Microdispersive superconductors in ceramic and polymeric matrix

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Abstract. The influences of the host material on the superconducting properties of the composite material are studied in the following cases: (i) niobium powder—aluminium oxide, (ii) technetium—rare earth oxides and (iii) Nb_3S_n powder—unsaturated polymer of fluorine derivative of ethylene. The critical temperatures, critical magnetic fields and the I – V characteristics of these systems are discussed.

Keywords. Microdispersive superconductors; ceramic matrix; polymeric matrix.

Studies on the influence of host materials on the superconducting properties of the composite material are of great scientific and technical interest. If the microdispersive superconductor is introduced into the matrix with high Debye temperature and high dielectric constant or with various conductivity mechanisms, one may investigate the dependence of the superconducting properties of metals on the matrix material. To avoid the shunting effect due to matrix metal it is necessary (i) to determine the limited metal concentration where the superconducting current exists and (ii) to reach the largest specific surface of contacts in the sample by preparation of very thin component powders (10^2 – 10^1 Å).

These systems are interesting for practical purposes due to the possibility of making superconducting materials with very high resistivity before their transition into the superconducting state. It may be important for superconducting switching devices and superconducting sensors of electromagnetic radiation.

Liquid eutectic alloy In–Ga–Sn in porous glass matrix was studied earlier (Alekseev *et al* 1975). It was found that the critical temperature did not increase but the “normal alloy–superconductor transition” was sharper ($\Delta T \sim 0.8$ K) than the one in the alloy without glass matrix In–Ga–Sn ($\Delta T \sim 1.6$ K) ($T_c \sim 4.9$ K).

Glass and other dielectric matrices have limited electronic properties for studying the matrix material dependence on T_c . We therefore attempted to solve the first of the two problems mentioned earlier by determining the metal concentration in the matrix at which the metal–insulator transition occurs. The mix of alumina powder and metal (Nb) powder (grain size of ~ 5 μm) was used as the model system.

Samples of various volume concentrations of components were sintered at 1800 °C. As a result, superconducting cermets Nb– Al_2O_3 with different metal concentration were obtained. For cermets T_c and J_c (at $T = 4.2$ K) were measured at $H = 0$ T. It is shown that T_c changes slightly with Nb concentration ($T_c = 5$ – 6 K). The resistivity ρ of the cermets before their transition to superconducting state is $\sim 10^{-1}$ – 10^{-2} Ωcm and the metal volume concentration and ρ decreases abruptly to 20% and $\sim 10^{-4}$ Ωcm respectively.

Cermets with Nb concentration $> 20\%$ indicate abrupt transition to superconduct-

tion state and those $< 20\%$ indicate step-like transition as shown in figure 1 (curves 1 and 2 respectively).

We assume that at low volume concentration of Nb the contacts on boundary metal-ceramics which were shunted by metal masses of matrix at larger metal concentrations begin to play an important role.

Figure 1. Transition to superconducting state in Nb-alumina cermets.

Figure 2. Critical current density versus Nb concentration for Nb-Al₂O₃ cermets.

The sharp decrease of ρ with increasing Nb concentration agrees qualitatively with the results of model experiments on small metallic balls (Alekseev *et al* 1975).

It is interesting that J_c of cermet samples of ϕ 1 mm changes with Nb concentration very slightly without sharp jumps (figure 2).

To study the influence of the ceramic matrix on T_c we have prepared the cermets "technetium-rare-earth oxide" R_2O_3 ($R = \text{La, Sm, Eu, Ga, Tb, Ho, Er, Yb, Lu}$) (Alekseev *et al* 1977). The resistance of the samples was measured by a four-probe method, and the temperature measured using an Fe–Au thermocouple. The results are shown in figure 3. T_c of base technetium was ~ 7.45 K. It is found that the cermets Technetium R_2O_3 have higher T_c compared with metallic Technetium. The Technetium- La_2O_3 cermet indicates abnormally high T_c . The resistance changes sharply at $T = 12$ K. It is obviously connected with the phase transition in lanthanum oxide at this temperature. The onset of superconducting transition in Technetium- La_2O_3 cermet takes place at 10.25 – 10.5 K.

Other cermets indicate higher T_c than T_c of the pure Technetium, but it was observed that T_c of these cermets decreases with increase of rare-earth element atomic number. All measured cermets indicate higher critical magnetic field than one of pure Technetium (for example H_c of Technetium- Sm_2O_3 is 10 times greater than H_c of pure Technetium).

Figure 3. Critical magnetic field (H_0) and critical temperature T_c versus atomic number of rare-earth elements for Technetium- R_2O_3 cermets. (The beginnings and the ends of arrows indicate the onset and the end of superconducting transition).

Figure 4. Superconducting transition in superconductor-polymer matrix system.

Figure 5. Current vs voltage characteristic of superconductor-polymer matrix system.

Table 1. Some characteristics of molecular cermets and their components.

Ln	T_k (°K)	R_{300}/R_{res}	Metal content (%)	Mean size of oxide phase particles, μm
La	9.35	—	50.80	5.0
Sm	4.2	6	52.30	2.3
Eu	7.90	17.5	52.08	3.5
Gd	7.97	14.5	51.35	2.7
Tb	7.57	12	51.13	1.25
Ho	7.52	16	—	1.2
Er	7.58	15	26.36	1.2
Yb	7.32	7	54.60	1.15
Lu	7.45	—	—	1.0

We feel that the T_c increase observed in Technetium- R_2O_3 cermets compared to T_c of pure Technetium is due to the influence of R_2O_3 .

We have tried to prepare superconductors in polymer matrix (Alekseev *et al* 1977). In contrast to the superconducting cermets case, the metal-insulator transition in the superconductor-polymer (unsaturated polymer of fluorine-derivative ethylene) system occurs at a metal concentration of 70%. The Nb_3Sn powder (grain size $\sim 5 \mu m$) was used as a superconducting metal. Superconductors with polymer matrix were prepared by mixing metallic powder and polymer at 150–200°C under pressure. Figure 4 shows the transition to superconducting state of the metal-polymer system for metal concentration 70% and 80%. The low J_c and nonlinear current-voltage characteristic (figure 5) may indicate the existence of tunnelling contacts in such superconductors.

It is also found that samples with 60–65% Nb_3Sn indicate high sensitivity to submillimeter radiation (more than 10^3 v/w for 8 mm radiation). The width of the superconducting transition in the superconductor-polymer system is 16–17 K.

References

- Alekseev V A 1972 *J. Non Cryst. Solids* **8–10** 723
Alekseev V A, Vedenov A A, Lelichko A V, Zaitseva L L, Konarev M I, Ryzhkov Yu F, Sukhikh A I, Parshin A I and Shishkov N V 1975 *Molecular superconducting cermets; Theses of conference on technical application of superconductivity*, Alushta
Alekseev V A, Baranovsky V M, Vedenov A A, Velichko A V, Zaitseva L L, Kovalenko A S, Konarev M T, Leshchenko G F, Mylnikova T S, Ryzhkov Yu F, Skidan B S, Sukhikh A I, Feklina L I, Usov N A, Parshin A I and Shishkov N V 1977 *Small-dispersive superconductors in ceramic and polymeric matrix; Superconducting materials*, Atomizdat