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Original Research Paper

Amorphization and nanocrystalline Nb_3Al intermetallic formation during mechanical alloying and subsequent annealing

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ABSTRACT

In this paper the formation as well as the stability of Nb_3Al intermetallic compounds from pure Nb and Al metallic powders through mechanical alloying (MA) and subsequent annealing were studied. According to this method, the mixture of powders with the proportion of Nb-25 at% Al were milled under an argon gas atmosphere in a high-energy planetary ball mill, at 7, 14, 27 and 41 h, to fabricate disordered nanocrystalline Nb_3Al. The solid solution phase transitions of MA powders before and after annealing were characterized using X-ray diffractometry (XRD). The microstructural analysis was performed using scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM). The results show that in the early stages of milling, Nb(Al) solid solution was formed with a nanocrystalline structure that is transformed into the amorphous structure by further milling times. Amorphization would appear if the milling time was as long as 27 h. Partially ordered Nb_3Al intermetallic could be synthesized by annealing treatment at 850 °C for 7 h at lower milling times. The size of the crystallites after subsequent annealing was kept around 45 nm.

1. Introduction

Various intermetallic compounds have been used as a matrix in a lot of nanocomposite materials. The production of nanocomposites in areas of intermetallic NiAl, NiTi, FeAl and Fe_3Al can provide a good example for such use. Niobium – aluminides, as one of the perfect replacements, are considered as one of the most important intermetallic compounds. They consist of three intermetallic compounds Nb_3Al, Nb_2Al and $NbAl_3$ [1]. The Nb_3Al intermetallic has some distinctive features. The spatial position of the atoms in the crystal lattice makes the intermetallic compound to benefit superconductivity as well as high elastic modulus and melting point and excellent resistance to oxidation [2]. Superconducting materials for magnets will be discussed from three viewpoints: firstly, the basic physical properties of the materials themselves, secondly the constraints and preferences imposed by the requirements of magnet building and finally, the manufacture of magnetic conductors as a commercial product [3]. As the previous studies, the ability of Nb_3Al superconductor to bear the high magnetic fields is more than other compounds such as Nb_3Sn superconductors; hence, this attracted the researchers' attention [4]. The most important processes applied in the manufacturing of niobium – aluminides, melted in electric arc furnaces and casting, powder metallurgy, mechanical alloying (MA), rapid solidification, and directional solidification can be mentioned. In recent years, the focus has been on niobium-base alloys, in order to prepare Nb_3Al superconductive wires based on manufacturing methods of mechanical alloying. It should be noted that the mechanical alloying process for the production of these compounds, is one the good mentioned methods because there are many constraints in producing these compounds via using the molten state. Furthermore, the formation of intermetallic compounds with nano-scaled grains is impossible by conventional casting methods. This method is also a process with high-energy to produce powders with controlled microstructures through repeated failure and then, cold welding of powder particles [5–10].

In MA processes, a blend of elemental powder is placed in a high-energy mill in order to give rise to solid solution phase, compounds or composites in the crystalline, quasicrystalline and amorphous phase [11,12]. Amorphization by mechanical alloying of elemental powders occurs by an interdiffusion reaction at relatively low temperature along constituent interfaces. The formation of amorphous phase by MA process depends on the energy provided by the milling machine and thermodynamic properties of the alloy system. It has also been reported that in some alloy sys-

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tems such as Ta-Al, Ti-Al, Zr-Al and several other alloy systems a solid solution forms first which on continued milling becomes amorphous. In some other systems, it was reported that MA of the blended elemental powder mixture results, with increasing milling time, in the sequential formation of phases of solid solution, followed by an intermetallic and finally an amorphous phase. It is interesting to emphasize that if the amorphous phase has the lowest free energy of all these competing phases, it forms directly without any other phase forming prior to that [13].

Hence, in this approach the desired intermetallic compounds, especially Nb_3Al with nano-metric structure, can be produced by grinding the elements such as niobium and aluminum at room temperature, followed by annealing of the milled powder. The structural evolutions and characteristics of the powder particles with an emphasis on the characterization of phases using X-ray-diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are studied in detail.

2. Experimental procedure

Niobium powder with 5-μm particle size and 98.5% purity, aluminum powder with less than 20 μm particle size and more than 99% purity, were used. Mechanical alloying was performed in a high-energy planetary ball mill (Retch PM100) in an argon gas atmosphere using hardened chromium steel vial and balls ($\Phi = 20$ mm). The ball-to-powder weight ratio was 20:1 and the rotation speed of the main disk was kept around 500 rpm (revolutions per minute). The MA was done nominally at room temperature although the temperature of the vial increased to around 50 °C during MA. The milling was interrupted at different selected times and a small amount of powder was taken out of the vial for further analysis [14].

For the annealing, milled Nb–Al powder was prepared in pills with a diameter of 10 mm, using a uniaxial hydraulic press with 500 MPa pressure. Then, this powder was put in a quartz tube in a furnace with 10^{-5} torr high-vacuity and 850 °C temperatures, for 7 h and argon was vented to avoid permeability or leakage. Applying an X-Ray Diffraction (XRD: Philips XPERT-MPD), the phase of synthesized powder was recognized before and after the treatment. All XRD experiments were carried out in the continuous scanning mode using Cu-Kα radiation ($\lambda = 0.1542$ nm), time per step of 1 s and 0.03° step size. The peaks were identified by the X'Pert HighScore software. The crystallite sizes of the samples were evaluated using the X-ray peak broadening based on Williamson-Hall analysis [15] as in Eq. (1). The instrumental peak broadening was corrected using a coarse grain strain-free sample of pure annealed Si.

$$\beta \cos\theta = (0.9\lambda)/d + 2\varepsilon \sin\theta \qquad (1)$$

where λ is the wavelength of X-ray, β is the full width at half-maximum (FWHM) intensity of peaks, θ the Bragg angle, d the average crystallite size and ε is the strain lattice.

TEM and SEM analyses were performed to study the morphology and structural changes in the forms and sizes of particles, and also to determine the structure type and the crystallite size.

3. Results and discussion

3.1. Phase evolution during mechanical alloying

Fig. 1 shows the XRD patterns of Nb-25 at% Al milled powders at different hours of milling. XRD pattern of as-received powder mixture is also shown for comparison. From the very first stages of milling, disappearing of aluminum peaks and widening of niobium peaks can be clearly seen. However, after 14 h of milling, aluminum peaks completely disappeared and (110) niobium peak, which is the only main peak in XRD pattern, remained after 27 h. Dissolving of aluminum in niobium and its entrance into the crystal structure of niobium can be a reason for decreasing of aluminum peaks. Based on Peng et al. [16], decreasing of aluminum peaks intensity and their disappearing cannot have any reason other technical dissolving of aluminum in niobium because MA is a non-equilibrium process. As the duration of milling increases, the halo of amorphous phase is apparently formed in the XRD pattern after 27 h and remain unchanged even on milling for up to 41 h. It is important to point out that both the fundamental and superlattice reflections show peak broadening due to a decrease in crystallite size and increase in lattice strain. After 14 h of milling time and longer, the superlattice reflections completely disappear, indicating that the compound has become completely disordered [13]. The broad peak around the (110) peak suggests that either the amorphous phase or the nanocrystalline phase or both are present in the milled powders [17]. The formation of amorphous phase during milling the powder mixture of Nb-25 at% Al is reported by different researchers [18–20]. Peng et al. [16] confirmed that amorphous phase will be formed even if the atomic percent of aluminum in this mixture is 60. The difference is that if the percentage of aluminum changes, the speed of amorphous phase formation will change. However, the desired Nb_3Al phase has not reached, yet.

A reason for supersaturation dissolving of aluminum in niobium can be related to those mechanisms, which occur during milling. During MA process, because of repetitive clashes between balls and powder particles, the density of crystal defects in structure increases. These defects can include atomic displacements, vacancies, dislocations and the grain boundaries. All of these defects provide the highest percentage of solubility of soluble element in the structure. As it was said, such interfaces increase the internal energy of the system. One way to decrease internal energy of the system is to dissolve more solute. It can be said that supersaturation dissolving of aluminum in the structure of niobium is a way that the system chooses to decrease interfaces of niobium and aluminum, and to reduce its internal energy [6,20].

The thermodynamic and kinetic principles for amorphization through mechanical alloying are discussed by Schwarz and Johnson [21]. They identified two rules for the formation of amorphous alloy by MA in an A–B binary system: I. A large negative heat of mixing, between the elemental constituents, II. A large asymmetry in the diffusion coefficients of the constituents. An amorphous phase is kinetically obtained only if the amorphization reaction is much faster than that for the crystalline phases.

In the coarse of MA process the increase in free energy of the crystalline phase is thought to occur through accumulation of lattice defects such as vacancies, dislocations, grain boundaries, and antiphase boundaries which are introduced into the material during MA. When the free energy of the crystalline structure exceeds the free energy of the amorphous phases, crystalline structure can transform to the amorphous phase. In the Nb-Al system, where an amorphous phase was obtained whether the starting material was an intermetallic or blended elemental powder mixture [13].

3.2. Measurement of crystallite size and lattice strain of milled powders

Fig. 2 shows the average crystallite sizes of powder particles and the strain of the lattice in Nb-25 at% Al at different times of mechanical alloying. Fig. 2a illustrates the sizes of crystallites according to the milling hours. According to the diagram, the crystallite size changes from 27 nm to about 5 nm during 14 h of milling; however, there is a lower slope at 20th h till it reaches 5 nm. The rate of refinement of the crystallite size is roughly loga-