel to the rolling plane, for the lower group of curves of H is perpendicular to the rolling plane

Fig. 7. Anisotropy of the critical current density on the calculated thickness of the NbTi-layer for composites of Cu(Nb/Nb31Ti) and Cu/Nb/Nb50Ti directly after rolling and after rolling and annealing at 360°C for 3 h and 400°C for 3 h in a field 6 T

2.5. Degradation of the second critical magnetic field

If we compare the dependences of the critical current density of the magnetic field $j_c(H)$ for the composite tapes with NbTi-layers of varying thickness (Fig. 8), we can see that j_c of composites with NbTi-layers ≤ 12 nm in the magnetic fields above 6 T drops sharply. In many cases, it became even smaller than j_c of the composites with layers of 80-120 nm thickness, while that in idles above 6 T the ratio of the critical current density was an order of magnitude or more in their favor. Such a course of the $j_c(H)$ is characteristic, if the external magnetic field H close to the second critical magnetic field of the measured sample. Therefore, experiments were undertaken to measure H_{c2} of Cu(Nb/Nb31Ti)-composites containing the minimum and maximum number of layers of the alloy.

The second critical magnetic field H_{c2} was determined from measurements of H_{c2} near the critical temperature [9]. Constructed dependence $H_{c2}(T)$, a straight line near T_c , and calculate the slope $(-dH_{c2}/dT)_{T=T_c}$. $H_{c2}(0 \text{ K}) = 0,69 \cdot T_c \cdot (-dH_{c2}/dT)_{T=T_c}$, $H_{c2}(4.2 \text{ K})$ was $\sim 95\%$ of the $H_{c2}(0 \text{ K})$. The experiment consisted of measuring the temperature of the superconducting transition at fixed magnetic field of superconducting solenoid. The transition temperature was measured by resistive method. The results of these measurements are shown in Fig. 9. It is seen that with increasing magnetic field the superconducting transition curve shifted toward lower temperatures. After the determining of the temperature of the superconducting transition $H_{c2}(T)$ dependents were constructed (Fig. 10). By analogy with the measurements of the critical current H_{c2} measured at the parallel (1) and the perpendicular (2) orientations of the rolling plane of the composite and the magnetic field. Directs $H_{c2}(T)$ out of one point. But for the Cu(Nb/Nb31Ti)-composite, containing layers of the alloy minimum (11.8 nm) thickness, the slope of $H_{c2}(T)$ -dependent in the case of perpendicular orientation of the rolling plane of the composite and the direction of H was significantly lower than for parallel orientation (see Fig. 10b). Hence and $H_{c2}(4.2 \text{ K})$ in this case will be lower than in the case when the plane of the composite and H are parallel. $H_{c2}(T)$ -directs of the composite with alloy layers of maximum (137.6 nm) the thickness are parallel (see Fig. 10a). Therefore, and $H_{c2}(4.2 \text{ K})$ will differ slightly.

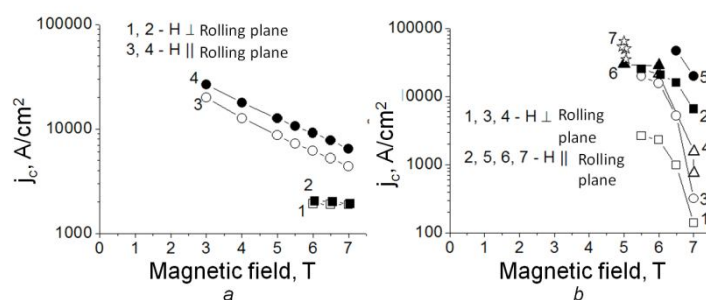


Fig. 8. The $j_c(H)$ of Cu(Nb/Nb31Ti)-composite: *a* and *b* – the thickness of the niobium and the alloy layers are equal ~ 91 and ~ 138 nm, ~ 8 and ~ 12 nm respectively

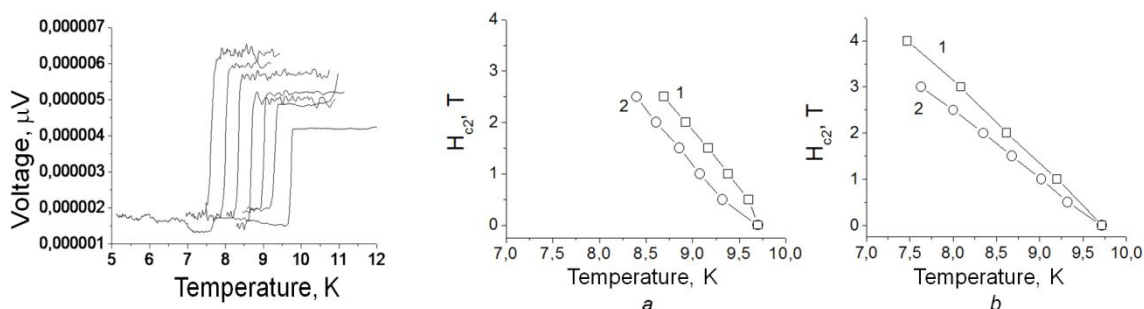


Fig. 9. The superconducting transition curves for the Cu(Nb/Nb31Ti) composite in a magnetic field 0, 0.5, 1, 1.5, 2, 2.5 and 3 T (right to left) for the perpendicular orientation of the rolling plane to direction of H. Annealing: 360°C for 3 h

Fig. 10. Dependence $H_{c2}(T)$ for Cu(Nb/Nb31Ti)-composites 1-st (a) and 5-th (b) variants (see Table 1.) for the parallel (1) and perpendicular (2) orientation of the rolling plane of the composite to the direction of the magnetic field. Annealing: 360°C for 3 h

The final results of the H_{c2} measurements are summarized in Table 2. For comparison, the results of similar measurements of H_{c2} were submitted for a regular ("single layer") tape of the Nb-31%Ti-alloy, as well as for the Cu(Nb31Ti/Nb31Ti)-composite thickness of 9.6 nm, in which all layers are made of Nb-31%Ti-alloy but their number is equal to 27791 what roughly corresponded to the total number of layers of niobium and the alloy in the composite of Cu(Nb/Nb31Ti).

For a composite tape that contains the highest number of layers, H_{c2} at the measurements, where the rolling plane parallel to the H, significantly less (11.8 T) than for the "single layer" tape from the alloy of Nb-31%Ti (14.8 T). The annealing at 360°C, with the result which in the alloy layers was separated α -phase, almost didn't effected on H_{c2} (11.5 T). The value of $H_{c2}(4.2\text{ K})$ of the composite thick layers on the order of magnitude greater at the same orientation of the rolling plane to H was 14.2 T, which almost coincided with the H_{c2} of conventional NbTi-tape. Greater decrease of H_{c2} observed in the case of perpendicular orientation of the rolling plane to H – up to 13.8 and 9.7 T for the composites with the lowest and highest number of layers, respectively.

In the composite of Cu/Nb31Ti/Nb31Ti the pinning of vortex filaments in parallel orientation of the rolling plane and H occurred at the interlaminar boundaries "superconductor-superconductor". The critical current density of such tapes in magnetic fields of 6.5 T (Fig. 11) was an order of magnitude smaller than in the ribbons with Nb-layers (see Fig. 8b). But a sharp drop in j_c from 6.5 T was not observed. This tape had parallel lines $H_{c2}(T)$ for both orientations of the ribbon plane on the field (Fig. 12a) and, consequently, the same slope value $(-dH_{c2}/dT)_{T=T_c}$ (2.36-2.39 T/K) and $H_{c2}(4,2\text{ K})$ (15.3-15.4 T), close to the values of the same parameters as "single layer» NbTi-tape.

For comparison, Fig. 12b shows the dependence of $H_{c2}(T)$ for bulk sample of the tape thickness of 0.3 mm of the Nb-31%Ti-alloy. It is evident that the $H_{c2}(T)$ -direct completely coincided, H_{c2} equals $\sim 15\text{ T}$ and does not depend on the orientation of the sample in an external magnetic field.

The behavior of the composites in an external magnetic field differs from that of bulk superconductors. The results can be explained by the proximity effect, whereby Nb-layers reduce the H_{c2} of NbTi-layers on the depth of the order of the coherence length $\xi(T) = (\Phi_0/2\pi H_{c2})^{1/2}$ [6], where Φ_0 – magnetic flux quantum. At $H_{c2} = 11\text{ T}$ $\xi(T) \approx 5\text{ nm}$. It is that the thickness of the layer below which H_{c2} of NbTi-alloy should decrease. Decrease in H_{c2} explains a sharp drop of j_c in fields 6.5 T

with its overall high values in excess of a 10^5 A/cm² in the field of 5 T, if count j_c on a section of the superconductor.

Table 2. The results of measurements of H_{c2} near T_c

Characterization of sample	$(-dH_{c2}/dT)_{T=T_c}$, T/K		$H_{c2}(4.2\text{ K})$, T	
	H $\perp$ rolling plane	H $\parallel$ rolling plane	H $\perp$ rolling plane	H $\parallel$ rolling plane
1-st variant, Cu(Nb/Nb31Ti), 360°C for 2 h	2.17	2.21	13.8	14.2
5-th variant, Cu(Nb/Nb31Ti), without annealing	1.50	1.82	9.7	11.8
5-th variant, Cu(Nb/Nb31Ti), 360°C for 3 h	1.46	1.78	9.4	11.5
Tape of Nb-31%Ti-alloy thickness of 0.3 mm, without annealing	2.34	2.27	15.2	14.8
5-th variant Cu(Nb31Ti/Nb31Ti) 300°C for 2 h	2.39	2.36	15.4	15.3

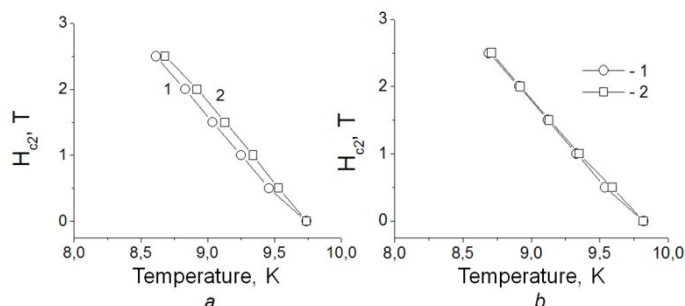
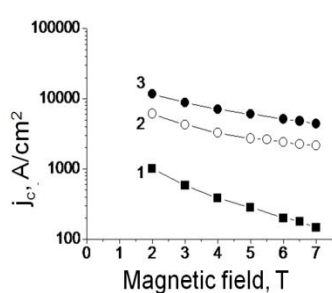


Fig. 11. Dependence $j_c(H)$ for the composite tape, containing no Nb-layers, at the perpendicular (1) and parallel (2 and 3) the orientations of the rolling plane and H in a state of "after rolling" (2) and "after rolling and annealing" at 300°C for 2 h (1 and 3)

Fig. 12. Dependence $H_{c2}(T)$ for the perpendicular (1) and parallel (2) orientations of the rolling plane and H for the composite containing no Nb-layers after the cold deformation and annealing at 300°C for 2 h (a) and "monolayer" tape of Nb-31%Ti-alloy (b)

2.6. Conclusions

1. Method 3-cycle the rolling deformation obtained prototypes of the superconducting multilayer tapes containing alternating layers of nanometer thickness of niobium and niobium alloys with 30, 31 and 50%Ti. Copper, as a stabilizer, could be present in the composites in the form of the inner layers, equally spaced multi-layer Nb/NbTi, and the outer layers.
2. Measurements of the critical current of the composites in an external magnetic field for the parallel and perpendicular orientation of the rolling plane to a direction of H is shown that Nb-layers shaped interlayer boundaries of "superconductor-normal metal", which were effective for pinning of the vortex filaments. This was evidenced by high values of anisotropy of the critical current density for the alloy layers the of ≤ 10 nm thickness. The critical current density, calculated for all section of the conductor, reaches $\sim 10^5$ A/cm² in field of 6.5 T.
3. Measurements of H_{c2} near T_c for the composites with layers of Nb-31%Ti alloy showed that $H_{c2}(4.2$ K) decreases with decreasing thickness of the layers. For the tape with a layer the thickness $\sim$ of 12 nm, it was 11.5-11.8 and 9.4-9.7 T, respectively, for parallel and perpendicular orientations of the rolling plane and H, which was much smaller than the regular tape of an alloy of the same composition. The results can be explained by the proximity effect, whereby Nb-layers reduced H_{c2} of NbTi-layers on the depth of the order of the coherence length.

3. STRUCTURE AND SUPERCONDUCTING PROPERTIES OF MULTILAYER TAPES FROM COMPOUND Nb₃Sn

Natural continuation of studies of superconducting multilayer composites were tested method of package rolling to produce the superconducting compound Nb₃Sn, which has practical significance. But, if in the case of Nb-Ti-alloys superconducting properties were realized in the composites of Cu(Nb/NbTi) and Cu/Nb/NbTi after deformation, then for the intermetallic compound Nb₃Sn is it basically impossible, due to its natural brittleness. Therefore, as "bronze technology" as a source of tin used bronze with 12 wt.% tin. Initially produces the multilayered nanostructure composite of Cu/Nb, which, together with segments of tape made of bronze was used for the formation of another composite Cu[(Cu/Nb)/Cu12Sn], as starting material to obtain multilayered tapes based on Nb₃Sn by the controlled heat treatment.

3.1. The starting materials and their preparation

The starting materials were oxygen-free copper of the grade MOF, niobium of the brand NHP and bronze of a composition Cu-12 wt.%Sn. To build the multi-package of Cu/Nb used Cu- and Nb-foils of 45 mm width. Copper foil required thickness obtained by rolling a sheet of 3 mm thick. Niobium in the initial state was in the form of plates with thickness of 10 mm, which rolled at room temperature to a thickness of 0.3 mm and cut into strips of 45 mm width. Before assembly into packages the Nb-foils were annealed in vacuum at 1100°C for 1 h.

Bronze in the form of flat ingots of $\sim 80 \times 40 \times 10$ mm the size were melted in an induction furnace with a casting into a massive Cu-mold. Ingots are rolled up the tape thickness of 0.3 mm at the room temperature with annealing or without them, but with pre-heating to 600°C.

3.2. Unoptimized superconducting tape based on Nb₃Sn

3.2.1. Obtaining of a composite (Cu/Nb)/Cu12Sn-tape

Multilayer composite tape of (Cu/Nb)/Cu₁₂Sn with nanometer thick layers of copper and niobium were produced by the package rolling over three cycles. The first two cycles were used for the manufacture of the laminated composite tape of Cu/Nb and only in the third cycle were used bronze foils to build the package.

In the 1-st cycle the package of 40 mm width and 80 mm long was assembled from 16 Cu-foils with thickness 0.15 mm, alternating with 15 Nb-foils with thickness of 0.3 mm. The package welded by the rolling on the vacuum mill with a heating to 950°C for two passes with the deformation in one pass ~30%, and the resulting blank rolled at the room temperature without intermediate annealing to the tape of 0.3 mm thick. At this stage, the thickness of the Cu- and Nb-layers, respectively, equal to 6.5 and 13 µm.

In the 2-nd cycle the package is the 31 segments of the tapes after 1-st cycle and subjected to the same as in the 1-st cycle, processing by the rolling to a tape of 0.3 mm thickness. Composite of Cu/Nb contained 496 copper and 465 niobium layers of ~210 and ~420 nm thick, respectively.

And finally, in the 3-rd cycle a package was assembled from 16 segments of tapes after 2-nd cycle, alternating with 15 foils of bronze of 0.3 mm thickness, i.e., so that the outer plates of the package were the laminated segments of Cu/Nb-tape. To prevent the possible formation of Nb₃Sn-compound at the time of the vacuum rolling the package is rolled in one pass with heating to 750°C and the compression of not less than 35%.

Before packages assembling in a 3-rd cycle segments of the Cu/Nb-composite and bronze annealed to relieve a work hardening after the deformation. If the HV hardness of the surface a cold deformed foils of Cu/Nb and bronze was 1.73 ± 0.03 and 2.68 ± 0.07 GPa respectively, then for Cu/Nb after annealing at 700°C for 2 h it decreased to 1.41 ± 0.05 GPa, and for bronze after annealing at 600°C for 1 h to 0.82 ± 0.02 GPa.

The ends of the multilayer packages at this stage of technology fastened with rivets.

Package of bronze and the multilayer Cu/Nb-segments of the tape rolled to a thickness of 0.4 mm. At the final stage the composite of (Cu/Nb)/Cu₁₂Sn contained a total of 7440 Nb-layers of 18 nm thickness, 7936 Cu-layers (9 nm) and 15 layers of bronze (~13 µm).

3.2.2. The microstructure of the composite tape before and after heat treatment

Microstructure studies were carried out by scanning electron microscopy using scanning electron microscope CamScan MV2300 and Vega 2, equipped with detectors of secondary and reflected electrons and x-ray microanalysis. Shooting in the reflected electrons allows to easily distinguish by means of a light contrasts the copper, niobium and bronze layers and also the layers containing superconducting compound of Nb₃Sn, which is formed after an annealing the composite tapes of (Cu/Nb)/Cu₁₂Sn. Composition of the layers was determined by local X-ray analysis.

The microstructure of cross sections of the composite tapes of Cu/Nb and (Cu/Nb)/Cu₁₂Sn along the rolling direction is shown in Fig. 13 and 14. After the 1-st cycle Cu/Nb-composite contained 15 layers of niobium (light strips) and 16 layers of copper (see Fig. 13a). Fig. 13b shows a fragment of the microstructure of its cross section after a 2-nd cycle, and Fig. 13c and d – the macrostructure of the finished (Cu/Nb)/Cu₁₂Sn-composite across and along the rolling direction. The composite contained 15 layers of bronze (dark strips) and 16 the multilayer nanostructure interlayers of Cu/Nb-composite. In the cross section perpendicular to the rolling direction layered structure look more correct than the longitudinal. Since all the deformation of layers occurs along the rolling direction, the unevenness of the thickness of the layers in this direction is often reached almost the critical moments when the interlayer's of Nb/Ti were on the verge of a break.

Each of the 16 interlayers of Cu/Nb contained 496 copper and 465 niobium layers of nanometer thickness. They can be seen in Fig. 14; where at high magnification shows the microstructure of one randomly selected multi-interlayer of Cu/Nb. Importantly to note well respected laminar structure and the absence of discontinuities of the individual layers. The thickness of the Nb-layers did not exceed ~50 nm, in order of magnitude close to its rated value.

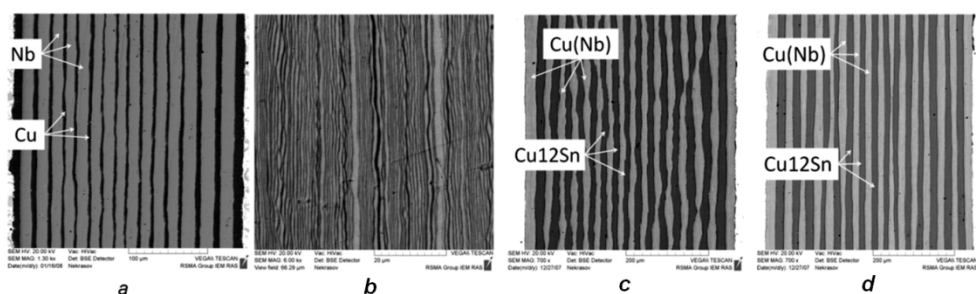


Fig. 13. The microstructure of the cross-section of composite strips along the rolling direction [a – Cu/Nb, 1-st cycle, b – Cu/Nb, the 2-nd cycle; c – the 3-rd cycle, (Cu/Nb)/Cu12Sn] and across the rolling direction [d – the 3-rd cycle, (Cu/Nb)/Cu12Sn]

According to X-ray analysis in layers of bronze contain from 12.4 to 12.7 wt% tin, which corresponded to its nominal composition.

To obtain the superconducting compound of Nb₃Sn (Cu/Nb)/Cu12Sn-tape subjected to a vacuum annealing at 750°C for 5 and 50 h. In the annealing process, due to the reactive diffusion, tin out of bronze diffuse into the multi-layers of Cu/Nb and formed with a niobium Nb₃Sn-compound. At the site of layers 12%-nt of the first tin bronzes was remained a solid solution of Sn in copper Cu(Sn) with a significantly lower tin content.

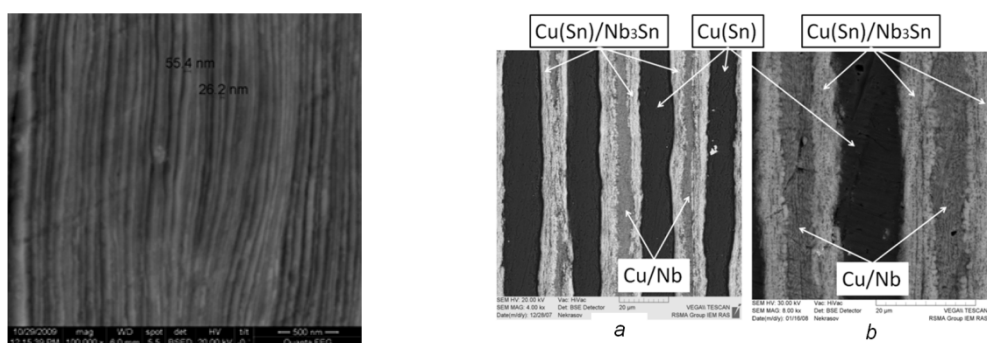


Fig. 14. Microstructure of multilayered Cu/Nb-interlayer in the composite tape of (Cu/Nb)/Cu12Sn. Inscriptions on the photo indicate the thickness of the randomly selected Nb-layers

Fig. 15. The microstructure of the Nb₃Sn-tapes after annealing at 750°C for 5 (a) and 50 h (b)

The results of microstructure studies of annealed composite tapes (Fig. 15) showed that the compound of Nb₃Sn was formed not by the entire volume of multi interlayers of the Cu/Nb-composite. Almost complete loss of bronze as a source of tin occurs already at the 5-hour exposure. After the annealing for 50 h have been no changes in the microstructure of cross section, compared with the

microstructure of the composite after the exposure for 5 h. This is also supported by X-ray analysis. In a layer of Cu(Sn), the former before the annealing layer 12% of the first bronze, after the 5-hour heating contain no more than 0.5 wt.%Sn. In addition, the complete absence of tin observed in the middle field of the multilayer Cu/Nb-layers, which occupies about the one-third part of them.

3.2.3. The critical current density and critical temperature of non-optimized tape-based compound Nb_3Sn

Despite the suboptimal phase composition, the tapes had a high current-carrying capacity. As is the case with the superconducting tape with nanoscale layers of Nb-Ti alloys, the sample was oriented such that its plane of rolling (ab) was parallel and perpendicular to the direction of the magnetic field H, but the current through the sample was always perpendicular to H. The critical current density j_c (Table 3), calculated on the entire cross-section in a magnetic field of 7 T for the perpendicular orientation of H and the plane of the sample was $1.47 \cdot 10^4$ and $2.00 \cdot 10^4$ A/cm² in the ribbons after annealing for 5 and 50 h respectively. However, if we consider that the superconducting current flows only in the section where the compound of Nb_3Sn was formed, then the true j_c was significantly higher – $4.53 \cdot 10^4$ и $6.02 \cdot 10^4$ A/cm². The parallel orientation of H and the sample plane $j_c = 3.51 \cdot 10^4$ and $1.08 \cdot 10^5$ A/cm², respectively, in the calculation of all cross-section and Cu(Sn)/ Nb_3Sn (for the tape after 5 hours of annealing).

Table 3. Superconducting properties of the composite tape of the Nb_3Sn

Annealing time at 750°C, h	j _c , A/cm ²				T _c , °K
	In the calculation of all cross-section		In the calculation of Cu(Sn)/Nb ₃ Sn-cross-section		
	H (ab)	H ⊥ (ab)	H (ab)	H ⊥ (ab)	
5	3.51·10 ⁴	1.47·10 ⁴	1.08·10 ⁵	4.53·10 ⁴	16.65
50	-	2.00·10 ⁴	-	6.02·10 ⁴	16.89

Anisotropy of the critical current density $j_{c||}/j_{c\perp}$, where $j_{c||}$ and $j_{c\perp} = j_c$, respectively, at ||- and ⊥-orientations (ab) relative to the direction of the magnetic field was 2.4.

Critical temperature, measured resistive method, was equal to 16.65 K for the tapes after annealing for 5 h and 16.89 K – for the tape after annealing for 50 h.

3.3. The optimum ratio of niobium and tin

The first results showed that the amount of tin, which contained in the bronze layers above mentioned the composite (Cu/Nb)/Cu12Sn-tape, was insufficient for the formation of Nb_3Sn in the entire volume of layers of multilayers Cu/Nb. Therefore, to Nb_3Sn formed throughout the volume of Cu/Nb-interlayers, the optimum amount of niobium being in Cu/Nb-layers of the tape, must match the amount of niobium in the compound Nb_3Sn , which can be formed from tin that is in bronze.

By a simple calculation was obtained by the following relationship:

$$\frac{t_{Nb} \cdot N_{Nb}}{t_{CuSn} \cdot N_{CuSn}} = \frac{\rho_{CuSn} \cdot \omega_{Sn}^{CuSn} \cdot \omega_{Nb}^{Nb_3Sn}}{100 \cdot \rho_{Nb} \cdot \omega_{Sn}^{Nb_3Sn}} = \frac{8,75 \cdot 12 \cdot 70,13}{100 \cdot 8,57 \cdot 29,87} = 0,288 \text{ or } t_{Nb} \cdot N_{Nb} \approx 0.288 \cdot t_{CuSn} \cdot N_{CuSn}. \quad (1)$$

Here: t and N – the thickness and the number of layers of niobium and bronze respectively, ρ - density of bronze and niobium, ω – the concentration of tin in bronze, niobium in Nb_3Sn and tin in Nb_3Sn .

Substituting in this expression parameters of the (Cu/Nb)/Cu₁₂Sn-tape, we obtained too an obvious inequality: $134 \neq 56$, i. e., construction of the tape is far from optimal. It niobium contained in large excess compared to the quantity that you need for education of the amount of Nb_3Sn , which is limited by tin being in bronze.

3.4. The composite (Cu/Nb)/Cu₁₂Sn-tape of optimal design

3.4.1. Getting the tape with an optimized ratio of tin and niobium

In the manufacture of multilayer (Cu/Nb)/Cu₁₂Sn-tapes, close to the optimum design that provides variants of the tape with some excess of niobium and some excess of tin (Table 4). For the first and second variants the tapes with the relations $t_{Nb} \cdot N_{Nb} / t_{CuSn} \cdot N_{CuSn}$, equal to 0.306 and 0.220 were consistent.

Unlike the tape of suboptimal design the composite of Cu/Nb with an excess of niobium after 2-nd cycle was subjected to rolling to thickness of 0.15 mm and, therefore, in the third cycle of a package was assembled from 16 multilayer foil after 2-nd cycle of 0.15 mm thick. In addition, the final strip thickness equal 0.3 mm.

If a receipt of production of the first version tape, compared with a tape suboptimal design differed slightly, then the technology of the composite (Cu/Nb)/Cu₁₂Sn-tape of the second version has been greatly improved.

Firstly, in the first two cycles of multilayered packages were kept in a vacuum chamber at a temperature of 800-850°C for 40 min under the pressure of ~25 MPa. As a result, packages were subjected to partial diffusion bonding. Such innovation freed technology from an unprogressive operation of riveting of the package.

Table 4. Parameters of the composite tape of the two designs in each of the three cycles

Cycles	Meaning of relations $t_{Nb} \cdot N_{Nb} / t_{CuSn} \cdot N_{CuSn}$	
	0.306	0.220
1-st	16 Cu-foil of 0.15 mm thickness; 15 Nb-foil of 0.3 mm thickness. Rolling up to 0.3 mm. The thickness of the Cu-layer – 6.5 μm^* ; The thickness of the Nb-layer – 13 μm .	16 Cu-foil of 0.3 μm thickness; 15 Nb-foil of 0.3 μm thickness. Rolling up to 0.3 mm. The thickness of the Cu-layer – 9.7 μm ; Nb-layer thickness – 9.7 mm.
2-nd	31 foil after 1-st cycle. Rolling up to 0.15 mm. 496 Cu-layers of 105 nm; 465 Nb-layers of 210 nm.	31 foil after 1-st cycle. Rolling up to 0.1 mm. 496 Cu-layers of 104 nm; 465 Nb-layers of 104 nm.
	16 foil after 2-nd cycle; 17 Cu ₁₂ Sn-foil of 0.3 mm thickness. Rolling up to 0.3 mm.	10 foil after 2-nd cycle; 11 Cu ₁₂ Sn-foil of 0.2 mm thickness; 2 outer Cu-foil 0.1 mm.

3-rd	7936 Cu-layers of 4.2 nm; 7440 Nb-layers of 8.4 nm; * Throughout the calculated thickness of the layers	Rolling up to 0.3 mm. 4960 Cu-layers of 9.2 nm; 4650 Nb-layers of 9.2 nm; 11 Cu₁₂Sn-layers of 17.7 mm; Outer Cu-layers of ~9 μm.
------	---	---

Secondly, in the 3-rd cycle the package turned a single layer of annealed copper foil. This operation was introduced in the first place, the desire not to use the diffusion welding because of the risk of premature formation of the fragile nature of Nb₃Sn-compound. The outer copper coating of ~9 μm thickness improved stabilizing properties of the tape on the cases of transition of its in normal state, and provides a reliable measurement contacts at the low temperature tests. In addition it is once again ruled out the riveting of the package. To show that the tape has a surface layer of copper, its symbolic image is recorded as Cu[(Cu/Nb)/Cu₁₂Sn].

Were modified and design parameters of the tape (see Table 4). Checking of the design of a composite for the optimality by substituting the numerical values of thickness and number of layers of niobium and bronze in the expression (1) evidence of a slight excess of tin.

3.4.2. Microstructure of nanostructure (Cu/Nb)/Cu₁₂Sn-composite of optimal design before and after annealing

In contrast to the non-optimized tape in the tapes of both variants with optimum design parameters multilayer interlayer of Cu/Nb had numerous refinement and regular breaks along its entire length (Fig. 16a).

Likely discontinuity interlayers of Cu/Nb is due to the thickness ratio of bronze and copper-niobium interlayers, and not by the thickness ratio of copper and niobium layers in themselves the Cu/Nb. Indeed, in a tape with non-optimal design parameters and the optimized tape with an excess of niobium an initial thickness of the Nb-foils was two times greater than the thickness of copper foils, and in the optimized tape with an excess of tin the initial thickness of Nb- and Cu-foils were the same. But in the ribbons with the optimum design parameters of both variants the thickness of the multilayer Cu/Nb-foils after a 2-nd cycle is half the thickness of the bronze foils, and in the non-optimized foil tape, both foils in the 3-rd cycle of the same thickness. But also the discontinuous of interlayers of Cu/Nb was not only in the non-optimized tape, i.e., the interlayer Cu/Nb are broken where they are thinner than a layer of bronze.

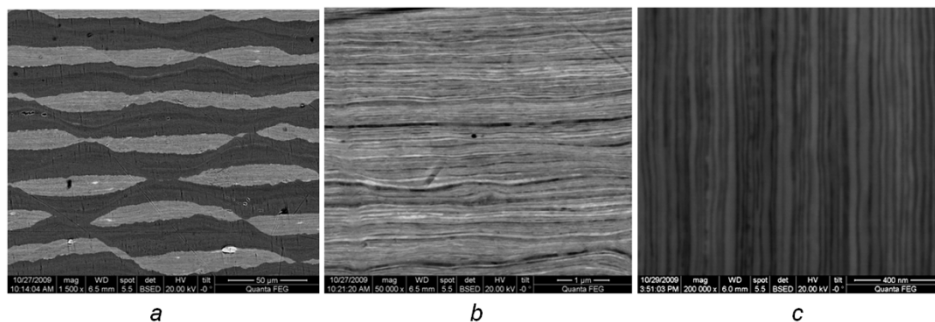


Fig. 16. The microstructure of the cross-section along the rolling tape (*a*) and multilayered interlayer of Cu/Nb (*b* and *c*): *a* and *b* – tape of Cu[(Cu/Nb)/Cu12Sn] with an excess of tin;
c – the tape of (Cu/Nb)/Cu12Sn with an excess of niobium

The layered microstructure of the Cu/Nb-interlayers in the unannealed tape (Fig. 16*b* and *c*) reflects the alternation of niobium (light bands) and copper (dark bands) layers. The thickness of the Nb-layers did not exceed 30 nm. Compliance with layers of a laminar and integrity pointed to the fact that the discontinuity of the Cu/Nb-interlayers is not linked to the achievement of reserve of plasticity of the individual Cu- and Nb-layers. The interlayers are busted spontaneously and at once over the section. This can be explained by the deformation of the layers of bronze, which occurs with the displacement angle of $\sim 45^\circ$ all the bronze layer at a time, used up their reserve of plasticity. These shifts were break and the neighboring interlayers of Cu/Nb. An appearance of such a process and its end is fixed in Fig. 17*a* (marked 1, 2 and 3). To prevent discontinuity of copper-niobium interlayers could the intermediate annealing in the process of a rolling at the room temperature.

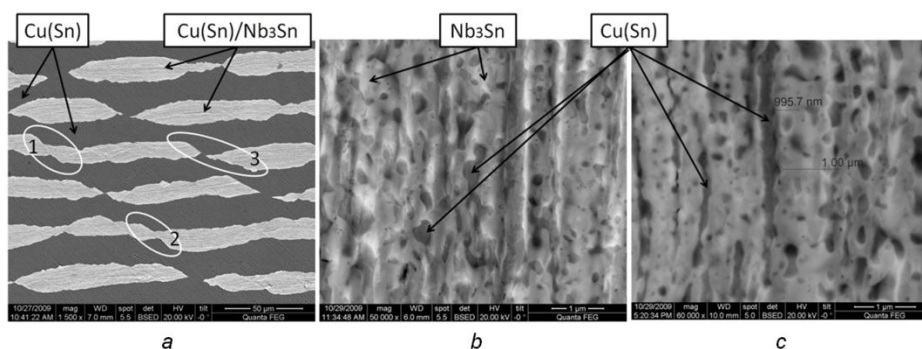


Fig. 17. The microstructure of the cross-section of an optimized composite tape of Cu[(Cu/Nb)/Cu12Sn] (*a*) and microstructure of single Cu/Nb-interlayer in an optimized tape of (Cu/Nb)/Cu12Sn (*b* and *c*) along the rolling direction after the annealing at 750°C for 3 (*a*) and 5 h (*b* and *c*)

After annealing at 750°C, which was conducted for the formation of the superconducting compound of Nb₃Sn, the strict alternation of nanoscale Nb- and Cu-layers that existed originally was absent (Fig. 17*b* and *c*). All Nb-layers were transformed into the layers of Nb₃Sn. However, compared with layers of niobium, their thickness becomes several times more. It seems such a pattern that in the process of diffusion formation of Nb₃Sn its neighboring layers merged, in turn, between the fused layers the jumper of different length are arose, and this led to the formation of even thicker layers. Enlargement

of the structural elements of Nb₃Sn could occur in the process of a formation of the compound, and after, when it occurred a depletion of bronze by tin.

Copper layers after an annealing remained as islands of a second phase in the form of a solid solution of Sn in Cu (indicated by arrows). These were some inclusions of gray 100-200 nm or the extended educations of thickness from 10 to 100 nm. Qualitative identification was carried out by their local X-ray analysis.

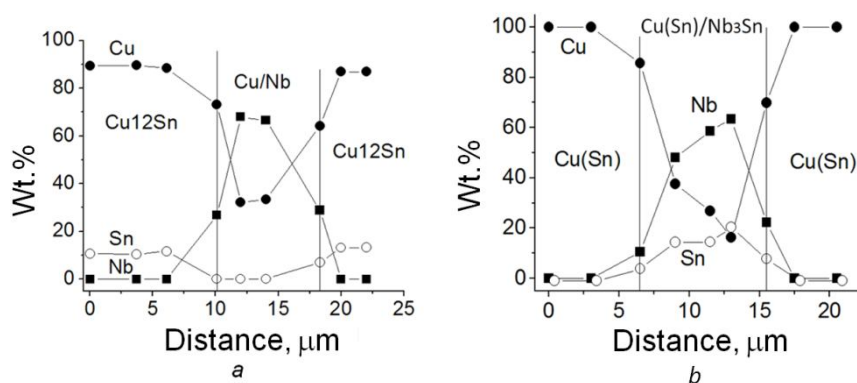


Fig. 18. Concentration profiles of niobium, copper and tin of the optimized composite (Cu/Nb)/Cu12Sn-tape with an excess of niobium to (a) and after annealing at 750°C for 5 h (b)

Fig. 18 shows the concentration dependence of the elements, involved in the diffusion process, for the optimized tape of (Cu/Nb)/Cu12Sn before and after an annealing. Scanning by a probe on the surface of section metallographic specimen conducted in a manner that it crossed an arbitrarily selected of a multilayer interlayer of Cu/Nb, if the sample of an unannealed tape is studied, or an interlayer of Cu(Sn)/Nb₃Sn, if a sample annealed ribbons is studied, partially capturing the right and left the layers of copper with tin. Before an annealing (see Fig. 18a) in the Cu/Nb-interlayer, as expected, there were only niobium and copper in the ratio ~2:1, respectively, and at the edges was bronze with ~12 wt% tin. After an annealing (see Fig. 18b) the concentration profiles showed only a redistribution of the tin. It is almost completely flowed into the interlayer of Cu(Sn)/Nb₃Sn. In layers of bronze it had less than 1 wt%.

3.5. Effect of annealing temperature on the structure of interlayers of Cu/Nb

An influence of the annealing temperature on the microstructure of the Cu(Sn)Nb₃Sn-interlayer in the range from 600 to 850°C was investigated using samples of the composite tape of Cu[(Cu/Nb)/Cu12Sn] of the optimized design with an excess of tin. The samples were annealed in a vacuum furnace with W-heaters for 3 hours

Even at 600°C (Fig. 19) between adjacent layers of Nb₃Sn formed jumper. With increasing temperature, the layered structure became all coarser and less pronounced. After annealing at 600 and 650°C layers of forming compound of Nb₃Sn and layers of Cu(Sn) be continuous, and their thickness does not exceed 100 nm. Notable merger of Nb₃Sn-layers started at 700°C and at higher temperatures this process becomes an avalanche-like character. At 750°C yet has been observed linear structure of the grains of Nb₃Sn, embedded in a matrix of Cu(Sn), but after annealing at 800°C and higher a coagulation of grains causes a complete break in continuity of the layers. After 850°C the Nb₃Sn-grains of predominantly elongated form grew to the size of 1 μm in length and 250-300 nm in diameter.

In this tape the original thicknesses of the Cu- and Nb-foils were the same, equal to 0.3 mm. In this regard, the microstructure of the interlayer of Cu(Sn)/Nb₃Sn in this tape after the annealing at 750°C is useful to compare with a microstructure the similar interlayer in the tape annealed at the same temperature, in the manufacture of which a Cu-foil was twice thin as against foils of niobium (see Fig. 19b and c). As expected, the microstructure of the interlayers of Cu(Sn)/Nb₃Sn strikingly different by the volume content of phase Cu(Sn). In terms of current-carrying capacity of Nb₃Sn layers of a more favorable option for a construction of tapes should be recognized the composite tape of Cu[(Cu/Nb)/Cu₁₂Sn] with the same volume content of Cu- and Nb-foils in the Cu/Nb-interlayers.

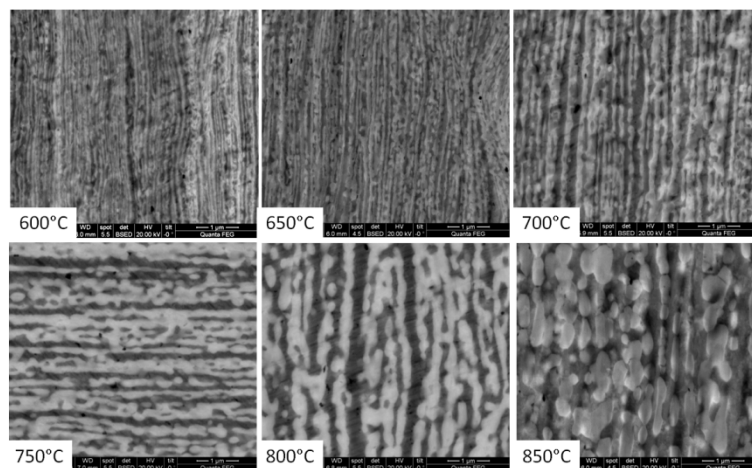
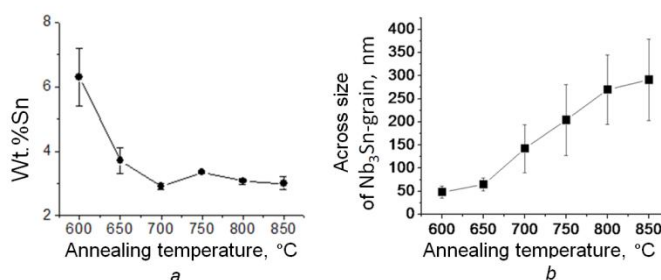


Fig. 19. Microstructure of interlayers of Cu(Sn)/Nb₃Sn in the composite Cu[(Cu/Nb)/Cu₁₂Sn]-tape after annealing in the temperature range 600-850°C. Exposure time – 3 hours

It can be assumed that the difference in the duration of annealing of the taps of two variants of a design not substantially affected on the results of the comparison.

Fig. 20 shows the dependence of the transverse grain size of Nb₃Sn-compound, which can be interpreted as the thickness of the layer, and remaining after the annealing of amount of tin in the bronze interlayers on the annealing temperature for the tape of an optimized design with an excess of tin.



20. Dependence of the transverse grain size Nb₃Sn-compound (a) and tin content in the interlayer of Cu(Sn) (b) on the annealing temperature of composite Cu[(Cu/Nb)/Cu₁₂Sn]-tape.

Annealing time – 3 h Fig.

Depending on the annealing temperature the average grain size of Nb₃Sn-compound in the transverse direction is increased from 48 at 600°C to 290 nm at 850°C (see Fig. 20b). Up to 850°C, we can assume that the thickness of the layer of the formed intermetallic compound corresponded to the cross-grain size. At 850°C as a result of coagulation the separation and the formation of more equiaxial grains of Nb₃Sn were began.

For the tape with an excess of tin its content in the former bronze interlayer with increasing of annealing temperature from 600 to 700-850°C decreased from 6.3 to ~3 wt.% (see Fig. 20a). Compare: in the Cu(Sn)-interlayer of optimized tape with an excess of niobium the tin content does not exceed 1 wt.%.

According to X-ray diffraction, patterns for the unannealed tapes of Cu[(Cu/Nb)/Cu₁₂Sn] contained lines of bronze, Cu and Nb. Complete transformation of niobium in Nb₃Sn occurs, starting from temperature of 700°C and above. In all these cases, the radiographs were observed two sets of lines, belonging to the compound Nb₃Sn with A15-structure and solid solution of tin in copper with fcc-lattice. The X-ray, taken from tapes after annealing at 600 and 650°C, was attended more and lines of the residual niobium. And for the tapes annealed at 600°C, the intensity of niobium lines was greater.

3.6. Optimized composite tape of Cu[(Cu/Nb)/Cu₁₂Sn] of new design

From the microstructure studies of composite Cu[(Cu/Nb)/Cu₁₂Sn]-tapes of the optimal design, as with a copper coating and without it, it followed that the multi-layer of Cu/Nb, containing nanoscale layers of copper and niobium in a process of a vacuum rolling and subsequent rolling at room temperature did not remain solid. This led to complete degradation of the critical current. It was therefore proposed a slightly different assembly technology of Cu[(Cu/Nb)/Cu₁₂Sn]-composites, taking into account the requirements of the optimum ratio of niobium and tin, and continuity of layers of Cu/Nb and bronze.

3.6.1. Three variants of Cu[(Cu/Nb)/Cu₁₂Sn]-tape of new design

In the 1-st cycle of a package assembled from alternating 16 Cu- and 15 Nb-foils with a thickness of 0.3 mm. To make the more laminarity in the future layered structure the package was subjected to partial welding by heating up to 800-850°C under a small (25 MPa) pressure for 40 min. Then the package is rolled first, on the vacuum rolling mill with pre-heating to 850°C and compression in a pass ~30%, resulting in it finally welding, and then at room temperature to tape of 0,3 mm thickness. The thickness of the copper and niobium layers in it at this stage was 9.7 μm.

In the 2-nd cycle a package going from 31 a multilayer foils after 1-st cycle and underwent the same operation as in the 1-cycle. Finite thickness of the multilayered composite of Cu/Nb was 0.1 mm. It contained 496 Cu- and 465 Nb-layers, the calculated thickness is 104 nm.

Third cycle. By design the packages of Cu₁₂Sn/(Cu/Nb) were the three variants (Fig. 21). First packs of 4, 5 and 10 multilayer foils of Cu/Nb after a 2-nd cycle were produced. This was done by the diffusion bonding under a pressure of 25 MPa at 850°C for 20 min. Package of Cu₁₂Sn/(Cu/Nb) of 1 variant consisted of 2 outer packs of 0.5 mm thick, each of which contained five foils of Cu/Nb after 2-nd cycle, and one bronze plate with thickness of 2.2 mm. The second version of the package: two plates of bronze of 1.1 mm thick and pack with a thickness of 1 mm of 10 foils of Cu/Nb. Composite of Cu₁₂Sn/(Cu/Nb) of third option was formed from three Cu/Nb-packs and two bronze plates of 0.4 and 1.1 mm thick, respectively.

Compiled packages turned a single layer of annealed Cu-foil with thickness of 0.1 mm and welded on the vacuum rolling mill in two passes with a reduction of not less than 30% per pass and heated to 850 and 800°C, respectively, before the 1-st and 2-nd drafts. Follow rolling was carried out at the room temperature without intermediate annealing to the tape of 0,3 mm thickness.

In the final the composite of first version is contained in each multilayer interlayer of Cu/Nb 2325 Nb- and 2480 Cu-layers with an estimated thickness of 9.2 nm. The number and thickness of layers of copper, niobium and bronze in the composites Cu[Cu₁₂Sn/(Cu/Nb)] of the three options listed in Table 5.

Volume ratio of Nb and bronze in the composite was chosen so that they become most fully in Nb_3Sn . For the $Cu[Cu_{12}Sn/(Cu/Nb)]$ -composites of all three variants the ratio $t_{Nb} \cdot N_{Nb} / t_{CuSn} \cdot N_{CuSn} < 0.288$ (see Table 5). All of them had some excess tin.

To form a compound Nb_3Sn a composite annealed at $750^\circ C$ for 5 h and $600^\circ C$ for 265 h. At this the tin out bronze diffuse into the niobium. As a result, multi-layer interlayers consisting of layers of copper and niobium were transformed into the interlayer containing superconducting compound Nb_3Sn and a solid solution of Sn in Cu: $Cu/Nb \rightarrow Cu(Sn)/Nb_3Sn$, and bronze – into a solid solution of Sn in Cu: $Cu_{12}Sn \rightarrow Cu(Sn)$. Ideally, multi-layer nanostructure Cu/Nb -interlayers must have been converted into the multi-layers consisted of Nb_3Sn -layers of nanoscale thickness, separated by layers of solid solution of Sn in Cu – $Cu(Sn)/Nb_3Sn$. Thus the composite of $Cu[Cu_{12}Sn/(Cu/Nb)]$ was transformed into a tape-based Nb_3Sn -compound, on the outside stabilized by the layer of copper: $Cu[Cu(Sn)/(Cu(Sn)/Nb_3Sn)]$ (Fig. 22).

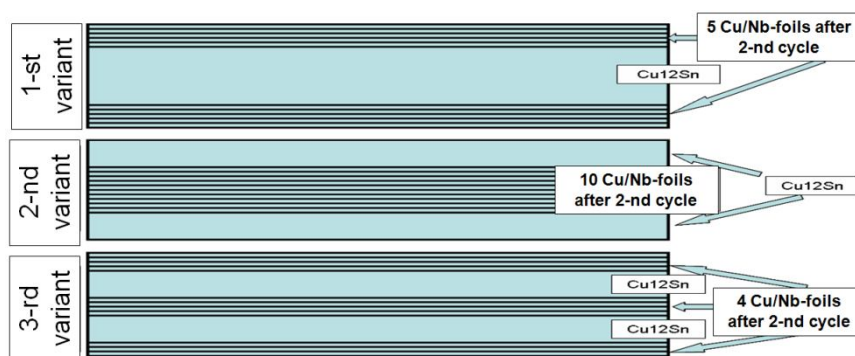


Fig. 21. Three variants of construction of the $Cu[(Cu/Nb)/Cu_{12}Sn]$ -composites

Table 5. The design parameters of $Cu[Cu_{12}Sn/(Cu/Nb)]$ -composite*

Variant	Nb		Cu		Cu ₁₂ Sn		$t_{Nb} \cdot N_{Nb} / t_{CuSn} \cdot N_{CuSn}$
	N	t, nm	N	t, nm	N	t, μm	
1	2×2325	9.2	2×2480	9.2	1	195.7	0.220
2	4650	9.2	4960	9.2	2	97.8	0.220
3	3×1860	8.7	3×1984	8.7	2	91.7	0.265

*Tapes of all options were outside the copper coating of $17.7 \mu m$ thick



Fig. 22. The second variant of the composite of the new design after heat treatment

In terms of the current-carrying capacity Nb_3Sn layers should have a fine grain structure, since the magnetic vortex filament in Nb_3Sn able to effectively pin in the grain boundaries. Therefore, annealing

of the composites is preferable carried out at 600°C when the Nb₃Sn-compound obtained with a more fine-grained structure.

3.6.2. Studies of the structure of tapes of a new design by method of scanning electron microscopy

As an example, Fig. 23 shows the macrostructure of one of the options for composite tape of Cu[(Cu/Nb)/Cu12Sn], made on the scheme described above, and microstructure of the interlayer (stack) Cu/Nb after the annealing at 600°C for 265 hours. A fairly orderly layered structure of Cu(Sn)/Nb₃Sn-interlayers was observed.

For the same composite in Fig. 24 shows the concentration dependence of tin, copper and niobium, obtained using X-ray analysis. Just in the composite of this option in the interlayer Cu(Sn)/Nb₃Sn observed the most uniform distribution of elements. The concentration of tin in them was 14.0-15.5 wt.%. In the interlayer Cu(Sn) near the superconducting layers tin remained from 3.0 to 4.4 wt.%.

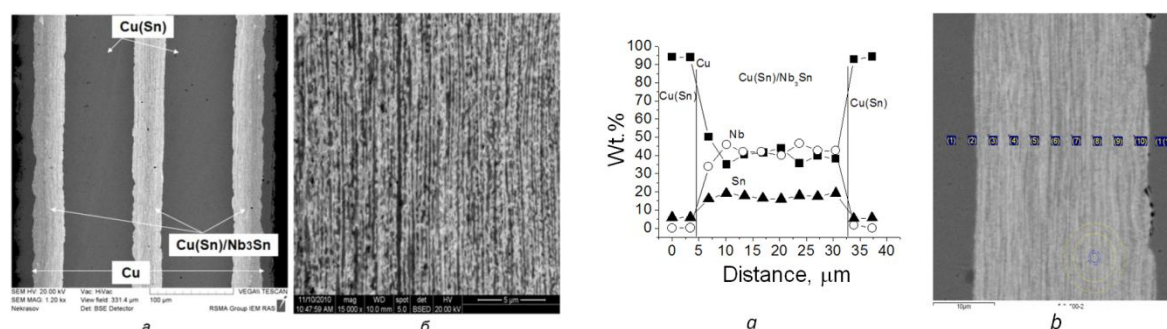


Fig. 23. Macrostructure of cross section of Cu[Cu12Sn/(Cu/Nb)]-tape of the third variant (a) and microstructure of multilayer Cu/Nb-layer (b) after annealing at 600°C for 265 h

Fig. 24. The concentration profiles of Nb, Sn and Cu (a) and a fragment of the structure of cross section, where analysis was made (b) for the composite of Cu[Cu(Sn)/(Cu (Sn)/Nb₃Sn] of the third variant (c) after annealing: 600°C for 265 h. The profile passed through the middle layer of Cu(Sn)/Nb₃Sn

A tape of a submitted variant rolled of the package, assembled in the 3-rd cycle of three packs of 0.4 mm thick, consisting of four foils after a 2-nd cycle of 0.1 mm thick, and two bronze plates of 1.1 mm thick (see Fig. 21). After rolling the tape with Cu-coating ~of 16.5 μm thick contained 5580 Nb-layers with an estimated thickness of 8.7 nm, and two layers of bronze with thickness of 91.7 μm. The ratio $t_{Nb}N_{Nb}/t_{CuSn}N_{CuSn} = 0.265$ (see Table 5).

3.6.3. Superconducting characteristics of the optimized composite tape based on the Nb₃Sn-compound of new design

Measurements of the critical current I_c and the second critical magnetic field H_{c2} as well as in the case of tapes with alloys of Nb-Ti, carried out in parallel and perpendicular orientations of the rolling plane relative to the direction of the magnetic field, which is produced by a superconducting solenoid. The critical current density was calculated on the entire cross-sectional area of tapes (so-called constructive critical current density) $(j_c)_\Sigma$ and the cross-sectional area, which occupied the interlayer of Cu/Nb, $(j_c)_{Cu/Nb}$.

The results of measurements of I_c for the tapes of all three variants are presented in Table 6 for annealing at two regimes. And as an example for a composite manufactured by a third variant, in Fig. 25 the experimental dependence of $(j_c)_\Sigma$ and $(j_c)_{Cu/Nb}$ for the two orientations of the rolling plane of the tape and the magnetic field were showed.

The critical current density j_c in the composites after the long 265-hour annealing at 600°C is significantly higher than after annealing at 700°C for 5 h. If the second case at the parallel and perpendicular orientations of the rolling plane of the composite and the magnetic field maximum out of a reached (j_c)_{Cu/Nb} did not exceed, respectively, $2.73 \cdot 10^4$ and $1.93 \cdot 10^4$ A/cm² in a field of 7 T, then after the long and the low-temperature annealing of its value reached $7.65 \cdot 10^4$ and $8.31 \cdot 10^4$ A/cm² in the fields of 7 T (see Table 6).

It was expected that, as in the case of multilayered composites with layers of wrought alloys Nb-Ti, the pinning of vortex filaments will occur at the interlayer boundaries of nonsuperconducting copper alloy Cu(Sn) and the superconductor Nb₃Sn. However, in contrast to composites with Nb-Ti alloys, in which the effective pinning of the superconducting vortex filaments occur at the boundaries of Nb-NbTi, and therefore a giant values of anisotropy j_c was observed, in a tape of Nb₃Sn high values of anisotropy were not observed. Moreover, it was < 1 after 265-hour annealing. This indicated that the boundaries of Cu(Sn)-Nb₃Sn in multi-layers of Cu(Sn)/Nb₃Sn were no more effective for pinning of vortex filaments than other structural defects, or are they simply "smeared" in process of the annealing. The high values of j_c obtained in this work after annealing at 600°C are provided by the pinning of the superconducting filaments on the grain boundaries, whose density at low temperatures of formation of Nb₃Sn was very large.

Experimental dependence of $H_{c2}(T)$ (Fig. 26) are linear throughout the measured temperature range, except for a small region in the immediate vicinity of T_c . There was a slight deviation from a straight line towards higher temperatures. The measured temperature of the superconducting transition for $H = 0$ was at 0.05-0.10 K to more than the temperature of intersection of $H_{c2}(T)$ with the horizontal axis.

H_{c2} measured in parallel mutual orientation of the rolling plane relative to the field were 1-1.5 T more than in the perpendicular orientation. This can be seen on different slopes of the lines $H_{c2}(T)$. For multilayered tapes with Nb-Ti alloys, where the such distinction was much more a result we have explained by the increase of H_{c2} with decreasing of layer thickness [10], which occurs only in a parallel orientation of the plane and the field [6]. Apparently, the same mechanism operates in the case of a multilayer tape of Nb₃Sn.

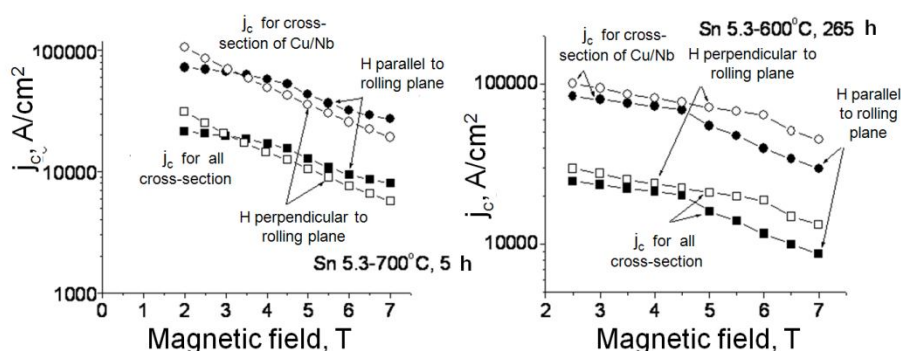


Fig. 25. Dependences of critical current density on the field for the optimized Nb₃Sn-tape of third variant after annealing at 700°C for 5 h and 600°C for 265 h for the two orientations of the rolling plane of tape to the direction of H

Table 6. The critical current density of the optimized Nb₃Sn tape (j_c)_Σ/(j_c)_{Cu/Nb} for the parallel (||) and perpendicular (⊥) orientations of the rolling plane (ab) relative to the magnetic field (H) and the anisotropy $j_{c||}/j_{c⊥}$ in field of 7 T.

Variant	700°C for 5 h			600°C for 265 h		
	ab H	ab⊥H	$j_{c }/j_{c⊥}$	ab H	ab⊥H	$j_{c }/j_{c⊥}$
1	6820/23300	3900/13300	1.75	-	-	-
1	-	-	-	13560/46104	-	-
1	-	-	-	-	11196/38066	-
1 ¹	-	-	-	22510/76534	24457/83154	0.92
1 ¹	3580/12200	1970/6700	1.82	15600/53200 ²	16500/56300 ²	0.95 ²
1 ¹	-	-	-	-	10900/37200	-
2	1170/3960	500/1700	2.33	11700/39700	13000/44100	0.90
3	8020/27300	5670/19300	1.41	8690/29600	13200/45000	0.66

¹The tape was obtained from a composite, at making which plates, recruited from foils of Cu/Nb after a 2-nd cycle, were not subjected to diffusion bonding. ²Date are in the field of 6.5 T.

The values of $H_{c2}(4.2\text{ K})$ for the parallel and perpendicular orientation (ab) relative to H (Table 7) were equal to 19-20 T, which is lower than those known in the literature. The reason was the low values of critical temperatures that are equal in our case 16.16 and 16.32 K. This is significantly less than 18 K for stoichiometric Nb₃Sn. However, this fact is common for compound Nb₃Sn, obtained by the "bronze technology."

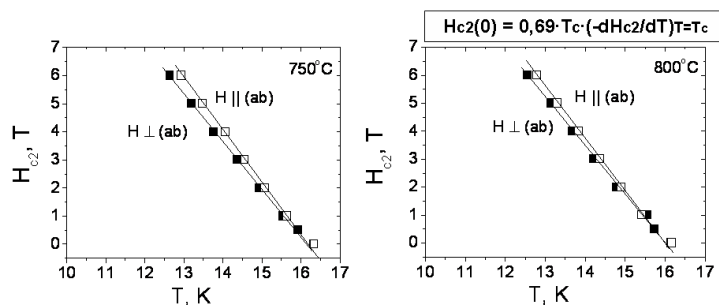


Fig. 26. Dependences of the second critical magnetic field on temperature near T_c for Nb₃Sn multilayer tapes after annealing at 750°C for 3 h and 800°C for 3 h for the two orientations of the rolling plane of the tape relative to the direction of H

Table 7. The results of measurements of the second critical magnetic field

Annealing regime and T_c	750°C for 3 h; 16.32 K		800°C for 3 h; 16.16 K	
Orientation	H (ab)	H ⊥ (ab)	H (ab)	H ⊥ (ab)
$(-dH_{c2}/dT)_{T=T_c}, \text{ T/K}$	1.88	1.71	1.91	1.78
$H_{c2}(0), \text{ T}$	20.9	19.9	21.0	19.6
$H_{c2}(4.2\text{ K}), \text{ T}$	19.1	18.1	20.0	18.6

3.7. Conclusions

1. Through the package rolling multilayer composite tape, consisting of interlayers of 12% of the tin bronze and nanostructure interlayers of Cu/Nb, containing Cu- and Nb-layers of nanometer thickness was manufactured. During annealing as a result of interdiffusion of niobium and tin composite was converted into a multilayered tape on base of superconducting compound of Nb₃Sn.
2. At the optimum volume ratio of composite components niobium and tin most fully converted into Nb₃Sn. For this attitude of $t_{Nb} \cdot N_{Nb} / t_{CuSn} \cdot N_{CuSn}$, where t and N are respectively the thickness and number of layers of niobium and bronze in the composite, must be equal to 0.288. However, in the composite of an optimal design the increasing of volume fraction of the bronze to the content of Cu/Nb-interlayers caused ruptures of the latter, which resulted in complete degradation of the superconducting critical current in the tape.
3. Given the experience of previous experiments, the technology for obtaining of three variants of the multilayer composite tape of Cu[Cu12Sn/(Cu/Nb)] as a precursor for a superconducting tape of Nb₃Sn, in which the nanostructure Cu/Nb-interlayers remain cohesive at all stages of rolling deformation was developed.
4. By scanning electron microscopy and X-ray analysis the microstructure of cross-section of the composite tape before and after annealing, depending on the volume ratio of composite constituents and the microstructure of itself Cu/Nb-interlayer as a function of annealing temperature were studied.
5. The high values of the critical current density were obtained after annealing at 600°C for 265 h. It reached $\sim 8.3 \cdot 10^4$ A/cm² in an external magnetic field 7 T calculated on the section occupied by interlayers of Cu(Sn)/Nb₃Sn. But in contrast to superconducting nanostructure tapes with Nb-Ti alloys, the anisotropy of the critical current density $j_{c\parallel}/j_{c\perp}$ was small or even smaller unit. This indicated that the interlayer boundaries of Cu(Sn)-Nb₃Sn in multi-layers of Cu(Sn)/Nb₃Sn were no more effective for pinning of vortex filaments what the other structural defects such as grain boundaries. The second critical magnetic field at 4.2 K reached 20 T (annealing at 800°C), the critical temperature – 16.2-16.3 K.

4. BEHAVIOR OF HARDNESS AND STRENGTH OF MULTILAYER COMPOSITES AT DEFORMATION BY ROLLING

Expression, reflecting the dependence of the mechanical characteristics of the material on its structure, is well-known Hall-Petch relation that relates the flow stress σ_t and grain size: $\sigma_t = \sigma_0 + K \cdot (1/\sqrt{d})$. Classical mechanism that explains it, is based on the occurrence of stress in the head of dislocation pileup at the grain boundary, which should initiate a slip in neighboring grains. Hall-Petch relation holds too in the deformed state, if in the structure of the metal present the effective lengthen obstacles to motion of dislocations, for example, the boundaries of a dislocation cells or sub grains [11]. Condition for this is consistency of coefficient K, i. e., the effectiveness of the obstacles to dislocations slip should not be changed. If the boundaries of grains, cells or sub grains are still in the process of testing the only or even the main obstacles to the dislocations, then the expression of the Hall-Petch relationship is applicable to the ultimate strength and hardness of the metal. Such is the case in bulk metals and alloys.

In [12, 13] for multilayer composites of Cu/Nb and Cu/Nb/Nb50Ti (see Table 1, variant 5) has been shown that a change in their hardness HV in the process of the rolling at room temperature is associated with decreasing in the interval from 500 to 5 nm thickness of layers t the same Hall-Petch relation. In the case of Cu/Nb/Nb50Ti-composite, comprising alternating layers of niobium and alloy of Nb-50 wt.% Ti, obtained the data were described by the expression $HV [MPa] = 1688 + 2125 t^{-0.5}$ (hereafter t in nm) [13]. For a multilayered composite containing layers of copper and niobium, two

intervals of thicknesses were observed – 100-25 and 25-5 nm, into which the changing of the hardness HV are given by $HV[MPa] = 700 + 9600 \cdot t^{-0.5}$, and $HV[MPa] = 2310 + 1580 \cdot t^{-0.5}$, respectively [12]. Significant result was a reduction of K to 6 times. This meant that alter the effectiveness of the interlayer boundaries of Cu-Nb, as the obstacles for slip of dislocations. Analysis of crystallographic texture in the layers of fcc-copper and bcc-niobium showed that when the thickness of 25 nm in both layers formed texture, in which the plane and slip direction in both layers became almost parallel to each other, and this facilitates the transfer of slip from layer to layer. In the composite of Cu/Nb/Nb50Ti both components have the bcc-lattice, textures in both layers is the same and a situation with the transfer slip is eased for all the layer thicknesses.

4.1. The dependence of the Hall-Petch relationship for a series of nanostructure Cu(Nb/Nb31Ti)-composites, differing in the number of layers

The purpose of the next study was to test the Hall-Petch relationship when the thickness of the layers is not changed in the rolling process of concrete composite, and regulated by a series of five composite Cu(Nb/Nb31Ti)-tapes (see Table 1.) at the final stage of their manufacture due to the changing of a design without the changing of technology.

The results showed that the measured range of thicknesses of layers as the hardness HV such and yield stress $\sigma_{0.1}$ (Fig. 27) can be described by the Hall-Petch relationship. Hall-Petch relation for the hardness can be represented as $HV [GPa] = 1.62 + 2.15 t^{-0.5}$. This expression is a very good agreement with previously obtained dependence for a single composite of Cu/Nb/Nb50Ti [4], when the hardness was measured during the cold rolling in the 3-rd cycle of its production ($\sigma_0 = 1.69$ GPa, and $K = 2.13$ GPa/nm^{-0.5}). For the yield stress $\sigma_{0.1}$, the Hall-Petch relation was as follows: $\sigma_{0.1}[MPa] = 584 + 1032 \times t^{-0.5}$.

4.2. Production of the microstructure composites of Cu/Fe, Cu/Nb, and Nb/Ti

Composite of Cu/Fe was obtained by diffusion welding and rolling package in the 1-st cycle consisting of 23 Cu- and 23 Fe-foils with a thickness of 0.2 mm. In the 2-nd cycle of a package was collected from 46 multilayer foils after 1-st cycle. At this stage, the composite contains more than 2100 layers of copper and iron with the average thickness of about 4 μ m.

From a series of Cu/Nb two composites were investigated in the process of the cold deformation in the 2-nd cycle with the total number of layers of copper and niobium, equal to 960. In the 1-st cycle the original packages were contained 16 Cu- and 15 Nb-foils.

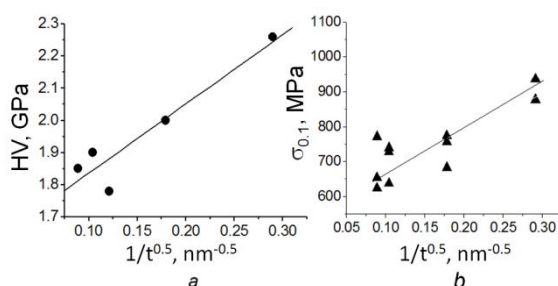


Fig. 27. Dependents of the hardness HV and yield stress $\sigma_{0.1}$ on $t^{-0.5}$ (t – thickness of the Nb- Ti alloy). Change interval of t – from 250 to 10 nm: a – each point corresponds to the average value of hardness of not less than five measurements

Microstructure composite of Nb/Ti was obtained by rolling of a packages composed of 24 Nb-foils with thickness of 0.18 mm and 23 Ti-foil with thickness of 0.15 mm.

Diffusion bonding of the packages was carried out under pressure ~ 20 MPa at temperatures from 800 to 900°C for 40-60 min. Subsequent packages rolling on vacuum rolling mill was carried out with pre-heating to a temperature of 850-900°C and the compression of 25-30% per pass. One or two passes were made.

The surface hardness of the composites was determined by Vickers method under a load of ~ 60 N and measured as a function of layer thickness, decreasing during the deformation by rolling in the 1-st and 2-nd cycles, both immediately after rolling and after annealing at 600°C for 2 h, which was conducted to remove cold work surface (Fig. 28 and 29).

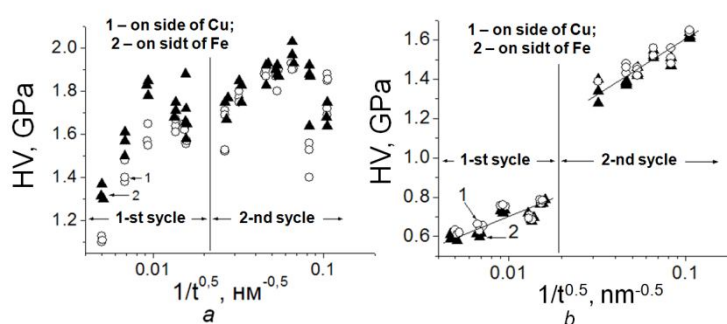


Fig. 28. HV dependence on $t^{-0.5}$ for the composites of Cu/Fe in a state of “after rolling” (a) and “after rolling + annealing” (b) (t – the average thickness of copper and iron layers, the change interval of t – from 40 to 4 μm and from 1.4 μm to 90 nm in 1-st and 2-nd cycles, respectively)

The design of the Cu/Fe-composite was such that on one side of the surface is a layer of copper, on the other – a layer of iron. Therefore, the hardness was measured in two sides. Immediately after the rolling the hardness of the iron was greater than that of the copper (see Fig. 28a). After annealing, the hardness's of the two surfaces becomes identical.

Give attention to the fact that all the dependence of $HV(t^{-0.5})$ for the microstructure composites directly after the rolling had a maximum. At the final stage of rolling the hardness, reaching a maximum, then drops a bit and the dependence, typical Hall-Petch relationship is not fulfilled. The latter is likely due to the fact that measurements take into account also and hardness induced a hardening. Hall-Petch relationship holds only after rolling and annealing.

When the thickness of the Nb-layer equaled to ~ 11 μm (see Fig. 29b), the dependence of $HV(t^{-0.5})$ changes a slope. This could be expected, since at room temperature niobium and titanium have different crystal lattices.

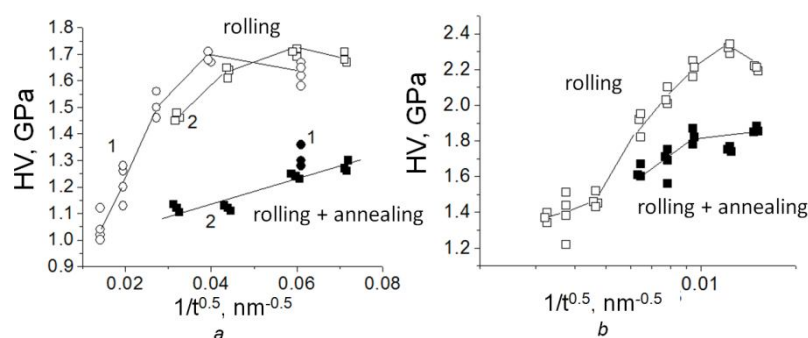


Fig. 29. HV-dependence on $t^{-0.5}$ for the composites of Cu/Nb (a) and Nb/Ti (b) in a state "after rolling" and "after rolling + annealing" (t – the average thickness of copper and iron layers). The change interval of t : a – from 5000 to 270 nm and from ~1000 to 200 nm for the composites of 1 and 2, respectively; b – from 93 to 45 μm

4.3. One component composite of Ti/Ti

Microstructure titanium composite was obtained by rolling a multilayered package consisted in 120 titanium foils of 50 μm thick.

The hardness of the composite was measured in the rolling process (Fig. 30). In the range of thicknesses of the individual Ti-layer from 16 to 2.2 μm the changing of HV satisfy to the Hall-Petch relationship. The hardness values were high. At the maximum degree of deformation, it reached the value of 3.4 GPa, while sufficient ductility of the composite was maintained.

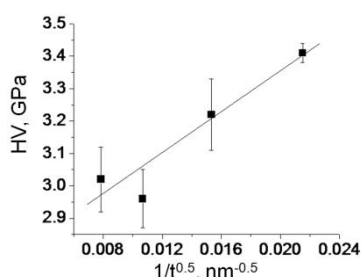


Fig. 30. Dependence of the hardness of the multilayer microstructure composite with titanium as a function of $t^{-0.5}$ (t – thickness of one Ti-layer)

4.4. Conclusions

1. It is shown that for multilayer nanostructure composite tapes of Cu(Nb/Nb31Ti) HV hardness and flow stress for small values of residual deformation during tensile tests (yield $\sigma_{0.1}$) in the range of thicknesses of Nb-layers and layers of NbTi-alloy from ~140 to 5 nm were described by the Hall-Petch relationship in which instead of the grain size was used the layer thickness t . The resulting Hall-Petch relationship for the hardness is in good agreement with previous results for a single composite of Cu/Nb/Nb50Ti, when the hardness was measured as far as rolling of it.

2. Dependences of the hardness on the $t^{-0.5}$ for microstructure composites of Cu/Nb, Cu/Fe and Nb/Ti were obeyed Hall-Petch relationship only after the annealing, which undertaken after the rolling at

room temperature and served to relieve hardening of the surface. All depends $HV(t^{-0.5})$ for these composite tapes immediately after rolling had a maximum.

3. Microstructure composite consisting of 120 layers of titanium with thickness of about 2 μm had a high hardness, equal to 3.4 GPa, while maintaining of sufficient flexibility.

5. MICROSTRUCTURE COMPOSITES OBTAINED BY DIFFUSION WELDING UNDER PRESSURE

5.1. Composites of Ni/Al

Compound of Ni_3Al is the main strengthening phase of a high-temperature Ni-alloys, which are used for the manufacture of parts and units, working in conditions of high temperatures and power loads. The disadvantage of Ni_3Al -based alloys is their low the melting temperature, $\sim 1400^\circ\text{C}$, which limits the temperature ceiling of their practical application. Meanwhile, there is a need to improve the working temperatures of power plants, in particular, aircraft engines, both to improve their efficiency and to reduce the environmental loads [14]. This initiated the development of high-temperature alloys based on NiAl, as a higher melting point and light, as Ni_3Al , and not in need of protection from oxidation [15].

The purpose of this study – to produce a NiAl by diffusion in a multilayered composite of Ni/Al, originally made from a package of alternating Ni- and Al-foils.

Flat composite of Ni/Al obtained by diffusion bonding of multilayer packages under pressure of 15-20 MPa for 1 h at temperatures below the melting point of aluminum, resulting in their partial sintering was occurred. Packages with outer Ni-foils were assembled from 12-20 Ni- and correspondingly 11-19 Al-foils. The thickness of the nickel foil was typically 100 μm , the thickness of aluminum foil could be varied from 10 to 150 μm . Already, even after diffusion bonding at the interface between the layers of nickel and aluminum the interlayers of $\sim 2 \mu\text{m}$ thick were formed, which were identified as NiAl_3 – the aluminum-rich intermetallic compounds. Intermetallic compounds of practical interest, formed during the subsequent heat treatment of composites under pressure as a result of an interdiffusion between the nickel and aluminum.

Table 8. Effect of heat treatment temperature on the microstructure of the diffusion zone of the composite of Ni/Al with the ratio of Ni:Al ≈ 2

Temperature, $^\circ\text{C}$	Composition of the diffusion zone
~ 600 (<1 h)	Al; NiAl_3 (2 layers of $\sim 2 \mu\text{m}$); Ni
800/1 h	Ni_2Al_3 ($\sim 25 \mu\text{m}$); NiAl (2 layers of 4-5 μm); Ni_3Al (2 layers of $\sim 3 \mu\text{m}$); Ni
950/5 h	NiAl (36-37 μm); Ni_5Al_3 (2 layers of $\sim 17 \mu\text{m}$); Ni_3Al (2 layers of $\sim 3 \mu\text{m}$); Ni
1000/1 h	NiAl ($\sim 35 \mu\text{m}$); Ni_5Al_3 (2 layers of $\sim 15 \mu\text{m}$); Ni_3Al (2 layers of 2-3 μm); Ni μm
1100/30 min	Ni_5Al_3 (balances); layers of Ni_3Al , interspersed with layers of Ni(Al) – a solid solution of Al in Ni

Effect of final temperature of the heat treatment on the composition of the diffusion zone in composites with a volume ratio (the "ratio") of nickel and aluminum Ni:Al, equal to 2, is presented in Table. 8. This ratio is consistent with the fact that in the final stages of the diffusion process of Ni and Al, exhausted, compound Ni_3Al were formed.

Based on the table, you can draw the following conclusions. (1) Aluminum is completely "consumed" for the formation of intermetallic compounds already at a temperature of 800°C , and at the same temperature begins to form compounds of NiAl and Ni_3Al . (2) As the temperature increases the thickness of NiAl -layer at the same exposure increased from 4-5 at 800°C to $\sim 35\ \mu\text{m}$ at 1000°C and the thickness of the layers once formed Ni_3Al -compound has not changed and equal to 2-3 μm . (3) Layers of pure nickel were observed up to 1000°C . (4) Only at 1100°C among all the intermetallics only compound Ni_3Al was remained. The heat treatment at relatively high pressure of $\sim 830\ \text{MPa}$ for 30 min was resulted in the formation of the layered structure of alternating layers of Ni_3Al and solid solution based on nickel, containing up to 15 at.%Al. Within the layers of Ni_3Al the remains of phase Ni_5Al_3 were found, which for some time could be a source of alumina for the formation of Ni_3Al .

Composite with the ratio of Ni:Al = 0.67. In the diffusion zone of a composite consisting of Ni- and Al-foils with a thicknesses of 100 and 150 μm respectively after heat treatment at 1100°C the same set of intermetallics are contained as in a composite with the ratio of Ni:Al = 2 after the heat treatment at $950\text{-}1000^\circ\text{C}$ (see Table 8) except that instead of pure nickel solid solution based on nickel, Ni(Al) , was formed, containing 13-14 at.%Al. Upon a completion of the diffusion process – 1300°C for 1 h (Fig. 31) – composite was turned into the laminate that entirely consists of NiAl -layers of $\sim 110\ \mu\text{m}$ thick. On the figure the boundary between the layers is marked of "lines" of small pores. Chemical etching revealed a fairly fine-grained structure of the compound (see box). According to X-ray analysis of aluminum contained in $\beta(\text{NiAl})$ -phase of 39-40 at.% (see Fig. 31b). This was combined with the diagram of Ni-Al [16], according to which the compound of NiAl at 1300°C has a wide homogeneity range, and the resulting composition is located within it. X-ray analysis confirmed the existence of a $\beta(\text{NiAl})$ -phase with a fct-lattice.

Composite of Ni/Al with the ratio of Ni:Al = 6 after heat treatment at 1300°C was converted into a solid solution of aluminum in nickel, with a gradually decaying change of composition in the direction on the surface to the section middle of the sample (Fig. 32).

Conclusion. The results showed that Ni and Al can easily engage in the diffusion interaction with the formation of all compounds known in the Ni-Al system. At the initial stage, regardless of the volume ratio of components, the formation and the disappearance of the compounds depending on the temperature obeys the laws of the reactive diffusion and occurred in a sequence from the compound with the maximum aluminum content (NiAl_3) to the compound with the minimum of its content (Ni_3Al). But the end result of diffusion of Ni and Al depend on the ratio of Ni:Al. Under the same heat-treatment regimes in a composite with the ratio of Ni:Al = 0.67 diffusion process ended on $\beta(\text{NiAl})$ -phase, while the composite with the ratio of Ni:Al = 6 – a solid solution of Al in the nickel Ni(Al) .

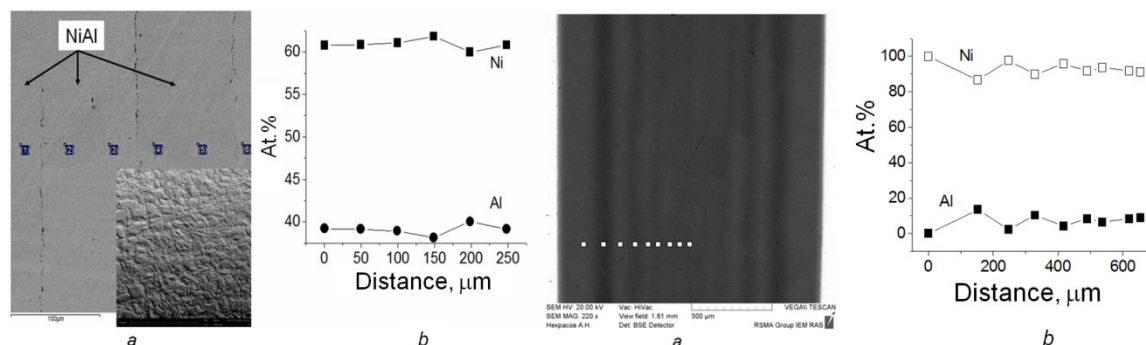


Fig. 31. Microstructure (a) and concentration profiles of Ni and Al (b) for the Ni/Al-composite with the ratio of Ni:Al = 0.67 after diffusion bonding at 460°C, for 1 h, and 14.8 MPa and heat treatment at 600°C for 2 h + 1300°C for 1 h under the pressure of ~ 20 MPa: a - the inset shows the microstructure after a chemical etching when the shooting in secondary electrons

Fig. 32. Microstructure (a) and concentration profiles of nickel and aluminum (b) for the Ni/Al-composite with the ratio of Ni:Al = 6 after diffusion bonding at 500°C for 1 h and 16.7 MPa and subsequent heat treatment at 600°C for 2 h + 1300°C for 1 h under the pressure of ~ 20 MPa: a - bright dots indicate the locations analysis

5.2. Composites of Ti/Ni

Ti-Ni alloys attract attention with its multifunctional capabilities. The high-strength and wrought Ti-Ni alloy with the martensitic transformation and associated with it the shape memory effect are designed and well-studied. Along with the traditional methods of obtaining alloys (alloying, thermal and mechanical treatment), the rapid quenching from the melt and the explosion welding, in recent times for the alloys based on TiNi have been used methods of severe plastic deformation. For most materials with sub microcrystalline and nanocrystalline structures, the high yield stress and strength are combined, as usual, with a low ductility at room temperature. However, metastable alloys of Ti-Ni, on the contrary, are acquired an unusually high deformation capability with large values of the reduction of area and the uniform elongation in tension [17]

Interest in the Ti-Ni alloys is partly explained by the fact that there are new types of a receiving and a processing of materials that their authors are trying to test at facilities already proven its prospect. Such methods include the multiple rolling of multilayer packages, combined with heat treatment.

Producing a multilayered tape of Ti/Ni. The package was about 10 Ti- and 11 Ni-foils with thickness of 0.32 and 0.19 mm, respectively. Ratio of t_{Ti}/t_{Ni} was ~1.6. This corresponded to the equiatomic alloy composition. The package was subjected to welding under a pressure ~21 MPa at 850°C for ~20 min and rolling in a vacuum for two passes with heating to 950°C and the compression of 35%. Welded blank rolled into a tape with the thickness of 0.2 mm at room temperature without intermediate annealing. The thicknesses of the layers of Ti and Ni in the film were ~120 and ~80 μm respectively.

After rolling TiNi-tape were annealed in the range from 500 to 800°C for 2 h to remove the surface cold working and a verification of the compatibility of components. The hardness decreased from 2.65-3.00 (immediately after the rolling) to ~2 GPa after annealing at 500°C (Fig. 33). However, with increasing of temperature it is increased and at 800°C becomes equal to 2.3-2.7 GPa

Effect of an annealing temperature on the microstructure of the composite. Already as a result of the short heating during the diffusion welding and the rolling in a vacuum at the boundary of Ti- and Ni-layers the formation of products of reactive diffusion was indicated. Total change in the structure of the composite was caused by heat treatment at 800°C (Fig. 34a). In its structure present layers of

intermetallic compounds of TiNi_3 (25.6-26.3 at.%Ti), TiNi (51.2-51.8 at.%Ti) and Ti_2Ni (67.3-67.4 at.%Ti) and β -solid solution of Ni in the Ti (~97.7 at.%Ti).

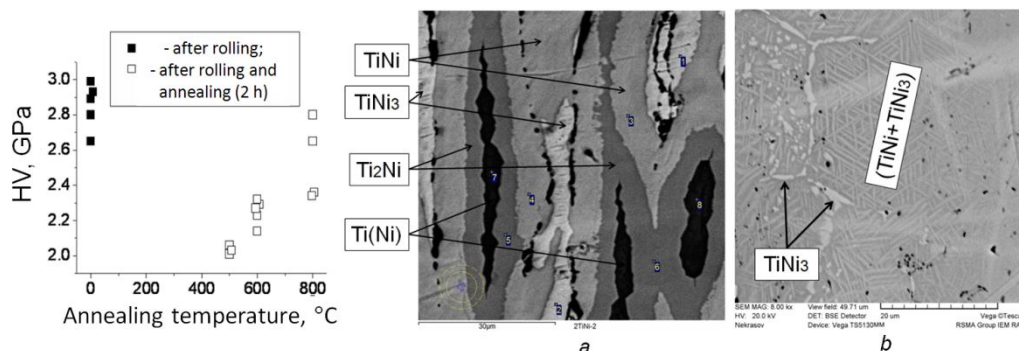


Fig. 33. HV dependence of composite on annealing temperature

Fig. 34. The microstructure of the composite TiNi -tape after rolling and annealing at 800°C (a) and after heat treatment at 1000°C in the pressure ~ 25 MPa (b)

A different structure was observed after heat treatment: 600°C for 1 h + 1000°C for 1 h under pressure (Fig. 34b). According to X-ray analysis and taking into account the phase diagram of Ti-Ni the main structural component is an eutectic of intermetallic TiNi and TiNi_3 (needle separation), and the selection of the second phase – the intermetallic TiNi_3 .

Conclusion. Titanium and nickel had a high reactivity with respect to each other. At 800°C due to the reactive diffusion they form three intermetallic compounds and solid solution of Ni in Ti. A heat treatment at 1000°C caused the formation of alloy with a homogeneous eutectic structure and secretions TiNi_3 .

REFERENCES

1. Karpov M.I., Vnukov V.I., Volkov K.G., Medved N.V., Chodos I.I., Abrosimova G.E. Capabilities of the method of vacuum rolling as a method for producing of multilayered composites with nanometer-scale thicknesses. *Materialovedenie*, 2004; № 1: 48-53.
2. Karpov M.I., Vnukov V.I., Korzhov V.P., Zheltyakova I.S., Kolobov Y.R. Method of manufacturing of multilayer nanostructure composite tape on base of the superconducting alloy of niobium-titanium. Patent RF № 2367043, priority 21.08.2008, registered 10.09.2009.
3. Adams D.P., Vill M., Bilello J., Yalisove S.M. Controlling strength and toughness of multiplayer films. *J. Appl. Phys.*, 1993; 17, N 2: 1015-21.
4. Karpov M.I., Korzhov V.P., Vnukov V.I., Volkov K.G., Medved N.V. The superconducting critical current in the nanocomposite of Cu/Nb. *Materialovedenie*, 2005; № 1: 43-7.
5. Bubnov I.V., Kopylov A.D., Korzhov V.P., Korzhova G.M., Marchenko V.A. The critical current of the multilayered tapes from the compound of Nb_3Al . *Metallophysics*, 1981; 3, № 1: 52-6.
6. Schmidt V. Introduction to the physics of superconductivity. Moscow: Nauka, 1982, 240 pp.

7. Baranov I.A., Bychkov Y.F., Korzhov V. P., Maltsev V.A., Slavgorodskii M.P., Shmulevich R.S. The influence of rhodium on the superconducting properties of zirconium and its alloys. *Sat: Superconducting alloys and compounds*. Moscow: Nauka, 1972, 140-7.
8. Karpov M.I., Vnukov V.I., Korzhov V.P., Zheltyakova I.S., Kolobov Y.R. Laminated tape nanostructure composite based on a superconducting niobium-titanium alloy. Patent RF № 2367042, priority 21.08.2008, registered 10.09.2009.
9. Hake R.R. Upper-critical-field limits for bulk type II superconductors. *Appl. Phys. Lett.*, 1967; 10, N 6: 189-92.
10. Korzhov V.P., Karpov M.I., Zverev V.N., Nikulov A.V. Degradation of the second critical magnetic field in multilayer composites with nanoscale layers of superconducting alloy of niobium and Nb-Ti. *Izvestiya of Russian Academy of Sciences. Series of physical*, 2010, 1974, № 11: 1570-5.
11. Trefilov V.I., Milman Y.V., Firstov S.A. Physical basis of the strength of refractory metals. Kiev: Nukova Dumka, 1975, 315.
12. Karpov M.I., Vnukov V.I., Gnesin B.A., Abrosimova G.A., Frolova L.A., Terekhova I.S., Korzhov V.P., Chodos I.I. Features of plastic deformation of laminated composite of Cu-Nb during rolling. *Deformation and Fracture of Materials*, 2007; № 11: 2-6.
13. Karpov M.I., Korzhov V.P., Vnukov V.I., Terekhova I.S., Abrosimova G.E., Chodos I.I. The structure and hardening at the rolling of nanostructure multilayer composite of Nb-NbTi. *Deformation and Fracture of Materials*, 2008; № 6: 18-21.
14. Mileiko S.T. The future of composites and kompozitovedeniya. *Science – Production*, 2007; № 2 (95): 10-24.
15. Povarova K.B., Skachkov O.A., Drozdov A.A., Morozov A.I. Especially light heat-resistant nanostructure powdered NiAl-Y₂O₃. Third All-Russian conference on nanomaterials. NANO-2009. 20-24 April 2009, Yekaterinburg. Abstracts. Ekaterinburg: Ural Publishing, 2009; 221-3.
16. ASM International Binary Alloy. The Materials Information Society. Massalski.
17. Pushin V.G., Lotkov A.I., Kolobov Y.R., Valiev R.Z., Dudarev E.F., Kuranova N.N., Dupin A.P., Gunderov D.V., Bakach G.P. On the nature of the anomalously high plasticity of high-strength alloys with a nickel-titanium shape memory effect. The initial structure and mechanical properties. *The Physics of Metals and Metallography*, 2008, 106, № 5: 537-47.