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Scale-up of silver – copper composite wires by spark plasma sintering and room temperature wire-drawing for use in 100 T triple coil at LNCMI

S. Tardieu, J. Béard, D. Mesguich, A. Lonjon, N. Ferreira, G. Chevallier, C. Estournès, C. Laurent
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Abstract— The generation of non-destructive pulsed magnetic fields of 100 T involves high mechanical stress, due to the Lorentz forces, which few conductors can resist. At LNCMI, in the inner coil (the most mechanically stressed) of the 100 T triple coil system a commercial conductor is used. It is presented the work on a new bi-material design of the inner coil allowing firstly reducing the use of this commercial conductor. Secondly, it is detailed how increasing the volume of Ag-Cu conductors produced at CIRIMAT and LNCMI by powder metallurgy, Spark Plasma Sintering and wire drawing at room temperature could allow the replacement of this commercial conductor.

Index Terms— High magnetic fields, Nanostructured conductors, Pulsed mag-nets, Spark plasma sintering, Wire-drawing.

I. INTRODUCTION

THE LNCMI has developed its first triple coil which made it possible to generate a pulsed magnetic field of 98.8 T [1]. The three coils being powered independently with three capacitor banks (energy 1, 6 and 14 MJ), they generate their own magnetic field. The outer coil generates a background field of about 11 T, the middle coil a field of about 27 T and the inner coil a field of about 60 T. For such device, it is essential to use electrical conductors having a resistivity as close as possible to pure annealed Cu, in order to maximize the duration of the pulse. Although the conductors are immersed in liquid nitrogen in order to limit their heating due to the Joule effect, the pulse is limited to a short duration

(a few ms). Moreover, conductors must have very high mechanical strength in order to withstand the stresses induced by the Lorentz forces during the generation of the magnetic field (1 GPa at 60 T and higher than 2.2 GPa at 100 T [2]). This triple coil system allows more flexibility in the development of the coil and allows using reinforced conductors to obtain a magnetic field of about 100 T while a monolithic coil would merely produce a magnetic field of 70 T. Currently, the inner coil consists of a winding of a copper-niobium (Cu-Nb) wire produced by Rusatom Metal Tech. Currently, it is one of the conductors strongest mechanically commercially available [3]. However, in order to avoid dependence on such conductors, which can only be produced by a single manufacturer, the LNCMI is working on solutions to limit their use or to replace them by new conductors. The first solution is to limit the quantity of Cu-Nb wire necessary for the manufacture of the inner coil. In order to achieve this, a new design is developed. This new design requires only about 200 g of Cu-Nb wire (current design requires 10 kg of Cu-Nb conductor), the rest of the coil being made up with macro-composite copper-stainless steel (Cu-SS) (manufactured by LNCMI [4] and already used in the middle coil [1]). Cu-SS wire is too hard to allow it to be wound on the first layers of the coil. The second solution is to completely replace the Cu-Nb conductor by another conductor. Among all conductors, Ag/Cu alloyed wires have been studied in detail [5], [6], [7], [8]. Ag/Cu (6-24 wt. % Ag) alloy wires have been prepared by metallurgy routes (melting, solidification and drawing), with an eutectic structure of Cu-rich and Ag-rich solid solutions. They exhibit a high ultimate tensile strength (UTS) (1160 MPa at 77 K), but the solid solution effect is responsible for their high electrical resistivity (2.10 to 2.65 $\mu\Omega\cdot\text{cm}$ at room temperature and approximately 0.80 $\mu\Omega\cdot\text{cm}$ at 77 K). The high electrical resistivity means that Ag/Cu conductors cannot be used in the winding of coils for non-destructive pulsed magnetic fields. Because composite wires show a better compromise between high UTS and low resistivity [3], [4], [9], it was proposed to prepare Ag-Cu wires with a composite microstructure. The preparation route has been adapted from previous studies on carbon nanotube-Cu composite wires prepared by powder metallurgy processes: spark plasma sintering (SPS) and wire-drawing [10], [11]. It was shown that the Ag-Cu composite wires containing only 1 vol. % Ag offers the best combination of high UTS

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(1000 MPa at 77 K) and low electrical resistivity ($0.44 \mu\Omega\cdot\text{cm}$). However, they are significantly weaker than those with 5 vol. % Ag or 10 vol. % Ag (1300 MPa at 77 K) [12]. These properties are due to the nanostructuring of the composite and the presence of two unalloyed phases, i.e. pure Cu (nanostructured matrix) and pure Ag fibers (1D reinforcement). This makes Ag-Cu wires good candidates for use in LNCMI inner coils. However, until then, the volume of the composite Ag-Cu wires produced by this method was too small to consider their use in magnets. This is why we are involved in scaling-up the production of these samples. The main risk is that the macroscopic properties will be modified during the upscale and do not longer fit the initial specifications.

II. NEW INNER COIL DESCRIPTION

It was chosen to produce a bi-material (Cu-Nb and Cu-SS) inner coil allowing to reduce the use of commercial conductor. Cu-SS (40 vol. % SS) wire, prepared at LNCMI, has a very high mechanical strength. Unfortunately, this material is so hard and cannot be wound on the 9.5 mm diameter of the inner coil bore. The deformation is so big that the stainless-steel sheath can be damaged by the winding. A reasonable diameter, knowing the cross section of about 6 mm^2 for such a coil is required, would be at least of 25 mm, thus the 4th layer inner diameter. Only 200 g of Cu-Nb make up the first three layers of the coil then the other layers are wound with a Cu-SS wire. A brass junction allows the connection between the conductors. This coil has been tested in a dual coil system and made it possible to generate several tens of magnetic fields pulses of 90 T. After integration in the triple coil system a maximum magnetic field about 92 T has been produced and the failure was due to the weakness of the Cu-SS wire and not to the junction between wires. Generating a higher magnetic field requires the use of a Cu-SS conductor with a higher UTS. Cu-SS 60 vol. % SS (6.0 mm^2 ; 1406 MPa; $0.61 \mu\Omega\cdot\text{cm}$) was therefore produced.



Fig. 1. Photography of the first bi-material inner coil prototype showing the output of the 3rd layer of Cu-Nb (right) connected by a brass junction to the entry of the 1st layer of Cu-SS (left).

TABLE I
INNER COIL DESCRIPTION

Conductor	Section (mm ²)	Length (m)	Number of layers	UTS at 77 K (MPa)	Electrical resistivity at 77 K ($\mu\Omega\cdot\text{cm}$)
Cu-Nb	6.6	6.9	3	1337	0.53
Cu-SS	6.0	165	15	980	0.45

These tests validate the design of a bi-material inner coil connected using a brass junction. It is therefore possible to consider a solution to replace the remaining 200 g of Cu-Nb. One of the solutions envisaged is the use of Ag-Cu composite conductors manufactured by the combination of powder metallurgy, SPS sintering and wire drawing. But first it is necessary to increase the volume of conductor produced.

III. Ag-Cu SCALE UP FOR PULSED MAGNET

A. Materials: fabrication

Our aim is a twenty-fold increase in volume, here the main risk is that the macroscopic properties will be modified during the upscale and do not longer fit the initial specifications. Increasing the volume of production requires some adaptation in the process compared to the preparation of smaller cylinder (diameter 8 mm, length 30 mm) [12]. In order to facilitate the scale up, it was decided to increase production step by step. A sample of 140 g (i.e. a ten-fold increase in) will be presented. The composite powder (1 vol. % Ag) is composed of Ag nanowires (NW) (diameter 200 nm; length $50 \mu\text{m}$) prepared in-house by reducing AgNO_3 with ethylene glycol in the presence of poly(vinyl pyrrolidone) [13] and a commercial Cu powder (Alfa Aesar, 99%, $1 \mu\text{m}$). The homogeneous composite powder was prepared by pouring the appropriate amounts of Cu and Ag NW into ethanol and mixing the suspension in a Kakuhunter planetary centrifugal mixer (400 rpm - 2 min). The dry composite powder was obtained after ethanol evaporation in an oven ($80 \text{ }^\circ\text{C}$). In order to reduce any copper oxide present at the surface of the Cu grains, the dry powder was heated at $210 \text{ }^\circ\text{C}$ under H_2 atmosphere (heating rate $2.5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$; dwell time 1 h; H_2 15 L/h). The increase in the reduction temperature that was found necessary compared to our previous study [12] could reflect the larger volume of powder processed. The Ag-Cu cylinders (diameter 24 mm, length 30 mm) were sintered by SPS (PNF²-Toulouse, Dr. Sinter 2080, SPS Syntex Inc., Japan). The sintering parameter described earlier [12] was adapted to the larger powder volume. In order to resist the radial forces generated by the compaction of the powder during sintering, a 24.4 mm inner diameter and 140 mm in length WC/Co die (93.5 wt.% WC and 6.5 wt.% Co) was used. A laminated sheet of graphitic paper (0.2 mm thick, PERMAFOIL®Toyo Tanso) was placed between the powder and the die to allow easy removal of the cylinder. The applied temperature was controlled by a K type thermocouple introduced in a half height hole (1.8 mm diameter and 3 mm deep). The sample is heated at $25 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from room temperature to $450 \text{ }^\circ\text{C}$ where a 5-minute dwell is applied. An uniaxial pressure (50 MPa) is applied gradually during the first

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1 minute of the dwell and is maintained for 4 min. Cooling (100 °C.min⁻¹) is applied down to room temperature and the pressure is gradually released. The graphitic paper remaining at the surface of the Ag-Cu cylinder was removed by machining before starting the wire-drawing. The resulting Ag-Cu cylinder has a relative density of 96 %. Our previous study has shown that a non-negligible residual porosity does facilitate the deformation during the drawing step and in fact too-dense cylinders cannot be drawn without breaking [12]. Compared to the smaller sized samples prepared previously [12], it was necessary to increase the sintering temperature as well as the pressure applied to maintain densification compatible with wire drawing. However, due to the solubility of Ag in Cu, it is important to limit the increase in temperature during SPS sintering in order to maintain a composite microstructure (i.e. composed of pure Cu and pure Ag). In fact, at 400 °C, the Ag solubility in Cu is below 0.1 vol. % and a composite microstructure should be obtained while at 600 °C it increases about 2.4 vol. %, as a total dissolution of the Ag NW is possible. The cylinder was wire-drawn at room temperature through conical WC dies, in about 60 passes, to obtain wires with decreasing wire diameters (D) down to 0.2 mm and making it possible to achieve a true strain rate ($\eta = \ln(A_0/A)$; A_0 is the cylinder section and A is the wire section) of 9.5. Samples with diameter ranging from 0.2 to 1.7 mm were taken for mechanical and electrical characterizations. It was shown that by adapting the manufacturing process it was possible to produce a sample volume 10 times higher with required density. The main changes are the choice of a more suitable mixing method and the modification of the SPS sintering parameters (450 °C, 5 min, 50 MPa vs 400 °C, 5 min, 25 MPa previously).



Fig. 2. Photography of a 24 mm precursor cylinder after the scale up step (on the left) and a 8 mm precursor cylinder having been used for the preliminary work on the Ag-Cu composite wires [12].

B. Electrical and Mechanical and Characterizations

The electrical resistivity of the wires was measured at 293 K and 77 K using the four-probes method with a maximum current of 100 mA in order to avoid heating by Joule effect of the wires. The values are reported in Table II and Figure 3. At 293 K, the electrical resistivity is ranging from 1.71 $\mu\Omega\cdot\text{cm}$ (D=1.8 mm) to 1.97 $\mu\Omega\cdot\text{cm}$ (D=0.2 mm). The higher resistivity of the finer wires is due to the increased density of grain boundaries, which act as scattering centers for conduction electrons [12]. The electrical resistivity at 77 K is between 0.46 and 0.50 $\mu\Omega$. The lower values at 77 K can be

explained by the negligible electron-phonon interactions at low temperature.

Tensile tests (1.7 x 10⁻⁵ m.s⁻¹) were performed at 293 K and 77 K. The values of the UTS are reported in Table II and Figure 3. The UTS ranging from 750 MPa (D=1,1 mm) to 931 MPa (D=0,2 mm) at 293 K and from 853 MPa (D=1,8 mm) to 1170 MPa (D=0,2 mm) at 77 K. The UTS values at 293 K and 77 K increase upon the decrease in wire diameter, reflecting the refinement of the microstructure [10], [12]. The higher UTS at 77 K are due to the lower mobility of the dislocations at liquid nitrogen temperature.

TABLE II
ELECTRICAL RESISTIVITY AND ULTIMATE TENSILE STRENGTH VERSUS WIRE DIAMETER AT 293 K AND 77 K

D (mm)	η	Electrical resistivity ($\mu\Omega\cdot\text{cm}$)		Ultimate Tensile Strength (MPa)	
		293 K	77 K	293 K	77 K
1.8	5.1	1.71	0.46		853
1.4	5.6	1.99	0.48		947
1.1	6.1	1.98	0.46	750	894
0.8	6.7	2.00	0.49	805	992
0.6	7.2	1.98	0.49	846	1046
0.5	7.5	2.00	0.50	870	1080
0.5	7.7	2.00	0.50	871	1087
0.4	8.1	2.00	0.51	891	1116
0.3	8.8	1.98	0.51	928	1154
0.2	9.5	1.97	0.50	931	1170

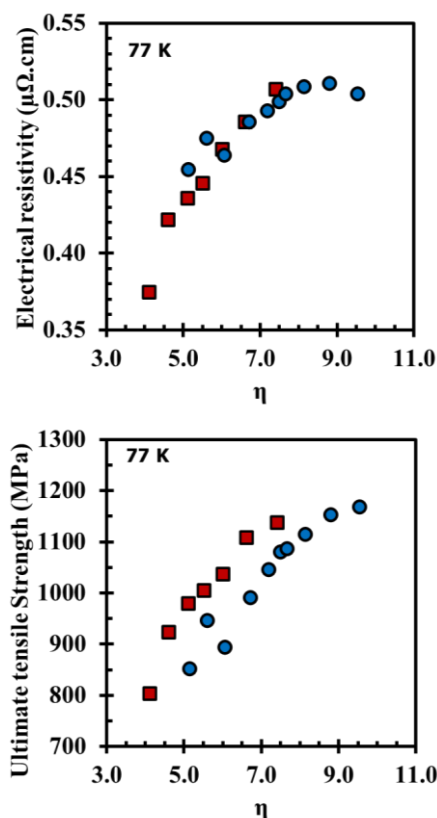


Fig. 3. Photography Electrical resistivity versus true strain rate and ultimate tensile strength versus true strain rate at 77 K for

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the present wires (●) and the wires obtained from a 8 mm cylinder [12] (■).

IV. DISCUSSION

The scaled-up Ag-Cu wires show UTS values ranging from 853 to 1170 MPa and electrical resistivity values ranging from 0.46 to 0.51 $\mu\Omega\cdot\text{cm}$ at 77 K. UTS and electrical resistivity values are similar to that of Ag-Cu wires made from a 8 mm cylinder obtained by the same production process (804-1137 MPa, 0.38-0.51 $\mu\Omega\cdot\text{cm}$ at 77 K) [12]. The wires properties are not impacted by scaling-up the process (Fig 4). Our approach through the use of innovative combinations of individually well-understood processes leads to high-electrical conductivity and high-strength Ag-Cu composite wires. Compared to Ag/Cu (24 wt.% Ag) alloyed wires, the present Ag-Cu composite wires show a better compromise between high UTS (similar) and low electrical resistivity (40 % decrease). Such composite wires are serious candidates for use in pulsed magnets. In addition, the low resistivity of scaled-up composite Ag-Cu made it possible to consider increasing the silver content in order to obtain a mechanically more resistant conductor. The 1 vol. % Ag wires are significantly weaker than those with 5 vol. % Ag (1300 MPa at 77 K) [12]. It is possible to consider doubling the volume of the Ag-Cu cylinder produced (about 280 g). This would lead to the manufacture of a cylinder with a diameter of 24 mm and a length of 60 mm. Thus, it would be possible to wind a first prototype of magnet with these Ag-Cu composite wires.

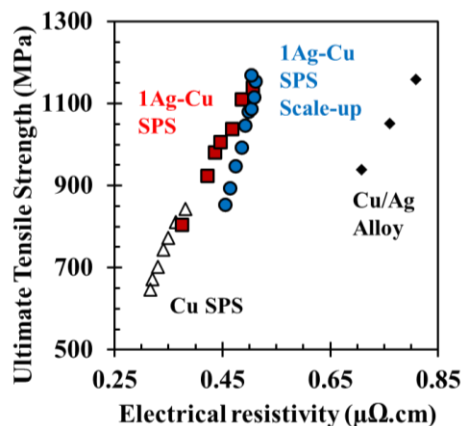


Fig. 4. Ultimate tensile strength versus electrical resistivity at 77 K for for the present wires (●), the wires obtained from a 8 mm SPS cylinder [12] (■), Cu SPS [14] (△) and Ag/Cu (24 % wt. Ag) alloyed wires [6], [7], [8] (◆).

CONCLUSION

The generation of non-destructive pulsed magnetic fields requires the use of high performances conductive wires (ie. exceptional mechanical and electrical properties). In the triple coil system of LNCMI, it is in the inner coil that the conductors are subjected to the greatest mechanical stress. The only commercial wire able to meet this request is produced by a single manufacturer. In a first step, LNCMI has redesigned its inner coil to reduce its dependence on this strategic

material. It was possible to make a coil using only 200 g of Cu-Nb (current design requires 10 kg of Cu-Nb conductor), the rest of the coil being wound with Cu-SS produced by LNCMI. This prototype made it possible to generate a non-destructive field of 90 T. This test confirms the strategy allowing the construction of an inner coil composed of two materials joined by a brass junction. In a second step, the scaled-up Ag-Cu wires show a UTS ranging from 853 to 1169 MPa and the electrical resistivity ranging from 0.46 to 0.51 $\mu\Omega\cdot\text{cm}$ at 77 K. The properties of the wires are not impacted by the upscale, making such a composite wire a very good candidate to replace the Cu-Nb wire in the inner coil. In addition, it is possible to increase the silver content in order to achieve higher UTS values.

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