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ARTICLE

Thermal Stability of Cu-18 vol%Nb Composites

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Abstract: The high strength and high conductivity Cu-18 vol%Nb composites (873^3 filaments) used in high pulsed magnets field were fabricated by bundling and drawing process (ADB). The influence of heat treatment on the microstructure, mechanical properties and magnetic properties of Cu-18 vol%Nb composites was investigated. The samples were characterized by XRD, SEM, and TEM. Results show that the intensity of $<110>_{Nb}$ texture decreases first and then increases with the increases of annealing temperature. At the same time, significant spheroidization and coarsening phenomenon of the Nb filaments are observed. The influence of the microstructural change on the mechanical properties and the magnetic properties of the Cu-Nb composites was also discussed.

Key words: spheroidization; Cu-Nb composites, thermal stability, magnetic properties

The Cu-Nb multi-filament composites have been investigated in the last several decades due to their high strength and high conductivity[1]. The advantages of these properties are adapted to the high field pulsed magnets, and the nano-sized filaments will be the key point of the high strength of the materials[2,3]. It is well known that the annealing effects on the microstructure and physical properties of such materials are very important. Remarkable changes take place in the microstructure, including recovery and recrystallization of copper matrix and niobium filaments depending on the annealing temperature. In addition, the high interfacial energy of the Cu/Nb is the main driving force for the spheroidization and the coarsening of Nb filaments[4]. Most of the stored energy in the Cu-Nb composite is attributed to the presence of geometrically dislocations in the Cu-Nb interface (compensation of strain mismatches). Sandim[5] pointed out that noticeable changes take place in the microstructure, including recovery and recrystallization of copper matrix and niobium filaments during annealing at temperatures above 850 °C. Sandim[6] reported that noticeable differences are observed in the isothermal magnetization curves of Cu-Nb composites, and moreover, there is a double-peak structure after annealing.

In this work, the annealing effects on the microstructure, mechanical and magnetic properties of Cu-18 vol%Nb composites were investigated, and the effects of microstructural evolution of Cu matrix and Nb filaments upon vacuum annealing on the mechanical and magnetic properties of the Cu-Nb composites were emphasized. The consistent changes of both mechanical and magnetic properties were also discussed.

1 Experiment

The high strength and high conductivity Cu-Nb wires were fabricated by the bundling and drawing process (ADB). The details of this process have been reported in Ref.[3, 4]. Fig.1 shows the microstructure of the multi-filament Cu-Nb wire, and it can be found that the filaments are arranged neatly and distributed evenly. Vacuum annealing was performed at temperatures from 400 °C to 830 °C. After heat treatment (HT), the samples were etched in HNO_3 to obtain pure Nb filaments for microstructure observation.

The diffraction patterns of the samples were investigated by X-ray diffraction (XRD, Bruker D8 Advance) using Cu Kα radiation. The microstructural characterization of deformed and annealed specimens was performed using an JSM-6700

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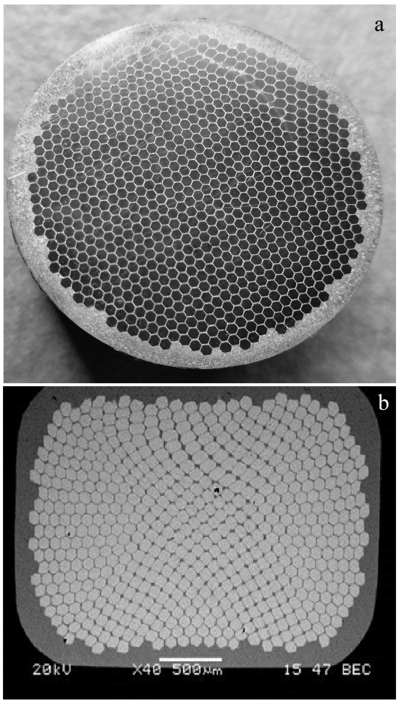

Fig.1 Cross section images of the multi-filament Cu-Nb wires: (a) round wire and (b) square wire

field emission gun scanning electron microscopes. The microstructures of Cu-Nb samples were observed by transmission electron microscopy (TEM, Japan NEC Corporation JEM-200CX). The stress-strain curves of the samples were measured by Instron mode 5982 electronic tensile machine. Magnetization measurements (*H-M*) were performed with a MPMS (XL-7)-Quantum design platform, and the samples were 15 mm in width and 30 mm in length.

2 Results and Discussion

2.1 XRD analysis

Fig.2 reveals the XRD patterns of the cross section of the as-drawn and annealed samples at 400, 600, 830 °C. It can be clearly seen that the intensity of $<110>_{\rm Nb}$ texture decreases at first and then increases with increasing the annealing temperatures, and the major Nb (110) diffraction peak becomes sharper and higher as the annealing temperatures increase, as shown in Fig.2, which is parallel to the drawing direction. It is found that the Cu phase develops strong <111> and <200> fiber textures during the drawing process. However, the <111> texture of the Cu matrix is significantly decreased at first and then increased with increasing the annealing temperatures. Finally, the main Cu orientation still maintains the <111> texture after high temperature annealing. Lim[7] indicated that Cu and Nb follow the $<111>_{\rm Cu}//<110>_{\rm Nb}$ relationship. Popova[8] studied the macro-texture in the annealing process by XRD, and pointed out that the <111> and <200> deformation textures of the Cu matrix produced during the deformation process are weakened due to the crystallization at low temperatures. Carpenter[9] explained this phenomenon that the recovery and recrystallization of Cu are inhibited by a large number of internal interfaces due to the larger strains at low temperatures.

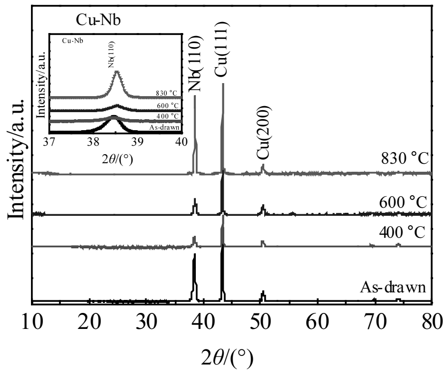

Fig.2 XRD patterns of as-drawn and annealed samples at different temperatures for 4 h in vacuum

During the annealing process, due to the recovery and recrystallization of Cu matrix and Nb filaments, the growth of the Cu phase can be changed to a new orientation along a specific direction[7], and a strong fiber texture is gradually developed[10]. As mentioned above, it is believed that the annealing treatment can change the orientation relationship of the Cu matrix and the Nb filaments, which is related to the recovery and the recrystallization of the Cu matrix and Nb filaments.

2.2 SEM analysis

Fig.3 shows the longitudinal-section SEM images of as-drawn and annealed samples. The edge portion of the Nb filaments is smooth, as shown in Fig.3a. However, after annealing temperature at 600 °C, the morphology of Nb filaments changes significantly, and partial depression appears at the edge of Nb filaments. During the high temperature annealing process, serious spheroidization and columnarization phenomenon occur in the Nb phase. Even the higher the temperature, the more serious the spheroidization. In addition to the spheroidization, the coarsening of the Nb filaments is also evident. Therefore, after high annealing temperatures, the combination of spheroidization and coarsening of the Nb filaments in the annealed state leads to a peculiar structure, as shown in Fig.3d. It is noticeable that the structural integrity of the Nb filaments is partially preserved, and the individual morphology can be clearly distinguished. An enlarged view of such a microstructure is shown in Fig.3e, where transverse grain boundaries are noted in the niobium filaments as well as contact points resulting from coalescence of neighboring Nb filaments. This unique morphology consisting of individual grains stacked one after another is known as the bamboo

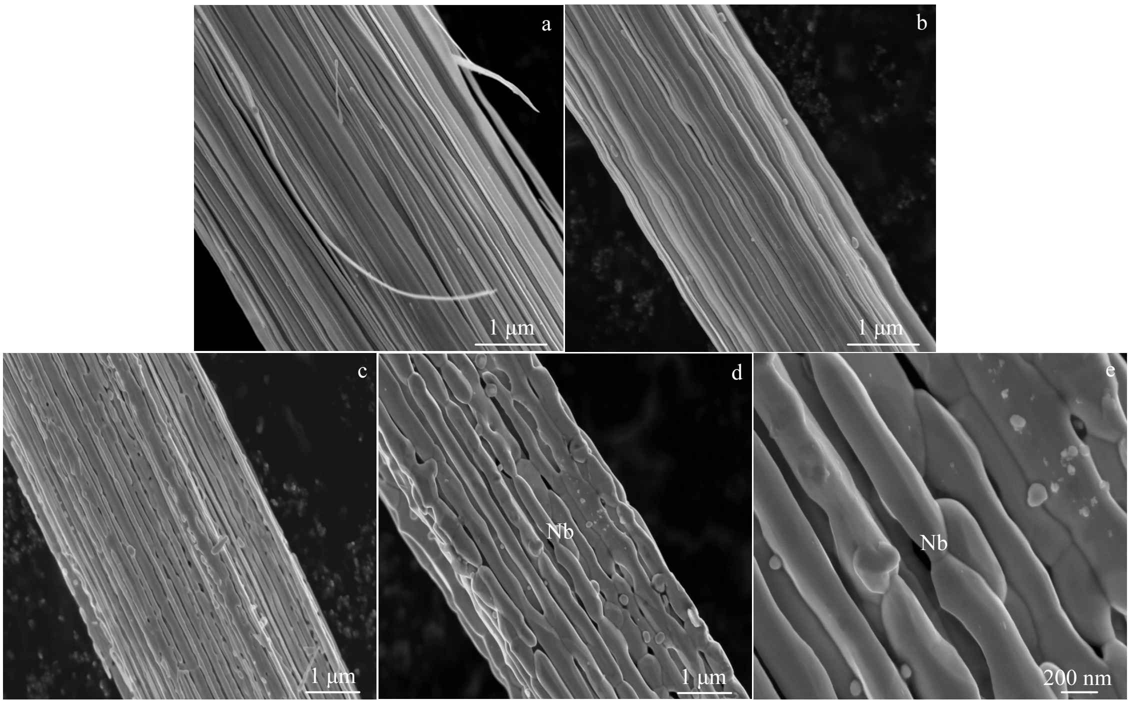

Fig.3 longitudinal-section SEM images of as-drawn and annealed samples: (a) as drawn, (b) 400 °C, (c) 600 °C, and (d, e) 830 °C

structure. The phenomenon is mainly attributed to the recovery and recrystallization of the Nb filaments during annealing process. The detail will be discussed later.

At this point of the discussion, it must be stressed that a grain boundary splitting mechanism is proposed to explain the spheroidization phenomenon[11]. During the heat treatment process, especially after high temperature annealing, the Nb phase is bent, which leads to the diffusion of atoms due to the imbalance of Nb phase. Now, the Nb atoms are continuously diffused to the Cu matrix, and moreover, the pits on the surface of the Nb filaments become deeper constantly as the temperature increases, which leads to the coarsening fracture of Nb phase, interface separation, and the formation of short columnar of Nb phase at last.

2.3 TEM analysis

Fig.4 is a TEM image of as-drawn and annealed samples. It can be seen that the Nb filaments show ribbons structure and disperse in the Cu matrix after annealing. After annealing at 600 °C, the microstructure morphology of both Cu matrix and Nb filaments changes obviously, that is, the grain grows, the Nb filaments are coarsened, and at the same time, the agglomeration phenomenon is serious. After further annealing, the nano Cu matrix between the Nb filaments begins to grow, and in addition, the Nb fiber is also accompanied by the characteristics of early ballooning necking. It is generally believed that high-density dislocations are important drivers for recrystallization, nucleation and growth[9]. After annealing at 830 °C, it can be clearly observed that the grains grow further, and some grains show an approximately isometric morphology. Furthermore, the boundaries between the crystal grains are clearer, and compared with annealing at 600 °C, the growth of grain is more obvious. At the same time, Fig.4d shows that corresponding selected area electron diffraction spots of Fig.4b are more scattered, indicating that the grain orientation of the Cu phase and Nb phase is relatively random.

The TEM observation of the microstructure of as-drawn and annealed Cu-Nb samples is scarcely reported. In summary, the high temperature annealing treatment leads to the occurrence of recrystallization of the Cu matrix and Nb filaments, which leads to grain growth and spheroidization. The occurrence of grain boundary and grain rotation changes the orientation relationship.

2.4 Mechanical property analysis

The stress-strain curves of Cu-Nb samples at different annealing temperatures are shown in Fig.5. As can be seen from Fig.5, the mechanical strength of Cu-Nb composites drops obviously as the heat temperature increases. However, for the first time, it is observed that the plasticity of Cu-Nb composites decreases at first and then increases. For the Cu-Nb as-drawn sample, the size of Nb filaments reaches the nanometer scale, and the internal interface density of the Cu-Nb composites is high. Therefore, the dislocation is hindered by the interface and the flaw, and thus the strength of Cu-Nb materials is high. In addition, the multi-scale structure is also formed in the Cu matrix, and the size of the Cu matrix and Nb filaments may increase greatly due to the high temperature

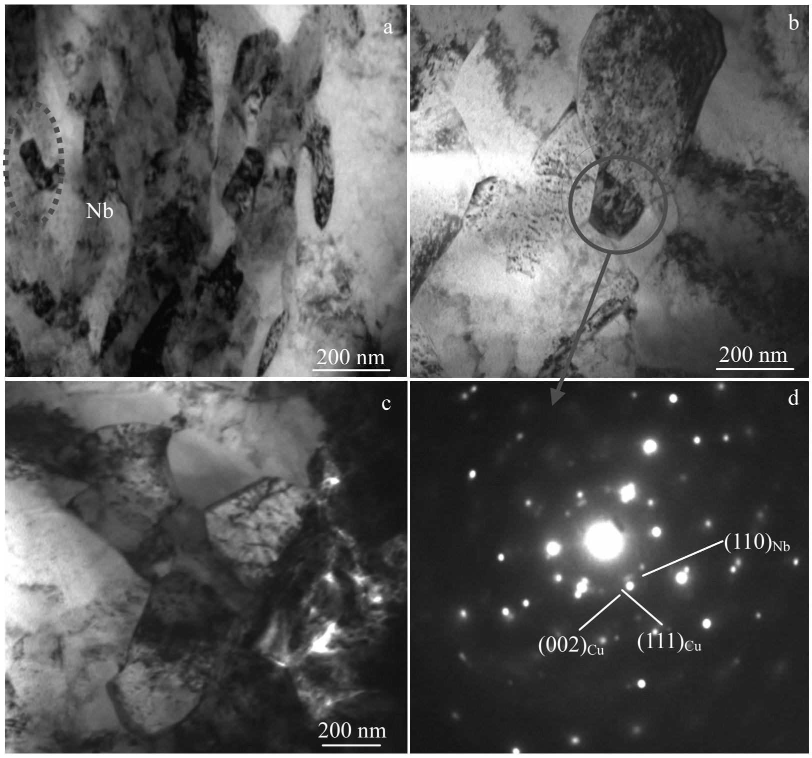

Fig.4 Cross-section TEM images of as-drawn and annealed samples: (a) as drawn, (b) 600 °C, and (c) 830 °C; SAED pattern of Fig.4b (d)

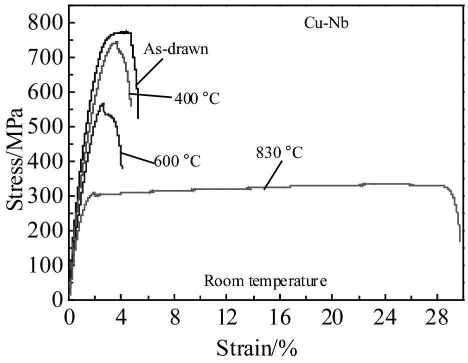

Fig.5 Stress-strain curves of the samples annealed at different temperatures

spheroidization, which may be the main reason for the good plasticity at high temperatures. As for the reason for poor plasticity at the low temperature, it is speculated that the Cu matrix and Nb filaments soften asynchronously at low temperatures, resulting in uneven force of the Cu matrix and the Nb filaments, which may cause the wires to break easily.

It is well known that the variation of the mechanical strength is closely related to the microstructural evolution of Cu matrix and Nb filaments due to the annealing[12]. This means that recovery of Cu matrix and Nb filaments is the predominant softening mechanism during the annealing process. It is emphasized that the annealing at different temperatures contributes to the grain growth, and the reduction of interface density, the stress restoration and the dislocation annihilation, which lead to the reduction of the strength. In short, recovery and recrystallization of Cu matrix and Nb filaments are the main reason for the declining of Cu-Nb properties. The research shows that the Nb filaments are completely broken during the recrystallization process, which promotes the reconnection of different grains by grain boundary diffusion, and then helps to maintain the good plasticity of the wire after subsequent processing[13].

2.5 Magnetic property analysis

Fig.6 shows the *M-H* (magnetization-magnetic field) curves at T=3 K for the samples with a size of 2.8 mm×4.3 mm annealed at 400, 600, 650 and 830 °C for 4 h. The only single-peak structure in the as-drawn sample is observed, as shown in Fig.6, and the magnetization peak at 3 K is located at H=48 000 A/m. After annealing at 400 °C, the Cu-Nb sample still maintains the single-peak structure, but the peak position shifts to the left. With increasing the annealing temperature to 600 °C, the second peak is observed at 1.2×10^5~2×10^5 A/m in the *M-H* curve. The first peak (H_{fp}) is located at low field region and the second peak (H_{fp}) is located at high field region, as shown in Fig.6. With increasing annealing temperature to 650 °C, the double peak structure

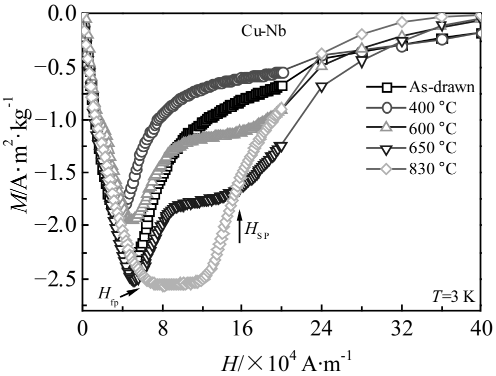

Fig.6 DC magnetization curves measured at different temperatures for the as-drawn and annealed samples

becomes more obvious. This means that the double peak structure in the *M-H* curve is closely related to recrystallization of the Nb filaments. However, after increasing annealing temperature above 830 °C, no additional magnetization peak is found in the *M-H* curve, but the only peak position moves to the right and widens. This can be interpreted by the fact that the decrease of interspacing between the Nb filaments does not lead to a significant proximity coupling due to spheroidization[4].

It is known that the low-field peak in the *M-H* curve is attributed to superconductivity of Cu-Nb composites due to the proximity effect in the Cu matrix, which demonstrates that this phenomenon is related to the filamentary spacing $d_{\mathrm{Cu\text{-}0}}$[14]. Sandim[14] pointed out that such a proximity effect can be controlled by distortion of the Cu-Nb interfaces during annealing experiments at high temperature of 1000 °C. The d_{Nb} of as-drawn sample in this research with a size of 2.8 mm×4.3 mm is about 50 nm and the $d_{\mathrm{Cu\text{-}0}}$ is about 80 nm. After annealing above 600 °C, the $d_{\mathrm{Cu\text{-}0}}$ is not distinguished. At this time, the $d_{\mathrm{Cu\text{-}1}}$ is about 140 nm. In addition, the Nb filaments grow up to about 170 nm, so the second peaks are observed. Such magnetization peak at the high field range is clearly originated from bulk pinning in Nb filaments due to the high temperature annealing[4]. With increasing the annealing temperature up to about 830 °C, two peaks change into one peak. In addition, Stamopoulos[15] proposed that the presence of two magnetization peaks should be related to two kinds of Cu-Nb interfaces. In short, as mentioned above, such proximity effect which may be close to the Cu-Nb interface, and the lattice misfit dislocation must be eliminated during annealing[4].

3 Conclusions

1) The microstructure, mechanical properties and magnetic properties of Cu-18 vol%Nb composites are investigated. It can be clearly seen that the intensity of $<110>_{\mathrm{Nb}}$ texture decreases at first and then increases as annealing temperatures increase. Annealing at higher temperatures promotes the spheroidization and coarsening of Nb filaments to a larger extent. The high temperature annealing treatment leads to the recrystallization of the Cu matrix and Nb filaments, which causes the growth and the spheroidization of grain. The occurrence of grain boundary and grain rotation changes the orientation relationship.

2) The mechanical strength of Cu-Nb composites drops obviously as the heat temperature increases, but the plasticity of Cu-Nb composites decreases at first and then increases.

3) Magnetic characterization shows that there is a hysteresis peak due to the proximity effect after the annealing at 600 °C, which will cause the proximity effect peak to be more pronounced as the temperature continues to rise to 650 °C. The interface structural change due to recrystallization of the Cu matrix and the Nb filaments leads to the proximity effect between Nb filaments in the annealed samples.

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Cu-18 vol%Nb 复合材料的热稳定性

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摘　要： 采用集束拉拔技术制备出应用于高脉冲磁场绕组材料的高强度和高导电性 Cu-18vol%Nb 复合线材（873^3 芯）。通过 XRD、SEM 和 TEM 对线材样品微观组织，力学性能及磁化曲线进行表征。结果表明，随着退火温度的升高，Nb（110）衍射峰的强度先减弱后增强锐，同时观察到了 Nb 芯丝显著的球化和粗化现象。最后探讨了材料微观结构变化对 Cu-Nb 复合材料力学性能和磁性能影响的微观机理。

关键词： 球化；Cu-Nb 复合材料；热稳定性；磁性能

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