Preparation of Nb$_3$Al by high-energy ball milling and superconductivity

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Abstract. The A15 phase superconductor Nb$_3$Al has been considered as an alternative to Nb$_3$Sn for high field and large scale applications. However, to prepare a stoichiometric Nb$_3$Al with fine grain structures is very difficult. High-energy ball milling is a solid state powder processing technique and is a very useful for preparing Nb-Al alloys (Nb$_3$Al). The effects of ball milling time and annealing temperature on the formation of Nb$_3$Al superconducting phase have been studied. Pure Nb and Al powders with stoichiometric ratio of Nb$_3$Al were mixed and milled, and the charging and milling were performed in an inert atmosphere. Phase formation and structural evolution during high-energy ball milling have been examined by X-ray diffraction. Al disappeared and Nb peaks broadened after about one hour of milling. With increasing milling time, the peaks ofNb became considerably broader and intensities decreased, the Nb-Al solid solution phase was extensive when milled about 3 hours. In order to obtain Nb$_3$Al superconducting phase, a subsequent anneal was required. We have annealed the as-milled powders at 800-900°C for different times to prepared Nb$_3$Al superconducting alloy. The results indicated that Nb$_3$Al with small amount of impurity phase can be obtained on annealing the Nb-Al solid solution phase and the superconducting transition temperature was about 15K, but it is difficult to obtain a homogeneous Nb$_3$Al phase by annealing the amorphous powder.

1. Introduction

Because of high critical current density in high field and excellent strain/stress tolerance, Nb$_3$Al superconducting alloy has attracted much interest in experiment studies and device manufacture. Enormous efforts have intensively focused on the preparations and properties of different form (or structure) Nb$_3$Al conductor and great progress has been made. Up to now, Nb$_3$Al superconductor can be achieved by many methods, such as powder metallurgy [1, 2], powder-in-tube [3], jelly-roll [4, 5], clad chip extrusion [6], rod-in-tube [7, 8], laser or electron beam irradiation [9, 10] and the rapid-heating, quenching and transformation method (RHQT) [11-13]. According to the phase diagram of the Nb-Al system, the A15 phase is formed by a peritectic reaction at about 2060 °C and shifted to lower Al concentrations with decreasing temperature. So the quenching from high temperature to
retain Al in composite is a good technology, and a bcc supersaturated solid solution forms in this process. Post-annealing is necessary to obtain stoichiometric Nb$_3$Al [14]. An excellent Nb$_3$Al conductor with multifilamentary structure can be obtained by the RHQT method. However, the RHQT techniques require specialized instruments to provide high reaction temperature and there exist some problems need to be solved.

High-energy ball milling or mechanical alloying is a very effective route in preparing nanosized solid solution or amorphous materials, including metallic alloys, intermetallics, composites and ceramics. It occurs by successive flattening, welding, fracturing and rewelding of powder particles in a high-energy ball mill [15]. High-energy ball milling has been proved to be a useful technique for preparing Nb-Al alloys [16-21]. NbAl$_3$ compound can be obtained directly by mechanical alloying, however, post-annealing is necessary to obtain Nb$_3$Al superconducting phase [19, 20]. In this work we investigate the effects of ball milling time and annealing temperature on the formation of Nb$_3$Al superconducting phase.

2. Experimental details

Pure elemental Nb (purity 99.99%, 325 mesh) and Al (purity 99.5% 325 mesh) powders were used as starting materials. Two grams of powder mixture was loaded in the vial with a weight ratio of powder to ball =1:10. The charging of powder was performed in an argon-filled glove box. A SPEX Mixer-Mill (Model 8000) with a stainless steel vial and balls were used. Mixtures with the nominal composition of Nb$_3$Al were high-energy ball milled in an argon environment. Samples were not exposed to the air until milling has finished. After milling, the mixtures were pressed into round pellet with a diameter of 10 mm and a thickness of 1.5 mm using hardened steel die with uniaxial 12 MPa pressure. Then, the pellet was sealed into a vacuum quartz tube. Finally, the samples were heat treated in a tube furnace and argon was vented in case a permeability or leakage occurred.

The crystal structure was studied by powder X-ray diffraction (XRD) using an X’Pert MRD diffractometer with Cu Kα radiation. All observed reflections were indexed. Lattice constants were determined from LeBail refinements. Microstructure and composition of the sample were analyzed using a field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray analysis (EDX). DC magnetization was measured with a SQUID magnetometer (MPMS, Quantum Design) and resistivity measurements were performed with a physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of powder mixture milled for different times. After 1 hours of milling, the peaks of aluminum were barely detectable and only the Nb was present. When the milling time is 3 hours, disappearance of Al peaks and broadening of Nb peaks are apparent. With increasing milling time, the peaks became broader and their intensities decreased and peak shift towards to greater diffraction angles after 5 hours of milling. The disappearance of Al peaks can be considered as dissolution of Al in Nb. The SEM images of sample milled for different hours (not shown here) indicated that the particle size decreased gradually with the increasing of milling time. Decrease of the particle size leads to the increase of surface area.

Figure 2 shows the XRD patterns of the samples milled and annealed for different times. The XRD pattern of sample milled for 3h and annealed for 10h at 800°C was shown in Figure 2(a), the Nb is the dominant phase which can be clearly observed. When annealing temperature increases to 900°C, as shown in Figure 2(b), Nb$_3$Al phase formed and Nb was observed also. Figure 2(c) shows the XRD patterns of the sample milled for 5h and annealed for 10h at 900°C. The sample is detected to be Nb$_3$Al phase with small amount of impurity phase and no Nb phase can be observed. Figure 2(d) and 2(e) show the XRD patterns of the sample milled for 3h and 5h respectively and annealed for 20h at 900°C. The better Nb$_3$Al phase can be obtained as show in Figure 2(d).

The morphology of sample milled for 3h and annealed at 900°C is show in Figure 3. The sample is brittle and the particle size is about 100nm~400nm. Figure 4(a)-4(d) show the temperature dependence
Figure 1. The XRD patterns of the Nb-Al powder mixture milled for different hours.

Figure 2. The XRD patterns of the samples milled and annealed for different time.

Figure 3. (a) Typical SEM images of the samples milled for 3h, annealed at 900°C, (b) shows enlarged view.

Figure 4. The temperature dependence of magnetization for the Nb3Al sample annealed at 900°C, (a) milled for 3h and annealed for 20h, (b) milled for 3h and annealed for 40h, (c) milled for 5h and annealed for 20h, (d) milled for 5h and annealed for 40h, inset shows the temperature dependence of magnetization for the Nb-26at.%Al sample milled for 3h and annealed for 5h at 900°C.

of magnetization for the sample milled for 3 h and 5h, annealed at 900°C for 20h and 40h respectively, and the highest $T_c$ is 14.3 K for sample milled for 3 h and annealed at 900°C for 20h. The increase of milling time and annealing time will decrease the $T_c$ value. EDX analysis indicates that sample compositions deviate from the stoichiometry of Nb$_3$Al. The inset of Figure 3 shows the temperature dependence of magnetization for two Nb-26at.%Al samples milled for 3h and annealed for 5h at 900°C. The values of $T_c$ are 15K, which is about 3K lower than the optimal $T_c$ value (18K) of stoichiometric Nb$_3$Al. Lower $T_c$ value arises from the deviation of Nb$_3$Al phase compositions from...
A15 stoichiometry. Another reason is the impurity phases. Although little impurity phase was indexed from the XRD patterns, the impurities (Fe or other magnetic impurities) introduced by milling would strongly destroy the superconducting properties. It should be emphasized that, no superconducting transition of Nb was detected which further confirms that the Nb has sufficiently reacted.

4. Summary
The effects of ball milling time and annealing temperature on the formation of Nb₃Al superconducting phase have been investigated. High-energy ball milling is effective in increasing activity of the powders by improving the mixing of the powders, simultaneously reducing the diffusion distance. The impurities are probably responsible for the poor-quality of superconducting properties. The achievement of stoichiometry is essential for producing high $T_c$ for Nb₃Al superconductor.

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