TERNARY CU – BASE IN SITU COMPOSITES – A NEW GENERATION OF HIGH STRENGTH CONDUCTORS

MAX-PLANCK PROJECT REPORT

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Project References

D. Raabe, J. Ball, G. Gottstein: Scripta Metall. 27 (1992) 211–216
„Rolling textures of a Cu-20%Nb composite“

D. Raabe, F. Heringhaus: physica status solidi (a) 142 (1994) 473–481
„Correlation of superconductivity and microstructure in an in-situ formed Cu-20%Nb composite“

F. Heringhaus, U. Hangen, D. Raabe, G. Gottstein: Materials Science Forum 157–162 (1994) 709–714.
„Textures of rolled and wire drawn Cu-20% Nb“

U. Hangen, D. Raabe: physica status solidi (a) 147 (1995) 515–527
„Experimental investigation and simulation of the normal conducting properties of a heavily cold rolled Cu-20mass% Nb in situ composite“

D. Raabe, U. Hangen: Materials Letters 22 (1995) 155–161
„Observation of amorphous areas in a heavily cold rolled Cu-20wt.% Nb composite“

F. Heringhaus, D. Raabe, G. Gottstein: Acta Metall. 43 (1995) 1467–1476
„On the correlation of microstructure and electromagnetic properties of heavily cold worked Cu-20 wt.% Nb wires“

D. Raabe, F. Heringhaus, U. Hangen, G. Gottstein: Zeitschrift für Metallkunde 86 (1995) 405–422
„Investigation of a Cu-20mass%Nb in situ Composite
Part I: Fabrication, Microstructure and Mechanical Properties
Part II: Electromagnetic Properties and Application“

U. Hangen, D. Raabe: Acta Metall 43 (1995) 4075–4082
„Modelling of the yield strength of a heavily wire drawn Cu-20%Nb composite by use of a modified linear rule of mixtures“

D. Raabe, U. Hangen: Acta metall. 44 (1996) 953–961
„Correlation of microstructure and type II superconductivity of a heavily cold rolled Cu-20mass% Nb in situ composite“

D. Raabe, U. Hangen: physica status solidi (a) 154 (1996) 715–726
„On the anisotropy of the superconducting properties of a heavily cold rolled Cu-20 mass% Nb in situ composite“

D. Raabe, D. Mattissen: Acta Materialia 46 (1998) 5973–5984
„Microstructure and mechanical properties of a cast and wire drawn ternary Cu-Ag-Nb *in situ* composite“

D. Raabe, D. Mattissen: Acta Materialia 47 (1999) 769–777
„Experimental investigation and Ginzburg–Landau modeling of the microstructure dependence of superconductivity in Cu–Ag–Nb wires“

D. Mattissen, D. Raabe, F. Heringhaus: Acta Materialia 47 (1999) 1627–1634
„Experimental investigation and modeling of the influence of microstructure on the resistive conductivity of a Cu–Ag–Nb in situ composite“

K. Miyake, N. Hanzawa, H. Takahara, S. Kobayashi, D. Raabe: Japanese Jornal of Applied Physics 39 (2000) 119-121
„Application of In Situ-Formed Metallic-Fiber-Reinforced Copper Matrix Composites to Cables Used for Robots “

D. Raabe, K. Miyake, H. Takahara: Material Science and Engineering, A 291 (2000) 186-197
„Processing, microstructure, and properties of ternary high–strength Cu–Cr–Ag in situ composites“

Report Abstract

A new generation of ternary *in situ* metal matrix composites, based on Cu-Ag-Nb and Cu-Ag-Cr, with high strength, high conductivity, and a comparatively low melting point are investigated in this project and suggested for applications in the fields of high field magnet design and robotics.

The samples were manufactured by inductive melting, casting, and wire drawing. The report concentrates on the investigation of the mechanical and electromagnetic properties and their relation to the microstructure, as well as on aspects associated with the industrial production of such compounds.

1 Introduction

Binary metal matrix composites (MMC) containing Cu as matrix and a bcc refractory metal [1-12] or fcc Ag [13-19] as a second phase represent of class of materials with a high strength and a high conductivity. Although substantial progress was made in optimizing these alloys with respect to particular applications in the field of robotics [20] and high field magnet design [21-27], some subtleties associated with the dislocation-filament interaction and the superconductivity (in alloys containing Nb) as well as their industrial mass production remain major unsolved issues [28-37].

This report introduces a new generation of ternary alloys [38], focussing on Cu-Ag-Nb and Cu-Ag-Cr composites, with the aim to combine the hardening effects of Ag (fine precipitates, filaments, eutectic) with those of the bcc phase (filaments), and at the same time simplify the processing through a decrease of the melting point. The alloys were processed by inductive melting and manufactured by wire drawing at room temperature with and without intermediate annealing. Due to the partial replacement of the high melting bcc elements (Nb, Cr) by Ag, the melting points of the alloys are much below those of the classical Cu-bcc composites. For a given chemical composition the filament morphology and topology mainly determines the strength and the electrical properties of MMCs. This report hence draws particular attention to the microstructure evolution in the course of manufacturing. The obtained data are used to explain the observed mechanical and electrical properties [39].

2 Material synthesis and experimental methods

A Cu-8.2%Ag-4%Nb and various Cu-(1-5)%Ag-(5-10)%Cr alloys were prepared by inductive melting (%=mass%). From the cast cylindrical ingots wires were produced by rotary swaging and drawing through hard metal drawing bench dies up to true wire strains above $\eta = 10$. The Cu-Ag-Nb alloy was drawn without intermediate annealing. For the Cu-Ag-Cr alloys various annealing treatments were used. Further manufacturing details are reported elsewhere [40].

Optical and scanning electron microscopy (SEM) was employed to determine the morphology and topology of the Ag, Cr, and Nb fibers. Due to insufficient contrast, an unambiguous optical identification of the various phases was sometimes not possible. The samples were thus additionally analyzed using energy-disperse X-ray spectrometry (EDX). The morphology of the isolated Nb fibers was additionally investigated by use of a selective etching technique, where the Cu and Ag were dissolved by dilute nitric acid. Vickers hardness measurements were carried out on samples which were prepared by grinding and etching. Tensile tests on deformed wire samples were conducted at 298 K and at 77 K.

3 Experimental results and discussion

3.1 Mechanical properties

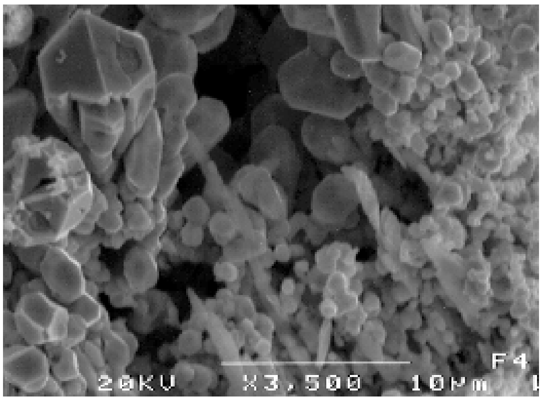

Fig. 1 Nb Morphology, as cast state.

Fig. 1 exemplary shows the Nb in the microstructure of as-cast Cu-8.2% Ag-4% Nb after removing the matrix and the Ag by etching. The Ag had a lamellar shape and formed a Ag-Cu eutectic. Some of the eutectic domains solidified around primary Nb. The Nb appeared in the form of Wulff-polyhedra and dendrites with an average diameter of $d_{Nb} \approx 1481$ nm. Fig. 2 shows the evolution of the Nb into filaments. At low strains ($\eta \leq 4$), the Nb morphology appeared inhomogeneous. While some dendrite arms revealed strong elongation, others appeared almost undeformed. With increasing strain ($4 < \eta < 10.5$), the filament morphology became more

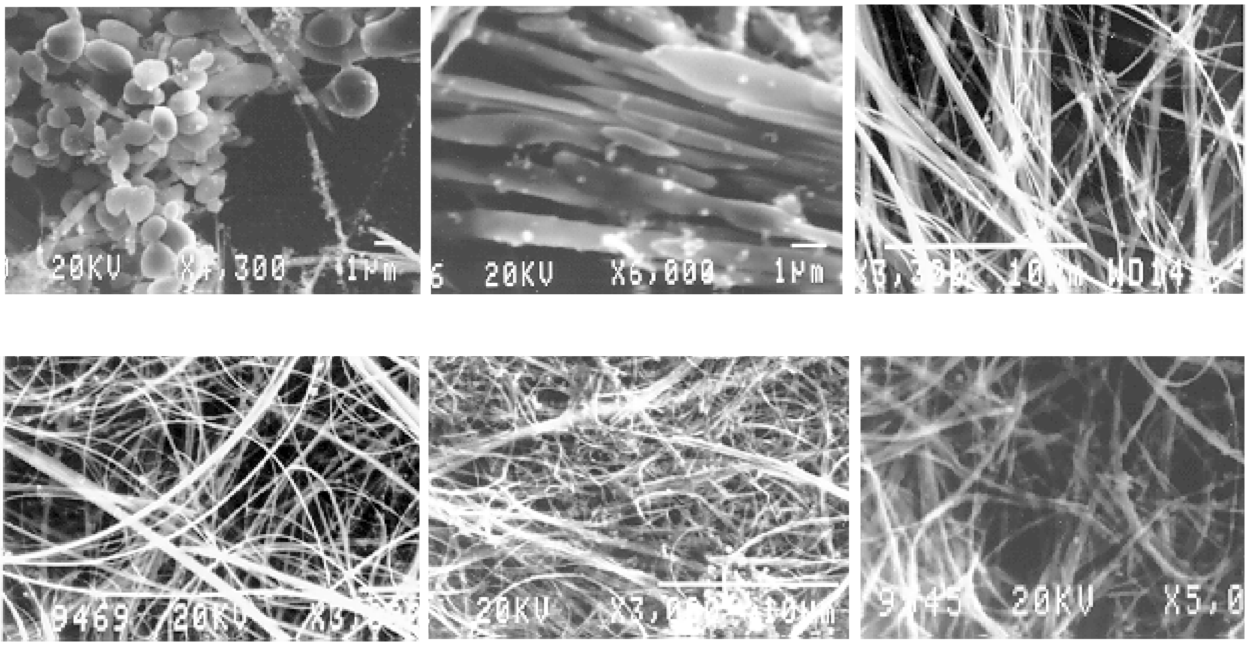

Fig. 2 Morphological evolution of the Nb filaments during wire drawing, $\eta = 2.59$-10.5.

uniform. At maximum strain ($\eta = 10.5$) the fibers had an average diameter of $d_{Nb} \approx 66$ nm. The smallest observed filaments were below 33 nm. The random distribution of the dendrites is a preparation artifact. Fig. 3 shows the Nb filament diameter, d_{Nb}, as a function of the wire strain. The Ag filaments in the Cu-Ag-Nb were at low strains shorter and thicker than the Nb filaments. With increasing strain their morphology became more similar to that of the Nb. At a wire strain of $\eta = 3.6$ the average Ag filament diameter amounted to $d_{Ag} \approx 676$ nm and at $\eta = 6$ to $d_{Ag} \approx 260$ nm. The corresponding data for the Cu-Ag-Cr are also shown in Fig. 3.

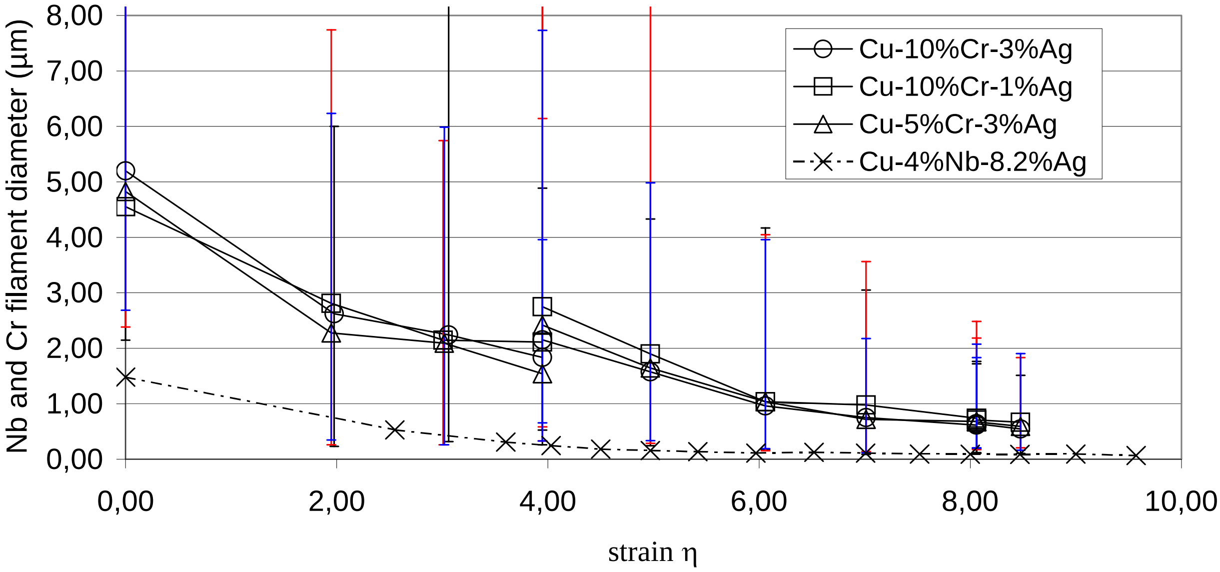

Fig. 3 Filament thickness of the Cr and Nb filaments in Cu-Ag-Cr and Cu-Ag-Nb.

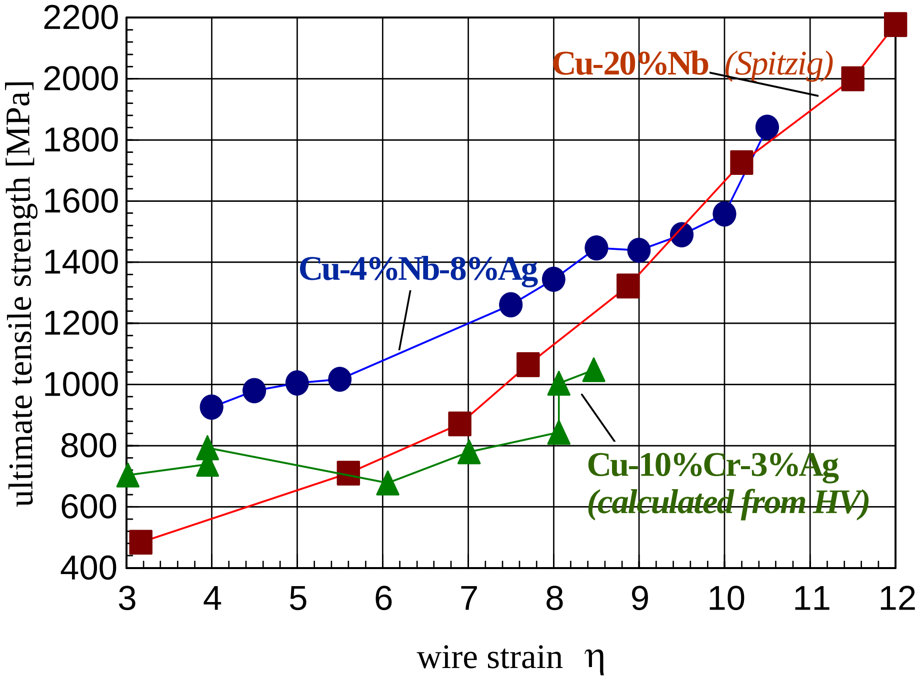

Fig. 4 Ultimate tensile strength for as a function of the true wire strain.

Fig. 4 shows the course of the ultimate tensile strength (UTS) for various alloys as a function of the true wire strain. The UTS of the Cu-Nb-Ag wire at ambient temperature increases exponentially and reaches a maxi-mum value of about 1841 MPa at a strain of η = 10.5. At 77 K it was even larger by about 300 MPa.

Fig. 3 substantiates that the diameter of the Nb in the investigated ternary Cu-Ag-Nb alloy is smaller than in the binary Cu-20 %Nb alloys[1]. This applies not only for the diameter in the as-cast state but also for the further thickness drop during drawing. A compa-rison of the fitted curves shows that the exponential drop of the Nb filament thickness is even steeper in the ternary than in the binary alloy. The ternary

[1] the Nb filament data for the Cu-20%Nb MMC were taken from the paper of Heringhaus et al. [12].

material thus contains small Nb filaments already at medium wire strains (η ≈ 4 - 6) with a thickness below those observed in the binary MMC.

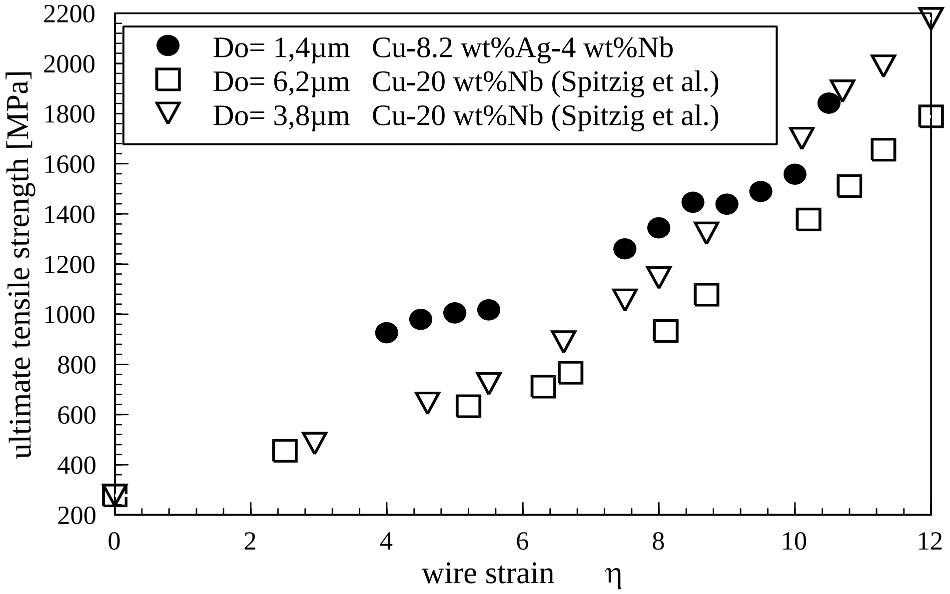

Fig. 5 Ultimate tensile strength of Cu-8.2 mass% Ag-4 mass% Nb and two Cu-20 mass% Nb alloys with different Nb dendrite diameters in the as-cast state (Cu-20% Nb data from [42]).

This evolution has two advantages. First, the various physical [28,29,43] and empirical mo-dels [4,5,9,44] pre-dict a Hall-Petch type increase in strength, inversely pro-portional to the square root of the interface spacing. Second, the rapid refinement in fiber scale as a function of wire strain pro-vides advantageous properties already at medium wire strains. This aspect is particularly re-levant, since in most electro-magnetic applications very thin wire dimensions are to be avoided. The effect of these microstructural improvements with respect to earlier Cu-Nb alloys is demonstrated in Fig. 5, which shows the UTS as a function of wire strain for Cu-8.2%Ag-4%Nb and two Cu-20%Nb alloys [42] with different Nb dendrite diameters in the as-cast state. This diagram sub-stantiates that the UTS of the ternary material with a total alloy content of only 12.2% exceeds that of Cu-20%Nb up to wire strains of η ≈ 8. At larger strains it shows a similar strength as Cu-20%Nb with an initial dendrite diameter of 3.8 µm.

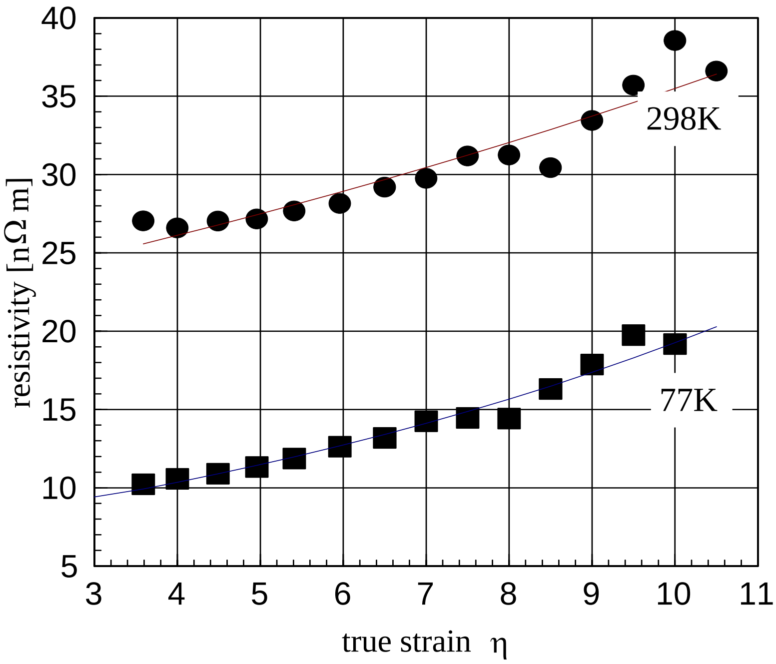

Fig. 6 Resistivity of the Cu-Ag-Nb MMC.

3.2 Electromagnetic properties

Fig. 6 shows the evolution of the electrical resistivity of the Cu-Ag-Nb alloy at 295K and 77K during wire drawing. The resistivity increases considerably with the degree of deformation. The strong dependence may be chiefly attributed to the scattering of conduction electrons at the various phase boundaries. This effect becomes particularly pronounced when the average filament spacing is, after heavy deformation, of the same order of magnitude as the mean free path of the conduction electrons in the Cu and the Ag phase. Since the Cu-Ag interfaces have a low, and the Cu-Nb and Ag-Nb interfaces a very high amount of inelastic scattering, the latter are assumed to be primarily responsible for the observed increase in resistivity.

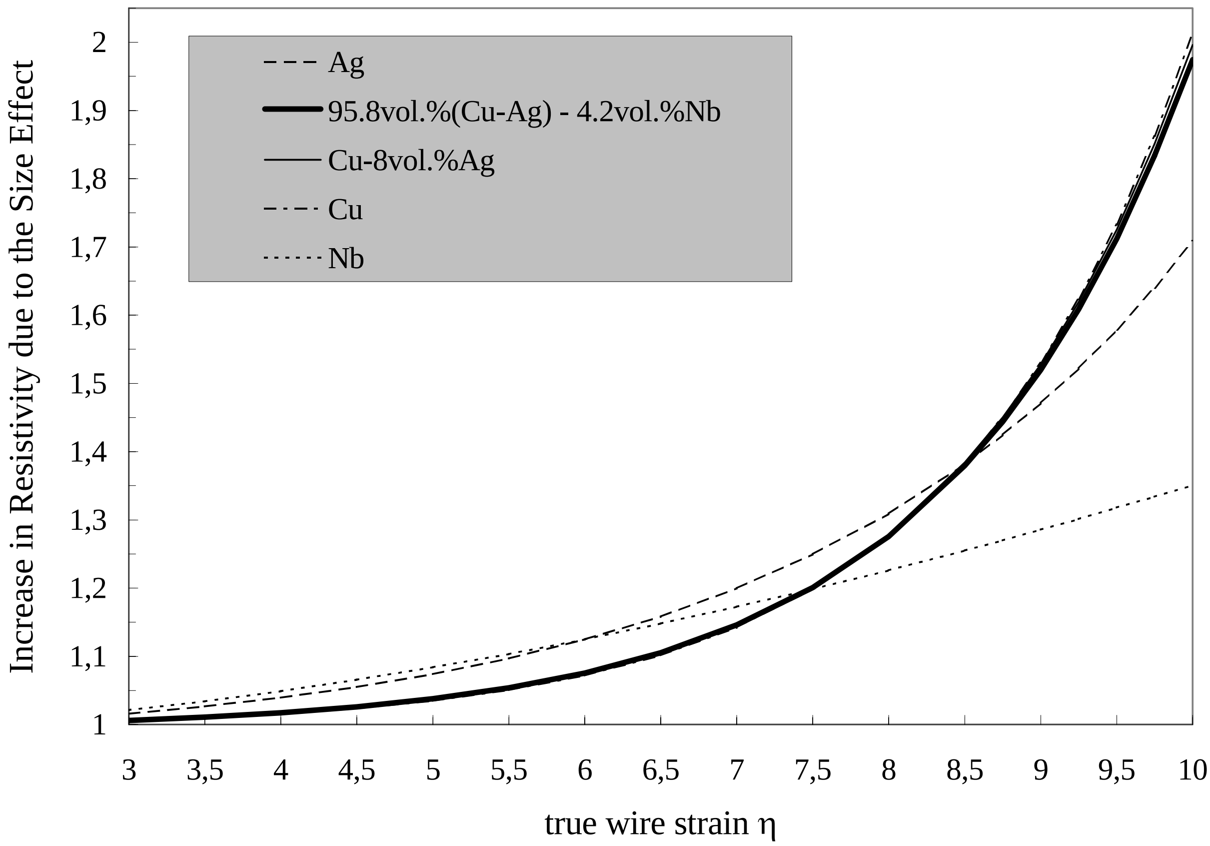

Fig. 7. Relative change in resistivity as a function of wire strain due to the size effect.

The mean free path of conduction electrons in pure Cu amounts to l=43-45 nm at 293K and l= 138-145 nm at 77K. Applying the theory of electron scattering at the surface of very thin wires [11,12,45-49] one can quantitatively assess the increase in resistivity as a function of strain by representing the three phases as linear resistors connected parallel, with the resistivity of each phase varying according to its actual filament thickness, Fig. 7. It is straightforward to show that the contribution of interface scattering to the overall resistivity considerably exceeds that of the inelastic scattering at the dislocation cores. The electrical resitivity of the various Cu-Ag-Cr alloys was for all investigated samples below that of comparable Cu-Ag-Nb samples.

Fig. 8 shows the transition of a Cu-Ag-Nb MMC wire (η=7) from the normal resistive to the superconducting state. This is a quite surprising result since only 4mass% of the sample should have superconducting properties (Nb, T_C =9.2K). In the microstructure investigation, however, no Nb filaments were observed to have a length comparable to the distance between the voltage leads (12-15cm). Thus it is not likely that a continuous connection of Nb ribbons existed over the distance examined.

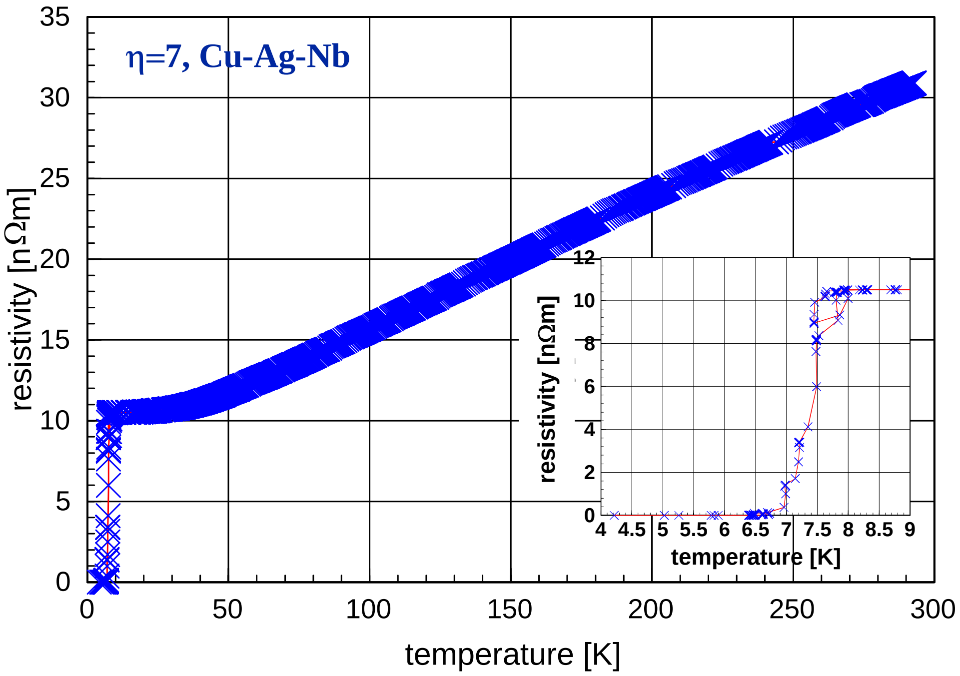

Fig. 8 Transition of the Cu-Ag-Nb MMC to the superconducting state

The observed superconductivity can hence only be explained in terms of the occurrence of weak links between the isolated Nb filaments, i.e. in terms of a local penetration of the superconducting state into the Cu matrix (metal-metal proximity effect). However, corresponding simulations using the Ginzburg-Landau theory, which essentially show that weak links can only exist within the order of the coherence length of Nb, give an unclear picture of the surprising stability of the superconducting state in this material.

4 Conclusions

A ternary *in situ* Cu - 8.2 mass% Ag - 4 mass% Nb and various ternary Cu - (1-5) mass% Ag - (5-10) mass% Cr *in situ* MMCs were manufactured by melting, casting, and wire drawing. The microstructure was investigated using electron microscopy and EDX. The mechanical properties were determined using tensile and hardness tests. The electromagnetic properties were examined using four probe DC tests at various temperatures. The main results are:

- The Cu-Ag-Nb material was very ductile. A maximum wire strain of $\eta = 10.5$ was reached without intermediate annealing. The various Cu-Ag-Cr alloys were more brittle, so that an intermediate annealing treatment had to be carried out during drawing as a rule.
- Cu-Ag-Nb wires of maximum strain ($\eta_{max} = 10.5$) had an UTS of 1840 MPa and 46% of the conductivity of pure Cu (IACS). The various Cu-Cr-Ag alloys generally had a lower strength and conductivity.
- The wire strength of all investigated ternary alloys was much larger than predicted by the linear rule of mixtures. Up to $\eta \approx 8$ the UTS of Cu-Ag-Nb was even larger than that of the classical Cu-20 mass% Nb compound, although it had a lower total alloy content of only 12mass%.
- The observed mechanical properties of the ternary MMCs can be interpreted in terms of a Hall-Petch or phase barrier type effect that chiefly arises from lattice dislocation pile ups at the interfaces.
- The electrical conductivity of the ternary composites at large strains decreased with increasing strain. This can be attributed to the size effect, i.e. to the inelastic scattering of the conduction electrons at the internal interfaces.
- The ternary Cu-Ag-Nb sample revealed type II superconducting behavior, although only 4% of the sample (Nb) had superconducting properties. This phenomenon could not be consistently explained on the basis of the phenomenological Ginzburg-Landau approach.

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5 References

[1] J. Bevk, J.P. Harbison, J.L. Bell, J. Appl. Phys. **49** (1978) 6031.
[2] K.R. Karasek, J. Bevk, J. Appl. Phys. **52** (1981) 1370.
[3] P.D. Funkenbusch, T.H. Courtney, Acta metall. **33** (1985) 913.
[4] W.A. Spitzig, A.R. Pelton, F.C. Laabs, Acta metall. **35** (1987) 2427.
[5] W.A. Spitzig, P.D. Krotz, Scripta metall. **21** (1987) 1143.
[6] P.D. Funkenbusch, J.K. Lee, T.H. Courtney, Metall. Trans. A, **18** (1987) 1249.
[7] L.S. Chumbley, H.L. Downing, W.A. Spitzig, J.D. Verhoeven, Mat. Sc. Eng. **A117** (1989) 59.
[8] P.D. Funkenbusch, T.H. Courtney, Scripta metall. **23** (1989) 1719.
[9] W.A. Spitzig, Acta metall. **39** (1991) 1085.
[10] W.A. Spitzig, H.L. Downing, F.C. Laabs, E.D. Gibson, J.D. Verhoeven, Metall. Trans. A **24** (1993) 7.
[11] D. Raabe, F. Heringhaus, U. Hangen, G.Gottstein, Z. Metallk. **86** (1995) 405.
[12] F. Heringhaus, D. Raabe, G. Gottstein, Acta metall. **43** (1995) 1467.
[13] H.E. Cline, D. Lee, Acta metall. **18** (1970) 315.
[14] G. Frommeyer, G. Wassermann, phys. stat. sol. A **27** (1975) 99.
[15] G. Frommeyer, G. Wassermann, Acta metall. **23** (1975) 1353.
[16] Y. Sakai, K. Inoue, H. Maeda, Acta metall. **43** (1995) 1517.
[17] Y. Sakai, H.-J. Schneider-Muntau, Acta metall. **45** (1997) 1017.
[18] F. Heringhaus, Ph.D. thesis, Institut für Metallkunde und Metallphysik, RWTH Aachen, Germany, and National High Magnetic Field Laboratory, Tallahassee, USA (1997) in press.
[19] K.Y. Sohn, Ph.D. thesis, Department for Materials Science and Engineering, University of Florida, Gainesville, USA (1997).
[20] D. Raabe, K. Miyake, H. Takahara, soon to be published.
[21] S. Foner, E. Bobrov, IEEE Magnetics **24** (1987) 1059.
[22] T. Asano, Y. Sakai, K. Inoue, M. Oshikiri, H. Maeda, IEEE Magnetics **28** (1992) 888.
[23] F. Heringhaus, Y.M. Eyssa, P. Pernambuco-Wise, M.D. Bird, G. Gottstein, H.-J. Schneider-Muntau, Metall **50** (1996) 272.
[24] J.D. Embury, M.A. Hill, W.A. Spitzig, Y. Sakai, MRS Bull. **8** (1993) 57.
[25] F. Heringhaus, R. Leffers, G. Gottstein, H.-J. Schneider-Muntau, Processing, Properties, and Application of Cast Metal Matrix Composites, TMS Fall Meeting, **1** (1996) 127.
[26] H.-J. Schneider-Muntau, IEEE Transact. on magnets **18** (1982) 32.
[27] J.T. Wood, J.D. Embury, M.F. Ashby, Acta mater. **45** (1997) 1099.
[28] J.G. Sevillano, Journ. de Physique III **6** (1990) 967.
[29] U. Hangen, D. Raabe, Acta metall **43** (1995) 4075.
[30] J.T. Wood, Ph.D. thesis, McMaster University, Canada (1994).
[31] J.D. Embury, private communication (1997).
[32] D. Raabe, F. Heringhaus, phys. stat. sol. A **142** (1994) 473.
[33] D. Raabe, U. Hangen, Acta metall. 44 (1996) 953-961.
[34] D. Raabe, U. Hangen, phys. stat. sol. A **154** (1996) 715.
[35] D.J. Chakrabati, D.E. Laughlin, Bull. Alloy Phase Diagramms **2** (1982) 936.
[36] G.I. Terekhov, L.N. Aleksandrova, Izvest. Akad. Nauk SSR. Metally **4** (1984) 210.
[37] J.L. Murray, Metall. Trans. A **15** (1984) 261.
[38] W.A. Spitzig, unpublished data.
[39] D. Raabe, D. Mattissen, soon to be published.
[40] D. Raabe, D. Mattissen, Metall, in press (1997).

[41] J.D. Verhoeven, W.A. Spitzig, F.A. Schmidt, P.D. Krotz, E.D. Gibson, Jour. of Mat. Sc. **24** (1989) 1015.
[42] J.D. Verhoeven, L.S. Chumbley, F.C. Laabs, W.A. Spitzig, Acta metall. **39** (1991) 2825.
[43] D. Raabe, U. Hangen, Comp. Mater. Sc. **5** (1996) 195.
[44] C. Trybus, W.A. Spitzig, Acta metall. **37** (1989) 1971.
[45] J.G. Rider, C.T.B. Foxon, Phil. Mag. **16** (1967) 1133.
[46] F.W. Reynolds, G.R. Stillwell, Phys. Rev. **88** (1952) 418.
[47] R.B. Dingle, Proc. Soc. London Ser. **201** (1950) 545.
[48] E.H. Sondheimer, Adv. Phys. **1** (1952) 545.
[49] D. Raabe: Comp. Mat. Sc. **3** (1995) 402.