Superconductivity in Cu-Nb with extremely fine structure

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Abstract. Electrodynamic properties of "three-dimensional" composites CuNb with extremely fine structure and different concentration of components are investigated. The samples have been fabricated from the melt using slow and extremely fast cooling rate. The slowly cooled samples (SCS) are characterized by a fractal niobium grid with a characteristic size of the micron scale immersed into a copper matrix. The fast melt cooling results in the nano-scale composite. It has a rather pure copper matrix in which almost pure isolated nano-inclusions of niobium are distributed. We have found the electromagnetic properties of these two (micron and nano scale) CuNb composites have some qualitative difference. The SCS shows features of superconducting transition, typical for granular superconductors. The superconducting transition in quenched samples (QS) carries the feature of an effective superconducting media which a critical temperature $T_c$ are renormalized to a rather lowered value for the small size of superconducting regions. On the basis of the experimental data we have estimated a coherence length of the effective superconducting media of the QS that occurs close to the Nb droplet diameter. Voltage–current characteristics (VCC) of the QS in magnetic fields parallel and perpendicular to the current show abnormally low slope in some intermediate current region while at lower and higher currents the VCC features are characteristic for a hard superconductor. The opportunity of a relation of the abnormal dissipation in the QS with the Josephson generation is discussed.

1. Introduction

The problems of development of large-scale and high-field superconducting magnets (e.g., for ITER project) generate hard requirements to structural materials of their windings. Properties of these materials have to combine an extremely high robustness and a good enough thermal and electrical conductivity. According to [1-4], CuNb nano-composites with Nb filaments of about 10 nanometers in diameter may meet these hard requirements. Owing to a pronounced size effect an electrical conductivity of such composites essentially depends on distance between filaments [5]. Moreover, when Nb filaments are in a superconducting state, the proximity effect is capable to modify essentially electrical and thermal properties of nano-composites. One may expect a strong anisotropy of an electrical and thermal transport in such materials, similarly to a case of "in situ" composite superconductors [6], and essential changes of an electron transport in a copper matrix as a result of a
reduction of effectiveness of a normal electron diffuse scattering at a metal-metal boundary when one of the neighbor passes into a superconducting state - Andreev reflection at N-S boundary [7].

Our experiment is devoted to a study of electrical and electromagnetic properties of "three-dimensional" CuNb nano-composites in which niobium nano-drops are immersed into a copper matrix. The transport properties of such system should be strongly affected by the size and proximity effects but free off a complicating anisotropy factor. In comparison with it, we consider CuNb composites with a micron scale structure. Samples of the first type represent the tapes prepared at extremely fast cooling of CuNb melt. The niobium drops and spacing between them have a measure of about 10 nm, and the drops are immersed into the Cu matrix with a low content (~1 at.%) of Nb. The system is similar to a granular superconductor but its structural sizes are less than coherence lengths of the materials forming it. Our experiment shows such system being superconducting even at Nb content low than a percolation threshold but its properties in comparison with the granular one fabricated at slow melt cooling have a distinction in kind.

2. Experiment

2.1. Samples

The composite samples CuNb were fabricated off a melted mixture of Cu and Nb powders of about 60 and 30 microns in size with an average Nb content indicated in a Table. Melting was done by an inductive heating up to 1800°C in an Ar gas with a subsequent natural and extremely fast cooling (slowly cooled samples – SCS and quenched samples - QS). According to a phase diagram of the CuNb system it has no intermediate phases. A solubility of Nb in Cu in a solid phase does not exceed 1 at.% and the solubility of Cu in Nb is of about 0.1%. As a result, cooling of the melt leads to a formation of a two-phase system.

At a slow cooling rate Nb nucleuses formed at an initial stage and comparatively Cu rich have a time to coagulate and they form a net of fractal clusters. The X-ray diffraction shows a characteristic diameter of the fractal regions of a micron scale and a cluster size distribution tending to a logarithmically normal one. According to a results of a CAMEBAX-SX50 micro-analysis of the sample with the average Nb content of 12 at.% the periphery regions of ingot occurs depleted with respect to average Nb content but a mid of the sample has of about 25 at.% of Nb.

The fast cooled samples were prepared by a flow turning method using a cold Cu wheel of 200 mm in diameter rotating with a speed of 4000 turns per minute [8]. They have a thickness of 30÷40 μm and a width of about 2 mm. Estimations give that in this case a decomposition of the solution limited by an ascending diffusion of the Nb atoms in liquid Cu has a time to complete but solid Nb nucleuses do not have a time to coagulate and form a superfine structure of isolated Nb drops of 200-300 Å in diameter. The latter follows from data of a transmission electron microscopy.

For detail electrodynamic measurement we picked out QS tapes CuNb12a, CuNb12b, CuNb15 and CuNb20 and slabs B1 and B2 cut off the middle part of the slow cooled ingot with the initial average Nb content of 12 at.%. Data of Table show the onset temperature \( T_c \) of a superconducting transition of the samples obtained from a resistivity \( R(T) \) and ac susceptibility real part \( \chi'(T) \) measurements. The dc resistivity measurements were done using a conventional four-probe method. The real and imaginary parts of ac susceptibility \( \chi = \chi' + i\chi'' \) were studied for directions of a probe ac field \( h \) put in the sample plane along the tape (slab) or perpendicular. The dc and ac (373 Hz) magnetic fields were collinear to each other.

2.2. Results

The main results are presented for the samples CuNb12a, CuNb12b and B2 the measurements for which were performed by both dc and ac methods(The samples CuNb15 and CuNb20 have demonstrated the electromagnetic properties almost the same as in CuNb12, but they are to brittle to prepare the proper samples for dc current study.). Figure 1 demonstrates the superconducting
transitions in slow cooled and quenched samples in the ac susceptibility (lines) and dc resistivity (symbols) at low values of the probe ac field $h$ and dc current $I$. (The room temperature resistivities of samples CuNb12a and both B1 and B2 are 7 $\Omega \cdot$ cm and 3.8 $\Omega \cdot$ cm correspondingly and their residual resistance ratio (RRR) are 2.3 and 8.3.) The onset of the superconducting transition in resistivity for Table 1.

| Sample     | Nb content, at. % | Nb content, at. % | Sample thickness $d$, mm | Sample width $a$, mm | $T_c$, K | $R(T)\parallel \chi'(T)$ |
|------------|-------------------|-------------------|--------------------------|----------------------|---------|------------------------|
| CuNb12a    | 11.2              | 17                | 0.039                    | 1.1                  | 7.0/7.0 |                       |
| CuNb12b    | 11.2              | 17                | 0.040                    | 1.5                  | 6.5/6.5 |                       |
| CuNb15     | 16.0              | 24                | 0.024                    | 0.7                  | -       | //6.2                 |
| CuNb20     | 18.9              | 28                | 0.027                    | 1.6                  | -       | //6.0                 |
| B1         | 24.9              | 35                | 0.500                    | 4.0                  | -       | //8.7                 |
| B2         | 24.9              | 35                | 0.500                    | 1.2                  | 9.2/8.7 |                       |

SCS is close to that of a bulk Nb, but in ac susceptibility the onset is shifted to the lower temperature at which the resistivity falls down to about 20% of its residual value. For the QS the $T_c$ value is significantly lower than for SCS, but the transitions in the former go almost coincident for both the ac susceptibility and resistivity.

Figures 1.

![Figure 1](image1.png)

The temperature variation of the ac susceptibility of the samples CuNb12a and B2 (lines) at the ac field amplitude $h=1$ Oe. The symbols show the dc data for these samples calculated as $\rho(T)/\rho_0 - 1$, where $\rho_0$ is a residual value measured a little higher than $T_c$.

Figures 2a., 2b. reflect qualitatively different influence of the external dc magnetic field $H$ on the resistivity of the QS and SCS. The transition in the SCS under the dc field shows the tailing typical for a granular superconductor. In the QS the external magnetic field only shifts the transition curve almost as a whole similarly to the case of a dirty hard superconductor. At $H=0$ the transition onset temperatures are 9.25 K and 6.27 K for samples B2 and CuNb12b correspondingly.

The results in Figures 3a and 3b present the qualitative difference in an ac field amplitude effect on the superconducting transition of our SCS and QS at comparatively small $h$ values. In particular, as the ac field amplitude increases the dependence $\chi'(T)$ of the slow cooled sample B1 reveals more clearly a kink near the transition onset at a value $|\chi'| = 0.2$ comparable to the Nb volume content in the
sample. The imaginary part $\chi'(T)$ of the sample B1 at some amplitude becomes clearly “two-humped”, that is characteristic of a granular superconductor too.

Finally, voltage-current characteristics of our two types of CuNb samples are qualitatively different too (Figure 4.). In general terms the VCC of the slow cooled sample B2 has an ordinary for a hard superconductor exponent view with a power decreasing as the current $I$ or field $H$ increases. The VCC of the quenched sample CuNb12b are abnormal. In intermediate current region at the electrical field $E$ of several micro-volts it has a flat slope being greatly lower than on the left and right side from it.

![Figure 2](image1.png)

**Figure 2.** The temperature dependence of the resistivity in the vicinity of the superconducting transition of the slow cooled (a) and quenched (b) samples.

The abnormal VCC view of the quenched sample is particularly visual for linear coordinates of Figure 5 presenting the influence of the dc field $H$ in a force (closed symbols) and forceless (open symbols) configurations. On reaching the sample critical current value estimated for a criterion $1 \mu V/cm$, the VCC slope decreases abruptly approximating linear one at a strong enough external dc field $H$. At this part the VCC does not depend on the dc field $H$ orientation with respect to the current $I$ direction. At higher $I$ values the VCC power becomes great again and a remarkable difference of the VCC in force and forceless configurations appears. As for a typical hard superconductor the voltage in our QS sample is higher in the force case ($H \perp I$).
2.3. Discussion

The presented experimental results indicate important qualitative difference of electrical and electromagnetic characteristics of the studied CuNb composite samples prepared at slow and extremely fast cooling from the melt.

First of all, the onset temperature $T_c$ of the superconducting transition of these two types of composites differs almost in one and half times (Figure 1.). The external dc field $H$ qualitatively in different manner shifts and deforms the superconducting transition curves of the SCS and QS and in the case of the SCS reveals two stages of the transition (Figures 2a, 2b) typical for the granular superconductors with a grain size $r_{\text{eff}} \geq \lambda_L$, where $\lambda_L$ is a London penetration depth. In a granular sample the superconductivity arises inside the grains and a width of corresponding part of the transition curve is determined by the material purity. If the grain size $r_{\text{eff}} \gg \lambda_L$, the absolute value $|\chi'|$ have to approximate the meaning of about the superconductor volume fraction. Only after completing the superconducting transition in the main part of the grains a formation of isolated and infinite superconducting clusters becomes possible. The external dc magnetic field essentially decreases the temperature of the infinite cluster formation or even prevents from its formation. Similar behaviour is observed for our CuNb SCS. In particular, the kink of the transition curves at the beginning of the second transition stage is observed at a value of the $|\chi'|$ comparable with the Nb volume fraction.

In contrast to the case of the slow cooled B2 sample, the superconducting transition in the quenched CuNb12 samples looks like to that in an ordinary hard superconductor. The absence of the “granular features” in studied characteristics of the QS gives arguments of the formation in them of an effective superconducting media which parameters may be remarkably modified with respect to the proper of the pure bulk Nb.

We have explained the great difference of the $T_c$ of the SCS and QS taking into account a size effect caused by a proximity effect (see, for example, [9]). According to [9] the size effect in the superconducting transition temperature may be written as $[T_c - T_c(r)] / T_c = (r_i / r)^2$, where $r_i$ is an
ultimate radius under which the particle inside the matrix can not become superconducting down to 0 K, e.g. \( r_1 \) satisfies to an equation \( T_c(r_1) = 0 \). Obviously, only the particles with \( r > r_1 \) contributes to the values measured in our experiment. For the calculation of the dependence \( \chi'(T) \) we have used a logarithmically normal distribution function \( f(r) \) of the particle size \( f(r) \propto (1/r) \exp\left[-\left|\ln(r/\bar{r})/4\sigma^2\right|^2\right] \), where \( \sigma \) is a dispersion of the distribution and \( \bar{r} \) is an average radius of the particle. The superconducting transition onset are determined by the equation \( T(r_{\text{min}}) = T_c \left[1 - (r_1/r_{\text{min}})^2\right] \) allowing to estimate the characteristic radius \( r_{\text{min}} \).

The comparison of the calculations and experiment in the case of the slow cooled sample B2 gives the best agreement for the characteristic particle size of about 800 Å and \( \sigma = 0.45 \). In the case of the nano-composite CuNb12 sample the calculation does not give a good result even for very narrow distribution \( \sigma = 0.06 \). We can reach a good agreement if cut the tail of the distribution from the side of a large particle size. The fit in this way gives the average particle size in the QS close to 170 Å. These results rather well agree with our estimations according to which coagulation processes in the quenched samples has a time to complete. As a result, a concentration of Nb particles have to be close to a concentration of the nucleuses of a new phase forming at the quench process and their distribution on size has to be narrow and correspond to the normal law.

![Figure 6](image)

Figure 6. Fragments of voltage-current characteristics of the sample CuNb12b (symbols) and results of a calculation (lines) by the formula \( V = R \sqrt{I^2 - I_c^2} \). The experimental VCC data are obtained for \( T = 4.2 \) K and \( (H \perp I) \). The values \( I_c \) were chosen to satisfy the close calculation and experimental results at the abnormal parts of the VCC. In calculation we have used \( R = 3.5 \) \( \mu \Omega \) for these three VCC. (The distance between the potential contacts of the sample is equal to 1 cm.)

Using the experimental data, in particular of Figure 2, and the relation for the upper critical field \( H_{c2}(T) = H_{c2}(0)\left[1 - (T_c/T)^2\right] \) which destroys a superconductivity at a temperature \( T_c \), we have estimated \( H_{c2}(0) = (8.3 \pm 1.6) \) kOe and the coherence length \( \xi_d = 220 \) Å of the sample CuNb12 effective superconducting media. This length is close to the size of the Nb particles and is approximately a half of the \( \xi_{\text{Nb}} = 380 \) Å. So, the coherence length is modified to the Nb particle size in the nano-composite CuNb12. Adding this fact to the absence of the granularity features in the superconducting transition characteristics we conclude that the effective superconducting media forms in the fast cooled CuNb samples.

The critical currents of this media is comparable with that of the CuNb granular micro-composite B2. The abnormal VCC of the CuNb nano-composites we have tried to connect to a possibility of Josephson generation. The generation results in a dissipation of the electrical current and a voltage drop in the sample. According to an RSJ model [10] valid near \( T_c \), this voltage \( V = R(I^2 - I_c^2) \), where \( R \) is the normal state resistance of the sample. Almost linear parts of the VCC shown in Figure 5
correspond to \(R = 3.5 \, \mu\Omega\). Using this \(R\) value and the \(I_c\) values indicated in the specifications of Figure 6 we calculated an expected voltage in the sample CuNb12 under the external dc field \(H\). The calculation results and the measured VCC are presented in Figure 6. One can see that the agreement between the calculation and experiment becomes better as the external dc magnetic field increases. It is natural for the RSJ model because the increase of the dc field approximates the experimental conditions to the vicinity of the superconducting transition.

If the Josephson generation in the sample CuNb12 is a fact, the resistivity at the abnormal part of its VCC should be close to the resistivity of the matrix normal metal. For the abnormal VCC part the experiment gives \(\rho \approx 2 \, n\Omega \times \text{cm}\) that almost in 2000 times less than the residual resistivity of the sample. Indeed, the extremely great residual resistivity of the sample CuNb12 is connected partly to very short spacing (~100 Å) between the Nb particles limiting the normal electron free path. One may suppose the scattering effectiveness of current carriers at a N-S boundary may be strongly reduced by the Andreev reflection. According to [10] the N-S boundary gives “an excessive resistance” \(R_{ex} = Z(T)\rho_{\lambda Q} / S\), where \(\rho\) is a normal state resistivity of a superconductor, \(S\) is a square of its cross-section, \(\lambda_q \approx (1 - T/T_c)^{-1/4}\) means an electric field penetration depth into superconductor, \(Z(T)\) is a coefficient taking into account a fraction of all electrons passing the N-S boundary without Andreev reflection. The coefficient \(Z(T)\) tends to zero as \(T \to 0\) and to unity as \(T \to T_c\). Assuming that a reduction of an electron scattering rate caused by the Andreev reflection takes place one may expect the significant decrease of the normal resistivity of the studied CuNb nano-composite at \(T < T_c\), \(I > I_c\). But even in this case it is very difficult to explain in considered way such low resistivity \(\rho \approx 2 \, n\Omega \times \text{cm}\) at the abnormal flat part of the CuNb12 sample VCC because the normal electron scattering rate \(\nu_{T < T_c}(T) \sim \nu_T + \nu_{Nv}Z(T)\) can not be lower than \(\nu_T\). The last is determined mainly by the Cu matrix purity and is limited by the presence of Nb admixture inside it.

3. Conclusion

The studied electromagnetic properties of the three-dimensional micro- and nano-composites CuNb reveal qualitative modifications of the material superconducting parameters in the last. The granular superconducting media transforms into the effective superconducting media. The coherence length of the last becomes close to the Nb nano-drops diameter that is remarkably less than the coherence length of the bulk Nb. The critical temperature of such media is considerably lower and the upper critical field higher than in a pure bulk Nb. Its voltage-current characteristic has the abnormal flat part in an intermediate region of current caused possibly by the Josephson generation of N-S boundaries like in mesoscopic N-S contacts.

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