Nanocrystalline Nb-Al-Ge mixtures fabricated using wet mechanical milling

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Abstract. An investigation into Nb-Al-Ge mixtures is presented with special attention to the superconducting compounds $Nb_3(Al_{1-x}Ge_x)$ with x = 0, 0.3 and 1, which are reported to provide the highest upper critical field values for Nb-based compounds. Wet mechanical milling using copper milling media and distilled water as a process control agent (PCA) was used with the intention of improving the yield, properties and the performance of these materials. Very high yields of nanocrystalline material were achieved but significant copper contamination occurred - confirmed using inductively-coupled-plasma atomic-emission-spectroscopy. Simultaneous thermogravimetric measurements and differential scanning calorimetry were performed on powders milled for up to 20 h with different PCA content, to quantify the work done on the powders. A typical grain size of a few nm was obtained for the Nb-Al-Ge mixtures after several hours milling. Powder ground for 20 h with 5 % PCA was processed using a hot isostatic press (HIP) operating at 2000 atm and temperatures up to 750 ^{o}C. The room temperature resistivity decreased as the temperature of the HIPing increased. Unfortunately, despite the nanocrystalline microstructure of the powders and the high HIP temperatures, if superconducting material was formed it was below the detection level of resistivity, Ac. susceptibility and SQUID measurements. We conclude that during milling there was widespread contamination of the powders by the PCA so that milling with distilled water as a PCA is not to be recommended for fabricating nanocrystalline $Nb_3(Al_{1-x}Ge_x)$ A15 superconducting compounds.

1. Introduction

$Nb_3(Al_{1-x}Ge_x)$ A15 compounds superconductors are recognised by the superconductivity community as an excellent source for future superconducting multifilamentary conductors capable of operation at magnetic fields higher than 25 T under extreme mechanical and irradiation conditions [1]. The superconducting properties of these Nb-based A15 intermetallic systems depend on the details of the manufacturing techniques [2, 3], heat treatment and annealing conditions [1, 4]. The best fabrication technology for producing the highest $B_{C2}(4.2K)$ values for Nb_3Al (30T), $Nb_3Al_{0.7}Ge_{0.3}$ (41T) and Nb_3Ge (37T) are the double rapidly heating quenching process [5], arc-melting [6, 7] and thin-film deposition [8] respectively. Although in the last few years excellent Nb_3Al wires [9] have been produced, a practical fabrication process for developing long length wires with $B_{C2}(4.2K)$ values close to 40 T has not yet been established because of the poor workability of the Al - Ge alloy [10]. Nevertheless, the developments in powder-in-tube technology means that long-length multifilamentary $Nb_3(Al_{1-x}Ge_x)$ wires may now be possible.

According to BCS theory, $B_{C2}(0)$ for a superconductor at zero temperature is given by [11]:

$$B_{C2}(0) = \frac{R(\infty)}{R(\lambda_{tr})}\left[8.3\times10^{34}\left(\frac{\gamma T_c}{S}\right)^2 + 3.1\times10^3 \gamma T_c \rho_n\right] \tag{1}$$

where $R(\infty)/R(\lambda_{tr})$ is a strong coupling correction close to unity, γ is the electronic specific heat coefficient (Sommerfeld constant), T_c is the critical temperature, S the Fermi surface area and ρ_N is the normal state resistivity. The increase in B_{C2} found in the nanocrystalline materials is explained by the decrease in γ and T_c being more than compensated for by the increase in ρ_N [11, 12]. Increasing disorder, both by increasing ρ_N and reducing the dimensions of the grains, increases B_{C2}. An effective technique for producing Nb-based nanocrystalline intermetallics is high energy mechanical milling [11]. The repeated welding, fracturing and rewelding of powder particles in a high energy mill produces structural or compositional inhomogeneities, such as small grain boundaries, which can produce strong flux pinning and potentially high critical current density [13].

Fabrication of nanocrystalline Nb-Al-Ge powders by dry high energy ball milling has been reported before as a means of producing A15 superconducting materials [14, 15]. In this work we report on the use of ball milling with a process control agent (PCA) to fabricate nanocrystalline material. It is known that using a PCA can increase yield, minimise powder agglomeration and produce finer powders in shorter milling times. We also present the properties of bulk materials that were produced by hot isostatically pressing (HIP) the milled powders. Thermal, XRD, electrical and magnetic measurements were made to characterise any superconducting material present. Finally we discuss the role of the PCA in fabricating superconducting materials and summarise our results.

2. Preparation of milled nanocrystalline powder

The starting materials were niobium powder (-60 mesh, purity 99.8%) from Alfa Aesar, aluminium powder (-325 mesh, purity 99.97%, particle size ~ 15 nm) from Alfa Aesar and germanium powder (purity 99.999%, particle size ~ 150 nm) from GoodFellow. A stoichiometric mix of these powders (~ 10 g) of atomic composition 3Nb + (1-x)Al + (x)Ge with x = 0, 0.3 and 1 were mechanically milled with a Planetary Ball Mill (Fritsh Pulverisette 6) using a copper vial and balls. Balls of two different sizes were used in this investigation to reduce the effect of cold welding of the powder to the vial. Seven 10 mm and two 20 mm diameter balls copper balls were used. Copper was chosen as the milling media because it has less adverse effect on the superconductivity than other (harder) potential milling media such as steel. A ball-to-powder ratio of 15 was chosen.

The quantity and type of PCA used depends on the materials being milled. There exists no general PCA that enhances the effects of milling for every combination of material powders. A PCA which can be either a solid, gas or liquid has the purpose of coating the surface of newly exposed material resulting from particle fractures. This reduces the surface energy of such particles and subsequently their tendency cold weld to other powder particles and to the milling apparatus. PCAs commonly used in milling include organic substances such as stearic acid, ethyl acetate, heptane, hexanes, methyl alcohol and ethyl alcohol [16]. The molecules constituting these commonly used PCAs contain a polar region which has an affinity to clean metallic surfaces. The relatively large molecules constituting organic PCAs however, have a tendency to break apart during milling and thus contaminate the resulting powder [17]. In this experiment, distilled water was chosen as a PCA because water is a relatively small molecule and thus will not break apart as easily as a significantly larger organic molecule. The hydrogen bonds in water make it polar which gives it the affinity required for the exposed metallic surfaces produced during milling.

High energy ball milling was completed in air using distilled water in the quantities of 2000, 20, 10 and 5 % of the initial powder mass at a rotational speed of 300 rpm for up to 20 hours. During all milling processes the apparatus stopped milling for five minutes followed by a reverse in the direction of rotation after every hour of milling time. Such a rest period was necessary to reduce the temperature of the vial contents so as to promote alloy and intermetallic compound formation through mechanical

processes rather than as a result of the melting. The change in direction of rotation increased the homogenisation of the powder produced. After every five hours of milling, the inside wall of the vial was scraped using a copper rod. We found that the use of a PCA only reduced the extent of cold welding and so such scraping was still necessary to remove as much powder attached to the vial wall and maximise yield. The mass of all the powder that could be obtained from the vial was also weighed to obtain the yield and ~ 0.2 g was extracted for X-Ray diffraction (XRD) analysis and differential thermal analysis (DTA). After 20 hours milling, all the powder that could be obtained from the vial was retained for making bulk material using the HIP.

It is likely during the milling process that flattened powder particles fold around small amounts of PCA and trap them. We chose to heat treat the powder after the milling process with the intention of causing the PCA to burst out of these enclosures. Two heat treatments were made: 250 $^{\circ}$C × 4 hrs. and 350 $^{\circ}$C × 4 hrs.

3. Properties of milled nanocrystalline powder

Figure 1 shows the typical XRD data for the Nb-Al powder made with a Siemens d5000 in conjunction with the commercial software EVA. The XRD peaks clearly change as the milling progresses. However there are many overlapping XRD peaks for the elements such as Nb, Al, Ge and their oxides as well as Nb_3Al, Nb_2Al and $NbAl_3$. This makes clear identification of which materials are present difficult. Nevertheless the A15 compound has a strong peak close to 25° which is not observed, suggesting no superconducting material has been fabricated during the milling. The particle size values were evaluated using the Hall-Williamson method [18]. Figure 1(b) shows that after just 5 hours of milling, grain sizes less than 8 nm were achieved, but that after that it does not change significantly. Indeed, after 15 hours, there is no further marked broadening effect as is evident from figure 1(a). The minimum grain size of milled Nb-Al powder was obtained using 5 % PCA so we chose this PCA content for producing Nb-Al-Ge and Nb-Ge mixtures for HIP'ing.

The yield provides a measure of the tendency of powder to become cold welded to the milling balls and vial wall. Figure 2 provides the yield as a function of milling time for different PCA content. Yield data are approximately 100 % where values higher than this are due to contamination by milling media. We conclude that the PCA has successfully reduced cold welding of the powders to the milling media although significant contamination by copper has occurred. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was completed to measure the relative concentration of Nb, Al, Ge and Cu. Consistent with the yield data, typically we find ~ 18 % Cu contamination in the powder milled for 20 h with 5 % PCA.
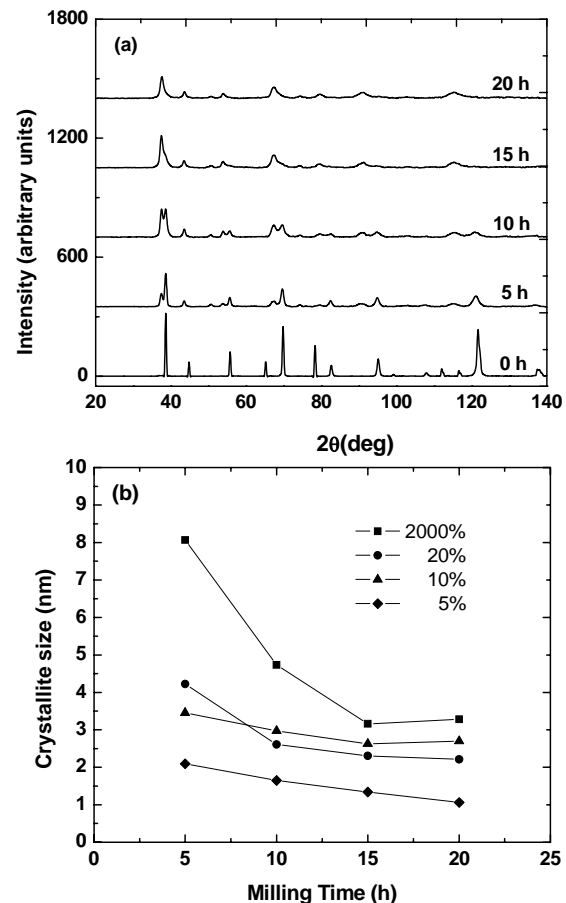

Figure 1 X-ray diffraction patterns for Nb-Al mixtures (a) Evolution of the XRD patterns of Nb-Al mechanically milled with 5% PCA for up to 20 h. (b) Average particle size versus milling time with different PCA content.

Simultaneous thermogravimetric analysis (STA) measurements were made in order to study the thermal response of the milled powder. We used a Netzsch Jupiter 499C which performed simultaneous high temperature thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Measurements were made while ramping the temperature at 10 ^{o}C.min^{-1} from 40 ^{o}C up to 1000-1100 ^{o}C (1st run) and during the dwell of 10 minutes at the highest temperature followed by a ramp down to 20 ^{o}C at 10 ^{o}C.min^{-1}. Figures 3(a) and 3(b) are for the Nb-Al sample milled with 5 % of PCA before and after the 350 ^{o}C × 4 h heat treatment. We associate the change of ~ ½ % in mass between 0 ^{o}C and 350 ^{o}C shown in the TG data in Fig. 3(a) with the liberation of the PCA from enclosed volumes. There are no similar mass changes in Figure 3(b) to with ~ 0.05 % suggesting the heat treatment has successfully removed most of the PCA. There are generally two peaks at ~ 600 ^{o}C and ~ 750 ^{o}C in the DSC data for Nb-Al (shown in Fig. 3(b)) and also Nb-Al-Ge and Nb-Ge. These peaks are not present when the sampler is cooled down during the 2nd run indicating they are not melting peaks. Consistent with other materials made in our group we suggest they are due to microstructure produced during the milling.

4. Fabricating HIP'ed materials

The powders milled for 20 h with 5 % PCA and heat treated at 350 ^{o}C × 4h were HIP'ed at a constant pressure of 200 MPa at temperatures of 450 ^{o}C, 550 ^{o}C, 650 ^{o}C and 750 ^{o}C. For comparison unmilled samples were also HIP'ed under the same conditions. Figure 4(a) and 4(b) show the XRD patterns for these samples. In contrast to the unmilled samples, with increasing HIP temperature, the XRD peaks of the milled samples narrow significantly, consistent with grain growth so that the sample HIP'ed at 2000 Bar and 750 ^{o}C has a similar grain size to the unmilled material.

5. Properties of HIP'ed materials

Rectangular shaped samples of about 10 × 1 × 1 mm were cut from the HIP'ed material. Standard four-probe measurements were completed. In table 1, the resistivity at room temperature of the HIP'ed samples are shown. The resistivity values are small characteristic of fully dense metallic materials. Consistent with the XRD data showing grain
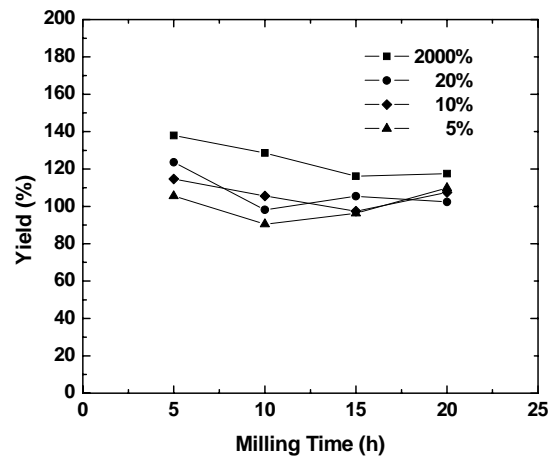
Figure 2: Yield for the Nb-Al-Ge mixture milled for up to 20 hours with different PCA content.
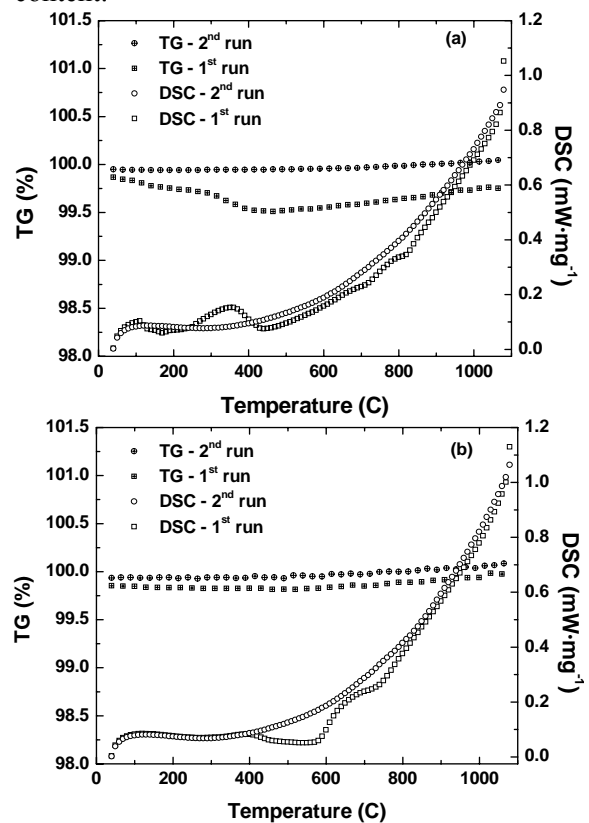
Figure 3: (a) Thermal analysis of Nb-Al powders. TG and DSC curves as a function of temperature for the powders milled for up to 20 h with 5% PCA and (b) after 350 ^{o}C × 4h in a furnace under Ar. Squares and circles are for the 1st (heating) run and the 2nd (cooling) run respectively.

growth, the resistivity decreases as the HIP temperature increases. Figure 5 shows resistive data taken below 30 K in high magnetic fields. At about 8 K one can see the superconducting transition of Nb in zero field. The sharp peak at 25 K occurred when the current through the sample was switched off and demonstrates that the thermal offset voltages during these measurements were negligible. Unfortunately these high field data do show any evidence for superconductivity due to the A15 structure.

Very careful measurements were made using SQUID magnetometry and Ac. susceptibility from 3 to 30 K in magnetic fields up to 9 T. The properties of superconducting Nb were found, but beyond the noise of the experiment and uncertainties associated with the temperature dependent background, there was no evidence for superconducting material with the A15 structure.

6. Discussion and conclusion

SQUID, resistive and Ac. susceptibility data confirm that no A-15 material has been formed in the Nb-Al, Nb-Al-Ge and Nb-Ge materials fabricated in this work. Different experimental techniques have allowed a thorough investigation of whether any trace nanocrystalline A15 materials were made but none were detected.

The high milling media contamination shown by ICP-AES might limit the Nb_3X layer formation. The air in the milling process probably also affected the final materials. The likely development of oxides such as Al-O, Ge-O, Nb-O may also have reduced A15 formation. Certainly these sources of contamination are important. We had expected that even if the samples fabricated were multiphase, we could have identified the potential of nanocrystalline $Nb_3(Al_{1-x}Ge_x)$ superconductors. However the contrast between the formation of A15 material when dry milling Nb-Al mixtures [1, 14, 15] and the results presented here for HIP'ed wet milled material is very stark indeed. It is very probable that no A15 material was produced during wet milling because the PCA both stopped the powders welding to the milling media and passivated the clean metallic surfaces produced during milling - preventing formation of A15 compound. The STA measurements suggest that PCA was trapped inside the metallic powder. Although most of the PCA was removed prior to HIP'ing, we suggest that the PCA is nevertheless
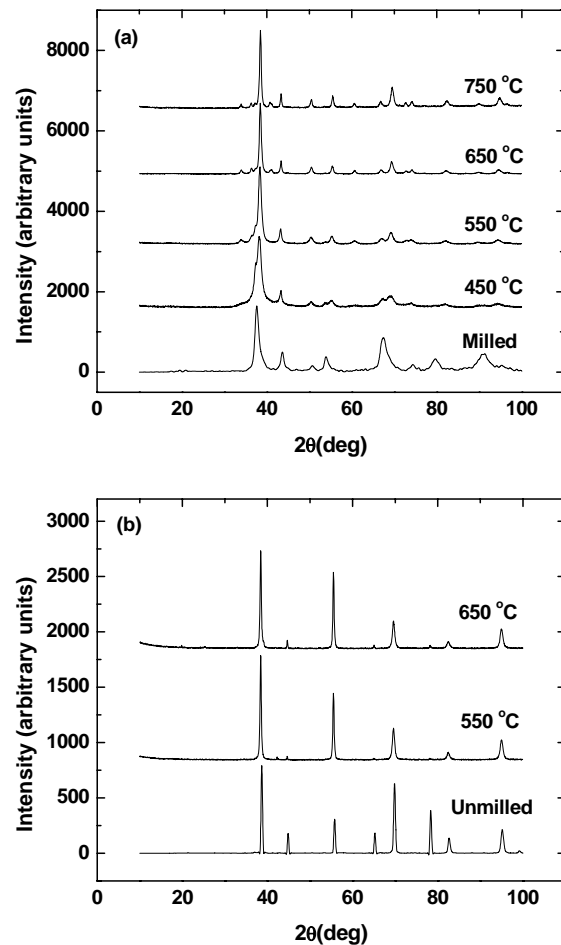
Figure 4 X-ray diffraction patterns of Nb-Al after HIP'ing (a) Powder milled for 20 h and HIP'ed at different temperatures (b) Unmilled powder HIP'ed different temperatures.
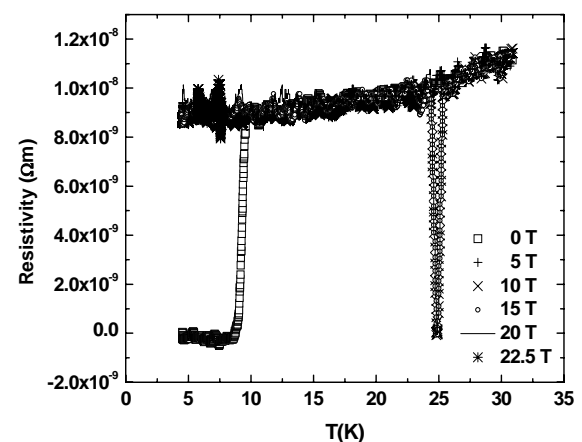
Figure 5 Resistive data of the milled Nb-Al sample HIP'ed at 750 °C as a function of temperature and magnetic field.

Table 1 Resistivity at room temperature for Nb-Al, Nb-Al-Ge and Nb-Ge and corresponding HIP processing conditions.

Type	HIP Processing	ρ_{300K} (10^{-7} $\Omega{\cdot}m$)		
		Nb -Al	Nb - Al - Ge	Nb - Ge
Unmilled	750 ^{o}C $\times$ 5 h	-	4.58	3.58
Unmilled	650 ^{o}C $\times$ 5 h	3.26	4.80	14.4
Unmilled	550 ^{o}C $\times$ 5 h	3.98	14.8	57.2
Milled	750 ^{o}C $\times$ 5 h	6.44	28.1	9.46
Milled	650 ^{o}C $\times$ 5 h	16.8	58.3	35.7
Milled	550 ^{o}C $\times$ 5 h	38.4	106	44.1
Milled	450 ^{o}C $\times$ 5 h	92.8	168	87.4

incorporated throughout the bulk of the milled powders during milling. This widespread contamination by the PCA prevented A15 material from being produced during HIP'ing. This study confirms that using a PCA with milling does lead to high yields and provides a fast method to decrease the grain size of the materials. However, in the context of fabricating superconductors in which inhomogeneities and second phase material on the scale of the coherence length can destroy the superconductivity, we conclude that fabricating nanocrystalline superconductors is best done in an inert environment and that using distilled water as a PCA during milling A15 compounds is not to be recommended.

Acknowledgments

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