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Fabrication of nanocrystalline and amorphous Chevrel phase $PbMo_6S_8$ powder by ball milling

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Abstract

Chevrel phase $PbMo_6S_8$ (PMS) superconducting powder ball-milled from 5 to 200 h has been investigated using X-ray diffraction (XRD) and scanning and transmission electron microscopy. Ball milling produced particles with crystallites of PMS in the range 10–100 nm and amorphous phase. From XRD data, it was found that the crystallite size decreased and lattice strain increased with increasing milling time until by 200 h the material was predominantly amorphous. The powder ball-milled for 100 h was subsequently annealed at temperatures from 400 to 1000 °C for 8 h. Annealing at 600 °C and above released the lattice strain. At 800 °C and above the amorphous phase crystallised and grains coarsened with sizes in the range 50–100 nm.

Keywords: $PbMo_6S_8$; Milling; Annealing; Nanocrystal; Amorphous

1. Introduction

The Chevrel phase superconductor, $PbMo_6S_8$ (PMS) is a promising candidate for producing the next generation of high field magnets because of its high upper critical field of ~50 T [1]. However, a further increase in critical current density (J_c) is required for industrial applications. This paper considers a fabrication route for decreasing the grain size of PMS. Small grain size produces high J_c by increasing the density of flux pinning centers [2]. Results are presented on the fabrication and analysis of ball-milled PMS powder which was then subsequently annealed. PMS powder with an onset critical temperature of ~15.3 K has been fabricated from elemental powders using standard powder metallurgy. The sintered PMS powder has been ball-milled from 5 to 200 h to form nanocrystalline and amorphous powder. High-energy ball milling is widely used for microstructural refinement, amorphisation and formation of nanocrystalline compounds [3]. In order to release lattice strain and recrystallise PMS, the milled powder was subsequently annealed in the temperature range 400–1000 °C.

2. Experimental

PMS samples were synthesised from elemental powders Pb (99.999%), S (99.998%) and Mo (99.95%) using a well-established technique and a final heat-treatment at 1000 °C for 40 h [4]. The

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sintered powder (5 g) was then put into the Syalon pot with six Syalon balls of diameter 20 mm and ball-milled from 5 to 200 h at 300 revolutions per minute. The weight ratio of ball to powder was ~16:1. Ball milling was carried out in a steel box under Ar gas flow. The powder milled for 100 h was subsequently annealed at temperatures of 400, 600, 800 and 1000 °C for 8 h. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to investigate powder microstructure.

3. Results and discussion

The sintered powder was single-phase PMS with a particle size of ~1–5 μm, as shown by the Figs. 1 and 2. Fig. 2 shows XRD patterns of PMS powder ball-milled for up to 200 h. Ball milling broadens XRD peaks by reducing the crystallite size and increasing the lattice strain. These properties have been evaluated using the Hall–Williamson method [5] in which

$$F\cos\theta/\lambda = 1/d + 4\varepsilon\sin\theta/\lambda \quad (1)$$

where F is the difference of the full width at half maximum between the milled sample and the sintered sample, d is crystallite size, ε is lattice strain and θ is Bragg angle. The d and ε values were obtained from plotting $F\cos\theta/\lambda$ versus $\sin\theta/\lambda$. Fig. 3 shows the change of the crystallite size and lattice strain with milling time. Increasing the milling time led to a rapid decrease of the crystallite size but an increase of lattice strain. Ball milling for 5 h resulted in a slight broadening of the diffraction peaks. After milling for 30 h, the crystallites were ~20 nm. After 100 h, the material was both amorphous and contained crystallite sizes of ~10 nm with a lattice strain of ~0.8%. After 200 h, the material was predominantly amorphous with particle size was 50–300 nm, as shown in Fig. 4. Fig. 5 shows how the XRD pattern of the milled PMS powder (100 h) changed with annealing temperatures up to 1000 °C. The effect of

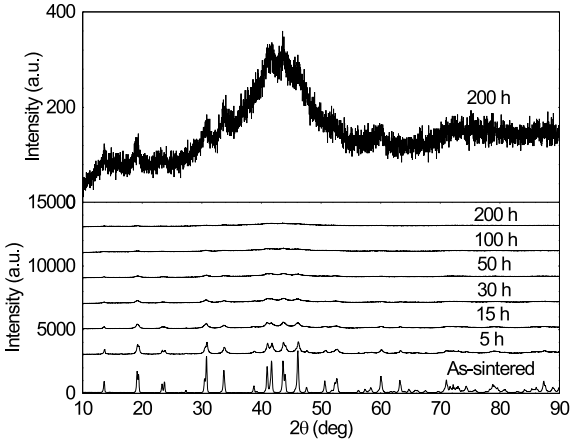

Fig. 2. XRD patterns of PMS samples ball-milled for different times.

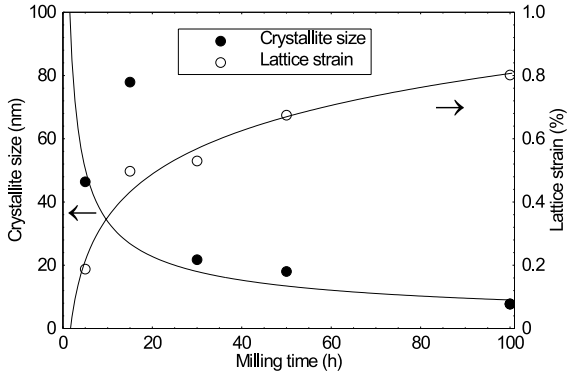

Fig. 3. Variation of crystallite size and lattice strain with milling time derived from the XRD analysis.

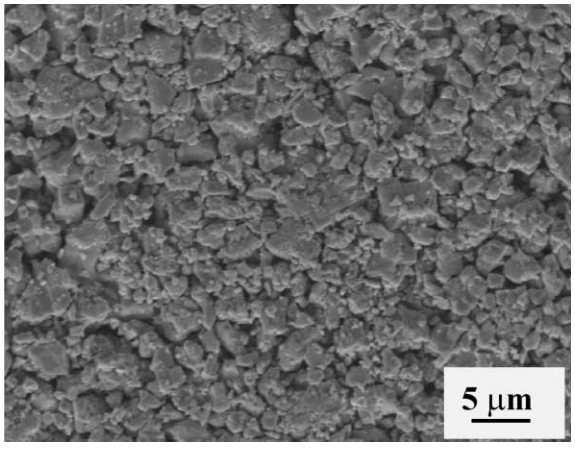

Fig. 1. SEM micrograph of the as-sintered PMS sample.

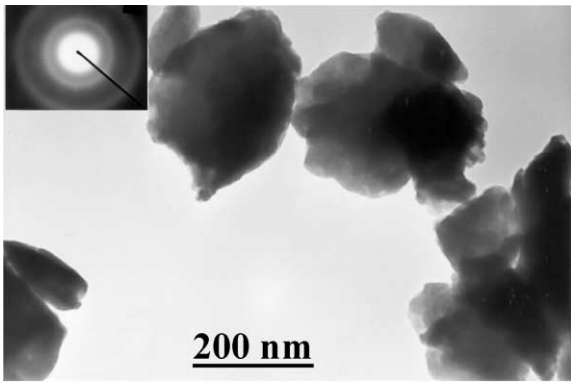

Fig. 4. Bright-field TEM micrograph and electron diffraction pattern of the PMS sample ball-milled for 200 h.

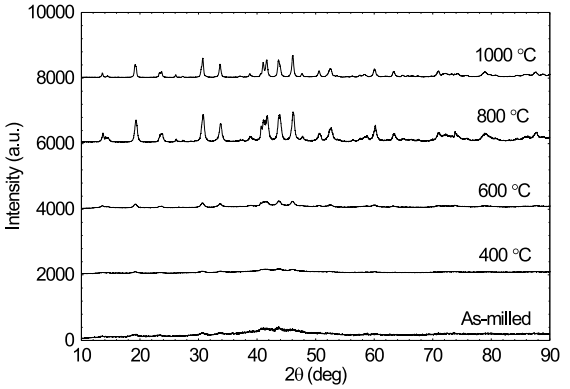

Fig. 5. XRD patterns of PMS samples annealed at different temperatures. The sample was ball-milled for 100 h before annealing.

annealing temperature on crystallite size and lattice strain is shown in Fig. 6. Annealing at 400 °C for 8 h produced no obvious structural change. However, the lattice strain decreased markedly after annealing at 600 °C and above and the amorphous phase crystallised at 800 °C, as shown in Fig. 5. Above 800 °C, a rapid increase of the crystallite size followed. The lattice strain decreased from ~0.8% for the as-milled powder to ~0.2% when annealed at 600 °C. The lattice strain eventually decreased to zero on annealing at 1000 °C.

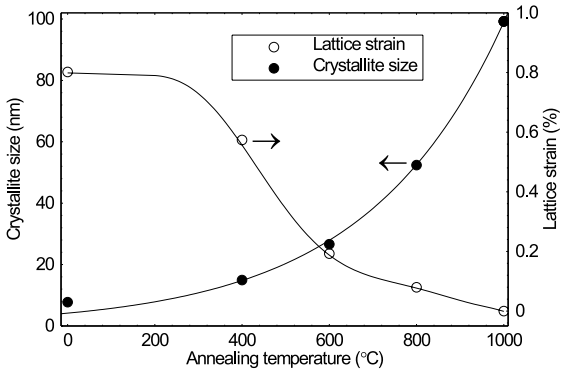

Fig. 6. Variation of crystallite size and lattice strain with annealing temperature derived from the XRD analysis for 100 h ball-milled sample. Lines shown are a guide to the eye.

4. Conclusion

Ball milling produced crystallite formation with sizes as low as ~10 nm and amorphisation. By subsequently annealing at temperatures above 600 °C, the lattice strain was released. The amorphous phase crystallised at 800 °C and above with crystallite sizes of 50–100 nm. This procedure offers the possibility of producing superconducting material with a high density of pinning sites and commensurately high J_c if consolidation of the milled PMS powder can be achieved.

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