Chapter 6

The Superconducting Tape of Nb_3Al Compound

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Additional information is available at the end of the chapter

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Abstract

Annotation. Compound Nb_3Al with critical temperature $T_c \approx 18.5$ K has the upper critical magnetic field H_{c2} of 30 *T*, which is significantly higher than that of the well-known Nb_3Sn. Besides, aluminum is lighter and cheaper than tin and is widely abundant in nature. With such properties, Nb_3Al is a good alternative to Nb_3Sn. The next chapter proposed steps for the development of manufacturing technology of superconductor Nb_3Al tapes from its approbation on a three-layer composite Nb/Al/Nb tape to obtain experienced semi-finished pieces of multilayer Nb_3Al-tape with length of about 100 *m*. This is despite the fact that in order to achieve the above values, T_c and H_{c2} needed exposure for 1–2 seconds at a temperature of 1850°C.

Laboratory technology allowed the investigation of such unknown during the time of obtaining the compound Nb_3Al as: a joint deformation of niobium and aluminum; reactive diffusion in semi-infinite pair niobium/aluminum; the dependence of the superconducting parameters from regimes of high-temperature heating and low-temperature annealing; fastening of superconducting vortices at the grain boundaries of compound Nb_3AlGe. Usage of duralumin (alloy Al–Cu) in a multilayer tape, instead of pure aluminum, has caused the need to investigate the effect of copper on superconductivity Nb_3Al. Its positive impact at that time was quite not obvious.

Keywords: superconductivity, type Cr_3Si structure, Nb_3Al and $Nb_3Al_{0.8}Ge_{0.2}$ compounds, the critical temperature, the critical current density, the critical current, the upper critical magnetic field, pinning, the superconducting tape, reactive diffusion, package rolling, extrusion

1. Introduction

Immediately after the discovery by Kamerlingh Onnes of superconductivity in 1911, work began on the practical use of this phenomenon in order to obtain large constant magnetic fields. However, the concrete development of superconducting materials, with the assurance that such goal is really achievable, began only after 1961, when Kunzler discovered that the compound Nb_3Sn has high critical currents in magnetic fields of the order of 7 Tesla. Since then, they started a new department of science of solids – «Metal science of superconductors», dedicated to the development of new hard superconducting materials and technologies for their production and processing. In about the same year, intensive researches of the deformable alloys Nb–Ti with continuous solubility in the liquid and solid states began as subjects of superconductivity. It turned out that at a content 40–50 at. %Ti alloy with a critical temperature ~9.5 K had the second critical magnetic field of 15 T at 4.2 K.

In the early 1970s, the class of intermetallic compounds with a structure of the A15 was distinguished, except for Nb_3Sn, including Nb_3Al, $Nb_3Al_{0.8}Ge_{0.2}$ and others, having a temperature of superconducting transition T_c up to 20 K and able to withstand magnetic fields up to 20 T and more. From the day of the discovery of superconductivity in mercury at $T_c = 4.25$ K, maximum critical temperature was adjusted to 23 K only in 1973, when almost simultaneously J.R. Gavaler and Yu.F. Bychkov with employees discovered superconductivity in thin films Nb_3Ge. This level was kept in the next 13 years – until the discovery of high temperature superconductivity.

Of course, in the near future, high-temperature superconductivity will come into modern life in a much larger scale than the low-temperature superconductors. But, most likely, they will always find a worthy place for themselves to use. Direct evidence are the international mega-projects such as «The Large Hadron Collider» and «Experimental Thermonuclear Reactor» (International Thermonuclear Experimental Reactor – ITER), in magnetic systems, which were designed low-temperature superconducting materials. The magnetic system of the modern MR-tomographs is also made of superconducting cable of an alloy Nb–Ti and owing to the reliability exceeding all conceivable standards without foreseen replacement.

Therefore, the main purpose of this chapter is to remind the scientific community, engaged in superconductivity, to look at the materials science of low-temperature superconductors with the new positions, using modern possibilities for their research.

2. About Nb_3Al and $Nb_3(AlGe)$ compounds

Superconducting intermetallic Nb_3Al compound belongs to the class of compounds with a structure of Cr_3Si type (A15 lattice). In initial studies, its critical temperature T_c depending on the composition was changed in the range from 15.2 to 17.6 K, but in recent studies [1] was brought to the 18.4–18.9 K. Interest in Nb_3Al was designated because its upper critical magnetic field H_{c2} has a higher value than Nb_3Sn and V_3Ga compounds. Values of H_{c2} at 4.2 K, measured by pulse method, reached 29.5–32.0 T [2, 3], at 12 K $H_{c2} = 13$ T [1].

The temperature of the superconducting transition T_c of compounds of A15 type is maximal at their stoichiometric compositions, and during the preparation, there are important factors to consider like the stoichiometric composition of compound whether it is located in its region of existence at room temperature or not. For example, the compound Nb_3Sn has maintained its stoichiometric composition from the temperature of its formation, which is about 2100°C, to the room temperature. Therefore, to get it with 25 at. % of tin, it is not necessary to use a temperature close to 2000°C (**Figure 1*a***). The compound Nb_3Sn with maximum critical temperature is readily formed at temperatures of about 800°C.

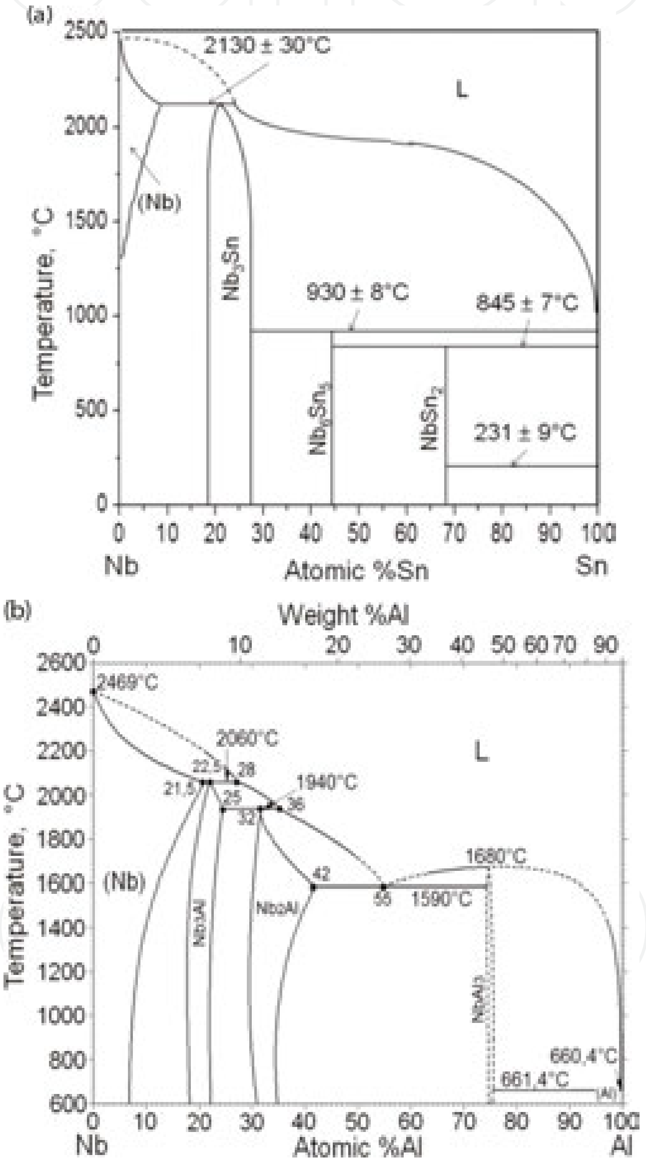


Figure 1. (*a*) State diagrams of Nb–Sn and (*b*) Nb–Al systems [4].

Compound Nb_3Al is another case. According to the state diagram, Nb–Al [5] (**Figure 1*b***) Nb_3Al with 25 at. % aluminum exists at temperatures above 1870–1940°C. Consequently, to obtain Nb_3Al with composition close to the stoichiometric composition and with high $T_c \sim 18.5$ K, it needs to use ~1850°C and higher temperatures. Therefore, with such value, the critical temperature has been obtained for him not immediately, and in later works.

In early 70s, when we began our researches, there were only a few works on the study of mutual diffusion of niobium and aluminum. Moreover, published works were devoted mainly to questions of formation of compounds $NbAl_3$ and Nb_2Al [6, 7]. Only in [7] at 1400°C with a 16-hour annealing in the diffusion layer the presence of interlayers of compound Nb_3Al was observed with 2 microns thick. The most complete data on Nb_3Al formation was given in [8], the authors who carried out a study of the interaction of niobium and aluminum to a temperature of 1550°C. The result of this work had a different slope of the linear dependencies of coefficients of mutual diffusion D dated the inverse value of the absolute temperature 1/T during the formation of compounds $NbAl_3$, Nb_2Al and Nb_3Al. In this case, the slope of the direct line D(1/T) was the greatest for Nb_3Al, however, with up to 1500°C, it was lower than the corresponding direct lines for $NbAl_3$ and Nb_2Al. If all the direct to extrapolate D(1/T) in the region are of higher temperatures, they cross in the range 1850–1900°C, i.e. the formation of compound Nb_3Al became predominant at higher temperatures (**Figure 2**). Subsequently, this was confirmed by our researches.

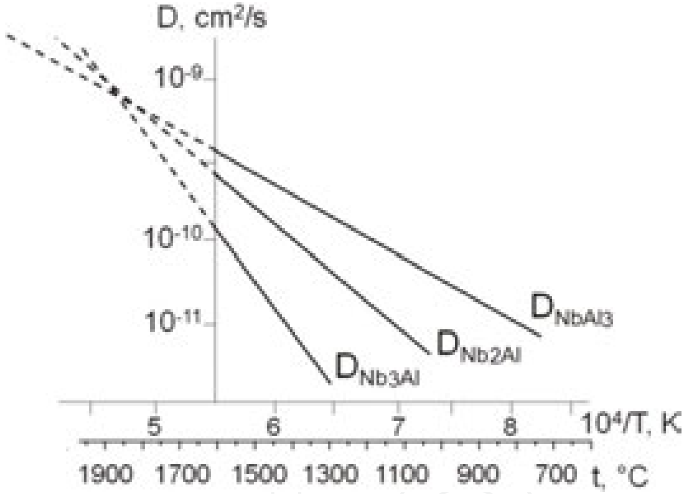


Figure 2. The coefficients of mutual diffusion for compounds $NbAl_3$, Nb_2Al and Nb_3Al depending on the inverse of the absolute temperature.

Consideration of compound Nb_3Al often occurs together with another compound in which a portion of the aluminum atoms is substituted with germanium – $Nb_3Al_{0.8}Ge_{0.2}$. It was discussed in 1967 by B.T. Matthias with colleagues. At that time, it had a record of critical temperature – 20.05 K and the upper critical magnetic field H_{c2} – 42 *T* at 4.2 K and 20 *T* at 14 K. The practical application of this material in the case of the development of manufacturing technology of wire or ribbon was to prove that it is more effective than the use of Nb_3Sn or V_3Ga especially with regard to the possibility to use it for cooling liquid hydrogen instead of helium.

The main disadvantage of intermetallic compounds is their natural brittleness. This is the reason why, in the case of application of the compound for the solenoid coils and magnets, it is prepared by methods that result in the intermetallic compound formed as a thin metal layer on a flexible substrate or inside the conductor. In this state, it retains its ability to deform while bending without destruction.

3. The joint rolling how laboratory technology for production of superconducting tapes on the basis of A15 connections

All the superconducting materials out of the A15 type compounds obtained by heat treatment in a tape or wire of thin section, one way or another can be attributed to the conductors of the composite type. Methods for the preparation of the composite, as we have seen, is very different: deformation of tube with the core out of components of the compound in the form of powder or of the compound (method Kunzler or "powder-in-tube"); coating of tape or wire out of niobium or vanadium with fusible component by passing them through a bath of molten tin or gallium (diffusion method from a liquid phase); niobium tape coated fusible component by spraying it in a vacuum (diffusion method from the gaseous phase) or by using gas-transport reactions (recovery with hydrogen of tin chloride); bronze technology and, of course, the method of deformation of dissimilar materials.

Among the laboratory technology of superconducting materials, we developed in the present research through the latter method. As mentioned, the lack of data on the superconducting characteristics in the obtained conductors of this type in the early 70s and the relatively small number currently suggest the specific difficulties are associated with this seemingly simple at first glance technology.

The first – is a great heterogeneity of metals, which is required to deform together. The second and the main difficulty are as follows. Manufacturing technology of bimetallic strip of any compositions must ensure durable bonding of layers. In practice, bimetals, the initial preform for making a flaky composite material, serve in a certain way assembled package is subjected to joint cold rolling. In this stage, lasting cohesion of layers must be achieved over the entire area of contact of joined metals. Only at this condition the process of further rolling is possible by preparing sufficiently long tape of thin section to avoid bundles.

To overcome the abovementioned difficulties on the initial stage of deformation, we used a vacuum rolling of bimetallic packets. With the help of vacuum rolling, we were able to obtain a monolithic planar blank for subsequent rolling at room temperature to the tape of thin-section subjected to a thermal treatment for solid phase formation of superconducting compound. This sequence of operations included the possibility of manufacturing the superconducting tape from almost all A15 compounds with high superconducting characteristics.

To obtain compounds such as V_3Ga, V_3Si, Nb_3Sn and $Nb_3(Al,Ge)$, we used copper alloys with gallium, silicon, tin (bronze) and aluminum alloy with germanium, respectively. However, it is difficult to roll bronze at room temperature. Additionally, their ductility decreases with increasing of gallium content, silicon and tin; also, for solid phase preparation of compounds, it is desirable to have copper alloys enrich with these elements. For ternary intermetallic compound $Nb_3Al_{0.8}Ge_{0.2}$ must have aluminum alloys 40–50 wt. % Ge, which are not deformed by rolling at room temperature without cracking.

Therefore, the joint rolling of bimetallic packets in a vacuum at elevated temperatures in the initial stage was what we needed. Firstly, the temperature was promoted firm adhesion of dissimilar metals. In most cases, when adhesion, or welding, cannot be achieved at room temperature, only the deformation in vacuum makes this possible. Secondly, bronzes and alloy Al–Ge are difficult deformable at room temperature, but when after vacuum rolling they are firmly cohesive in the bimetallic monolithic preforms with plastic metals – niobium and vanadium, we were able to deform this alloys at room temperature without intermediate annealing. The thickness of the bimetallic tape $Nb_3(Al,Ge)$ in the final stage equals 50–70 microns.

3.1. Questions about Joint Plastic Deformation of Metals

Practical achievements of metal welding by joint plastic deformation (rolling, pressing, explosion welding) so far were outstripped theoretical ideas about the nature and the mechanism of adhesion, although there are a number of hypotheses to explain this phenomenon. This question else in the 70s with insufficient detail was illuminated in a number of fundamental works. It should be noted that certain provisions of the proposed hypothesis well explain the phenomena in clutch area of metal strips when the joint deformation by rolling occurs. The essence of these provisions are as follows:

1. Clutch of similar and dissimilar metals in the process of plastic deformation is conditioned by "grasp" phenomenon, which occurs due to the formation of metallic bonds between atoms of adjacent physically clean (juvenile) surfaces when their rapprochement at a distance of action of interatomic forces.

2. The ability of metals to "grasp" is the physical property of juvenile surfaces and depends on their nature.

3. In ideal conditions, the grasping is a beneficial thermodynamic process and should occur spontaneously, as the energy of the system of two connected metal is reduced by the elimination of free surfaces. Under ideal conditions, it should be understood that rapprochement of atomically smooth surfaces free from oxide and adsorbed films, over a distance equal the sum of atoms radii of connected by metal.

4. The joint plastic deformation of metals is one of the ways of obtaining juvenile surfaces, their convergence and increase of the actual area of the clutch.

3.2. Preparation of Packages for a Joint Rolling of Dissimilar Metals in Vacuum

The initial workpiece for the experienced tape samples of superconducting compounds V_3Ga, V_3Si, Nb_3Sn, Nb_3Al and $Nb_3(Al,Ge)$ was served with package assembled from two plates of refractory and one plate of fusible component (**Figure 3*a***). In the case of Nb_3Sn compound, five-layer packages with copper plates from the outside were also collected (**Figure 3*b***).

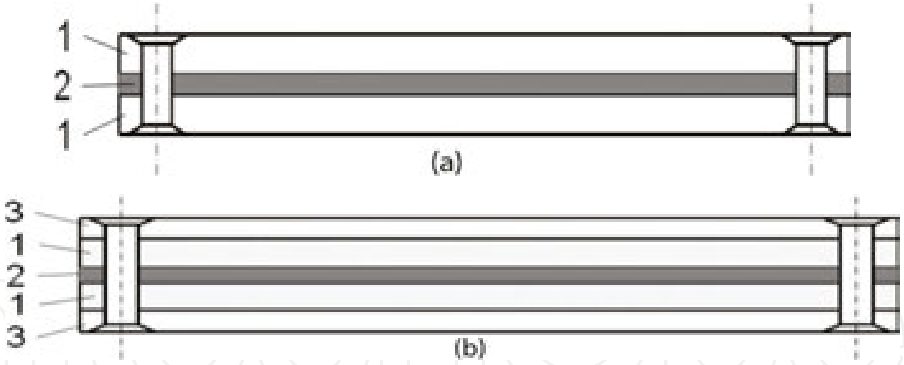


Figure 3. (*a*) Construction of collected packets without copper and a copper-clad; (*b*): 1 – niobium, vanadium, niobium alloys; 2 – aluminum, Al–Ge alloy, bronze; 3 – copper.

Bronze was smelted by the induction method in an argon atmosphere, Al–Ge alloy – by flash smelting. Massive flat copper molds were used for casting. Then, the ingots were rolled at room temperature with intermediate annealing in a vacuum, and, in some cases, with heating in air to 500–600°C.

To ensure grasping and obtaining of reliable clutch between connectable metals from the contact surfaces, oil and fat film were removed, and water vapor and oxides were adsorbed. This was achieved by immediately chemical etching of plates before assembling packages for rolling. The package was assembled from plates of the same width to prevent cracking of the tape edges. The ends of plates fastened conventional rivets (see **Figure 3**). Package size for laboratory tests: width 15–20, length ~70 *mm*.

3.3. Vacuum Rolling of Packages.

The rolling of packages in vacuum efficiently protects the surfaces of the connected metals against oxidation, which was one of the conditions for lasting clutch of dissimilar metals.

In our works, vacuum rolling of packages was made on the rolling mill DUO–170, basic design of which was developed in the Physical-Technical Institute of the National Academy of Sciences of Ukraine. The diameter of the work rolls – 170, length of barrel – 144 *mm*. Clearance between the rolls can be adjusted from 0 to 20 *mm*. The mill – two reverse, has 5 speeds: 8, 16, 22, 34 and 54 *rpm*. Permissible design pressure on the rolls is 30 tons. The pressure of residual gas in the chamber is $\sim 5 \cdot 10^{-5}$ *mm Hg*.

The most problematic object for joint rolling proved to be a pair of niobium/aluminum. This interests the study of the properties of relatively thin layers Nb_3Al since all of its connections by nature are very brittle at room temperature, where in such state, it retained the ability to bend without breaking. Assuming the possible technical use of the Nb_3Al in the future, it is necessary to obtain it in the form of a thin layer within a conductor.

Studies of optimal modes of rolling showed that the volumetric content of aluminum in the package:

- decreased from 9.8 to 0% with an increase of the heating temperature of package before rolling in vacuum of 400 to 700°C (reduction ratio per pass from 22 to 24.4%, the initial thickness of Al-foil – 1 *mm*);
- decreased from 18 to 9% with increasing of degree of reduction per pass from 10 to 22.5% (heating – 500°C; the initial thickness of Al-foil – 1 *mm*);
- increased from 4.7–5.6 to about 13% at an increase of the initial Al-foil thickness of 0.1 to 1 *mm* (heating – 470°C, the reduction ratio per pass 17–25%).

Optimal modes of vacuum rolling: the heating temperature of the package 450–500°C, the degree of reduction per pass of 15–25% and the initial thickness of the Al-foil of 0.5–0.8 *mm* at a thickness of Nb-plate equal 1.5 *mm*.

Selecting of reduction per pass at rolling of packages for compound Nb_3Al became looser after the replacement of pure aluminum on a more durable duralumin brand D16.

Vacuum rolling of packages Nb/(Al–Ge)/Nb to obtain intermetallic compound $Nb_3(Al,Ge)$ was carried out at the temperature range of 390–410°C, which was limited by the melting temperature alloys Al–Ge. Unlike the packages of Nb/Al/Nb, they were allowed rolling with a reduction of 35 to 55% per pass. At this alloy content in packages after the rolling (or in composite tape of final thickness) varied from 4.8 to 10.0 vol. %.

3.4. Cold Welding of Packages Nb/Al/Nb

Apart from welding in vacuum at a temperature above the room temperature experiments by the cold grasping (cold welding) of packages Nb/Al/Nb using a twin-roll mill with 300 *mm* diameter rolls were performed. Reliable welding of packages, after further rolling into a ribbon the exfoliation was not observed, was achieved at a reduction per pass of more than 60%.

It should be noted that the grasping is dependent on the low-melting component. For example, the cold joint rolling of packages, which consisted of plates niobium and SAP-1 (sintered aluminum powder, which is much stronger than pure aluminum) did not give positive results. However, packages Nb/Sn/Nb attempt to obtain the intermetallic compound Nb_3Sn. (Packages of Nb/SAP/Nb grasp was implemented by joint rolling in a vacuum at a temperature of 400°C).

Eventually, we preferred to obtain a three-layer tape Nb/Al/Nb out of packets welded by rolling in vacuum.

3.5. Rolling of Thin Tapes at Room Temperature

The monolithic workpiece after welding with a vacuum rolling mill (or cold welding) was rolled at room temperature to the tape of a thin section. At present stage, it did not attempt to get long pieces of tape. The length of the piece was determined by the original thickness of package and final thickness of the rolled tape (**Table 1**). For example, length of tape Nb/Al/Nb could be from ~4 *m* if the initial thickness of the package and its final thickness were 4 *mm* and 65 *μm*, respectively, until ~11 *m* – at a thickness of the package of 8 *mm* and the final thickness of tape 50 microns.

For further studies, the obtained tape of width 15–20 *mm* was cut by the disk scissor for a few tapes 2 *mm* wide.

Initial thickness of package Nb/Al/Nb, *mm*	**Thickness of tape, *μm***	**Length of tape piece, *m***
4	50	5.5
	65	4.0
8	50	11.0
	65	8.5

Table 1. Geometric parameters of packages and pieces of the three-layer tape Nb/Al/Nb. The length of welded packages is 70 *mm*.

The rolling of packages at room temperature was simultaneously done by estimation of the grasp niobium with aluminum. With rare exceptions, an exfoliation of tape was not observed. This indicated that the joint plastic deformation of the packages in the selected parameter range of rolling provided a strong clutch between metals.

However, the quality of the outer surfaces of the 3-layer composite tape with aluminum depended on its volume content. It was found that up to 8–8.5 vol. % aluminum was not adversely affected. But, at higher content during the process of cold rolling on Nb-surfaces of tape, emerged local discontinuities through which was looked through aluminum. The tape preserved integrity, but after the heat treatment in these places, it broke down because of brittleness. Based on our observations, this was due to high ductility of internal component of the composite. For a more durable alloy Al–45 wt. % Ge such a phenomenon was not observed at 10 vol. % alloy in tape.

3.6. Heat treatment of tapes Nb/Al/Nb and Nb/(Al–Ge)/Nb

To obtain superconducting compounds Nb_3Al and $Nb_3(Al,Ge)$, heat treatment was carried out which resulted in the formation of inside tapes in a thin diffusion layers. It included high-temperature heating (h.-t. h.) and a low-temperature annealing (l.-t. an.).

Strictly speaking, intermetallic compounds were formed in the first stage. During this stage, the optimum temperature of heating was exceeded at 1700–1750°C, and the time was measured by a few seconds. This regime was carried out in a vacuum chamber ($\sim 10^{-5}$ *mm Hg*) by direct passing of electric current through the tape sample attached between two the massive copper contacts. Temperature *t* was monitored by magnitude of an electric current *i* through the sample.

Dependencies *t*(*i*) for the tapes with thickness of 50, 60, 65 and 70 microns were constructed in individual test experiments in which the temperature of the sample was determined by (W–Re)-thermocouple WR 5/20 and was controlled by indications of the pyrometer. Thermocouple junction was joined by spot welding directly to tape. The diameter of thermocouple wire was 0.1 *mm*. In actual experiments, 10 tape samples of the same thickness connected in parallel were placed at once into the camera. The distance between contacts equaled to 100 *mm*. After heating the edge of the tape ~15 *mm* was cut, mid of 60–70 *mm* was used for research.

The low temperature (600–900°C) annealings of samples undertaken for the ordering of crystal structure of the compounds was carried out in vacuum furnace of resistance with a W-heater.

Figure 4 shows the results of the measurement of the critical temperature of Nb/Al-tapes depending on the volume content of aluminum after heating at 1750°C for 5 seconds, and 2-hour annealing at 800°C. It is seen that T_c is not dependent on the aluminum content and is ~17.5 K.

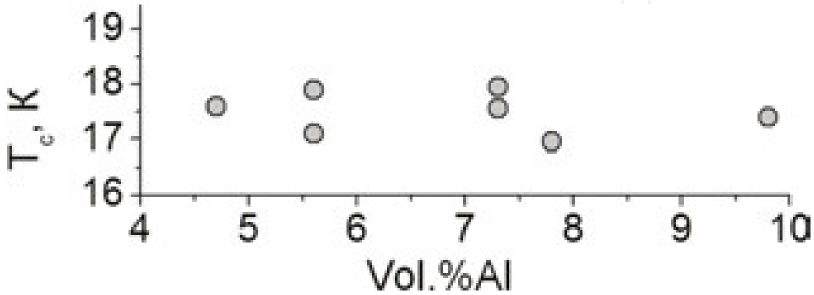


Figure 4. The dependence of the critical temperature T_c of tape Nb/Al/Nb from aluminum volume content Heat treatment: 1750°C, 5 *s* + 800°C, 2 *h*.

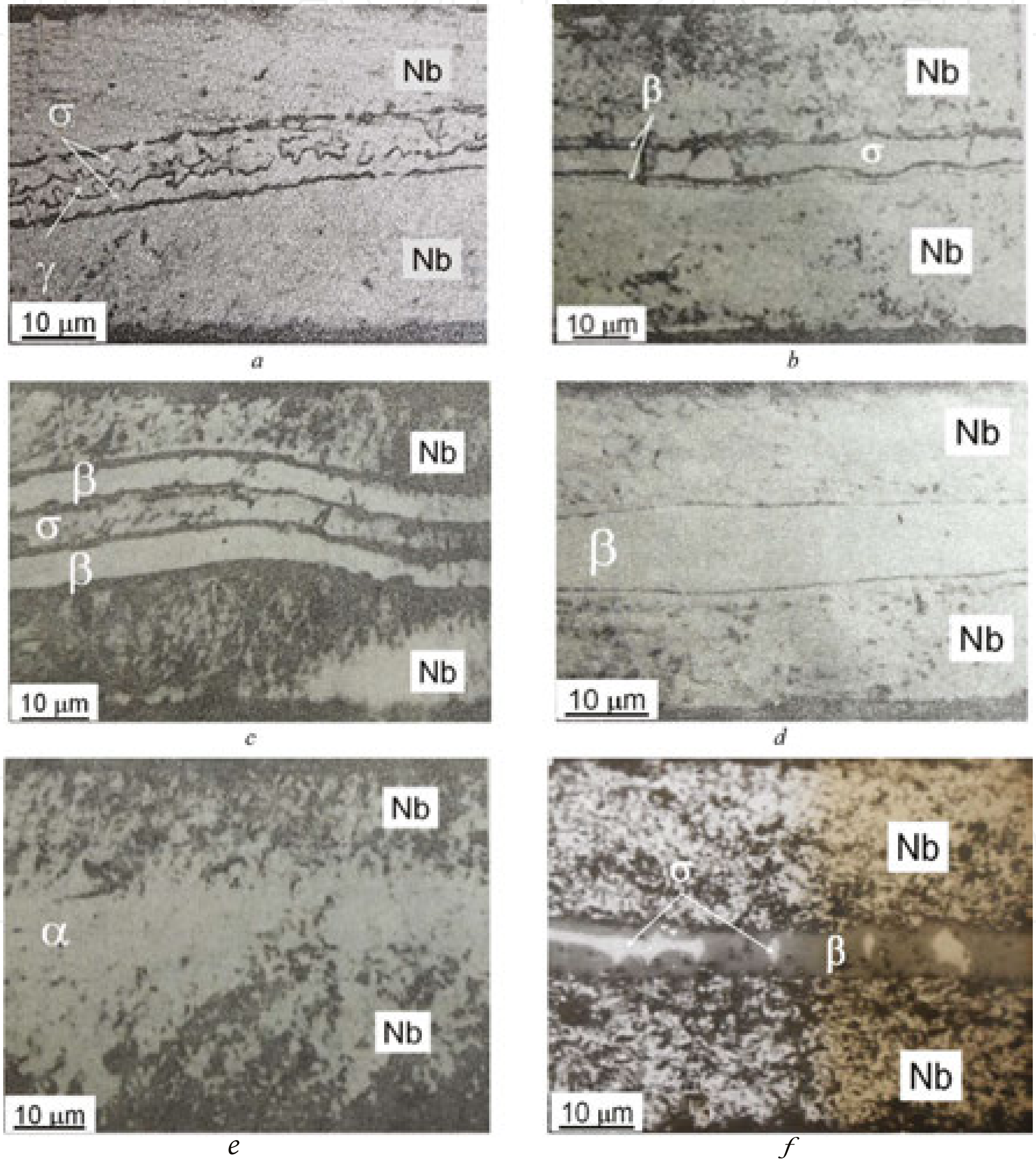
4. Microstructure and superconducting properties of the tapes Nb_3Al and $Nb_3(AlGe)$

4.1. The Cross-section Structure of Tapes

The phase structure of the diffusion layers was formed in the process of high-temperature heating and depended on the heating time and the volume content of aluminum in the initial tapes. Heating for 1 second at 1750°C led to the formation of the diffusion layer out of $\sigma(Nb_2Al)$- and $\gamma(NbAl_3)$-phase (**Figure 5*a***). Compound Nb_3Al (β-phase) is hardly viewed as separate inclusions on the boundary of σ-phase with Nb. With the increase of time and temperature of heating, layer structure is changed by increasing the thickness of the interlayer β-phase (see **Figure 5*b*** and **5*c***). Furthermore, ß-phase became too occupied with the entire volume of the diffusion layer (see **Figure 5*d***). A further increase of the heating time caused the diffusion of aluminum over the entire cross-section of the sample and the formation *α*-solid solution based on niobium (see **Figure 5*e***).

Figure 5*e* shows the cross-sectional microstructure of the composite tape out of niobium and alloy Al-30 wt. % Ge, which occupies 7.4% of its volume. After a 5-second heating at 1850°C in the tape, the diffusion layer with thickness of 8–5 microns was formed consisting of an intermetallic compound $\beta[Nb_3(Al,Ge)]$-phase with σ-phase splashes of compounds $Nb_2(Al,Ge)$.

After subsequent low-temperature annealing, the ratio of phases in the resulting diffusion layer did not change. However, in the beginning, an annealing at 900°C then formed γ-phase, that is, already before h.-t. h. It contained 35–43.5 wt. %Al and had a tetragonal lattice with the ratio $c/a = 1.63$. The X-ray patterns of specimens with β-phase set of lines corresponded to cubic lattice of type Cr_3Si with parameter a equaled to 5.178–5.207 Å. For chemical compound Nb_3Al in the cast state $a = 5.187$ Å.



a *b* *c* *d* *e* *f*

Figure 5. The structure of the cross-section of tape samples out of Nb/Al /Nb- (*a-e*) and Nb/(Al-30Ge)/Nb-composites (*f*) with thickness of 50 microns. H.-t. h, °C: *a* – 1750, 1 *s*; 7.4 vol. %Al; *b* – 1750, 5 *s*; 7.4 vol. %Al; *c* – 1850, 3 *s*; 8.1 vol. %Al; *d* – 1850, 5 *s*; 4.7 vol. %Al; *e* – 1850, 8 *s*; 4.7 vol. %Al and *f* – 1850, 5 *s*; 7.4 vol. %(Al–30Ge).

A layer of β-phase quickly arises, grows rapidly, and reaches a maximum value, ceased to exist. At temperatures of 1750°C and higher a heating, an excerpt and a cooling are continuing during several seconds (see **Figure 5**). However, even against the backdrop of such fleeting process, one may note that in the tapes, which contained about 7.4 vol. % Al, β-phase was maintained for a longer time than in tapes with 4.7 vol. % Al. In **Figure 6** (curve 2), in the samples with less volume content of aluminum equal to 4.7 vol. % aluminum layer, β-phase existed only for 5 seconds. During this time, it has grown to 5.5 microns, and then formed α-solid solution of aluminum in niobium. A similar case can be observed by comparing microstructures of the cross-sections of two identical samples *d* and *e* in **Figure 5**, which differed only by the duration of the heating at 1850°C: after 5 *s* – layer of β-phase, after 8 *s* – α-solid solution. In the tape samples with 7.4 vol. % Al (see **Figure 6**, curve 1), β-layer with thickness of 4.5 micron was observed after heating for 10 seconds.

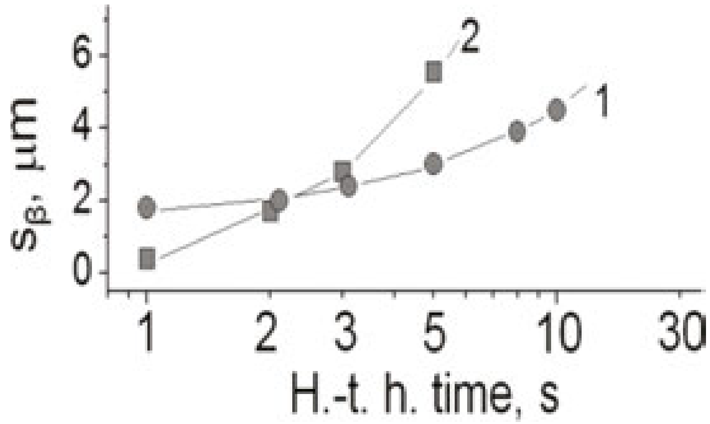


Figure 6. Layer thickness of β-phase versus time of h.-t. h. for samples of tape Nb/Al/Nb with 7,4 (1) and 4.7 vol. % Al (2) after heating at 1750°C. L.-t. an.: about 1 – 900°C, 2 *h*; 2 – 800°C, 2 *h*.

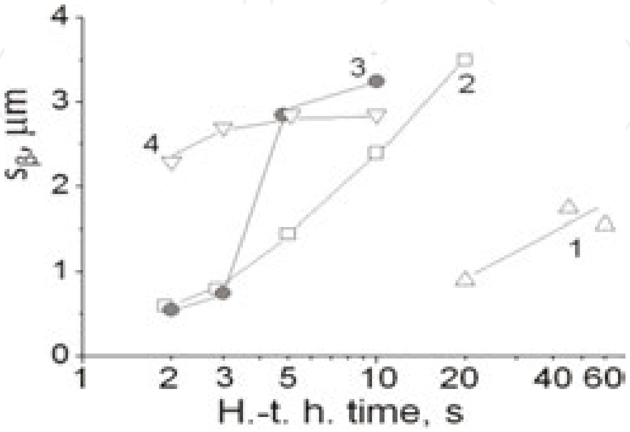


Figure 7. Layer thickness of β-phase versus time of h.-t. h. for samples of tape Nb/(AlGe)/Nb with 7,4 vol. % of alloy Al–30 wt. %Ge. Temperature of h.-t. h., °C: 1 – 1650, 2 – 1800, 3 – 1850, 4 – 1900.

Graphical dependence of β-layer thickness from the holding time at high-temperature heating of samples out of tape Nb/(AlGe)/Nb was shown in **Figure 7**. The layer thickness was calculated as the average of 10–15 measurements. At identical volume content of AlGe-alloy, β-layers after heating to a temperature in the small interval 1800–1900°C reached approximately the same thickness, ~ 3 μm at times of h.-t. h. equals 10 seconds. At 1650°C, to obtain the same thickness of β-layer, significantly longer times of the heating were required.

4.2. Tape Nb/Al/Nb. The dependence of the critical temperature from temperature and time the high-temperature heating

Before moving to an exposition of research results, dwell upon the interpretation the experimental data derived directly at measurements of the critical temperature T_c.

Figure 8 displays an experimental curve of the transition to the superconducting state, resulting to an inductive method of measurement T_c, which we appreciated. Two transitions were observed – the low-temperature transition at ~ 9.3 K, relating to the layers of niobium and the transition that begins and ends in the present experiment, at ~13.5 and ~18 K, respectively (this refers to the diffusion layer). In our studies of the transition temperature to the superconducting state, we took the beginning of the transition T_{CB}. This is caused by the fact that the received critical temperature in the literature as the middle of the transition does not entirely satisfactorily reflect its essence in the case of diffusion layers. As can be seen from the figure, the transition into district of high temperatures is greatly smeared to its left side, and a large portion of the signal occurs in the region near the beginning of the transition to the superconducting state. Therefore, the middle of the transition T_c, which is equal to 15.75 K, will not have any significance since it depends on the measurements of the critical temperature of the massive superconducting samples. In this study, to characterize samples of such, magnitudes were taken: T_{CB}, T_c and $\Delta T_c/2$ (see **Figure 8*a***). Parameter $\Delta T_c/2$, correlating with a half-width of the superconducting transition, was calculated as the difference of $T_{CB} - T_c$,

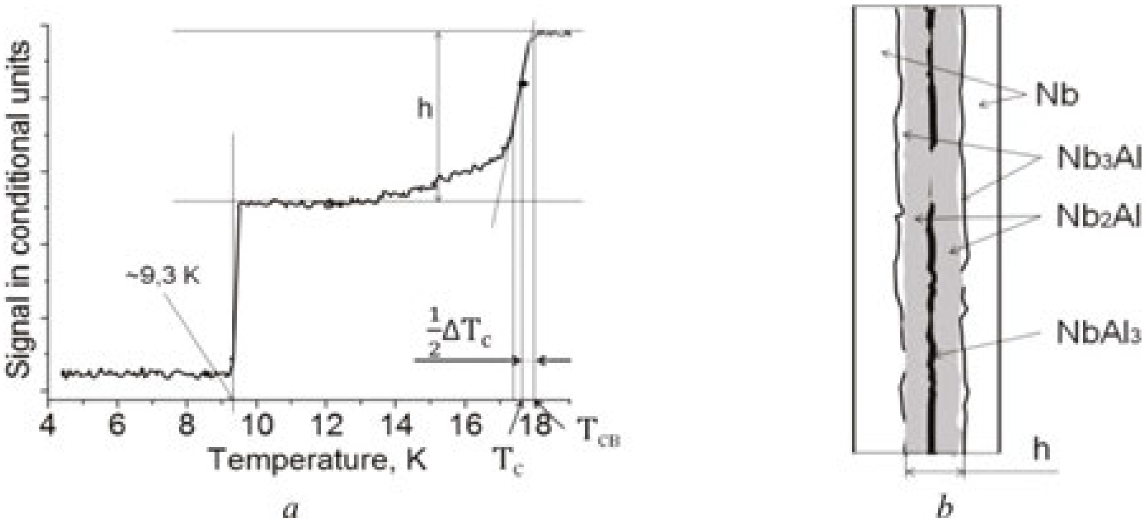


Figure 8. The experimental curve of the superconducting transition for the tape sample Nb/Al/Nb: 7.4 vol. %Al; 1750°C, with 1 *s* + 800°C, 2 *h* (*a*) and a schematic representation of the phase structure of the diffusion layer (*b*).

where T_c corresponded to the temperature of point of a flexion for the high-temperature transition on the experimental curve.

The height of the superconducting transition (designated as *h*) is determined by the volume of the superconducting phase in the sample the higher it is, the higher the jump of the signal. This also happens in bulk samples. Here, Nb_3Al is the superconducting layer with the highest critical temperature which is adjacent to the niobium and has bordered the whole diffusion layer (**Figure 8*b***). In the transition to the superconducting state, it screens the entire volume of the diffusion region h, where there are other compound Nb_2Al, non-superconducting at 18 K, and the intermetallic compound $NbAl_3$, not possessing superconductivity. Moreover, shielding occurs also if the layer Nb_3Al is not continuous.

Dependencies of the critical temperature T_{CB} and the parameter of $\Delta T_c/2$ from the time of high temperature heating at different temperatures were conducted in the range from 1400 to 1950°C. There are such dependencies for temperatures h.-t. h., equivalent to 1750, 1850 and 1900°C (**Figure 9**). Almost all dependencies characterized with a flat maximum for T_{CB} and minimum for $\Delta T_c/2$. Annealings at 800 and 900°C for 2 hours were followed after the short heating increased in T_c on 0.5–1.5 K (see **Figure 9**, top row, curves 1 and 2). There were excepted samples that were initially heated at 1500 and 1600°C for 1–5 seconds. Low-temperature annealing was decreased T_{CB} in these samples. The best samples had values of T_{CB} in the range of 18–18.5 K and minimum values of $\Delta T_c/2$ = 0.2–0.9 K. Such values of the superconducting parameters corresponded to tapes with time h.-t. h. from 3 to 5 seconds.

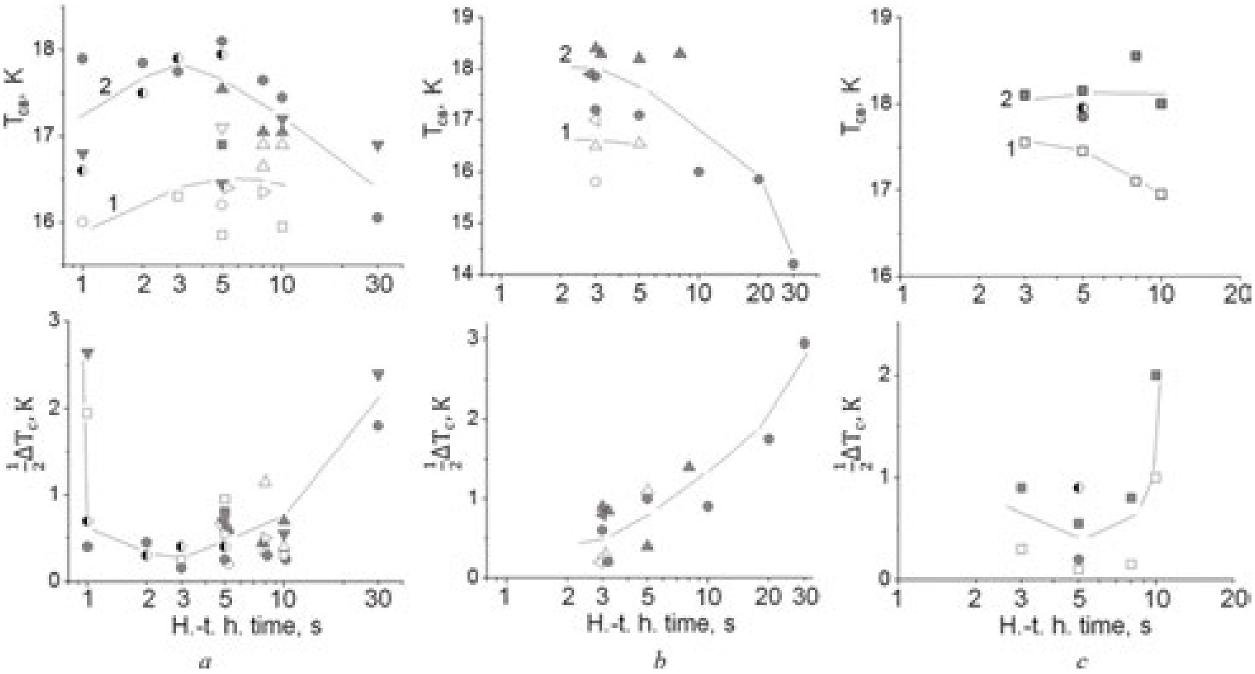


Figure 9. Dependence of the critical temperature T_{CB} (top row) and half-width $\Delta T_c/2$ of superconducting transition (bottom row) for tape samples Nb/Al/Nb from time h.-t. h. at 1750 (*a*) 1850 (*b*), and 1900°C (*c*): 1 – no l.-t. an., 2 – annealing at 800°C for 2 hours. Vol.% Al: △, ▲ – 4.7; ▽, ▼ – 5.6; ▷ – 6.3; ○, ● – 7.4; □, ■ – 7.8; ◁, ◀ – 8.1; ◐ – 7.4; 900°C, 2 h.

A dependence of T_{CB} from the temperature of h.-t. h. at a constant exposure during 5 seconds was presented in **Figure 10**. It shows that the maximum T_{CB} is equivalent to 18 K, observed at temperatures of the heating 1850–1950°C.

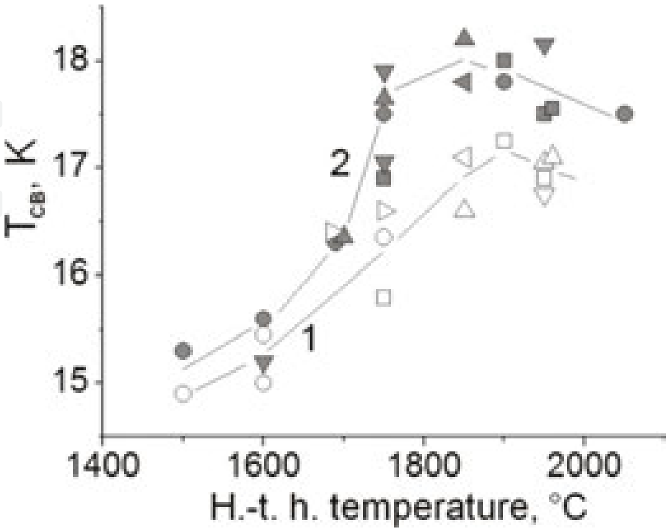
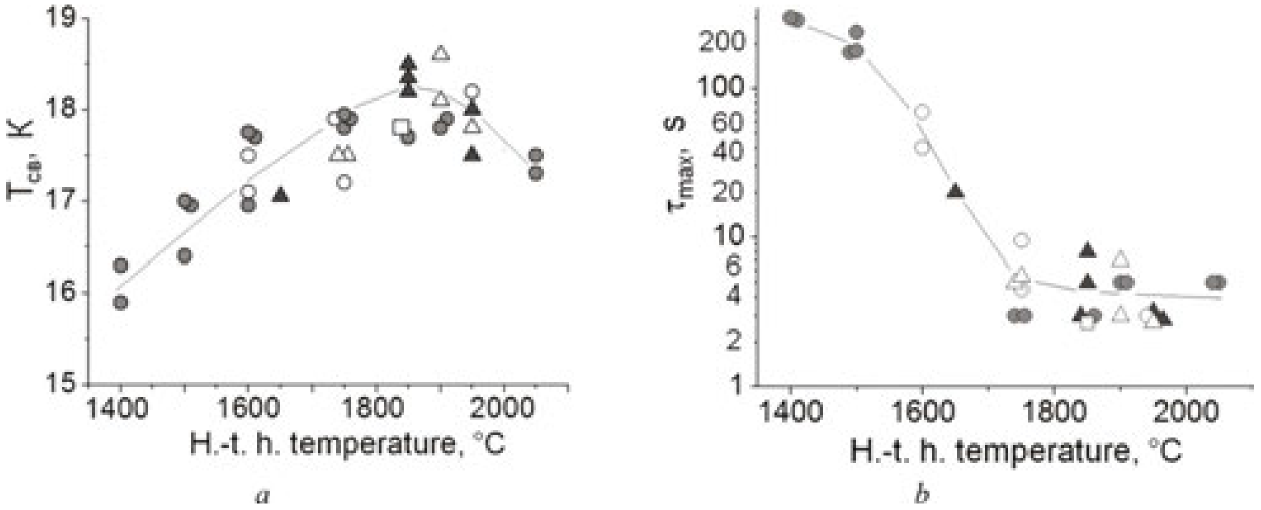


Figure 10. Dependence of the beginning temperature of the superconducting transition T_{CB} from temperature of the initial heating at the time of heating during 5 *s*: 1 – without l.-t. an.; 2 – annealing at 800°C for 2 *h*; designation similar to **Figure 9**.

Figure 11 shows that the maximum attainable (at a given temperature of h.-t. heating) temperature of the beginning of transition to the superconducting state T_{CB} (*a*) and the time of heating, at which maximum is reached (*b*), from the temperature of the h.-t. heating. On 1st curve is still more pronounced than in the previous figure, the maximum at 1850–1900°C, and on the 2nd – the bend in the range 1550–1700°C.



a

b

Figure 11. Dependence of maximum attainable critical temperature T_{CB} (*a*) and the time at which it is achieved τ_{max} (*b*) from temperature of the heating. L.-t. an. – 800°C, 2 hours. Vol. % Al: ▲ – 4.7; ○ – 5.6; ● – 7.4; △ –7.8; □ – 8.1.

Monotonic increase of T_{CB} with increasing of heating temperature from 1400 to 1950°C is due to the approximation of the composition of β-phase to the stoichiometry. As already mentioned, this is due to a shift of existence region in the phase diagram Nb–Al (**Figure 12**) toward the increasing aluminum content. The maximum of $T_{CB} = 18.5$ K. Some drop T_{CB} beyond 2050°C connected with a transition in the region above the line of peritectic reaction of formation Nb_3Al. In this case, β-phase is formed by the decay of a supersaturated solid solution of Al in Nb. Composition of such β-phase is always <25 at. % Al.

The temperature interval of an inflection on the curve τ_{max} depending on the temperature of h.-t. h. was in the range of 1500–1700°C and coincides with a melting point of $\gamma(NbAl_3)$-phase. According to different authors, it ranges from 1550 to 1660°C. This affects the formation of Nb_3Al so much that the diffusion from liquid phase is faster than in the solid phase. At temperatures of heating 1400–1500°C $\tau_{max} = 3$–5 minutes and at 1750°C and above – 3–5 *s*.

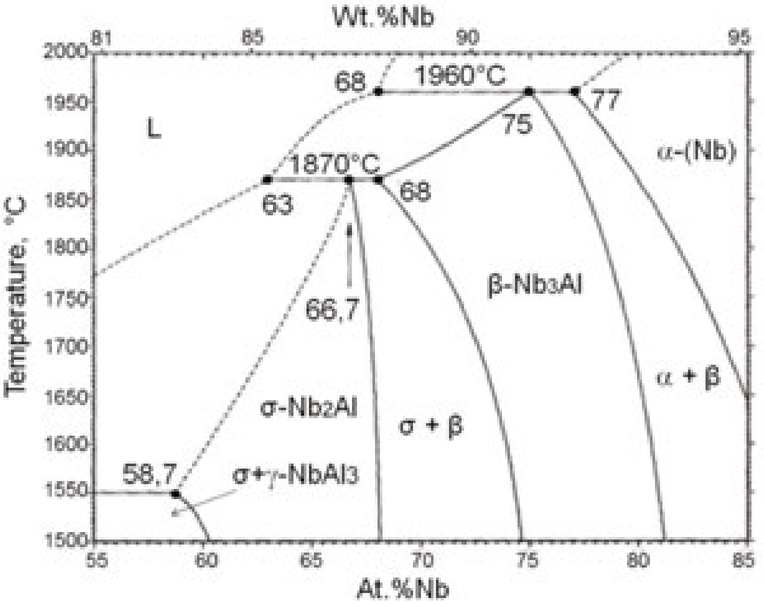


Figure 12. The state diagram Nb–Al system.

In the works of V. I. Arkharov, the appearance of new phases during reactive diffusion is described as follows. At first, in the regions adjacent to the phase boundary (in our case – to the boundary Nb-σ), the solid solutions are formed. When reaching of the saturation the solid solution lattice is rearranged to form a new phase. In a recent paper, the theory of "activated complex" was developed, which states that in the first stage of reactive diffusion, a border zone with a composition close to a new phase is formed, but the order of the arrangement of atoms differs from the order in the final structure of the product. This is the "activated complex", which is a highly distorted part of crystal lattice of product reactive diffusion with a concentration of point defects in excess of the equilibrium concentration. The accumulation of atoms within the reaction zone increases distortions and the achievement of their critical value is happening in the transmission of distortion into the reaction product. That is "complex" as a whole begins to move from reaction zone in depth of the layer of reaction product and to leave behind myself already an undistorted lattice. In order to establish this balance is needed time the less the, the higher the temperature at which there is mutual diffusion.

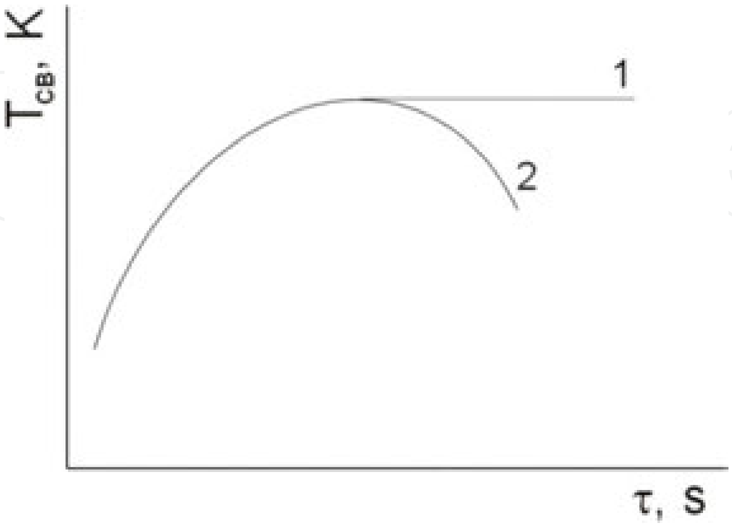


Figure 13. The dependence of the critical temperature T_{CB} from exposure time at a constant temperature of mutual diffusion in a semi-infinite diffusion pair (1) and in diffusion pair with a limited source of aluminum (2).

For diffusion couple Nb–Al, final reaction product is β-phase, the critical temperature depends on the concentration of point defects. At a constant temperature over time, T_{CB} should increase since the amount of defects in its crystalline lattice will become smaller. For the case of a semi-infinite diffusion couple (**Figure 13**, curve 1) T_c during the heating time τ should reach saturation. (Semi-infinite body – this body is extending from one side to a distance much greater than the diffusion length of on the other side is limited by plane $x = 0$). In investigated tapes, the aluminum is noticeably smaller than niobium and $T_c(\tau)$ has a maximum as a result the diffusion of aluminum on the entire volume of the tape. This was clearly observed mostly in the experimental T_{CB} depending on the heating time (see **Figure 9*a***).

Composition of the β-phase, corresponding to certain the temperature of heating is determined by the phase diagram. The higher the heating temperature, the faster equilibrium is established for the mutual diffusion. At a heating to 1850°C and above the time of stationary regime is so small that the maximum T_{CB} achieved almost immediately after switching on the electric current to heat the sample – for 1–2 seconds.

According to the local X-ray spectral analysis of σ- and β-phases layers were built on the dependencies T_{CB} of Nb_3Al tapes on the content of aluminum in σ- and β-phases (**Figure 14*a*** and ***14b***, respectively). Growth of T_{CB} with decreasing aluminum content in the σ-phase is evidenced on one hand, the directionality of flow the aluminum atoms from σ-layer, that is from the center of sample. On the other hand, due to the limited source of Al-atoms, the interface between σ- and β-phase is moved toward the central axis of the tape section. In line with this, it created a mistaken impression that niobium diffuses into the aluminum layer. In fact, the diffusion process is derived, at least in consequence of contrary streams of aluminum and niobium atoms and is not only owing to niobium as it may seem.

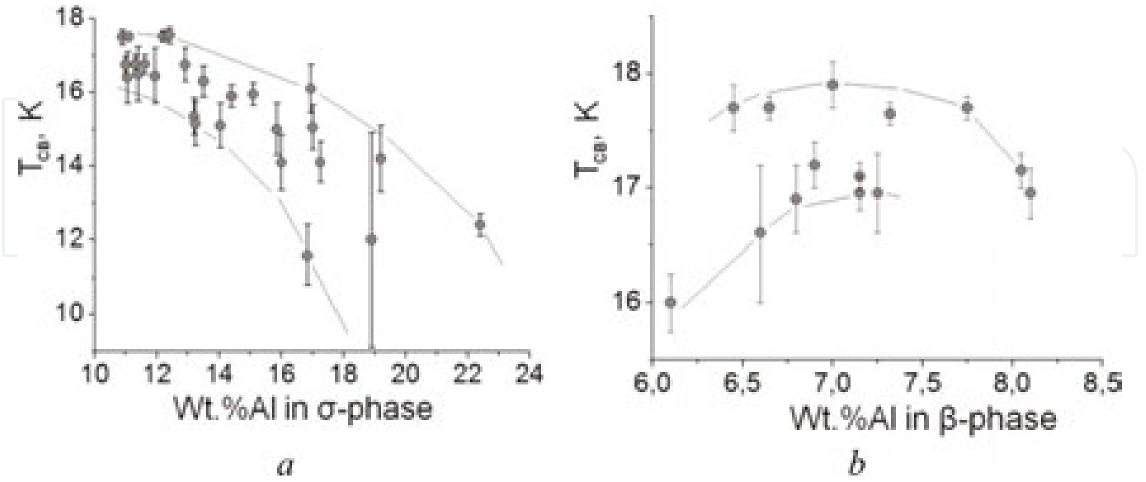


Figure 14. The dependencies of the critical temperature T_{CB} of tape samples Nb/Al/Nb from content of aluminum in the σ-phase (*a*) and in the β-phase (*b*). Vertical line segments are showed the doubled half-width $\Delta T_c/2$.

As the aluminum content in the σ-phase decreased, the content in β-phase increased, approaching the stoichiometric composition, which led to higher T_{CB}. Maximum values T_{CB} were observed at the content of aluminum in the β-phase, equal to 7.0–7.5 wt. % (see **Figure 14*b***). By stoichiometric compositions, Nb_2Al- and Nb_3Al-phases correspond to 11.0 and 7.6 wt. % Al, respectively.

In **Figure 14*a***, it is seen that the aluminum content in the σ-phase layer in a large number of measurements exceeds the content allotted by state diagram Nb–Al (see **Figure 12**). This is because real in σ-layer contained γ-phase (compound $NbAl_3$), mostly aluminum-rich. The data in **Figure 14*a*** were compiled for the samples in the diffusion layers which prevailed σ-phase. Afterwards, as the sample cooled down, it is very possible to observe an "imaginary σ-layer". In fact, it was a layer of σ + eutectic, which is a mechanical mixture of the two phases – σ and $NbAl_3$. Moreover, by using a micro analyzer, average composition of layer was determined.

The fact that in the investigated Nb/Al/Nb-tapes at temperatures of interdiffusion 1700–1900°C for formation a micron-layers of superconducting compound Nb_3Al enough 2–5 seconds time, there is nothing exceptional. This follows the Fick's 2nd law equation

$$\frac{\partial C}{\partial \tau} = D\frac{\partial^2 C}{\partial x^2}$$

for the finite body, where: C – the concentration, τ – time, *x* – the distance, *D* – the diffusion coefficient. When considering the diffusion from a layer in which the distribution of matter at T = 0 satisfies such boundary conditions:

$$f(x) = \mathrm{C}_0 \text{ at } 0 < x < h$$

$$f(x) = 0 \text{ at } h < x < l\,(l > h),$$

a solution of Fick's looks

$$\mathrm{C} = \mathrm{C}_o\left(\frac{h}{l} + \frac{2}{\pi}\sum_{1}^{\infty}\frac{1}{h}\exp\left[-\left(\frac{n\pi}{l}\right)^2 D\tau\right] cos\frac{n\pi x}{l} sin\frac{n\pi x}{l}\right).$$

Here, *2h* – Al-layer thickness in the initial tape Nb/Al/Nb, *2l* – tape thickness, *x* – β-thickness layer. The time is defined in which a layer of β-phase with thickness of 1 micron grows. For our case: $h = 1{\cdot}10^{-4}\ cm$, $l = 25{\cdot}10^{-4}\ cm$, D ≈ $5{\cdot}10^{-9}\ cm^2/s$ at 1800°C [7], C_o = 100 at. %Al, C = 25 at. %Al. We restrict ourselves to n = 2. Having a numerical substitutions and calculations, we find that β-layer of thickness 1 micron is grown for 30 seconds. At 1300°C $\tau = 9\ h$ (D ≈ $5{\cdot}10^{-12}\ cm^2/s$ [7] and with the same values *h, l* and *x*). In our experiments, in samples of niobium-aluminum tape at 1300°C β-phase was formed during 5 *h*. However, T_{CB} of these samples was equal to 15.7 K. At temperatures of 900–1000°C, a layer of β-phase is formed only during 900 hours (with *h* ~ 1 micron).

In the present studies, layers of β-phase were formed after heating for 2–5 (at 1850°C) and not after 30 seconds as what we have been calculated using the Fick equation. This discrepancy is possible since values of mutual diffusion coefficients are taken from the literature. But our tapes should expect higher values of D because the interacting metals were contacted physically clean – juvenile – surfaces which were formed by their joint rolling. Based on our data, that is, $x \sim 2{\cdot}10^{-4}\ cm$, $h \sim 1{\cdot}10^{-4}\ cm$, $l \sim 25{\cdot}10^{-4}\ cm$ and $\tau \sim 3\ s$, the diffusion coefficient D ≈ $6{\cdot}10^{-8}\ cm^2/s$ at 1850°C. This is an order of magnitude higher than in [7].

4.3. Tapes Nb/AlGe/Nb. Dependence of T_{CB} on the content of germanium in the alloy Al–Ge

For obtaining of tape samples with intermetallic compound Nb$_3$(Al$_{0.8}$Ge$_{0.2}$), instead of aluminum, AlGe-alloys c 30, 40, 45 and 50 wt.% of germanium were used. As a trial alloy, alloy Al–7.5 wt. % Ge was used. The alloys were prepared by melting in a suspended state with casting in a massive copper mold in the form of flat bars of thickness about ~2.5 *mm*, which prior to assembly of three-layer packages were rolled with heating to 400–410°C on air: the temperature close to the melting temperature of eutectic. To form a layer of the intermetallic compound Nb$_3$(Al,Ge) and to plot of the dependencies critical temperature on the germanium content in the alloy Al–Ge, the tape samples were heated to a high temperature heating at 1650–1850°C. Then, there was low-temperature annealing in two regimes: 750°C, 50 hours and 800°C for 2 hours. Part of the results obtained on measuring critical temperature is shown in **Figure 15**. Almost for all the samples T_{CB} values after low temperature annealing lie above the 19 K. The greatest value of critical temperature was equated to 20.2 K, obtained from the tape with the alloy Al–45 wt. % Ge after treatment on the regime: 1850°C, 2 *s* + 750°C, 50 *h*.

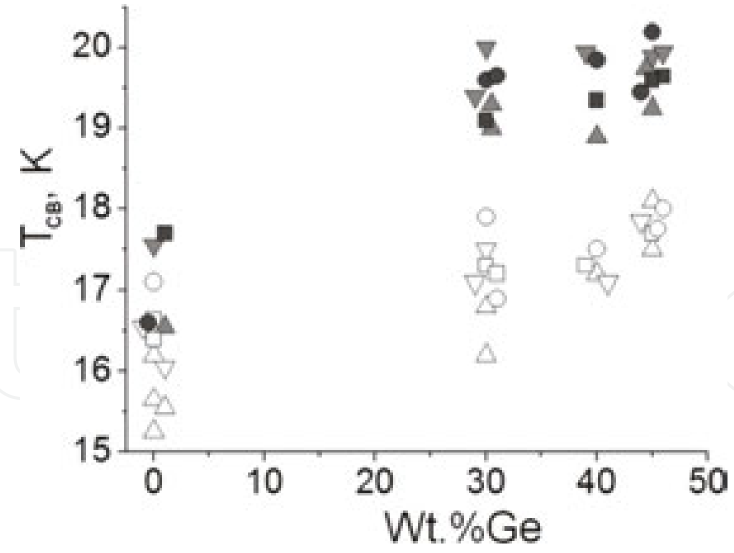


Figure 15. Critical temperature T_{CB} of tapes Nb/AlGe/Nb depending on the alloy composition of Al–Ge. Heat treatment, °C: △ – 1650, 20 *s*; ▽ – 1650, 30 *s*; □ – 1750, 3 *s* и ○ – 1850, 2 *s*; ▲, ▼, ■ и ● – the same + 750, 50 *h*.

With the addition of germanium in an amount of 7.5 wt. % T_{CB} is decreased a little compared with samples of Nb/Al/Nb-tape. This was observed on several samples with different modes of h.-t. h.

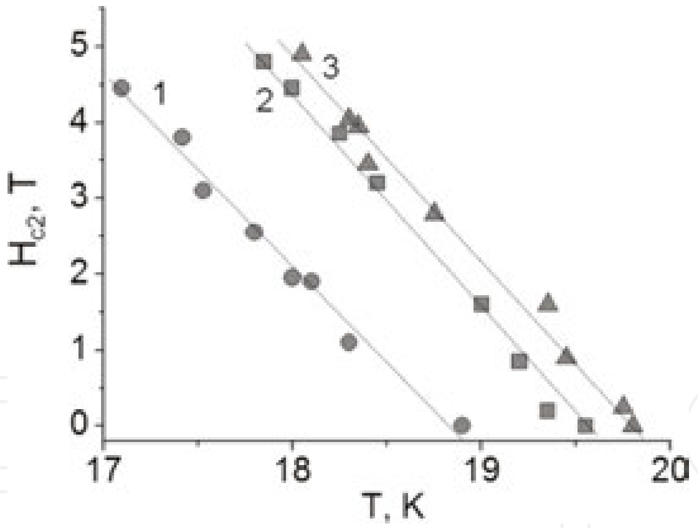


Figure 16. Experimental dependence H_{c2} on temperature near T_c for Nb/Al30Ge/Al tape after h.-t. h. at 1900°C. Heating time, *s*: 1 – 2, 2 – 3 and 3 – 10. L.-t. an.: 800°C, 2 *h*.

4.4. The critical magnetic fields of tapes Nb/Al/Nb and Nb/AlGe/Nb

The upper critical magnetic fields $H_{c2}(4.2\ K)$ at liquid helium temperature were determined by the method proposed in [9], measuring its near the critical temperature, and calculating by the following formulas:

$$H_{c2}(0) = -0,69 \cdot T_c \cdot (dH_{c2}/dT)_{T=T_c}$$

and

$$H_{c2}(\mathrm{T}) = \mathrm{H}_{c2}(0) \cdot [1 - (T/T_c)^2],$$

where: T = 4.2 K.

The numerical value of the slope $(-dH_{c2}/dT)_{T=T_c}$ is calculated from the experimental direct $H_{c2}(T)$. Such dependencies are shown in **Figure 16** for niobium-aluminum-germanium the tape after heat treatment at 1900°C.

The calculated values of H_{c2} at 0 and 4.2 K for Nb/Al/Nb tape and Nb/AlGe/Nb tapes with 50-hour annealing at 750°C are summarized in **Tables 2** and **3**, respectively.

Heat treatment, °C	**T_{CB}, K**	$(-\mathrm{dH}_{c2}/\mathrm{dT})_{\mathrm{T}=\mathrm{T}_c}$, ***T/K***	**H_{c2}, *T***	
			0 K	**4.2 K**
1650, 10 s	15.4	2.1	23	21.3
1650, 20 *s*	15.9	2.0	22	20.5
1650, 10 *s* + 800, 2 *h*	16.0	2.2	24	22.3
1650, 20 *s* + 800, 2 *h*	17.4	2.4	29	27.3
1750, 8 *s*	16.0	2.6	28	26.1
1750, 10 *s*	16.4	2.3	23	21.5
1750, 5 *s* + 800, 2 *h*	17.0	2.5	32	30.0
1750, 8 *s* + 800, 2 *h*	16.5	2.4	28	26.2
1750, 10 *s* + 800, 2 *h*	17.0	2.4	29	27.2
1850, 3 *s*	16.3	2.4	27	25.2
1850, 5 *s*	16.3	2.3	26	24.3
1850, 8 *s*	17.0	2.2	25	23.5
1850, 3 *s* + 800, 2 *h*	17.5	2.2	26	24.5
1850, 5 *s* + 800, 2 *h*	17.7	2.0	25	23.6
1850, 8 *s* + 800, 2 *h*	17.4	2.0	23	21.7

Table 2. Results of measurements of the upper critical magnetic field H_{c2} near the critical temperature for the tape samples Nb/Al/Nb c 4.7 vol. % Al.

A tilt of straight lines $H_{c2}(T)$ for Nb/Al/Nb tape varies in the range of 2.0–2.6 *T*/*K* regardless of heat treatment. Low-temperature annealing, raising T_{CB}, is increased H_{c2}. Its best values at 4.2

were accounted for tapes with heating at 1750°C. After annealing at 800°C, H_{c2}(4.2 K) is equal 30 *T* by heating for 2 seconds and with the increase of its duration to 8–10 *s* it was reduced to 26–27 *T*.

The niobium-aluminum-germanium tape with alloy of Al–45 wt. % Ge having the maximally out of achieved critical temperature of 20.2 K (see **Table 3**), possesses and the highest H_{c2}(4.2 K), equal to 50.7 tesla. As a consequence of annealing at 750°C for 50 *h*, the value of the slope $(-\mathrm{dH}_{c2}/\mathrm{dT})_{T=T_c}$ increases to 3.8 *T/K* in comparison with samples without the low-temperature annealing.

Wt.%Ge	**L.-t. annealing, °C**	**T_{CB}, K**	$(-\mathrm{dH}_{c2}/\mathrm{dT})_{T=T_c}$, *T/K*	**H_{c2}, *T***	
				0 K	**4.2 K**
30	Without annealing	17.8	3.4	42	39.5
30	750, 50 *h*	19.8	3.8	51	48.7
40	Without annealing	17.5	3.5	42	39.6
40	750, 50 *h*	19.7	3.8	51	48.7
45	Without annealing	18.1	3.3	42	39.7
45	750, 50 *h*	20.2	3.8	53	50.7

Table 3. Results of measurements of the upper critical magnetic field H_{c2} near the critical temperature for the tape samples Nb/AlGe /Nb after h.-t. h. at 1850°C for 2 seconds.

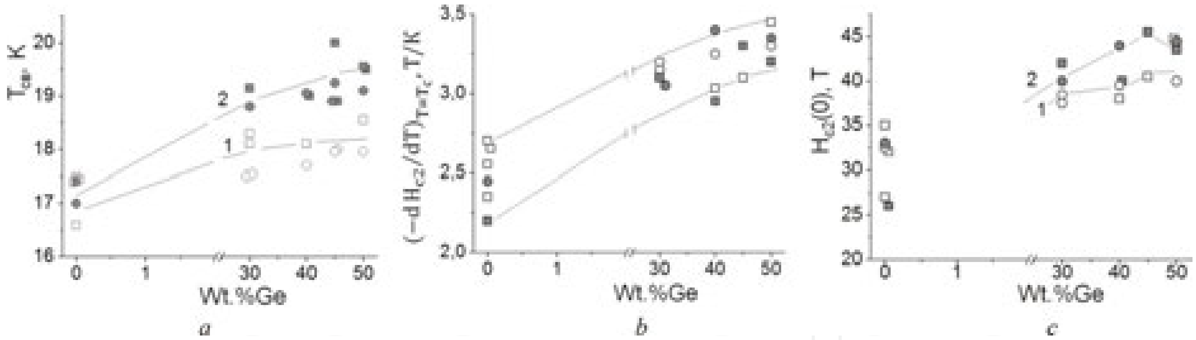


Figure 17. The dependence of the transition temperature to the superconducting state T_{CB} (*a*), the slope of the straight $H_{c2}(T)|_{T=T_c}$ (*b*) and the upper critical magnetic field at 0 K $H_{c2}(0)$ (*c*) on the germanium content with the alloy Al–Ge for tapes Nb/AlGe/Nb after h.-t. h. and after h.-t. h. + l.-t. an. Heat treatment, °C: ○ – 1750, 5 *s* and □ – 1850, 3 *s*; ● and ■ – the same + 800, 2 hours.

Towards the values of H_{c2}(4.2 K) ~ 50 *T* should be treated critically, since direct measurements of H_{c2} with use the pulse technique were not carried out.

Dependencies of tilt $(-dH_{c2}/dT)_{T=T_c}$ and H_{C2} as well as T_{CB}, measured in experiments to determine the H_{C2}, depending on the germanium content in the alloy Al–Ge for the second series of Nb/AlGe/Nb tapes are shown in **Figure 17**. Concentration diapason of germanium in the alloy was extended up to 50 wt. % Ge.

The maximum superconducting characteristics were for the samples with 40–50 wt. % Ge. The critical temperature after heating and annealing was 19–19.5 K, $H_{c2}(0) = 42–45$ *T*. At 4.2 K $H_{c2} = 40–43$ *T*. The two-hour annealing at 800°C significantly increases the T_{CB} and H_{c2} compared with samples without annealing, but any effect on the slope of $H_{c2}(T)$. The latter circumstance is somewhat contrary to the results obtained for samples previous series (see **Table 3**). In those tapes 50-hour annealing increased the slope of dependences $H_{c2}(T)$ from 3.3–3.5 to 3.8 *T*/*K*.

Increasing of the upper critical magnetic field of the diffusion layers Nb_3Al and Nb_3AlGe was explained by the collapsing of the superconducting phase with allocation $\sigma(Nb_2Al)$- and $\sigma(Nb_2AlGe)$-phases accordingly. The upper critical field of superconductors II-kind equal $H_{c2} = \sqrt{2}\cdot\varkappa\cdot H_{cm}$, where $\varkappa$ is the parameter of the Ginzburg-Landau and H_{cm} is the thermodynamic critical field. The parameter $\varkappa$, defined by the ratio of the penetration depth of the magnetic field λ to the coherence length ξ ($\varkappa = \lambda/\xi$), in alloys and compounds can be great. In dirty superconductors II-kind with a high concentration of impurities, coherence length will decrease with decreasing the mean length of free path of electrons in a normal state l_e, what and should occur during the decay β-phase in the process of low-temperature annealing. According to the theory of Gorkova: $\varkappa \sim l_e^{-1}$.

Wt.%*Ge*	**Regime of temperature treatment, °C**	**T_{CB}, K**	**$H_{c2}(0)$, *T***	**Content of element in β-layer, *wt.%***			**Chemical formula of β-phase**
				Nb	**Al**	**Ge**	
30	1750, 5 *s*	17.6–17.7	36–37	90.4	5.2	1.8	$Nb_{3.2}Al_{0.7}Ge_{0.1}$
45	1750, 5 *s*	17.8	-	91.5	5.9	2.3	$Nb_{3.1}Al_{0.8}Ge_{0.1}$
45	1850, 3 *s*	18.1	41	90.8	5.1	3.7	$Nb_{3.2}Al_{0.6}Ge_{0.2}$
50	The same + 800, 2 *h*	19.6	48	90.9	5.7	4.6	$Nb_{3.1}Al_{0.7}Ge_{0.2}$

Table 4. Data local of X-ray spectral analysis for Nb/Al/Nb-tape samples with the alloys Al–Ge of different composition and their values of T_{CB} and H_{c2}.

On the decay of the superconducting β-phase, we will get back when considering critical currents, but now, let us compare the change of superconducting parameters T_{CB} and H_{c2} of compound $Nb_3Al_{1-x}Ge_x$ with a change in its composition. Increasing of T_{CB} compound of niobium with aluminum and germanium is due, firstly, to the approximation of composition β-phase to stoichiometric and, secondly, to the approximation of composition β-phase to a range of concentrations of aluminum and germanium, which is considered optimal in terms of the critical temperature and critical field ($x = 0.2$). If a greater or smaller difference in the composition of the superconducting phase from the stoichiometry is rigidly dependent on the temperature of the high-temperature heating, then the correlation of germanium and alumina into the β-phase, we can adjust by arbitrary change the germanium content in the alloy Al–Ge in the range from 30 to 50 wt.%. To determine the composition of the β-phase, a local X-ray spectral analysis was used. These data and values T_{CB} and H_{c2} for the two tested tape samples are summarized in **Table 4**.

With the increase of germanium concentration in the Ge–Al alloy with 30 to 45–50 wt. % Ge its content in the β-phase was increased from 1.8 to 3.7–4.6 wt. %, and the ratio of Al and Ge in the phase varied from 0.7/0.1 to 0.7/0.2. With this, T_{CB} has risen by 17.6–17.7 to 19.6 K and $H_{c2}(0)$ – from 36–37 to 48 Tesla. Note that niobium in the β-phase containing germanium was always more than its stoichiometric composition. It is very likely that such a deviation explained by the fact that the compound Nb_3Ge at 1750–1850°C is stable in the range of compositions sufficiently far from the stoichiometric. Then, it is possible to conclude that high temperature of transition to the superconducting state and the critical magnetic field of compound $Nb_3(AlGe)$ are caused advantageously by how close the relation of aluminum and germanium to the ratio of 0.8/0.2.

4.5. Current-carrying capacity of superconducting tapes Nb_3Al and Nb_3AlGe. Influence of temperature and time h.-t. h. (on example tapes of Nb/Al/Nb)

Measurements of the critical current I_c of tape samples was performed in a superconducting solenoid at a temperature of 4.2 K. The sample was placed in such a manner (**Figure 18**), that the direction of electric current I, flowing through the sample was perpendicular to the magnetic field H, which was produced by a solenoid ($I \perp H$), and plane (of rolling) of sample (*ab*) was parallel H – (*ab*) | | H. In this position, the Lorentz force F, acting on the superconducting vortices in the layer of superconductor is directed perpendicular to the (*ab*). Width of the tape is 2 *mm*.

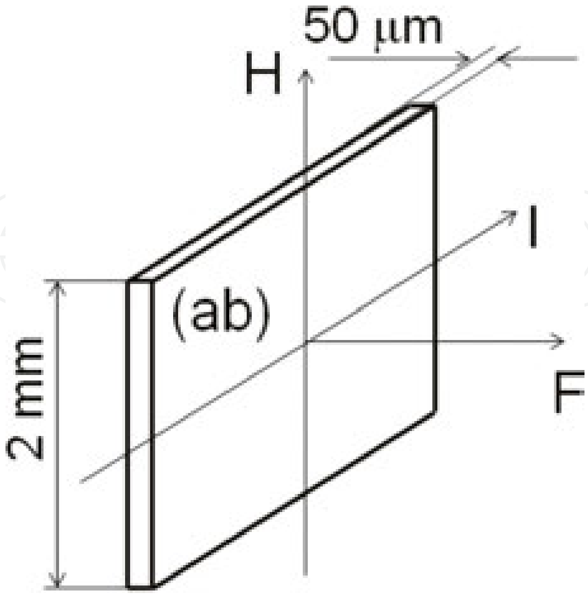


Figure 18. Disposition of tape specimen in the working area of the superconducting solenoid: H – magnetic field, I – transport current through the sample, (*ab*) – plane of the surface of the tape, F – Lorentz force.

Numerous measurements of the critical current I_c showed (**Figure 19**) that their maximum values in the tapes Nb/Al/Nb fall on the a fairly narrow temperature range of the initial heating of 1700–1750°C and reach 15 *A* (or 7.5 *A*/*mm* – amperes per millimeter of the tape width).

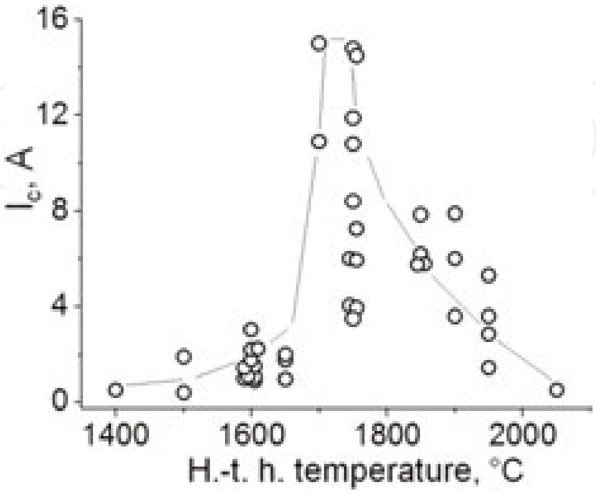
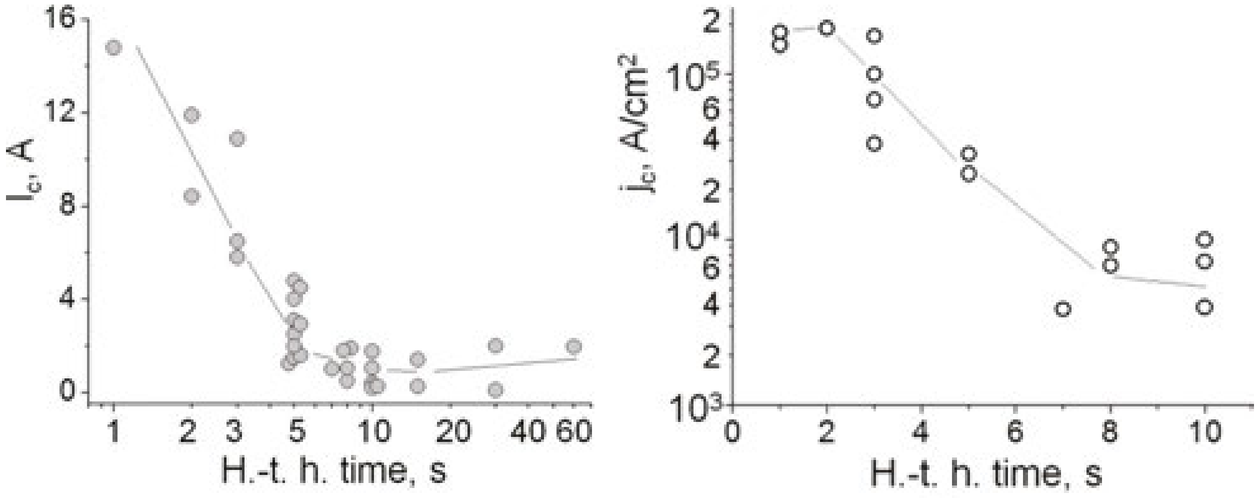


Figure 19. The dependence of the critical current I_c tapes Nb/Al/Nb on temperature of h.-t. h. Heating times were corresponding to the larger of the achieved values I_c at a given temperature. Regimes of l.-t. an.: about 800 and 900°C for 2 *h*.

From the viewpoint of the critical current I_c and the critical current density j_c most optimal are the shortest times of heating of 1–3 *s* at 1700–1800°C (**Figure 20**). The value I_c in the magnetic field of 5 *T* in the best samples were the same 15 *A*. This corresponded to $j_c = 2 \cdot 10^5$ *A*/*cm*^{2} in calculation on layer Nb_3Al.



a *b*

Figure 20. The dependence of the critical current I_c (*a*) and the critical current density j_c (*b*) tapes Nb/Al/Nb on the time of h.-t. h. in a magnetic field of 5 Tesla. Temperatures of the heating 1600, 1750, 1850 and 1900°C were corresponding to the larger of the achieved values I_c for a given duration of heating. Regimes of l.-t. an.: 800 and 900°C for 2 hours.

Increasing the heating time to 8–10 *s* leads to a decrease of the critical current to ~1 *A*, and the critical current density to (4–8)·10^3 *A/cm*^{2} in a magnetic field of 5 Tesla.

4.6. Influence of the diffusion layer structure on the critical current and critical current density.

In considering the dependence of the critical current I_c on the structure of diffusion layer Nb–Al, namely the thickness of β-phase, the layer s_β might be expected to increase in a monotone. However, measurements of I_c showed that the current was rapidly increased with s_β only in a narrow, 0.5 to 2 microns, range of layer thickness, and then just as quickly fallen even below its initial level (**Figure 21*a***).

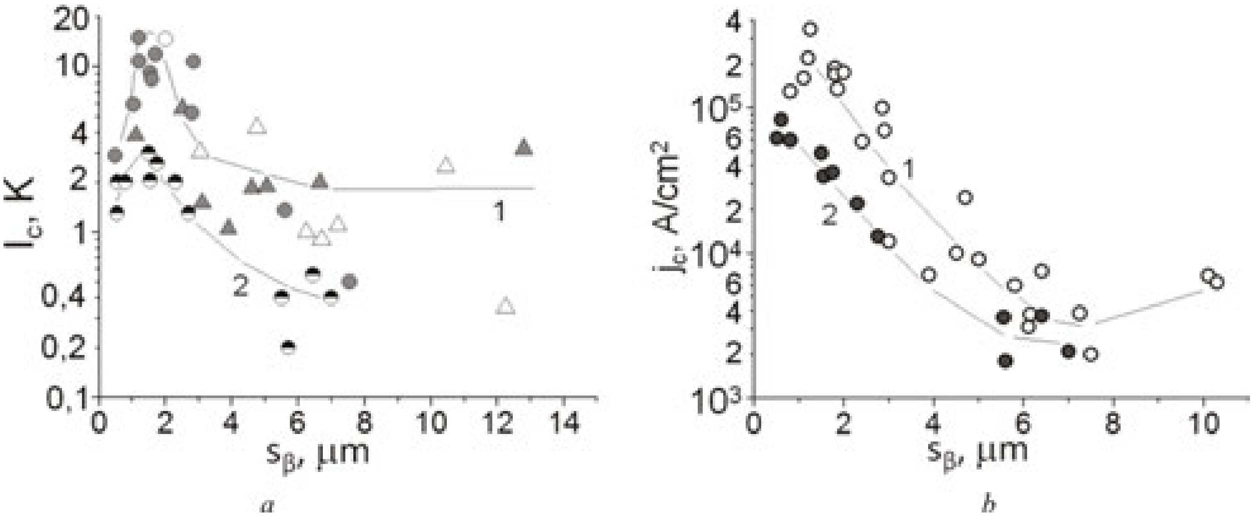


Figure 21. The dependence of the critical current I_c (*a*) and the critical current density j_c (*b*) on layer thickness of β-phase in tapes Nb/Al/Nb (1) and Nb/AlGe/Nb (2) in a magnetic field of 5 *T*.

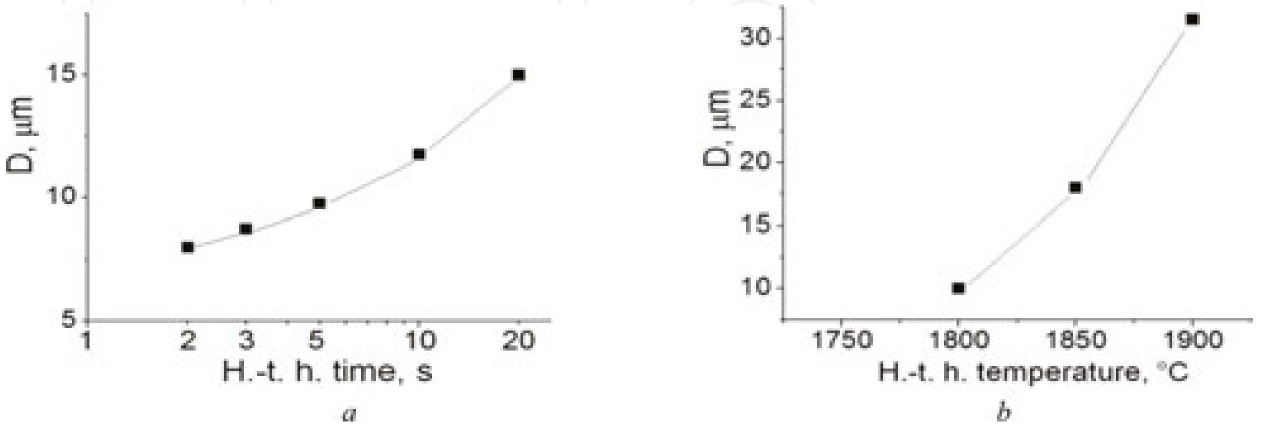


Figure 22. The dependence of the average grain size of β-phase in the tape Nb/Al30Ge/Nb on the temperature (*a*) and time (*b*) of the high temperature heating: *a* – 1800°C; *b* – 5 *s*.

That is, the critical current in tapes with diffusion layers containing, along with the β-phase, σ- or σ- + γ-phase, was significantly greater than in the tapes with diffusion layers only of β-phase. Maximum value of I_c observed in the tapes Nb_3Al with thickness of its layer equal 1–2 *μm*, and then dropped to 1–2 *A* in the layers of 10–14 microns thick. It was sharply decreased with the increase of β-layer thickness and critical current density (**Figure 21*b***). With s_β, equal to 1–2 microns, j_c reached ~ $2 \cdot 10^5$ *A*/*cm*^{2} but in a layer of thickness of greater than 5 microns current density dropped two orders of magnitude.

Similar behavior demonstrated tape out of compound Nb_3AlGe: the critical current in the tapes with $s_\beta = 2$ *μm* equal 3 *A* was decreased to 0.2–0.5 *A* at a thickness of β-layer 5 and more microns, the critical current density at this point ranged from ~$7 \cdot 10^4$ to about $3 \cdot 10^3$ *A*/*cm*^{2} in a field of 5 Tesla.

4.7. Effect of the grain size of β-phase on the critical current density Nb_3AlGe

Critical current in A15 compounds such as Nb_3Sn and V_3Ga, is dependent on the grain size, and the centers of fastening the superconducting vortices in them are mainly grain boundaries. Therefore, the smaller the grains of the compound, the higher the critical current density. This was shown in compound Nb_3AlGe, obtained in composite tapes out of niobium and alloy Al–30 wt. % Ge.

In studied tapes, which were subjected to heat treatment at relatively high temperatures, the grain size of β-phase in formed diffusion layers is very sensitive to temperature and time of the high temperature heating. Based on the data of metallographic analysis (**Figure 22**), the average grain size Nb_3AlGe D depending on the heating ranged from about 8 micrometers after h.-t. h. at 1800°C for 2 seconds (**Figure 23*a***) to 33 micron after 5-second heating at 1900°C (**Figure 23*b***). That is why, the increase of critical current was observed at the initial stage of formation of the compound and associated with an increase of thickness of its layer (see **Figure 21**) are not accompanied by the increase of the critical current density, since at an increase s_β very rapidly grew and grain of β-phase (**Figure 24**). It comes to the size of grains in a plane parallel to the rolling tape. It is understood that the grain size of the phase in the perpendicular direction cannot exceed the thickness of its layer.

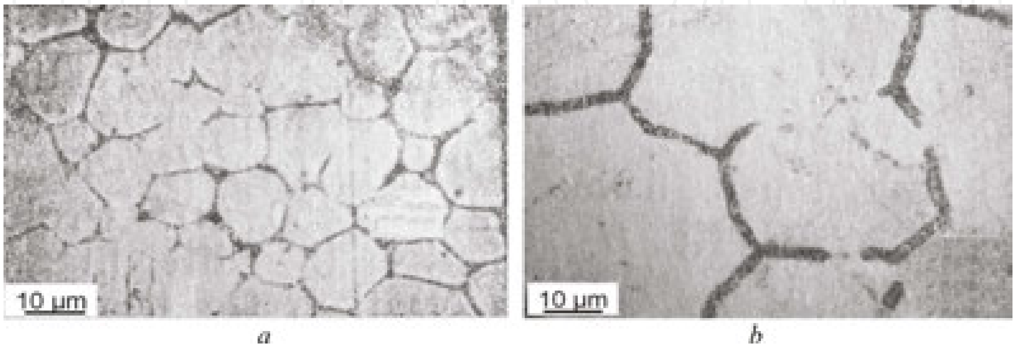


Figure 23. The microstructure of β-phase layer in the tape Nb/Al30Ge/Al after h.-t. h. at 1800°C for 10 seconds (*a*) and 1900°C for 5 seconds (*b*). L.-t. an.: 800°C, 2 *h*.

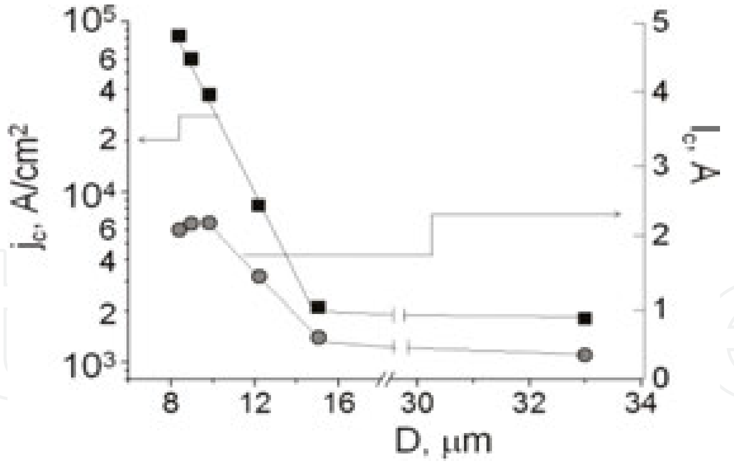


Figure 24. The dependence of critical current density j_c and a critical current I_c on the average grain size of β-phases in tapes Nb/AlGe/Nb with the alloy Al–30 wt. % Ge. L.-t. an.: 800°C, 2 *h*.

4.8. Effect of low-temperature annealing on critical temperature and critical current of tapes Nb/Al/Nb

Dependencies T_{CB} and I_c on temperature of l.-t. an. at constant time of annealing of 2 hours are shown in **Figure 25**. Compared to tapes without annealing, the critical temperature after low temperature annealing in the range of 500–700°C was on 1 K less, and the critical current was equal to 0.4 *A*. In samples without annealing I_c = 1.5–3 *A*. However, basing on the graphs for the starting point to take the room temperature, then both dependencies in that temperature interval will have a minimum. At the next increase of the annealing temperature T_{CB} and I_c are increased, can reach maximum and further fall. The maximum value of the critical current, relative to the maximum value of critical temperature is shifted to a much higher temperature, 900–1100°C, which depends on the high-temperature heating. The largest I_c equal to 7–10 *A*.

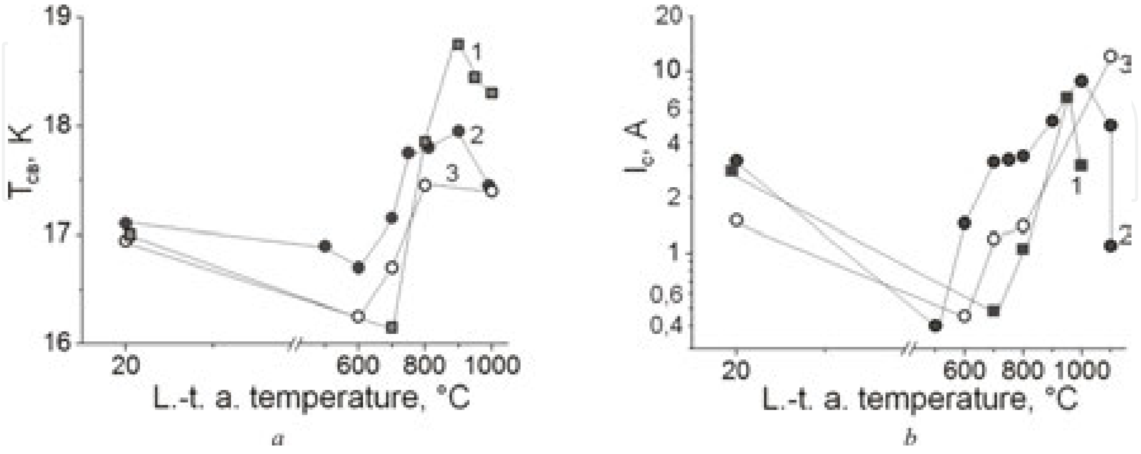


Figure 25. Critical temperature T_{CB} (*a*) and the critical current I_c in magnetic field of 5 *T* (*b*) for the tapes of Nb_3Al depending on temperature of l.-t. an. Time of the annealing – 2 *h*. Temperature of h.-t. h., °C: 1 – 1850, 2 *s*; 2 – 1850, 3 *s*; 3 – 1950, 3 *s*.

Dependencies T_{CB} on the annealing time were of two types (**Figure 26**).

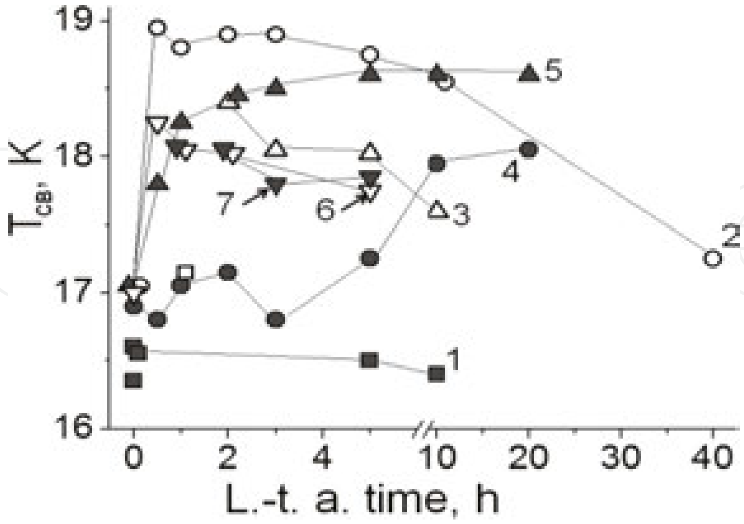


Figure 26. Dependencies of the critical temperatures T_{CB} on the time of l.-t. an. for tapes Nb/Al/Nb and Nb/Al30Ge/Nb (2). Temperature treatment, °C: 1 – 1750, 3 *s* + 1000; 2 – 1850, 2 *s* + 900; 3 – 1850, 2 *s* + 1000; 4 – 1850, 3 *s* + 700; 5 – 1850, 3 *s* + 800; 6 – 1850, 3 *s* + 900; 7 – 1950, 3 *s* + 900.

1. At annealing temperatures of 700 and 800°C (curves 4 and 5) the critical temperatures monotonically increase and, reaching a maximum, remained on constant level.
2. The tapes, annealed at 900°C (2, 6, and 7) have a gently sloping maximum. Pronounced maximum was of sample with temperature of annealing at 1000°C (3). Their T_{CB} came back after 5 hours annealing to a level of the critical temperatures for the samples not subjected to annealing. It is very likely that the rise, a maximum and drop of T_{CB} have occurred earlier than 5 hours (1). The time at which the maximum values of the critical temperatures were reached, with the increasing of annealing temperature was decreased. At 700 and 800°C maximum of T_{CB} advanced, after annealing for 10 and 3–5 hours. At 900°C was after a half-hour annealing.

To trace the dependencies of the critical currents on the annealing time for the samples with the same regimes of the high-temperature heating failed. From all the number of measurements, it is possible to confidently state that only the general level of I_c values increased after 10 hours of the annealing.

4.9. Low-temperature annealing – a necessary tool to enhance critical temperature and critical current of compounds Nb_3Al and Nb_3AlGe

As a result of the low-temperature annealing in the range of 700–1000°C in the layers of superconducting compounds Nb_3A land Nb_3AlGe should be observed in two processes:

- an increase of order degree in the arrangement of atoms in knots of the crystal lattice and
- decay with allocation σ-phase, due to the non-equilibrium of resulting β-phase.

If the initial and final crystal structures of the compounds are though somehow the same type, the ordering process consists of an exchange of atoms places and does not require diffusion over long distances. The rate of process depends on the temperature and by the parameter of the estimation of speed its change will the change T_{CB} on time and temperature of annealing. The rate of process depends on the temperature. Then the change T_{CB} on time and temperature of the annealing will be the parameter of the estimation of speed its change. Effect of ordering on T_{CB} of Nb_3Al and Nb_3AlGe is reflected by curve 1 in **Figure 27**. The maximum established Nb_3Sn and V_3Ga, is located at 700–750°C. For similar compounds of niobium with aluminum, it is achieved at somewhat higher temperature, about 900°C (see **Figure 25*a***). It is thought that the ordering processes are actively occurring in the initial stage of annealing. Since the diffusion mobility of atoms increases with increasing temperature, then and T_{CB} reach their maximum values at a given temperature in more short time – at 900°C for 30 minutes, at 700°C for 10–20 *h* (see **Figure 26**, curves 4 and 6).

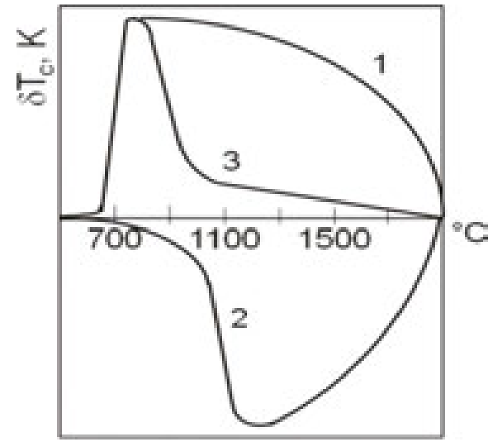


Figure 27. Change the critical temperature T_c depending on the annealing temperature under the influence by the degree of ordering (1) and the equilibrium composition (2): 3 - summary curve.

Precipitation of σ-phase, in contrast to the ordering process should reduce T_{CB} (see **Figure 27**, curve 2). It was already mentioned that in the systems of Nb–Al and Nb–Ge, the temperature boundaries of homogeneity areas of β-phases are changed and so the percentage composition of phases also changed. Characters of the change in composition such that:

- at 1700°C Nb_3Al stably in the ranges of 23–26 at. % Al, at 1000°C – in the ranges of 19–23 at. % Al;
- Nb_3Ge is stable with compositions that are far from the stoichiometric, namely, at 1700°C – in the range of 16–19 at. % Ge, at 1000°C – in the ranges of 15–18 at. % Ge.

Therefore, at low-temperature annealing Nb_3Al- and Nb_3AlGe-phases necessarily are undergoing the disintegration with a precipitation of σ-phase. A matrix consisting of β-phase is depleted with aluminum or aluminum and germanium, resulting in the removal of β-phase composition from stoichiometric composition and decrease of T_{CB}.

The present study shows that in the tapes of Nb_3Al at 2 hours of exposures at annealing up to 900°C, the ordering affects to a greater extent than the process of decay. The ordering completely is dominated at relatively long annealing in the range of 700–800°C. Falling of T_{CB} in this temperature range is not observed at exposure up to 20 hours (see **Figure 26**, curve 5). This accounts for the decrease of T_{CB} beginning from 900°C observed on its annealing temperature (see. **Figure 25*a***) and on depends on the annealing time at 900°C (see **Figure 26**, curve 2).

Unlike the critical temperature, the critical current is important in the decay process since it is accompanied by the precipitation within the grains of the superconducting phase particles of σ-phase which, together with the boundaries of the grains should be additional superconducting vortex pinning centers. In the scientific literature on superconducting materials the fastening of vortices accepted to call "pinning" and fastening centers – "pinning centers". Therefore, I will continue to use this term.

Stages of decay process with the precipitation of σ-phase particles, how they appear to us, will be considered later. Here the same we note the following. For vortex pinning more favorable is the stage when the final phase (in this case – it σ) becomes incoherent with the matrix (β-phase), that is, when there is the interphase boundary. By this explains the earlier marked shift of the critical current maximum on 50–200°C with respect to the maximum of critical temperature towards higher temperatures l.-t. an. (see **Figure 25*a*** and ***25b***). It can be assumed that after 2-hour annealing at 900°C, particles of σ-phase are the intermediate product coherently associated with β-matrix, although it already have a tetragonal structure and a composition near to composition of equilibrium precipitates. This stage of the disintegration process is critical for T_{CB}. Matrix is already enough depleted in aluminum in order for T_{CB} to drop, but still is such that the ordering remains predominant. At this stage, the pinning force on σ-precipitates has not yet reached the maximum value. Its maximum will come at a temperature slightly higher when the particles of σ-phase will separate and the interphase boundaries are formed. But, becoming isolated, σ-particles begin to grow and rapidly to coagulate. The particles size becomes more than the efficient size from the standpoint of the pinning. Upon reaching the maximum value, the critical current drops sharply.

The minimum of I_c at 500–700°C (see **Figure 25*b***) explained by a simple removal of thermal stresses in the diffusion layer of β-phase, typically occurs at low temperatures of the annealing.

Explanation of complex dependencies of the critical current and the critical temperature on regimes of low-temperature annealing, and even earlier, and increasing the upper critical magnetic field as a result of l.-t. an. are based on classical concepts that the non-equilibrium alloys until the formation of the precipitates during annealing was preceded changes inside of a supersaturated solid solution (matrix). By Genie with employees on the basis of results of the analysis of a thin X-ray structure studies first it was concluded about education of the certain zones at a very early stage of decay process.

1. Initially are formed Genie-Preston zones 1 which were presenting itself areas of matrix with an increased content of the dissolved element but with the same arrangement of atoms as in the matrix. The difference in the size of components atoms initiates an occurrence of distortion of the crystal lattice around the area. Exactly by the existence of

significant distortions in matrix are explained diffraction effects, which were observed in the study areas. In our case the matrix was been by β-phase supersaturated with an aluminum or aluminum and germanium.

2. In the process of annealing in zones, a new crystalline structure corresponding to arrangement of atoms in the crystalline structure of precipitates (tetragonal – for the case of decay β-phase) is formed. The precipitates on the second stage of the low-temperature annealing or Genie-Preston zones 2 are similar to the coherent precipitates. While they are not in equilibrium and represent itself an intermediate product coherent with the β-matrix and having tetragonal structure and composition near to the composition of the equilibrium precipitates σ-phase . In the supersaturated solid solutions, such zones (clusters) are formed very quickly with the most significant changes in the physical properties taking place till the fixed structural changes.

   When implementing such mechanism disintegration of β-phase, a decrease in mean length of free path of electrons in a normal state must occur at these two stages of the structural changes in β-matrix. At relatively low 750–800°C, temperatures of the annealing the disintegration β-phase was not completely realized.

3. Increase annealing temperature to 900–1100°C leads to the formation of the final σ-phase. It is already non-coherent with the matrix. Phase boundaries were formed, leading to a marked increase in the critical current.

So our reasoning on the effect of low temperature annealing on superconducting characteristics of tapes compounds Nb_3Al and Nb_3AlGe can be summarized in the following.

1. The stage of disintegration with the formation of Genie-Preston zones 1 and 2:
   - increase of the upper critical magnetic field H_{c2}, due to a decrease in mean length of free path of electrons in a normal state l_e;
   - increase of the critical temperature T_{CB} due to the predominant influence of the ordering process in comparison with the process disintegration;
   - a small increase of the critical current I_c.
2. Stage of disintegration of with the formation of σ-phase:
   - maximum of I_c;
   - drop of T_{CB} in resulting of depletion β-phase toward aluminum or aluminum and germanium.
3. Coagulation stage of particles σ-phase: drop I_c because of that the size of σ-precipitates become larger its optimum size with point of view for the pinning of superconducting vortices.

Likely the results of the local X-ray spectral analysis, which inflicted on the fragment of the triple phase diagram Nb–Al–Ge (**Figure 28**) correspond to one of three stages beta-decay in the tapes of superconducting compound Nb_3AlGe.

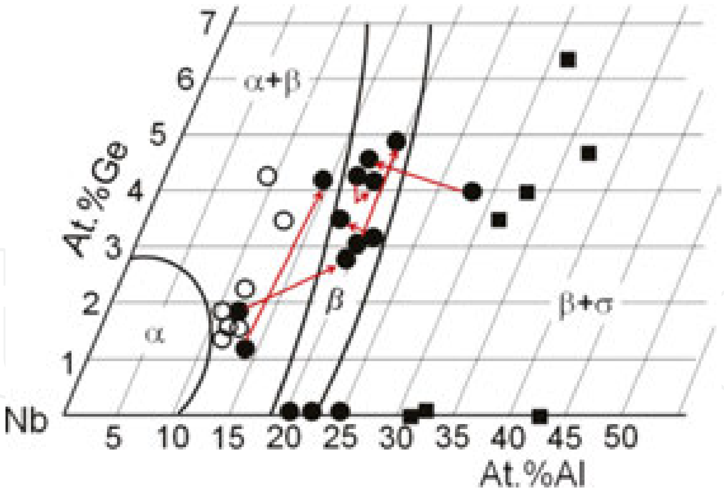


Figure 28. Isothermal section of the niobium angle of state diagram of the system Nb–Al–Ge at 1000°C: ○ – α, ● – β, ■ – σ. Heat treatment, °C: 1800–1900, 3–20 *s* + 800, 2 *h*. The changing of the phase contents of elements in β-phase after Low-temperature annealing is shown by arrows.

It is unclear why points that concerns the β-phase, after high-temperature heatings found themselves on either side of its region of existence. It is important to note that the "β-points" are going to the existence region of β-phase. But the points of β-phase, which already before the annealing were in its homogeneity region, were moving within it. According to the selected time and temperature of the annealing, and a change in the content of elements in the β-phase can be assumed that the ordering here was the dominant process.

4.10. Conclusions

1. The diffusion layers of compounds Nb_3Al and Nb_3AlGe in three-layer composite tapes Nb/Al/Nb and Nb/AlGe/Nb with high superconducting characteristics with thickness of 1–2 microns are formed at temperatures of 1750–1850°C for 2–3 seconds. In these cases, the diffusion layers, in addition to β(Nb_3Al)- or β(Nb_3AlGe)-phase, are also σ(Nb_2Al)- or σ(Nb_2AlGe)-phase and also σ- + γ($NbAl_3$)- or σ- + γ[$Nb_5(AlGe)_3$]-phases. With the increase of heating time, the thickness of the β-layer was increased. The diffusion layer only consisted of one β-phase after the heating during 5 seconds. After the heat treatment, tapes were flexible and able to bend with a certain radius without destroying the superconducting layer.

2. For Nb/AlGe/Nb tapes dependencies of the critical temperature and the upper critical magnetic field from the germanium content of the alloy Al–Ge were studied. The best parameters of superconductivity were observed in tapes with an alloy of 40 to 50 wt. % Ge.

3. An influence of regimes the low-temperature annealing was investigated for tapes Nb/Al/Nb. It is shown that there is a principle possibility by choosing regime of the annealing to increase the critical current of tapes by 2–3 times, compared to non-annealed tapes. Dependencies T_{CB} and I_c from time and temperature of annealing are explained by the

laws of reactive diffusion and by features of the diagrams state of systems Nb–Al and Nb–Al–Ge.

4. It is found that the critical current and critical current density j_c decrease with increasing layer thickness of β-phase. Their highest values are reached in tapes with layers of β-phase, with thickness of 1–2 microns. With the help of metallographic analysis for samples of Nb_3AlGe it is found that with the increase in thickness of β-layer, the average size grain of the compound is increased. This was the reason for the fall of j_c at the growth of thickness of the layer of β-phase.

5. It is established that at low-temperature annealing of the samples Nb_3AlGe, 750°C for 50 h, the slope of the straight $H_{c2}(T)$ near T_c is increased with 3.3–3.5 to 3.8 *T/K*. Then, the calculated values of $H_{c2}(4.2\ K)$ are reaching ~50 *T*. The increasing H_{c2} as compared with samples without annealing was the consequence of the decrease in mean length of free path of electrons in a normal state l_e. The decrease l_e is explained in the light of the Genie-Preston theory about the decay of supersaturated solid solutions.

6. Tapes Nb_3Al and Nb_3AlGe, made according to the best regimes have values of the superconducting parameters are presented in **Table 5**.

The tape	**T_{CB}, K**	**$H_{c2}(4.2\ K)$, *T***	**At 4,2 K in field поле 5 *T***	
			I_c, *A/mm*	**j_c in β-layer, *A/cm²***
Nb/Al/Nb	18.0–18.5	30	7.5	$2\cdot10^5$
Nb/AlGe/Nb	19.5–20.2	43	1.5	$9\cdot10^4$

Table 5. The values of the superconducting parameters of the tape samples from Nb_3Al and Nb_3AlGe compounds prepared according to optimum regimes of heat treatment.

5. Influence of copper on the structure and critical current of superconducting tapes from Nb_3Al

5.1. Samples and determination method of the grain size of β-phase

Studies were performed on composite tape that was produced by joint rolling of two plates made of niobium and one plate of an alloy of Al–Cu. Aluminum alloys with a sufficiently high content of copper are not deformed by rolling without breaking. Therefore, the concentrations range of copper in alloys Al–Cu was from 0.7 to 12 wt. %. The width of the tape is 2 *mm*, the thickness – 50 *μm*. To obtain layer Nb_3Al tape was heat treated by mode: 1650°C for 20 and 30 *s*, 1750°C for 3 and 5 *s*, and 1850°C for 3 *s*. Then annealing at 800°C for 2 hours was followed.

The grain size of the β-phase was determined on surfaces of the tapes parallel to the rolling plane. For this, surfaces was ground and polished until appearance of the intermetallic compound layer. Polishing and successive etching was performed several times. The layer β-phase is bordering on niobium. A layer of β-phase borders with niobium. But to distinguish β-phase from niobium was easy, since niobium is not etched at those times at which layer of β-phase is etched. Etching time was 5–10 seconds.

Furthermore, measurements of micro hardness showed that micro hardness of niobium considerably smaller micro hardness of portions β-phase. To reveal the grain boundaries of β-phase, chemical reagent of equal parts of hydrofluoric and sulfuric acids and water with a small amount of hydrogen peroxide was used. The grain size was calculated through "cutting".

5.2. Critical current

The best results were obtained in tapes with the heat treatment at 1850°C. A critical current I_c equaled 38 *A* is observed in samples with alloy Al–12 wt. %Cu in the magnetic field of 5 *T*. After heating at 1650 and 1750°C I_c are smaller.

Dependence of I_c on the alloy composition of Al–Cu must divided into two regions (**Figure 29**). The area 2 is the increase in critical current of tapes with increasing concentration of copper from 4–8 to 30–38 *A*. The area 1 is the same, but has the values of I_c are much lower – I_c is increased from ~1.5 to 3.7 *A*. The width of tapes is of 2 *mm*.

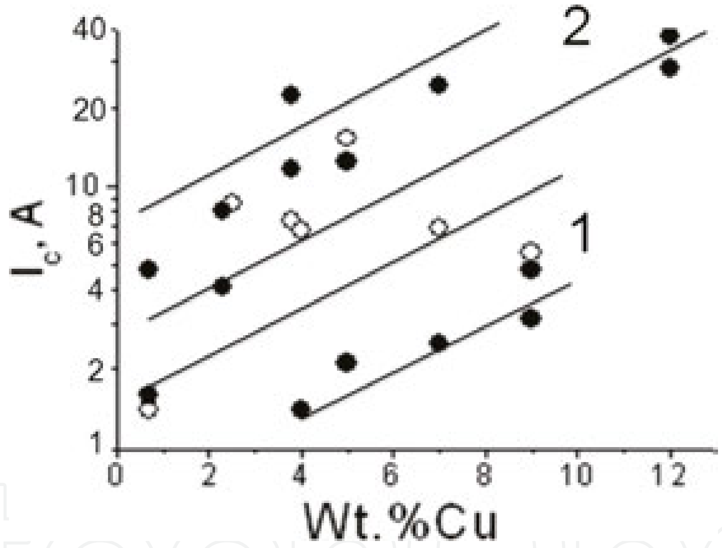


Figure 29. The critical current I_c of Nb/AlCu/Nb-tapes on the copper content in magnetic field of 5 *T* and at 4.2 K after the h.-t. h 1850°C for 3 *s* (○) and the same as + 800 for 2 *h* (●): 1 – samples with the diffusion zone of the β-phase, 2 – samples with zone of β + α. The width of tape – 2 *mm*.

5.3. Discussion

The existence of two ranges of critical current values is explained by the different microstructure of the diffusion zones in the samples. In samples of the first range the diffusion zone consists of only layer β-phase (**Figure 30*a***), samples in the region 2 have the diffusion zone out of the two layers β(Nb_3Al)-phase and one layer σ(Nb_2Al)-phase (**Figure 30*b***). Copper is present in the layer β-phase in quantity of 0.1–0.2 % if the diffusion zone is two-phase and 0.7 wt. %, if it is a single-phase.

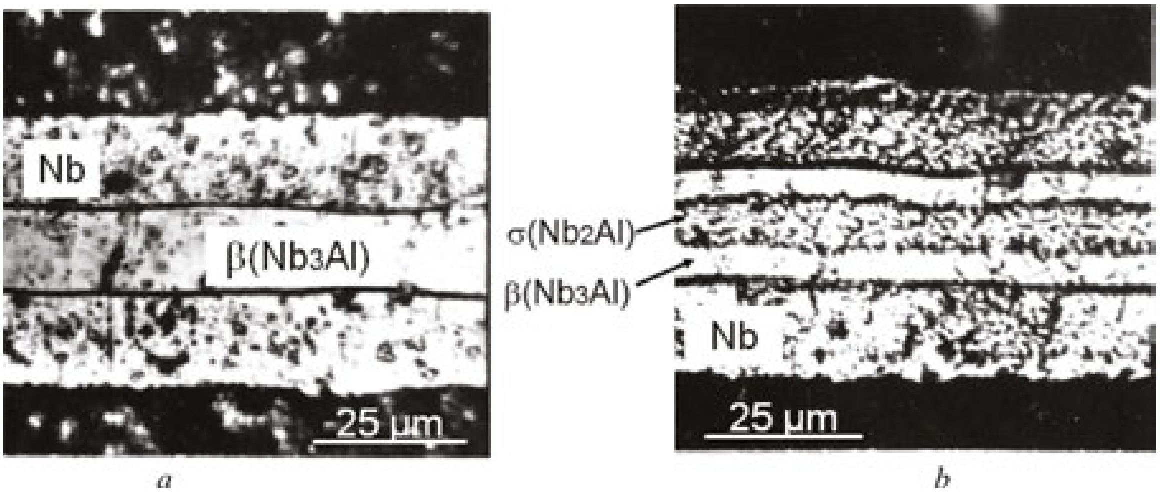


Figure 30. Microstructure of the cross-sectional Nb/AlCu/Nb-tape, wt. %Cu: *a* – 5, *b* – 12. Heat treatment: 1850°C for 3 *s* + 800°C for 2 *h*.

The diffusion region is one third the volume of the tape. It can be observed that after high-temperature heating for 3 *s*, the diffusion zone can consist of two layers of β-phase with a thickness of 5 *µm* and one σ-phase layer with a thickness 8.6 *µm* so and only one layer of β-phase with thickness 13–15 *µm*. Such cases are explained by deviations of ratio Nb-thickness to the thickness of the alloy Al–Cu along the length of the tape and the inaccuracy of compliance 3 seconds exposure at heating. At the second exposure, even a slight deviation could lead to significant deviations of the microstructure of the diffusion zone.

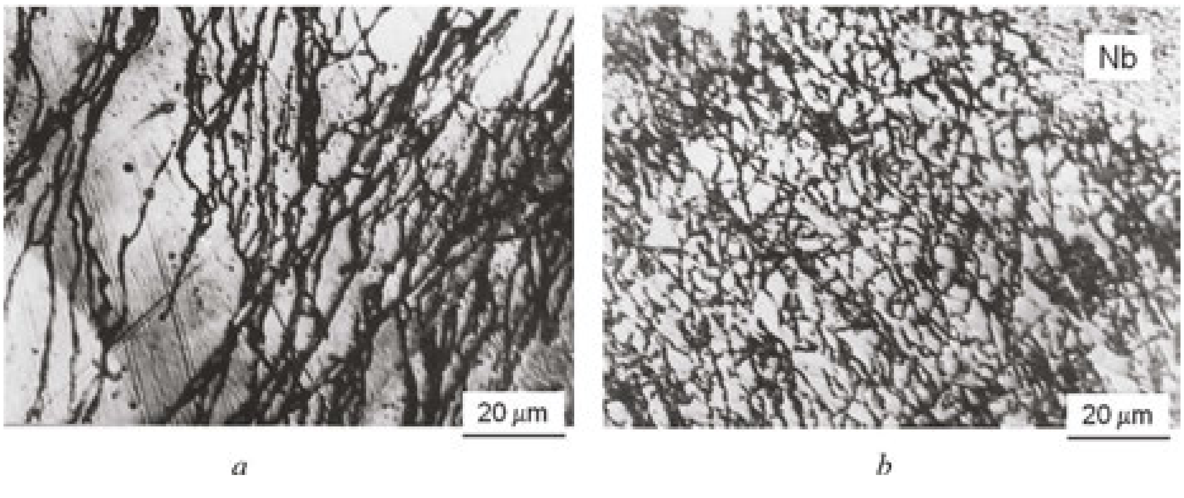


Figure 31. The microstructure of β-phase layer in a plane parallel to the rolling plane of the tape Nb/AlCu/Nb after h.-t. h.: 1850°C for 3 *s* and l.-t. an.: 800°C for 2 *h*. Visible small area of no etched Nb, wt. %Cu: *a* – 5, *b* – 3.8.

Metallographic studies showed that the average size of grains of intermetallic compound Nb_3Al D for the samples which belong to the one- and the two-phase areas are significantly differed. The grains of β-phase in samples out of zone 1 are greatly differed in size and many of them are elongated along the rolling direction (**Figure 31*a***). In the direction of the minor axis, the average grain size of β-phase is equal to 4 *μm* and in the direction of the major axis it is equal 25–30 microns. The grains of β-phase in samples from second zone were significantly smaller (**Figure 31*b***).

It is known that the pinning of the superconducting vortex in compounds A15 occurs mainly at grain boundaries. Here, it can be seen that though the copper improves the critical current of tape, but the transition from two-phase structure of the diffusion zone (β + ▽) to a single phase dramatically reduces the critical current, since the size of grains has become much greater.

The critical current density j_c for the tape with the alloy of Al–12 wt. %Cu and with the maximum I_c, equaled to 39 *A*, is $1.35 \cdot 10^5$ *A/cm*^{2} in the β-layer with thickness of 5.5 *μm* (**Table 6**). Note that in the tape with aluminum in β-layer of the same thickness j_c was equal to ~$6 \cdot 10^3$ *A/cm*^{2}. The increase in critical current density of layers Nb_3Al doped with copper is due to fineness of compound grains. The method we used for determining the grain size D has allowed to receive β-phase accurate value D ~ 3 *μm* (see **Figure 31*b***). In samples with pure aluminum, D was 7–8 *μm* [10].

The tape	The thickness of β-layer, *μm*	5 *T*; 4.2 K; H ⊥ I	
		I_c, *A/mm*	j_c in β-layer, *A/cm*^{2}
Nb/Al/Nb	1.5	5.0	$1.7 \cdot 10^5$
Nb/Al/Nb	5.5	0.7	$6.0 \cdot 10^3$
Nb/AlCu/Nb	1.5	17.0	$5.7 \cdot 10^5$
Nb/AlCu/Nb	5.5	14.5	$1.3 \cdot 10^5$

1. Notes: I – transport current in the sample.
2. In the calculation should take into account the two β-layers.

Table 6. The influence of the thickness of the β-layer on I_c and j_c.

The result of the alloying of β-phase by copper deserves special attention since the critical current and critical current density with increase of β-layer thickness is reduced much smaller than in samples which do not contain copper. This is shown in **Table 6** – an increase of the thickness of β-layer from 1.5 to 5.5 *μm* is causing a decrease of j_c in the tapes with aluminum at about ~30 times but in the samples with copper – only at 4–5 times.

5.4. Conclusions to section

1. The influence of copper on the current carrying capacity Nb/Al/Nb- apes was investigated. Copper was added to the aluminum in the concentration range from 0.7 to 12.0 wt. % and tape Nb/AlCu/Nb was examined. The value I_c is increased to 19 *A/mm*, the critical current density in a layer of β-phase with thickness ~1 *μm* – to $5.7 \cdot 10^5$ A/cm^2. In samples out of the tape without copper, with the conditions of being equal, I_c was equaled 7.5 *A/mm* and j_c – $2 \cdot 10^5$ *A/cm*^{2}.

2. The increase of I_c in the samples with copper due to the fineness of grain β-phase. In the samples with the alloy Al-12 wt. %Cu it was 3 *μm* after the high temperature heating by regime: 1850°C for 3 *s*. In the tapes without copper D was more than 8 microns.

3. In layers β-phase copper-doped the critical current density with the increasing of β-layer thickness is reduced to a much lesser extent than in β-layer does not contain copper.

6. Manufacture, structure and critical current of multilayer Nb_3Al

We would like to summarize the presented research in the following form:

I. The effect of copper on T_c of diffusion layers Nb_3Al is as follows. Firstly, T_c for samples with the addition of copper equalled to 18.6-18.8 K, is somewhat higher than in the samples without copper, and secondly, the high values of T_c were achieved after heat treatment at 1650°C, 20–30 *s* + 800°C, 2 *h*. The samples without copper after this treatment regime had T_c from 17.0 to 17.7 K. This suggests that copper makes the formation temperature of stoichiometric Nb_3Al less on 150–200°C.

The lowering of the formation temperature of the compound Nb_3Al is important to achieve a high current-carrying capacity in its layers because that the heating of a tape in the range of 1850–1950°C, even for a few seconds, is causing a rapid growth of β-phase grains. It was shown (see **Figure 24**) that the critical current density decreases with ~10^5 to $2 \cdot 10^3$ *A/cm²* in magnetic field 5 *T*.

II. The second conclusion is based on the first one. In terms of the formation of compound Nb_3Al by reactive diffusion for reducing the building time of its layers, it is advantageous to have small diffusion distances, which will be overcome by aluminum atoms. Taking into account that the aluminum atoms before meeting with the niobium surface, it must be overcome the distance equal to the thickness of $\sigma(Nb_2Al)$-phase layer formed earlier let us estimate the thickness of Al-interlayer in the composite Nb/Al-tape in order to the formation of β-phase at 1000°C for 10 *h*. Solving the second diffusion equation for final of the body in the assumption that the thickness of β-layer will be equal to 1 micron, we find that the thickness of Al-interlayer to be 0.6 *μm*. The diffusion coefficient is ~$7 \cdot 10^{-14}$ cm^2/s [8]. Layers of aluminum with such thickness can be obtained in multilayer tapes by rolling.

III. An advantage of the multilayer tape in comparison with the three-layer tapes consists of the possibility to create in tape the structure of alternating layers from superconducting compound and niobium (strictly speaking – solid solution of aluminum in niobium). In the multilayer tape with large number of layers Nb_3Al and due to their mutual shunting the critical current will be not sensitive to change in the thickness of β-layers or even to their local discontinuities. However, the mechanical properties of aluminum and niobium are very different. Therefore, to achieve laminar (right) structure along the rolling direction is challenging enough. Therefore, instead of aluminum for the manufacture of multilayer tapes Nb_3Al, it was decided to try an industrial aluminum alloy with 4.4 wt. %Cu of class D16. It is more durable than pure aluminum at room temperature.

6.1. The initial preform

Thus, to improve the process of joint deformation of metal components of the composite for the obtaining of the multi-layered tapes was used duralumin D16 instead of pure aluminum.

The starting preform for extrusion was assembled as follows. Niobium strip 0.25-0.30 *mm* thick and duralumin ribbon 0.06-0.09 *mm* thick were folded together, and by means of special clamping device tightly wound on Nb-rod with diameter 10 *mm* until an outer diameter of the received twist equal 35 *mm*. The twist was placed in thick-walled Nb-tube and the whole assembly was laid in the Cu-glass with an outer diameter of 75 *mm*. The glass was closed densely with copper lid. The fully assembled preform had height of 100 *mm*. Copper at the extrusion is fulfilled a useful role of lubricant, as niobium have an ability to stick on the walls of a tool.

An extrusion of copper glass with embedded in it a twist happens so, that niobium and duralumin tapes are drawn out across the direction of their rolling. Mechanical tests on stretching for specimens of the deformed cold Nb-tape cut transversely and along its rolling (**Table 7**) shown that an elongation $\delta_\perp$ in the direction perpendicular to the rolling direction was equal to only 0.4%. Therefore, to improve ductility of the metal foils Nb-foil prior to winding in twist was annealed at 1100°C and the duralumin foil was annealed at 400°C for 1 *h* and quenched. Then $\delta_\perp$ of Nb-tape was increased to 9–10%.

Heat treatment, °C	**Along the rolling direction**			**Across the rolling direction**		
	σ_b, *MPa*	**σ_t, *MPa***	**$\delta_{\|\|}$, %**	**σ_b, *MPa***	**σ_t, *MPa***	**$\delta_\perp$, %**
deformed at 99%	520	340	3.0	390	260	0.4
1100, 1 *h*	255	180	22.0	265	140	9.0
1100, 5 *h*	250	190	23.0	260	150	10.0

Table 7. The mechanical properties of niobium foil: σ_b – ultimate strength, σ_t – yield strength, $\delta_{||}$ and $\delta_\perp$ – elongation of Nb-foil in a direction parallel and perpendicular to the rolling direction respectively.

The extrusion of preforms were conducted on a hydraulic press with a maximum force of 630 tons in a container of diameter 76 *mm*. Before the extrusion preforms were heated to 200-300°C in air. As a working tool the matrix with channel of 30 *mm* diameter was used. The obtained rod is cut into chunks, which in the first experiments extruded again into rods of 10 *mm* diameter and in the subsequent experiments – into billets (sutunkas) ~6×20 mm^2. A macro-structure of the cross-section of one of them is shown in **Figure 32**. Rods and billets were rolled at the room temperature to 50–70 *μm* thick tape without intermediate annealing. On one of the initial stages of rolling both edges of the band were cut off and the outer Cu-covering quite easily was removed by mechanical means. To facilitate the last operation, the inner surface of the cupper glass before the assembly of billet for extruding was lubricated with fine powder alumina. The edges were cut off using a disc scissors.

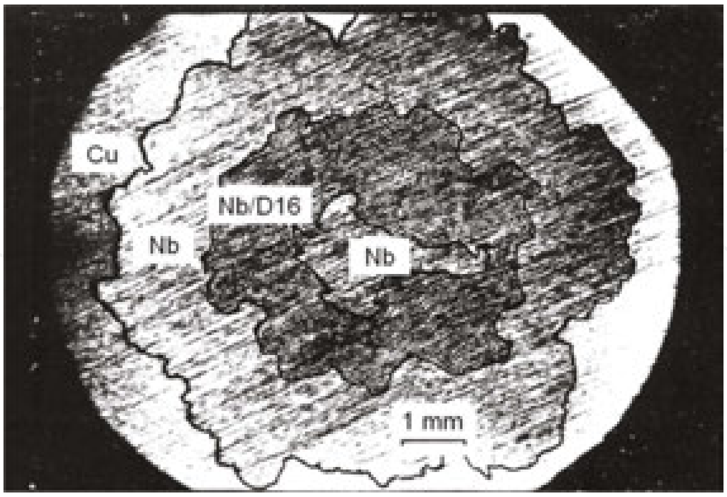


Figure 32. Macrostructure of the Nb/Al-rod cross-section in Cu-shell diameter of 10 *mm*.

For the formation of Nb_3Al-layers samples of the tape were subjected to heat treatment in a vacuum: high-temperature heating + low-temperature annealing. For research purposes, high temperature heating of the multilayer tape was performed in analogy with the three-layered tapes – by direct passing of an electric current.

6.2. The microstructure of the multi-layered tapes

After rolling and cutting of edges tape had a width of 10–15 *mm*. To research a wide ribbon was cut into strips 2 *mm* wide (**Figure 33**).

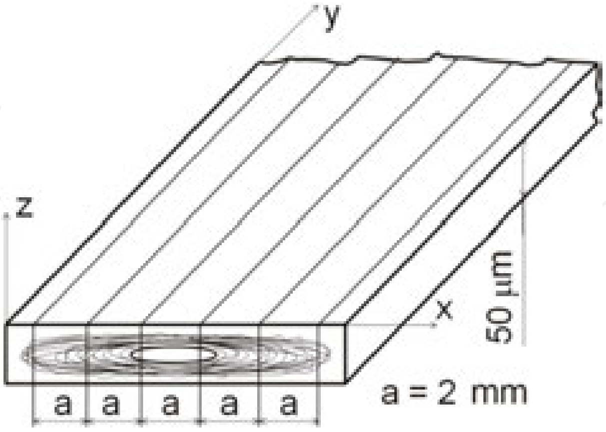


Figure 33. Schematic representation of the cross-sectional structure of a wide tape, being cut into tapes of 2 *mm* wide.

In the multilayer structure of the tape cross-section may be a three- and five-layer. If narrow ribbon was cut from the middle of a wide tape, in the cross section were two multilayer layers

Nb/D16 derived from the twisting, two outer wall layers of Nb-pipe and the middle layer of Nb-rod (**Figure 34*a***). Narrow tape was cut at a certain distance from the middle, have only three layers: the average Nb/D16-layer formed from twisting and two extreme Nb-layers formed from the walls of Nb-tube (**Figure 34*b***).

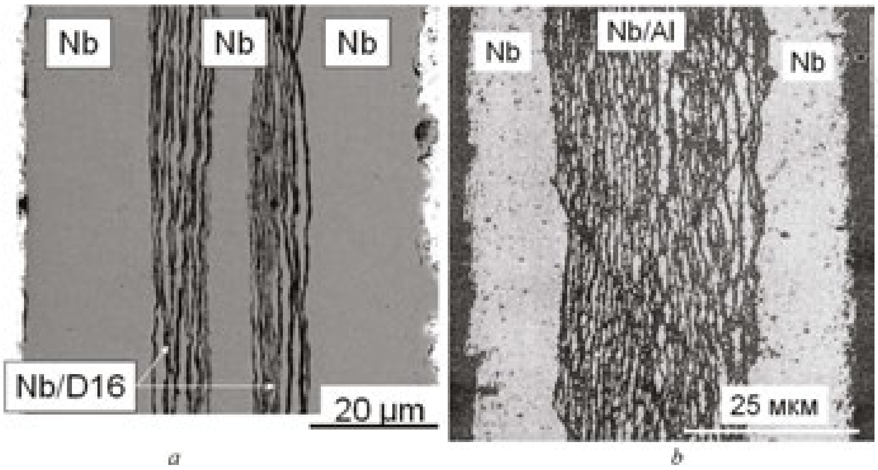


Figure 34. The microstructure of the cross section of the multilayer tape after rolling width of 2 *mm* cut from a wide tape in its middle (*a*) and at a distance from the middle of the (*b*).

After heat treatment at 1200°C for 30 minutes, the layers Nb/D16 transformed into a layered structure of two phases differing slightly light contrast (**Figure 35**). According to the local X-ray analysis in dark elongated areas was contained ~29.5 at. % Al, which corresponded to the σ-phase, in lighter areas was contained 18.7–19.9 at. % Al, which were been β-phase.

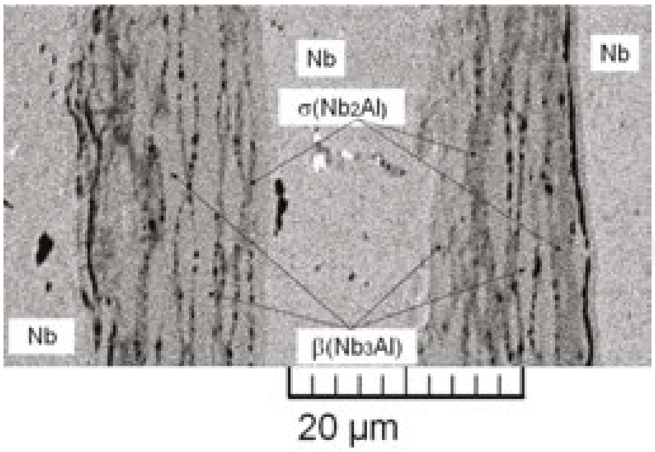


Figure 35. The microstructure of the cross section of the multilayered tape after heat treatment at 1200°C for 30 minutes.

After high temperature heating at 1850°C for 2 *s* in diffusion zone was only β-phase. Layers of diffusion zone were differed so little contrast from niobium layers. Therefore, for this it will show the concentration dependencies of niobium and aluminum over the cross section of tape

(**Figure 36**). In a tape of 2 *mm* width, cut from the middle of the wide band, clearly looked two layers of β-phase. In the tape cut at some distance from the center of a wide band, observed one β-layer with thickness approximately equal to the previous two layers.

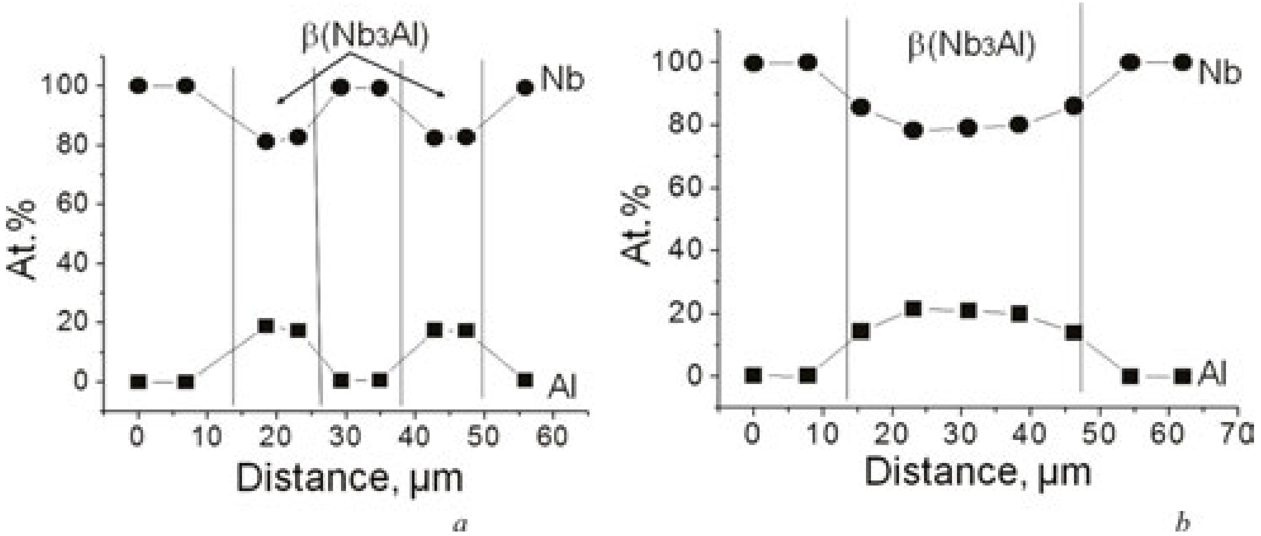


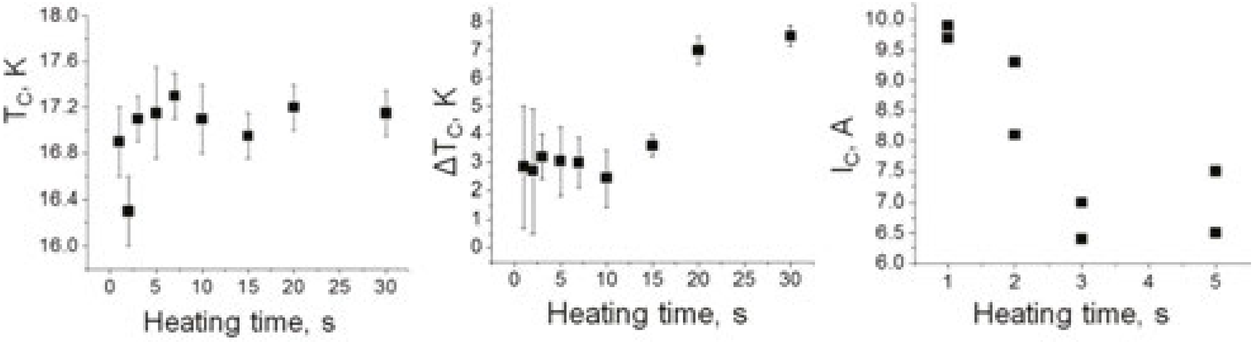
Figure 36. Concentration Nb- and Al-sectional profiles of multilayer Nb/D16-tape with a width of 2 *mm* after the heating at high temperature for 1850°C for 2 *s* cut from the middle of (*a*) and at some distance from it (*b*) of wide tape.

Concentration profile shows that the aluminum content of the β-layers is substantially less stoichiometric composition. It has changed from 17.5 to 21.5 at. %. But the values of the superconducting transition temperature after the heat treatment at such a regime were ~18 K. This indicated that the composition formed β-phase is close enough to 25 at. %. From this it can be assumed that in β-layer there are interlayers of niobium unreacted with aluminum, which is risen content of niobium in diffusion zone.

6.3. Superconducting properties of multilayered Nb/D16 tape after heat treatment at 1700°C

High temperature heating was conducted with times ranging from 1 to 30 seconds. Dependence of T_c and the width of the transition from ΔT_c from heating time are shown in **Figure 37**. Each value T_c and ΔT_c was calculated as the average of 6 samples. It is seen that the dependence of T_c on the heating time has slightly pronounced maximum after heating for 7 *s* equal 17.2–17.4 K when $\Delta T_c = 3.0$ K. However, after exposure exceeding 10 *s* the transition width abruptly is increased. This is indicative of "blurring" of the concentration of elements in the superconducting β-phase and the degradation of its superconducting parameters. On the curve of transition to the superconducting state, conforming to the sample with a 30-second heating, observe a broadening of Nb-transition toward lower temperatures. This is evidenced by the formation of a significant amount of solid solution of aluminum in niobium in a concentration sufficient to reduce the T_c of pure niobium.

The critical current I$_c$ were measured for a 2 *mm* wide strips cut from the middle of the wide tape. I$_c$ dependence on the heating time (**Figure 37*c***) showed that his best its values were observed in the samples after heating for 1 second and equal to 9–10 *A* in a magnetic field of 5 *T*. Increasing time to 3 and 5 *s* to reduced I$_c$ = 7 *A*.



a *b* *c*

Figure 37. The dependencies of the critical temperature T$_c$ (*a*), the width of the transition from ΔT$_c$ (*b*) and critical current I$_c$ at 4.2 K in magnetic field 5 *T* (*c*) of multilayered Nb/D16-tape on the heating time at 1700°C.

The upper critical magnetic field H$_{c2}$(0) and the slope $(-dH_{c2}/dT)_{T=Tc}$, depending on the heating time are changed respectively between 24 and 30 *T* and within 2.1–2.5 *T*/*K*. An additional 5-hour annealing at 800°C is increased H$_{c2}$(0) to 32–35 *T*.

7. Lengthy tapes Nb$_3$Al

The laboratory technology developed for the preparation of superconducting tape Nb$_3$Al can be successful if used for manufacturing and other functional materials, for example, alloys with shape memory effect or heat-resistant composite materials with a layered structure. It is somehow impossible to obtain monolithic preforms with the use of the rolling in vacuum – process much better than the cold welding using rolling at room temperature. But at the same time, this technology cannot provide the making of long superconducting tape at least 100 meters.

Furthermore, it was clear that the heating up to ~1850°C by direct passing of an electric current through the tape specimen, clamped in the fixed contacts, unacceptable for heat treatment of a lengthy tapes. From here, there were two big problems: to develop the technology of long pieces of the composite Nb/Al-tape and to create equipment for the high-temperature heating of ribbons in a continuous mode by manner "to passage".

More or less fully technology of manufacture of a multilayer tape of large length was described in [11]. But in that work multi-layered Nb/Al-tape was investigated with the aim of testing and heated as before – directly by passing an electric current through the sample. Here we denote the stages of technology and present the value of current-carrying capacity of the multilayer Nb$_3$Al-tape. The manufacture of tape was included: collection of the preform, its extrusion, and rolling at room temperature. First let us dwell on the hydro-extrusion for manufacture of the long multilayer tape of Nb_3Al.

7.1. Hydro-extrusion in production process of multilayer tape Nb_3Al

The high hydrostatic pressure has been widely use in a metalworking. Hydro-extrusion method is ideal for the cold processing of metal materials in general and composite materials in particular. Implemented through the hydro extrusion a comprehensive schema of high pressure allows to process the materials with a high degree of deformation without destruction and to deform the materials which in normal conditions difficult or not at all deformed. For the last the hydrostatic extrusion is the only possible way their processing.

In the manufacturing of superconductors using hydro-extrusion are solved two problems with the original rod-preform for the rolling from which must to obtain a long tape. This is its length and relatively small diameter of ≤10 *mm*. And especially actually it for the compounds with the structure of the A-15 is prepared by co deformation of dissimilar metals. The tape length is conditioned by the size of the rod-preform.

Conventional pressure by the extrusion of multilayer preform Nb/D16 cannot be affected by a high degree of deformation, for example, from 75 to diameter of 10–15 *mm*. In the process of pressing the workpiece warms up to the 200–300°C. The resistance of deformation due to such a low temperature is too large, and pressing of workpiece cannot be executed. But if the pressing been success to carry out, then due to the high reduction ratio the workpiece in the deformation zone so was heated that led to the melting of duralumin.

For obtaining of long pieces of multilayer tape Nb/D16, a tentative technological cycle was conducted using hydro extrusion, which consisted of the following steps: manufacturing-assembly of an original workpiece with diameter of 75 *mm*, conventional pressing of workpiece in rod with diameter ~30 *mm*, hydrostatic extrusion of it into a rod of 10 *mm* in diameter and a rolling of last rod into a strip. At the assembly of the initial workpiece, the thickness of copper glass wall was calculated so that after pressing it in the rod diameter of 30 *mm* and processing of the rod on the lathe to a diameter of 20–22.5 *mm* on it still remained the copper layer with thickness of 0.5–1.5 *mm*. Thereafter, rods were cut into bars 200 *mm* in length, which were subjected to hydro extrusion on an installation of the Institute of High Pressure Physics, Russian Academy of Sciences [12]. As a lubricant of rods before the extrusion is used ktiol CT-15 or MoS_2. Working matrix has the angle $2\alpha = 30°$, degree of deformation – 76%, the working pressure of a fluid is 12.5–16.0 *kbar*, final diameter of rods – 9 *mm*.

Hydro extrusion positively characterized at any of its stage, the multilayer preform is not required to pre-heat despite the great degree of deformation. The length of rods after hydro extrusion was ~0.8 *m*. It should be noted that the length of the starting bars at the pressing with the use hydro extrusion are limited by the size of the reception chamber which, if desired, can be increased. A meltdown of duralumin, located inside bar, was not observed as not been and discontinuities of the material as the whole.

After hydro-extrusion rods of 9 *mm* in diameter were rolled at room temperature without intermediate annealing's in the multilayer tape with the breadth of 10.5 *mm* and the thickness of ~50 microns.

7.2. Facility of the high-temperature heating of long Nb/D16-tapes

Thus, the scientific results have brought us a purely engineering task to create an apparatus similarly designed for the thermal treatment at temperatures higher than 1500 (one) for a few seconds (two) long (three) thin multilayer tapes Nb/D16 by mean of "to pass ". Others simply do not give . A description of such installations in the foreign and domestic literature of course did not meet. Itself task is hidden the solution of many complex issues – from the choice of the type and the material of the heating device to the sagging of tape due to its elongation under the influence of high temperature heating. Approximately similar can be found in Müller's research [13] of Nb/Al- and Nb/AlGe-tapes after the heat treatment at 1700–1900°C. As can be understood from a brief description of the method of heating, the latter is similar to the heating realized in the proposed installation.

The main components of high-temperature heating installation we developed are vacuum chamber, vacuum pumping system and the control unit. The vacuum chamber is made of pipe with an inner diameter of 300 *mm* horizontally laid on a welded frame, with chamber length is 800 *mm* (**Figure 38**). The ends of the chamber is equipped with flanges that can be opened. The end covers and the pipe itself have four viewing windows made of quartz glass for observing of movement and heating of tape. The pipe in its middle part has a water jacket for protection against thermal radiation emitted by the heating device. There were electrical insulation required from the hull, a pyrophyllit was used. Its details before the assembly were subjected to calcination at 1200°C for 2 hours.

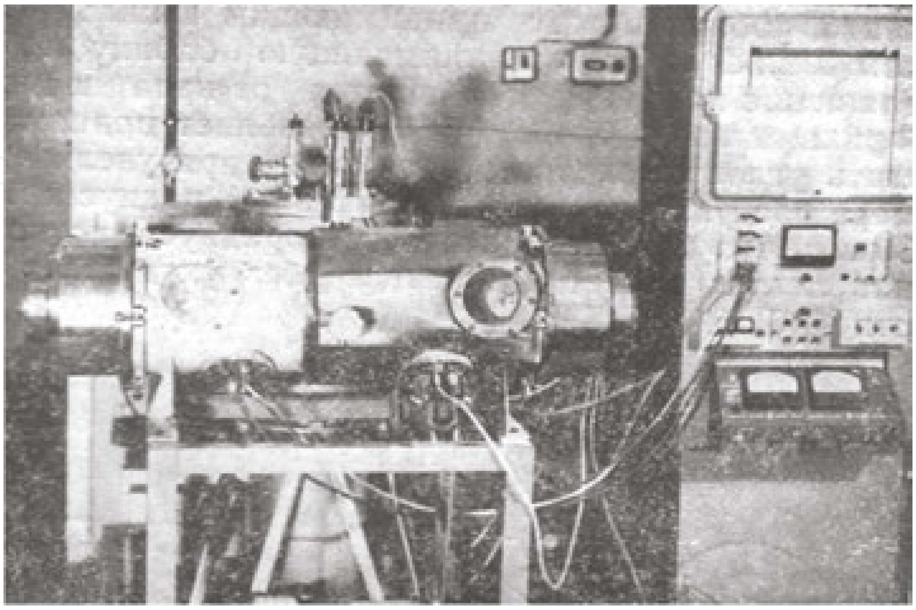


Figure 38. Installation for the high-temperature heating of the long multilayer Nb/D16-tapes.

A pressure in the chamber ~10^{-5} *mm Hg* was achieved within 40 mines with the moment of pumping the inclusion. In the process of high-temperature heating it was fallen, but not lower than the ~$5 \cdot 10^{-5}$ *mm Hg*.

7.3. Heating device

The heater is tantalum tube with a diameter of 10 and a length of 150 mm, welded out of the foil with thickness 0.3 *mm*. Copper bars are served at its ends and an electrical current of industrial frequency is discharged. The installed length of a working zone is 50 *mm*. To achieve temperature of 1800°C current flowing through the heater is ~200 *A*. To control the temperature of the heater, W-Re-thermocouple has been used, tucked away in the isolation of beryllium oxide. The signal from the thermocouple was fed to a regulator of temperature maintenance. The heater is surrounded by a system of screens collected from the W-foils.

The heater with screens for the isolation against walls of the chamber has been mounted on the pyrophyllite plate with thickness of 15 mm, which is fixed inside the chamber.

7.4. Kinematic scheme of tape passage

The movement of the tape was carried out by means of two pulleys (for supply and receiving coils). Their rotation was set by DC servomotors arranged on the same axis with the coils. On the way from the coil filled with tape (supply) to the receiving coil the tape, except heater, passes still through pinch, tension and guide rollers. By means of a reducer the speed of tape movement can vary in a fairly wide range. The friction device allows for the receiving coil reduce the angular velocity at an increase of the winding radius of the tape. An initial radius of winding is 30 *mm*. It exceeds the critical radius at which the tape after the heat treatment can be bent without affecting on the current carrying capacity of the tape.

7.5. The electrical circuit of installation

Passage of the tape through the heater (or rather the speed of passing) is adjusted automatically. Electric circuit of the speed regulator is built on the principle of the tracking system. It includes the following: a sensor, a control for the circuit of speed of servo motors, a high frequency

Figure 39. Apparatus for a speed control of tape passage.

oscillator, an amplifier, the subtracting device, power supply and a safety unit. Exterior view an apparatus which contains the entire electric scheme is shown in **Figure 39**.

Mismatch voltage of the two circuits depends on the bias of tape $\pm \Delta y$ relative to the average situation.

The sensor depends on the accuracy and stability of the whole tracking system. Specifically for the occasion, a proximity (noncontact) sensor is designed. It works on the principle of change of the coupling coefficient. The sensor represents two resonant contours, interacting on of differentiated communications. Contours are spaced apart at some distance. For protection against extraneous electromagnetic fields contours are enclosed in screens with cutouts facing each other. The tape moves freely between the contours and on it through the brush is transmitted a current from the high-frequency generator. The tape is the third circuit, generating its electromagnetic field of a certain frequency. And together with the two previous differentially coupled contours the ring circuit is obtained. As soon as the tape is shifted to $\pm \Delta y$ from the middle position between the first two contours a mismatch of their voltages arises.

The amplifier receives signals from the sensor, amplifies, filters, and transmits them to the inputs of the subtracted device and the safety unit.

A signal proportional to the displacement Δy of the walking tape is transmitted to the input of the subtracted device, is recorded and reproduced the micro ammeter, located on the front panel of the apparatus (see **Figure 39**).

If the heated tape is cut off, the safety device disables the amplifier and the subtracted device. Then the servomotors stops and a light signaling includes.

7.6. Test results of tape after heat treatment in continuous mode

Installation for heating high-temperature long pieces Nb/D16 layered strip in a continuous mode examined for three modes (**Table 8**). The output data was the critical current of tapes (**Table 9**). Alloy D16 is an industrial aluminum alloy with 4.4 wt. %Cu. The residence time of the tape portion in a working zone (zone length – 50 *mm*) was calculated from the rate of movement of the tape given by the receiving coil. Initial angular velocity ω of the coils was set depending on the linear velocity υ which is remained constant during the entire heating of tape for the selected mode.

Temperature of high-temperature heating, °C	ω, *turn./min*	υ, *mm/s*	Heating time, *s*	Performance, *m/h*
1700	0.2	0.8	62.5	2.9
1800	5.4	25.8	2.0	92.9
1800	8.6	39.0	1.3	140.4

Table 8. Modes of tape passage.

The first trial pieces of tapes 2 *mm* wide have a length of ~5.5 *m*. After the high temperature heating, from their middles cut out piece of ~3 *m* long, which was cut in half. The obtained pieces of tape 1.5 *m* long in its turn cut into six lengths of 250 *mm*. In threes such lengths of 250 *mm* from each of two 1.5 *m*-pieces of tape were selected for measurement of the critical current immediately after h.-t. h. in a continuous mode and for measurement I_c after h.-t. h. and subsequent low-temperature annealing at 800C for 3 hours. The l.-t. an. was performed in furnace of resistance at vacuum.

Mode of high-temperature heating, °C	**The average value of I_c, *A***		**The range of changes of I_c, *A***	
	Without the l.-t. an.	**800°C for 3 *h***	**Without the l.-t. an.**	**800°C for 3 *h***
1700, 62.5 *s*	1.1 ± 0.2	1.8 ± 0.3	0.4 ÷ 1.8	1.2 ÷ 2.6
1800, 2.0 *s*	4.1 ± 1.5	71.0 ± 12.0	1.8 ÷ 11.0	36.0 ÷ 96.0
1800, 1.3 *s*	10.8 ± 4.0	106.0 ± 8.2*	4.1 ÷ 27.5	92.0 ÷ >120

*For samples which became non-superconducting

Table 9. Results of measurements of I_c of tape Nb_3Al (5.5 *T*, 4.2 K, tape width – 2 *mm*).

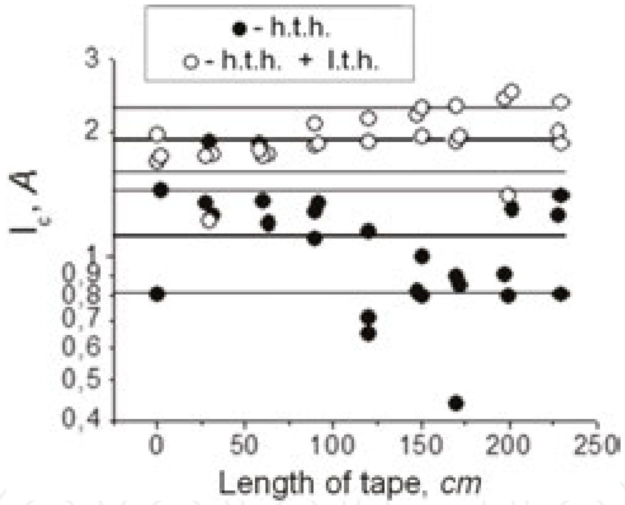


Figure 40. The values of I_c of the tape after h.-t. h. at 1700°C for 62.5 *s* (υ = 0.8 *mm*/*s*): ● – without the l.-t. an. and ○ – after l.-t. an. at 800°C for 3 *h* (5.5 *T*; 4.2 K).

From each 250 *mm*-part of the tape, 9–10 samples of the length 15 *mm* for I_c were selected. Three parts of tapes intended for the measurement of critical current only after heating and three after heating and annealing. Therefore, the average value I_c, in **Table 9** is calculated from samples in an amount of from 54 to 60 taken from a piece of tape 1.5 *m* long.

The values of I_c along the length of the three 250 *mm*-parts of tape, heat treated for one of three modes are summarized in a single graph and presented in **Figure 40**–**Figure 42** respectively. Heating at 1700°C for 62.5 seconds gave a small critical current value I_c, equal to about ~1 *A* in a magnetic field of 5.5 *T*. Low-temperature annealing increased the critical current twice (see

Figure 40). Judging by our studies [14, 15], heating for 1 minute at 1700°C is far from optimal. It may be assumed that layer of compound Nb_3Al is not continuous. Most probably the β-phase preserved only as islands and strongly depleted by aluminum. Most of the tapes volume has already turned into a solid solution of Al in niobium.

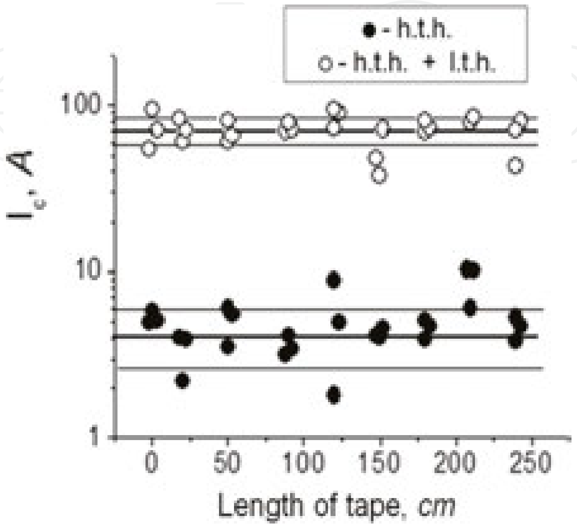


Figure 41. The values of I_c of the tape after h.-t. h. at 1800°C for 2 *s* (υ = 25.8 *mm/s*): ● – without the l.-t. an.) and ○ – after the l.-t. an. at 800°C for 3 *h* (5.5 *T*; 4.2 K).

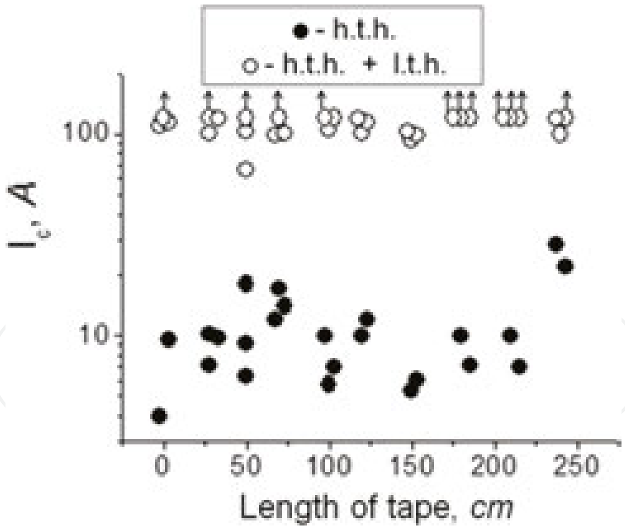


Figure 42. The values of I_c of the tape after h.-t. h. at 1800°C for 1.3 *s* (υ = 39.0 *mm/s*): ● – without the l.-t. an. and ○ – after the l.-t. an. at 800°C for 3 *h* (5.5 *T*; 4.2 K). An arrow pointing upwards indicates that I_c is greater than the current shown by the arrow, that is, an electric current of this magnitude does not put the sample in the normal state.

A completely different pattern was observed in the tape after the h.-t. h. at 1800°C for 2 seconds (see **Figure 41**). However, the level of critical current values immediately after heating was not high total 4–5 *A*. But the subsequent annealing at 800°C was increased critical currents of more than an order of magnitude – up to 70–80 *A*. Higher I_c were obtained in tapes after 1800°C for 1.3 seconds (see **Figure 42**). Without annealing is 9–10, with annealing is 100–120 *A*. A significant number of samples are not transferred to the normal state by electric current 115–120 *A*. This is the maximum current of source, which we possessed at that time.

Analyzing the results, we can say that the critical current is strong enough and varied along the length of tapes. For this, we need to turn to the 4th and 5th columns of **Table 9**. In samples without the low-temperature annealing, minimum value of critical current is different from the maximum in 4.5, 6.1 and 6.7 times. But after a low-temperature annealing, this difference is reduced to 2.2, 2.7 and ≥1.3 times, respectively. The higher the current carrying capacity of tapes, the more times the monitored parameters are improved.

The average arithmetic deviation from the mean values I_c for tapes without low temperature annealing which has undergone the heating in a continuous mode according to the second and third embodiment, is 37%. The lowest value of the critical current of the sample are different from the maximum, as we have already established, an average of 6.5 times (see **Table 9**). But be noted that out of the total number of samples that heated at 1800°C for 2 *s*, the samples with critical current equal 2 *A* or less there were only two. The number of samples after heating for 1.3 seconds, having I_c about 6 *A* or less there are only three.

The most common reason for the change of the critical current over the length of the tape became intelligible from **Figure 45** and is explained by change of the cross-sectional structure of the tape in the direction of axis *y*. This is a consequence of the method of the tape manufacturing. Because of the fact that the tape is narrow – only 2 *mm* width – under excision out of wider tape its structure of cross-sectional owing to random circumstances may have as 3-layer so and 5-layer. The case is very unfavorable when it is found on the outer regions of a wide tape. They account for the smallest number of layers D16. The use of a wider tape will be smooth out and level the structural changes along the length of tapes and thereby decrease the distinction of the critical current values.

The common property of the analyzed data is a significant decrease of the arithmetic average after the low-temperature annealing. That is, the scatter of the critical current value after annealing becomes smaller. For samples with heating at 1800°C for 2 *s* the scatter of I_c values after annealing at 800°C was decreased from 37 to 17%. At that the average critical current value has increased from 4.1 to 71.0 *A*, or in 17 times.

In these studies, we have used 2 *mm* in width ribbons in order to have to deal with wittingly lower values of electrical current. This was done to facilitate the measurement of the critical current at liquid helium temperature. The narrower the tape, the smaller its critical current is needed for the transfer of sample in the normal state. From here, wires will be less heated, lead-in electric current to the sample, which is in liquid helium, and will be less losses of helium due to its evaporation.

7.7. Conclusions to part

One. Quite a promising factor is that already in the first experiments have been received very high values of the superconducting characteristics for the tapes of compound Nb_3Al. Of particular importance is the fact that the high values has structurally dependent characteristic, which is the critical current. The critical current of tapes Nb_3Al was equal 50–60 *A* in 1 *mm* of width tape in a magnetic field of 5.5 *T*, which corresponded to a current density in the β-phase $(1.0–1.2)\cdot 10^5$ A/cm^2. The critical temperature (at the beginning of the transition to the superconducting state) is equal to 18.5 K. The upper critical magnetic field H_{c2} (4.2 K) = 30–32 *T*. Considering that the alloy of D16, is commercially available, and is much cheaper than tin, could have been expected that the multilayer Nb_3Al, would be very competitive with Nb_3Sn. Further are seen the following paths of improving of the critical current Nb_3Al:

- modes optimization of high temperature heating and low-temperature annealing;
- optimization of the construction and structure of the cross section of composite tapes Nb/D16;
- alloying of niobium [16, 17].

Two. The optimal modes of high-temperature heating for the obtaining of maximum possible the critical current in the three-layer tapes Nb/Al/Nb and multi-layer composite tape Nb/D16 (1800–1850°C, 1–2 *s*) by means the passing of an electric current through a short immovable samples [16] are matched with the third mode of high-temperature heating of the long multilayer tape Nb/D16 (1800°C, 1.2 *s*) by means "to pass" through permanently installed Ta-heater.

Three. At fast heating of multilayer tapes by passing an electric current not infrequently was observed the so-called "swelling" of tapes the surface. To avoid this, before the high-temperature heating is conducted 1 min-calcination of the tape at 1000°C. At the heating by "to pass" this procedure is not required. Evidently in order to "swelling" is not occurred, for tape was sufficiently smooth entry into the heating zone. Evidently, the time there was enough for formation out of aluminum and niobium the intermetallic compound $NbAl_3$.

Four. The presented results demonstrated that the developed high-temperature heating technology at some improvements of individual units of installation can be used for manufacture of the long (~100 *m* or more) pieces of multilayer tape Nb_3Al. Implementation of short-term (1–2 *s*) and high temperature (1800–1850°C) heating of a moving tape was quite solvable problem. Short times allow the leading of the heating process with high performance around 100–150 meters of tape per hour.

8. The dislocation structure of the superconducting layers in multilayer tape Nb_3Al

Electron microscopic studies [18] were conducted on three-layer tapes Nb/(AlGe–Cu)/Nb, in which Al–Ge alloy contain copper. In layers $Nb_3(AlGe)$ was discovered precipitation of fine particles of the second phase as inside so and on grains boundaries of the compound. The samples were subjected to heat treatment: 1650–1800°C, short time + 800°C, 2 *h*. By this was explained a significant (more than an order of magnitude) increase in the critical current after the low-temperature annealing. In the tapes without annealing of the second phase was not observed, and I_c was remained small.

The difficulty of preparation of the foils was "hit" on the layers of Nb_3Al, concluded between the Nb-layers (**Figure 43**).

Here, were studied the layered tapes Nb/D16 of 50 microns thickness and a width of 5 *mm*, after heating at the high temperature at 1850°C for 1.2 to 6.4 seconds. The structure of β(Nb_3Al)-phase layer was investigated using transmission electron microscopy. Foils for studies were prepared by thinning at room temperature in an acidic electrolyte of composition H_2SO_4 : HNO_3 : HF = 3 : 2 : 5. The cathode was stainless steel. The difficulty in preparing of foils was in that to appear in process of the thinning in layer of the β-phase, which is between the layers of Nb-solid solution (**Figure 43**).

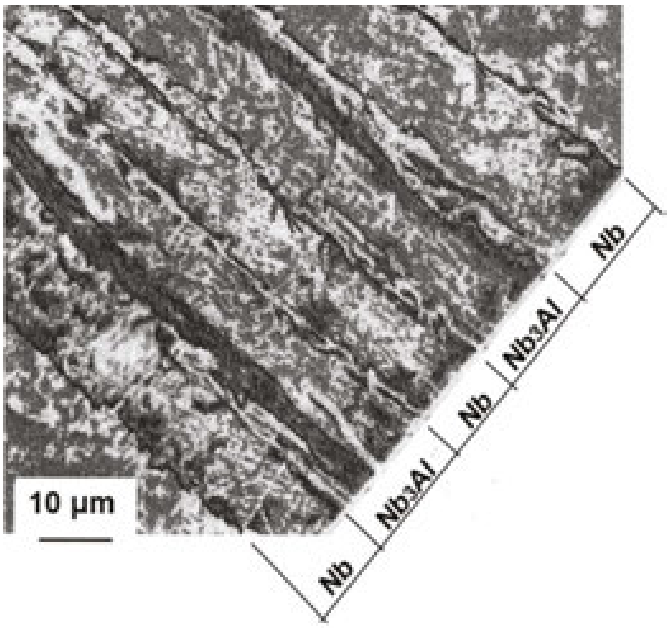


Figure 43. Microstructure of the cross-sectional of multi-layered strips of Nb_3Al after the h.-t. h. at 1850°C for 1.3 *s*. Actually designations of Nb_3Al and Nb are: Nb – two outer layers and one central layer of the solid solution of Al in Nb, Nb_3Al – two multilayer layers out of alternating considerably more thin layers of Nb_3Al and Nb-solid solution.

Heating at 1850 C for 1.3 s (**Figure 44*a***): beta-layer has structure of equiaxed grains. Its average size is 0.2 *mm*. Period of crystal lattice is 5.185 *Å*. Increasing the heating time to 4.6 seconds leads to the development of polygonization with the manifestation of its symptoms from education "honeycomb" structure, dislocation walls and dislocation grids to small-angle boundaries. The result is the formation of elongated sub-grains perpendicular to the former boundaries (**Figure 44*b***). A size of blocks is of 0.2–0.3 *µm*. A further increase of heating time to 6.4 *s* leads to formation of a three-dimensional network Frank. This is accompanied by an increase in the thickness of the layer of β-phase and increasing of its grains size to 2 or more microns (**Figure 44*c***). The contrast of the dislocation image made it possible to judge about atmosphere of impurities accompanying dislocation.

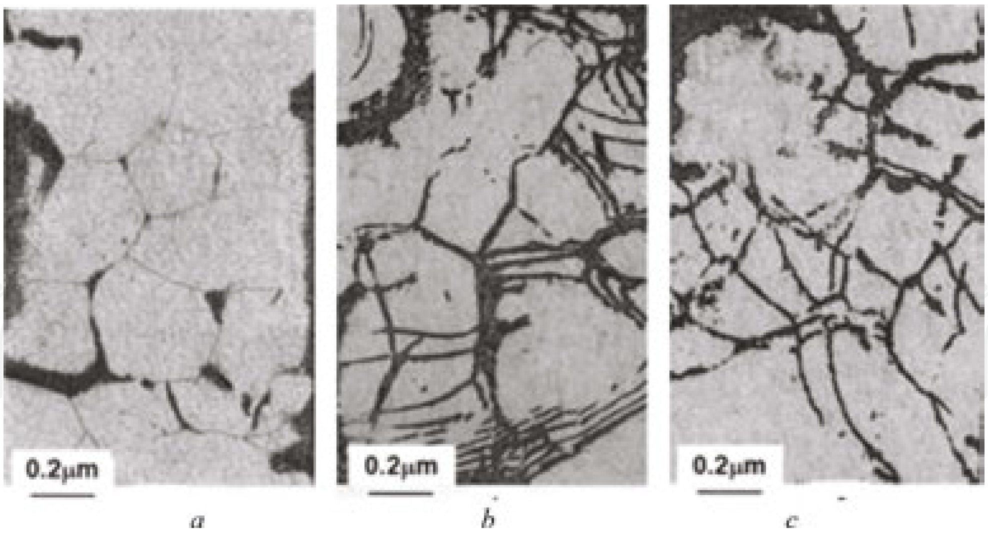


Figure 44. The microstructure of β-layer in a multi-layered tape Nb/Al after the h.-t. h. at 1850°C for 1.3 (*a*), 4.6 (*b*) and 6.4 *s* (*c*).

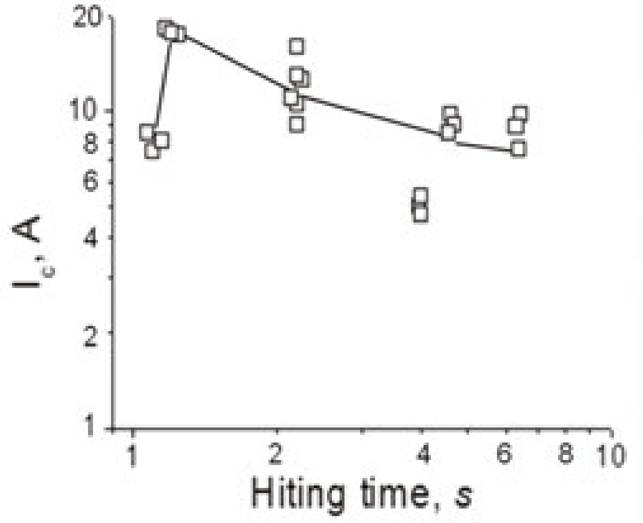


Figure 45. Critical current I_c of Nb$_3$Al multi-tape depending on the time of h.-t. h.

The maximum current carrying capacity corresponded to the heating time for 1.3 *s* (**Figure 45**). At the following grain growth and evolution of the dislocation structure I_c was decreased. It was another confirmation of concept that in compounds with A-15 structure grain boundaries are the most effective pinning centers of superconducting vortices.

9. Conclusion

1. Research works which are described in the presented chapter began in the 70s of the last century. The aim was to develop and test the semi-industrial technology to produce a

superconducting material on the basis Nb_3Al connection. At that time industrial production of superconducting materials were presented alloys Nb–Ti with T_c little more than 9 K. Technological developments of for superconducting material out of the more advanced at the time of the compound A-15 Nb_3Sn already were, but none of them has been implemented in the industrial of variant as the superconducting material. Compound Nb_3Al with a critical temperature equal to T_c of Nb_3Sn, has a much greater than Nb_3Sn the upper critical magnetic field of 32 *T* and, therefore, seems more promising for use in magnetic fields exceeding 10–15 *T*.

2. The samples of superconducting tape Nb_3Al were tested in magnetic fields up to 22 *T*. The so-called "constructional" or "engineering" critical current density calculated on the entire cross-section of the superconducting tape at 4.2 K in an external magnetic field of 14 *T* (**Figure 46**), and 18–22 *T* equal to (7–8) 10^4 [19] and (3.4–4.5) 10^4 *A/cm²* [20], respectively. Measurements in magnetic fields up to 14 *T* of Bitter magnets were conducted in the Laboratory of strong magnetic fields and low temperatures (Wroclaw, Poland), measurements in magnetic fields up to 22 *T* of the combined superconducting solenoid – in the Institute of Atomic Energy of name I.V. Kurchatov (Moskow, Russia).

3. The multilayer tape is capable of withstanding very small critical bend radius without degradation of critical current equal to 6–7 *mm* (**Figure 47**).

4. Semi-industrial of technology for long pieces production of multi-layer composite tape Nb/D16 developed and tested on one of a plant. The technological cycle consists of the following major steps:

   - the hydro extrusion of composite rod Cu/Nb/D16 on the press of horizontal type,
   - a profiled cold rolling of the resulting rod of diameter 10 *mm* on 8-stand rolling mill to the profile of the flat section,
   - a removing of the copper sheath,
   - an intermediate rolling of the profile to tape with thickness of 0.3 *mm* and
   - the rolling at room temperature using a four-roll mill of thin rolling equipped by coilers with regulated tension (**Figure 48**).

   One piece of the tape Nb/D16 of final thickness is shown in **Figure 49**.

5. Superconductivity, which was before the discovery of high-temperature superconducting ceramics and which is dedicated to this chapter, now called low-temperature superconductivity. Was a short time when on the wave of HTS-euphoria an opinion existed, that the previous superconductivity would lose prospect for its practical application. But this did not happen and could not happen. Low-temperature superconductivity was used up to HTS, even wider uses at present and will peacefully co-exist with high-temperature superconductivity in the foreseeable future.

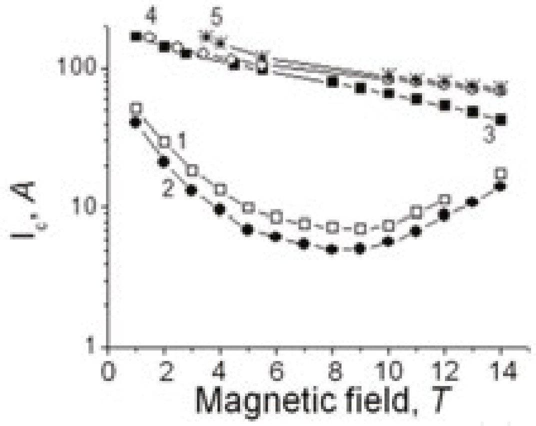


Figure 46. Critical current I_c of multi-layered Nb_3Al tape depending on the external magnetic field. Width of tape is 2 *mm*. Heat treatment, C: 1 and 2 – 1000, 1 *min* + 1850, 2 *s*; 3, 4 and 5 – the same + 900, 0.5 *h*, + 800, 3 *h* and + 900, 1 *h*.

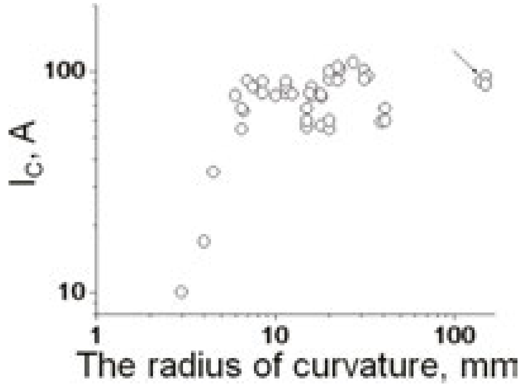


Figure 47. I_c on the radius of curvature (4.2 K, 5.5 *T*). Heat treatment, °C: 1750, 2 *s* + 800, 2 *h*. The tape thickness of 50 *μm* and width of 2 *mm*.

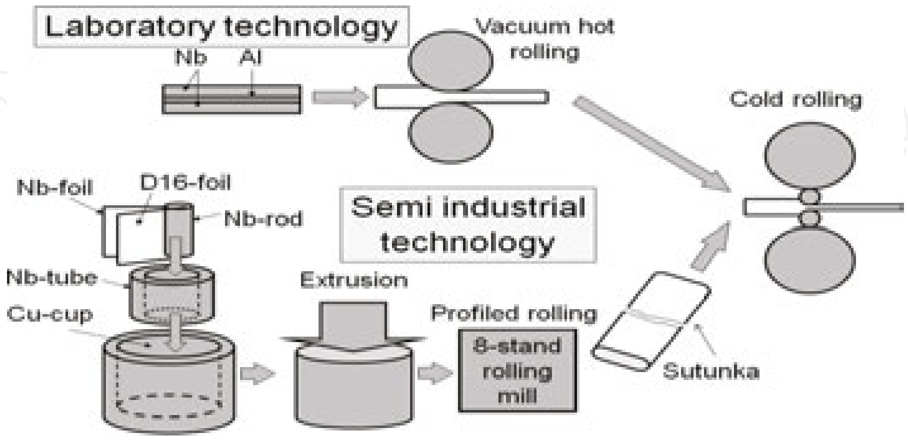


Figure 48. Simplified schemes of operations of the laboratory and semi-industrial technology for obtaining composite tape of Nb_3Al.

Figure 49. Segment of multilayer Nb/D16 tape.

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