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Superconducting Multilayered Ribbon for MRI Scanners, Produced Using Solid-Phase Technology

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Abstract—A solid-phase technology is described for producing a superconducting multilayered ribbon with layers ~150 nm thick from a solid solution of titanium in niobium and an Nb–50% Ti alloy. The ribbon is 0.1 mm thick. Measurements of the critical current of the ribbons at perpendicular and parallel orientations of external magnetic field H relative to the plane of the layers reveals considerable anisotropy in magnetic fields $H > 1$ T. This testifies to the pinning of superconducting vortices on the non-superconducting layers of the niobium solid solution. The critical current in a field of 5 T reaches 50 A per 1 mm of the ribbon width.

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INTRODUCTION

The first magnetic resonance imaging (MRI) scanner with an open superconducting magnet having a field of 0.35 T was marketed in 1997 by Toshiba. Magnetic resonance imaging is a highly informative and harmless diagnostic technique based on the principle of the magnetic resonance of hydrogen nuclei (an element very common in the human body). Superconductive MRI scanners are now becoming more widespread. Two models of such an MRI scanner were built in the Russian Federation in 2017 [1]: a compact orthopedic MRI scanner and a full-size MRI scanner with a field induction of 1.5 T and a scanner bore 90 cm in diameter and 170 cm long.

Russian cable 0.8 mm in diameter with 19 cable cores of Nb–50 wt % Ti alloy in a copper matrix was used to fabricate a superconducting magnetic system for MRI scanners in the Russian Federation. This is a wrought alloy with a superconducting transition temperature of 9.6 K. It was the first industrial superconductor for practical use in the Soviet Union and elsewhere.

The industrial technology for the production of multicore superconductors based on NT-50 alloy (Nb–50% Ti) was developed by studying superconducting Nb–Ti alloys in the 1960s–1970s. No such research is being done today.

In studying the dependence of the mechanical properties of multilayer materials obtained by rolling artificially formed multiple sandwiches on layer thickness, we became interested in layered composites of superconducting alloys of Nb–31 and 50 wt % Ti [9, 10]. Our goal was to measure their critical current density j_c. In type II superconductors, j_c depends on how effectively the superconducting vortices are pinned to structural defects. In other words, the critical current density is the same as, e.g., hardness or strength. It can be more of a structure-dependent characteristic of the material.

V.V. Schmidt theoretically studied the interaction between vortices and the flat surface of a superconductor [11]. He showed that even defect-free superconducting plates with thickness $d \gg \lambda$, where λ is the depth to which an external magnetic field penetrates into a material, can carry a considerable current of $\sim 10^5$ A cm^{-2} in a mixed state. Let us assume a thick plate is replaced by a set of thin superconducting plates artificially separated from one another by layers of normal metal. The current in this case flows through each plate and the multilayered superconductor carries a strong transport current. This situation is observed in multilayered composites of Cu/Nb [12] and Nb/NbTi [9, 10]. In a Cu/Nb composite, the layers of superconducting niobium are separated by layers of normal copper; in a Nb/NbTi composite, superconducting niobium is used as a normal metal. However, since the critical current is measured in magnetic fields tens of times higher than the second critical magnetic field of the niobium layers, they are stoppers or pinning centers of superconducting vortices in the (Nb–Ti) layers of a composite.

Anisotropy $j_{c\parallel}/j_{c\perp}$ of critical current density j_c measured at parallel (‖) and perpendicular (⊥) plane orientations of the composite layers and the magnetic field, is evidence of effective vortex pinning on extended thin copper layers between niobium layers, or on thin layers of niobium between layers of NbTi alloy. In a Nb/Cu composite, $j_{c\parallel}/j_{c\perp} = 410$ in magnetic fields of

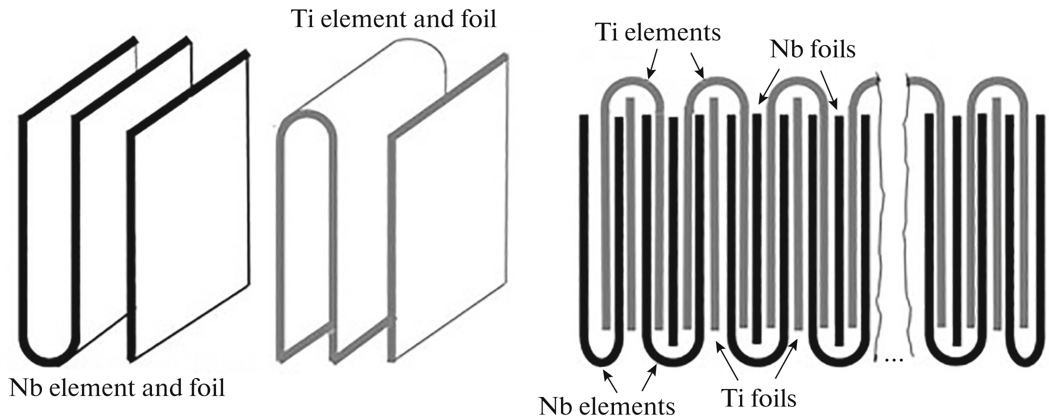

Fig. 1. Elements for assembling the sandwich and its schematic design with external niobium foils.

0.5–0.6 T [12]. In a Nb/NbTi composite, anisotropy grows from 3–5 (for composites with a layer thickness of ~140 nm) to 235 (for ribbons with a calculated layer thickness of ~3 nm) in magnetic fields of 5–6.5 T. In some cases, ratio $j_{c\|}/j_{c\perp}$ was more than 2000 [9, 10].

One aim of this work is to propose a solid-phase technology that does not require foils from a previously melted Nb–50 wt % Ti alloy to obtain a superconducting multilayered Cu/Nb/Nb50Ti composite. In contrast to [10], the first stage of the work was based on multiple sandwiches being formed not from foils of niobium and (Nb–Ti) alloy of required composition, but from foils of niobium and titanium, Nb/Ti/...Nb/Ti/Nb. (Nb–Ti) alloy of the required composition thus formed as a result of mutual diffusion between niobium foils and titanium foils during diffusion welding in two stages of multiple sandwiches that initially consisted of niobium, titanium, and copper foils.

The proposed solid-phase technology for producing a multilayered ribbon from Nb–50% Ti alloy does not include smelting a niobium alloy of the required concentration and subsequent processing of its ingot into, e.g., a hexagonal rod or foil (1). Neither does it require prolonged annealing of a partially finished composite ribbon or conductor for 300–320 h at 280–300°C in a vacuum or inert environment using bundled technology (2).

Solid-phase technology focuses on obtaining ribbons of multilayered superconductor from (Nb–Ti) alloy, but there is also a solid-phase technology for producing cable from a copper matrix with Nb/Nb50Ti cores.

EXPERIMENTAL

A superconducting multilayered ribbon made of Nb–50% Ti alloy stabilized with copper was obtained in two cycles, each of which consisted of diffusion welding sandwiches assembled in a specific manner and rolling at room temperature.

In the first cycle, the sandwiches were composed of niobium and titanium foils, plus U-shaped elements from the same foils. Each sandwich was a set of alternating niobium and titanium layers. Figure 1 shows the design of a sandwich whose outer layers were niobium. The nobium foils were 50 μm thick, and the titanium foils were 45 μm thick. Their total number in the sandwiches was 61 or 79. The assembled sandwiches were 2.9–3.0 and 3.7–3.8 mm thick, respectively.

Each sandwich was a consolidated structure so that the required technological procedures could be performed.

Diffusion welding of the sandwiches was done in a vacuum no lower than 10^{-4} mm Hg. Each sandwich was positioned between pistons made of high-strength graphite. Foils made of TEG (thermally expanded graphite) 0.3 mm thick were placed between the sandwich and pistons. In the first cycle, diffusion welding of Nb/Ti sandwiches was done for 10 min at 1050°C at a pressure of 16–17 MPa. The sandwiches contained external and internal copper layers, so the temperature of diffusion welding in the second cycle fell to 900–950°C at pressures of 17–19 MPa, and the period of diffusion welding grew to 1.5–2 h.

The rolling deformation of the welded sandwiches was done at room temperature on a four-roll thin rolling mill. The degree of deformation per pass was 2–3%. The direction of rolling the sandwiches corresponded to that of the foils laid in the sandwiches. In the first cycle, the ribbon was rolled to a thickness of 0.2–0.25 mm and cut into pieces of the length required for assembling the sandwiches in the second cycle.

Sandwiches were assembled from pieces of a multilayered ribbon after the first cycle, using two or three copper strips (0.15 mm thick) as stabilizers of the

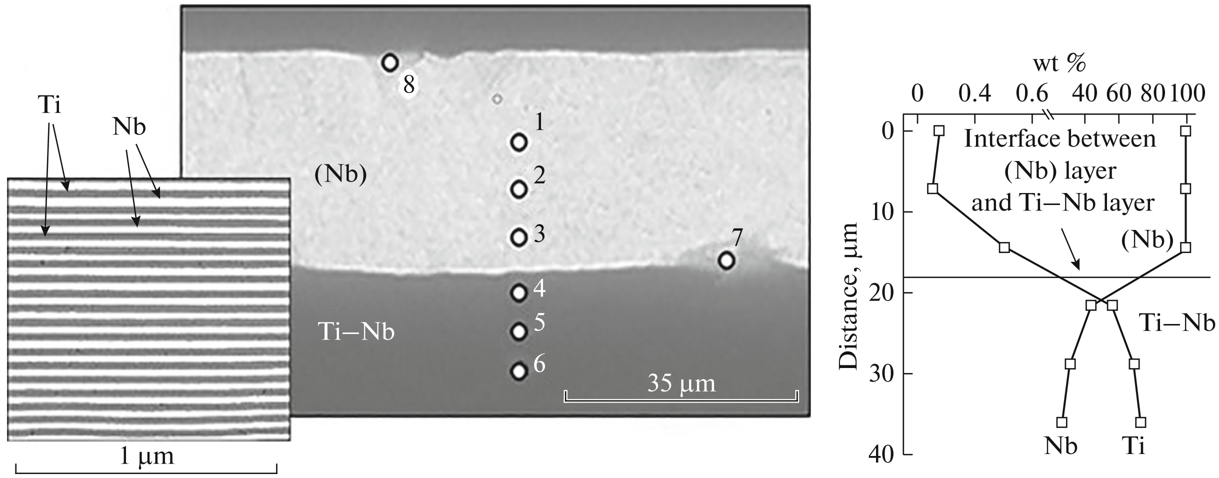

Fig. 2. (a) Macrostructure and microstructure of the Nb/Ti composite and (b) concentration profiles of titanium and niobium at the interface between the layers of niobium solid solution and Ti–Nb alloy. The points of local X-ray spectral analysis are 1–6.

superconducting state of the composite, and two or four thin niobium foils (20 μm thick) as diffusion barriers. If there were two pieces of copper, they were placed outside the sandwich; if there were three pieces of copper, one was placed in the middle of the sandwich.

Niobium foils were inserted between copper pieces and a set of multilayered segments after the first cycle to prevent interaction between copper and titanium during the subsequent diffusion welding. It is known that niobium does not interact with copper at the temperatures we used.

After the second cycle, the welded sandwich was rolled at room temperature into a ribbon 0.1 mm thick.

The calculated thicknesses of individual layers of a solid solution of titanium in niobium (Nb) and an NbTi alloy in a ribbon of finite thickness were ~150 nm.

STRUCTURE OF MULTILAYERED COMPOSITES

The structure of the composites was investigated via scanning electron microscopy and X-ray spectral analysis. The microstructure, including images of objects in secondary and reflected (backscattered) electrons and X-ray spectral analysis, was investigated using digital Tescan VEGA-II XMU and CamScan MV230 electron scanning microscopes. The microscopes contained W cathodes, YAG detectors for secondary and reflected electrons, and an X-ray microanalyzer. The depth of the region of characteristic X-ray radiation was 5–6 μm. This was a circle in the cross section; in the volume, it was a pear-shaped zone with a maximum diameter of ~10 μm.

Composite Structure after the First Cycle of Diffusion Welding and Rolling

After the first diffusion welding, the structure of the Nb/Ti composite consisted of light and dark layers (Fig. 2). The light layers were niobium; the dark ones, titanium (these were also the outer layers in Fig. 2).

The layers were identified by means of local X-ray spectral analysis (Figs. 2a and 2b). The concentration profiles near the interface between the niobium and titanium layers showed that layers of (Ti–Nb) alloy with titanium and niobium concentrations varying in direction from the boundary to the middle of a layer from 56 to 73 and 44 to 27 wt %, respectively, formed in place of titanium layers after just 10 min of diffusion welding at 1050°C and relatively low pressure.

On the other hand, titanium did not dissolve appreciably in the niobium layers. Its concentration in the middle of a niobium layer was less than 0.2 wt % (Fig. 2b). Our results showed that there was solid-phase interaction between layers, due to the diffusion of niobium atoms into the titanium. After the first diffusion welding, a multilayered structure of a superconducting alloy formed in the composite. The alloy was 25–40% Nb–75–60 wt % Ti, which was close to the desired composition with 50 wt % Ti that had the best combination of superconducting characteristics in the Nb–Ti system. The other layers had to be niobium with a low titanium concentration in order to be non-superconducting in low magnetic fields. It is known [13] that non-superconducting defects in superconductors are more effective centers for pinning superconducting vortices than superconducting defects.

Diffuse formations with anomalously high concentrations of titanium (75–85 wt %) were also found in a niobium layer at a Nb/Ti interface (points of spectra 7 and 8; see Fig. 2a).

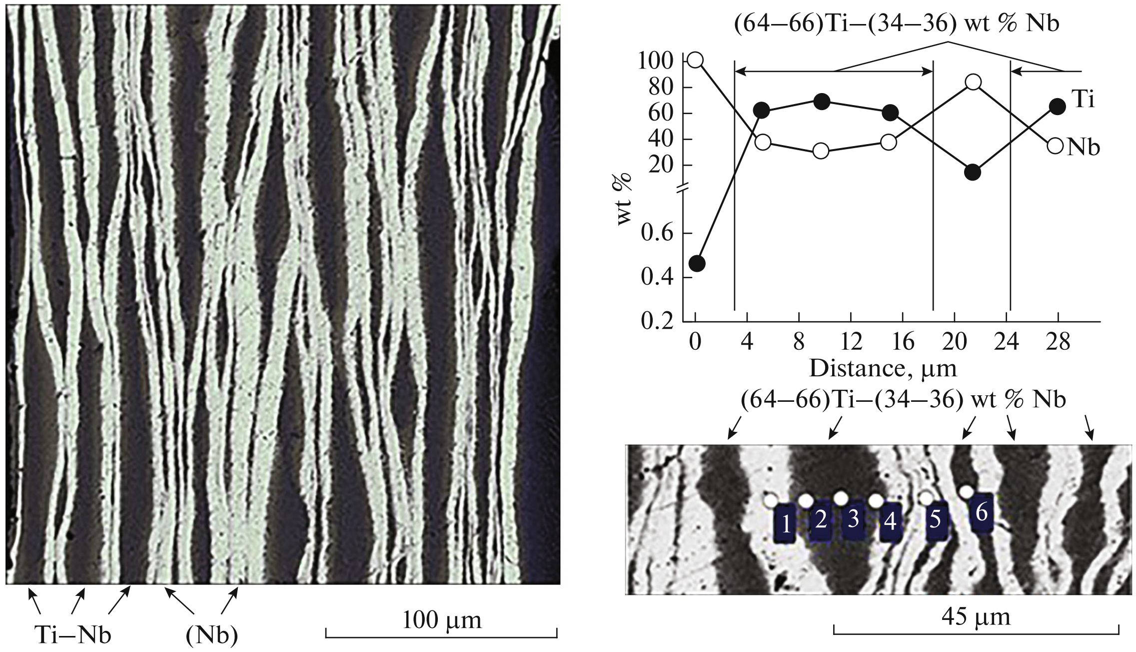

Fig. 3. Structure of a 0.2-mm-thick composite ribbon of (Nb)/Nb–Ti alloy (a) across rolling and (b) along rolling after the first cycle of diffusion welding and rolling. Concentration profiles of titanium and niobium. The points of local X-ray spectral analysis are 1–6.

Figure 3 shows the microstructure of the cross section of a 0.2-mm-thick ribbon after diffusion welding and rolling. The initial workpiece was an Nb/Ti composite containing 40 layers of niobium and 39 of titanium. The light layers were niobium solid solution (Nb) containing titanium in an amount of a few tenths of a percent. The dark layers were niobium alloy with 75–60 wt % Ti . The laminarity of the layered structure in the direction across that of rolling was expressed to a much greater extent than along that of rolling. The section coinciding with the direction of rolling (Fig. 3b) contained a great many disc-shaped formations in the NbTi alloy layers, due largely to cold rolling. We are confident the laminarity of the layered structure of the ribbon can be greatly improved if the cold rolling mode is selected correctly.

The calculated thicknesses of the layers of niobium solid solution (Nb) and Ti–Nb alloy in the rolled ribbon after the first cycle were 2.7 and 2.4 μm, respectively. The actual thickness varied from several micrometers to 10–15 μm (see Fig. 3a).

Local X-ray spectral analysis of the microstructure of the (Nb)/Nb–Ti ribbon confirmed our earlier results. The dark layers of the Ti–Nb alloy were ~34.5 wt % Nb, which was the mean concentration of niobium calculated from four points of the spectrum (2, 3, 4, and 6) for Ti–Nb layers (Fig. 4).

Composite Structure after the Second Cycle of Diffusion Welding and Rolling

Figure 5 shows the macrostructure of the composite after diffusion welding for 1–2 h in the second cycle at 900–950°C and 16–17 MPa. The section of the composite is oriented parallel to the direction of rolling. The sandwich consisted of six multilayered pieces of (Nb)/(Nb–Ti) ribbon after the first cycle (see 1, 2, 3, 4, 5, and 6 in Fig. 4), two outer copper plates, and niobium foils that served as diffusion barriers during diffusion welding (see inset). Local X-ray spectral analysis (Fig. 5) done for one of the sections of its cross section at high magnification showed that the stabilizing plates were 100% copper, and the diffusion barriers were 100% niobium.

Two regions located on both sides of the disc-shaped inclusion with an alloy of ~35Nb and ~65 wt % Ti (spectrum points of 11, 12, and 13) marked as Nb–Ti in the upper part of Fig. 5 are interesting in the context of superconductivity. Using data from local X-ray spectral analysis, we can distinguish both points of analysis with equiatomic concentrations of niobium and titanium. This corresponds to layers of 50Nb–50Ti alloy and points of analysis with titanium in amounts of 10 to several wt % that correspond to layers of a titanium solid solution in niobium. These were the areas responsible for the superconducting properties of the composite ribbon. They consisted of thin layers of Nb–50 wt % Ti alloy that were titanium foils in the

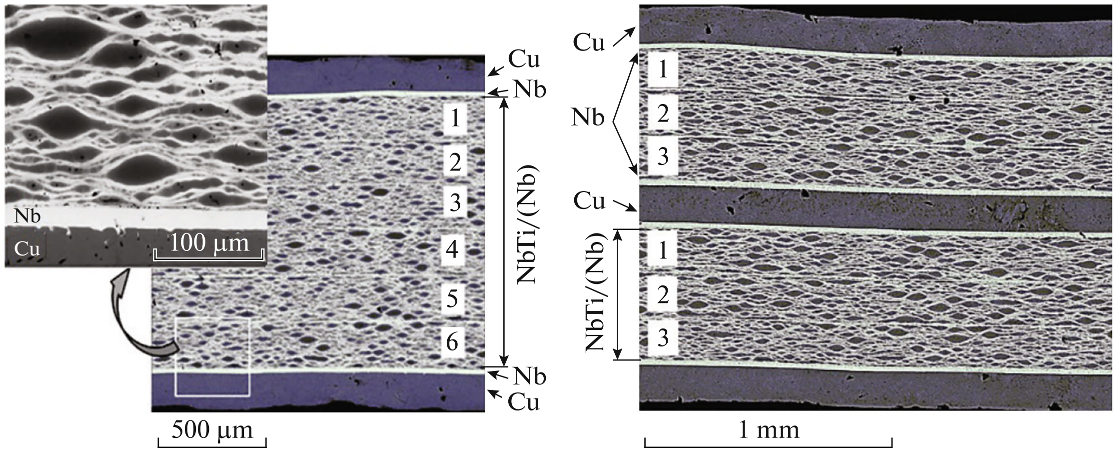

Fig. 4. Macrostructure and microstructure of a sandwich with six sections of ribbons after the first cycle of diffusion welding and rolling with (a) outer stabilization and (b) outer and inner stabilizations. Cu is outer and inner layers; Nb is diffusion barriers; 1–6 and 1–3 are ribbons of (Nb)/(Nb–Ti) alloy after the first cycle of diffusion welding and rolling.

first sandwiches, and niobium layers with very low concentrations of titanium that were niobium foils in the first sandwiches. It was not possible to accurately determine the content of elements in such thin objects, since their thicknesses are comparable to the diameter of the characteristic X-ray radiation region of ~10 μm.

Figure 6 shows the structures of the other two sandwiches after diffusion welding in the second cycle. The first sandwich (1.5 mm thick) contained seven multilayered segments of (Nb)/(Nb–Ti) after the first cycle, two outer copper stabilizers 0.15 mm thick, and two niobium screens 20 μm thick. The second sandwich (2 mm thick) contained two external copper stabilizers, the same copper plate for internal stabilization of the superconducting state, and thus two more niobium diffusion barriers. The superconducting volume of the composite was two sandwiches of four multilayered segments of the (Nb)/(Nb–Ti) ribbon after the first cycle.

The volumes with a two-phase layered structure responsible for the superconducting state in the first and second composites, determined from the coloration of functional structural elements, were 79.5 and 70.2 vol %, respectively.

After the second diffusion welding, the sandwiches were rolled to a thickness of 0.1 mm. The microstructures of such ribbons are shown in Fig. 6.

Analysis of macrostructures and microstructures showed that their layering, connectivity, and continuity were determined only by the light component, in which the concentration of titanium did not exceed 10–15 wt % at best. The concentration of titanium ranged from 1 to 3–4 wt % much more often. The grey component from a niobium alloy with titanium in amounts of 50–70 wt % formed elongated discontinuous inclusions, often in the form of disks. This meant that the niobium alloy responsible for the high superconducting current of the layered composite had no connected current paths.

The microstructures of thin multilayered ribbons after two cycles of diffusion welding and rolling refute

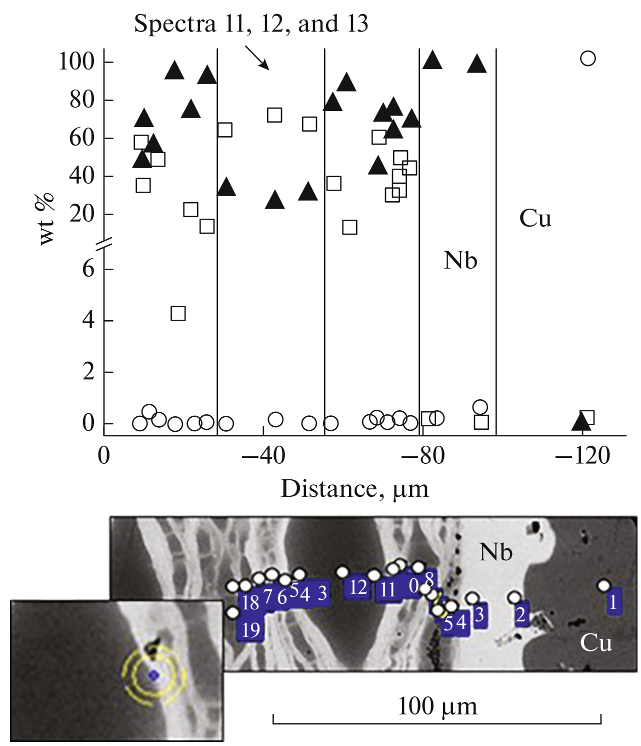

Fig. 5. Local X-ray spectral analysis of the Cu/Nb/[(Nb)/(Ti–50Nb)] sandwich after the second cycle of diffusion welding. Denotations are ▲ (Nb), □ (Ti), and ○ (Cu). The points of local X-ray spectral analysis are 1–19. The area of characteristic X-ray radiation with a radius of ~5 μm is located at the bottom left.

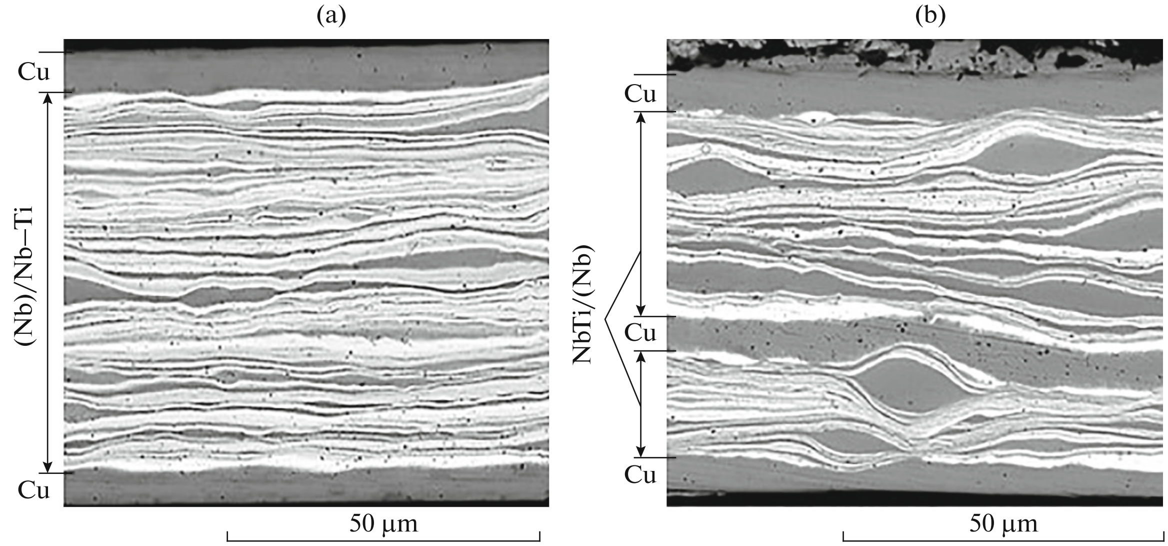

Fig. 6. The final structure of 0.1-mm-thick superconducting ribbons based on an Nb–50 wt % Ti alloy with (a) an outer stabilizing layer and (b) outer and inner stabilizing layers.

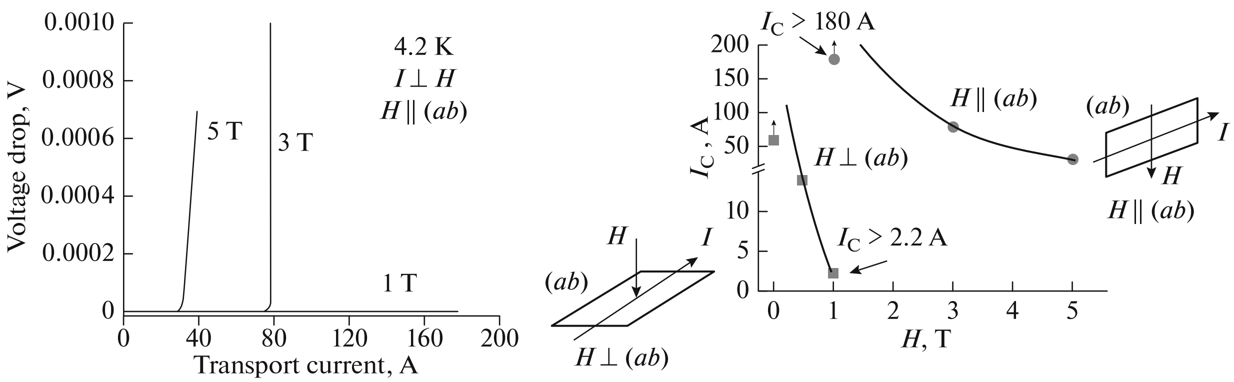

Fig. 7. Current–voltage characteristics of a multilayered superconducting ribbon made of an Nb–50Ti alloy at $H \parallel (ab)$ and H = 1, 3, and 5 T (a) and the dependence of I_C on the magnetic field strength H at $H \parallel (ab)$ and $H \perp (ab)$ (b).

the above concepts. After rolling, the layered structure of the ribbons consisted of continuous layers of (Nb–Ti) alloy of gray and dark gray contrast and light layers of a niobium solid solution with a low content of titanium.

CURRENT-CARRYING CAPABILITY OF THE COMPOSITE RIBBON

The critical current was measured on samples of a multilayered ribbon after the second cycle of diffusion welding and rolling. The ribbon was 0.1 mm thick and 1 mm wide. Measurements were made in a cryostat with liquid helium in magnetic field H generated by a superconducting solenoid with perpendicular $H \perp (ab)$ and parallel $H \| (ab)$ orientation of magnetic field H and the rolling plane of the ribbon (ab). In both cases, transport current I through the sample was perpendicular to the magnetic field of the solenoid $I \perp H$.

Current–voltage characteristics of multilayered ribbons in magnetic fields of 1, 3, and 5 T at $H \parallel (ab)$ are shown in Fig. 7a. In magnetic fields of 5 and 3 T, the critical current was 30 and 75 A per 1 mm of ribbon width, respectively. A transport current of 180 A did not destroy the superconducting state of the sample in a magnetic field of 1 T.

The dependences of critical current I_C on the magnetic field for two orientations relative to the rolling plane of the ribbon ($H \perp (ab)$ and $H \parallel (ab)$) are shown in Fig. 7b. The two experimental points with upward arrows show that the transport current did not destroy the superconducting state of the ribbon.

For the $H \perp (ab)$ orientation, critical current I_C dropped sharply upon an increase in the magnetic field in the range of 0 to 1 T. However, the critical current for the $H \parallel (ab)$ orientation fell gradually, remaining ~30 A at 5 T, which corresponds to the design (or engineering) critical current density of 3×10^4 A cm^{-2}. Anisotropy I_C equal to ratio $I_{C\parallel}/I_{C\perp}$ calculated for H = 1 T was less than 82. This indicates the superconducting vortices localized in the (Nb–Ti) layer, which carries the transport current, are pinned in the non-superconducting layers of the niobium solid solution (Nb).

CONCLUSIONS

Particles of the α-phase, precipitated over many hours of the low-temperature annealing of such finished composites as cable or ribbon, are pinning centers in industrial multicore superconductors made of (Nb–Ti) alloy. In a solid-phased superconducting composite material of Cu/Nb/NbTi, in which vortices are pinned on non-superconducting niobium layers, high critical current density in the Nb–Ti alloy was achieved without low-temperature annealing (i.e., annealing is excluded from the existing technology for producing a superconducting material).

The use of solid-phase technology for producing a Cu/Nb/Nb50Ti composite is better than the energetically more expensive skull melting of Nb–50 wt % Ti alloy ingots and processing them into composite billets of complex design.

Our X-ray structural analysis and measurements of the current-carrying capacity of layered ribbons show that the layers of a superconducting niobium alloy with 50 wt % titanium form in two cycles in a multilayered Nb/Ti composite as a result of solid-phase interaction between niobium and titanium layers.

Layers of Nb50Ti alloy are capable of conducting high electric currents in magnetic fields ≥5 T. Interlayers of a niobium solid solution with low concentrations of titanium transition into the normal state even in low magnetic fields and become effective pinning centers for superconducting vortices. This is confirmed by the high anisotropy of critical current $I_{C\parallel}/I_{C\perp} > 82$ at H = 1 T.

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