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Synthesis and Characterization of Fe₈₀B₂₀ Nanoalloys Produced by Surfactant Assisted Ball Milling

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In this present study attempts have been made to synthesize $Fe_{80}B_{20}$ crystalline/amorphous nanocomposite powder by using surfactant-assisted high-energy ball milling. Comparison has been made for the differences in evolved microstructure via solidification and solid state phase transformation under equilibrium and nonequilibrium processing conditions. Structural analysis reveal that initially observed Fe₂B and Fe₃B intermetallic phases tend to disappear even at 1 h milling time and eventually lead to the stabilization of α -Fe nanoparticles and possible formation of amorphous phase by increasing milling time. This resultant structure governs the magnetic behaviour of the Fe₈₀B₂₀ nanoalloy.

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1. Introduction

Amorphous and/or nanocrystalline alloys are the main research interests of scientists for the last decades because of their unique material properties and characteristics in comparison with their crystalline counterpart. Following the recent introduction of nanoalloys to engineering applications, in addition to the limited parameters, temperature and composition employed for phase tuning in conventional alloys, there emerged a third parameter, namely, *particle size*, which made the properties attainable from materials nearly unlimited [1]. Despite, due to their low surface area they have limitation on industrial usage. To overcome this barrier, there are variety of ways to synthesise the nanoparticle such as chemical method and surfactant assistant ball milling [2].

Surfactants help in achieving the smaller particle size during the milling time and the solvent scatter the fine particles. Although the particle which are produced with ball milling are varying in size in comparison with chemical method, due to their success in synthesis of hard--phase magnetic nanoparticle of rare-earth compounds are used [3, 4]. Nanoalloys, having diverse fields of applications such as data storage, catalysts, biosensors, and cancer treatment, demand theoretical predictions more than ever due to their complex structures and varieties. In this context, Fe–B based amorphous alloys are suitable candidates for magnetic applications such as magnetic imaging due to their excellent soft magnetic properties with very low coercivity and high saturation magnetization in bulk form [5, 6]. Moreover, bimetallic FeB glassy alloy and crystalline/amorphous nanoparticles of FeB have unprecedented usage in biomedicine such as cancer therapy, drug delivery, etc., in addition to magnetic imaging applications [7, 8].

For new generation nanoalloys to take part in mentioned fields of applications, it is required that synthesis conditions, i.e., structure-property relations can be predicted in advance. In this present study, therefore, attempts have been made to synthesize the $Fe_{80}B_{20}$ crystalline/amorphous nanocomposite powder by using surfactant-assisted high-energy ball milling and to establish a relationship between structures, size of nanoparticles, and their morphology on the magnetic properties of this nanoalloy.

2. Experimental procedure

The Fe₈₀B₂₀ alloy ingots with specified chemical composition were prepared by melting the appropriate amounts of high purity constituents by using arc melting in Zr-gettered Ar atmosphere. In order to achieve higher composition homogeneity, the ingots were melted for several times and then suction cast into a cylindrical-shaped copper mould with a diameter of 3 mm. Suction cast samples were then crushed down to particle size of 70 μ m to be utilized for subsequent ball milling operation. High energy ball milling was performed up to 60 h in hardened stainless steel vials under high purity Ar atmosphere by using stainless steel ball where the weight ratio of ball--to-powder was 13:1. Heptane (> 99%) and oleic acid (90%)/oleyl amine (> 98\%) were used as solvent and surfactant, respectively. Powder samples were taken out at various milling times for structural analysis and characterization for which thermal, spectroscopic, and e-beam techniques were utilized. Hysteresis (B-H) loop, saturation inductions (B_s) and coercivity (H_c) measurements were done with an ADE Magnetics EV9 vibrating sample magnetometer (VSM) with maximum field strength of 1750 kA/m. Besides this general procedure, attempts have also been made to produce almost equilibrium solidification microstructure by cooling the sample very slowly

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from liquid state to room temperature in the furnace in order to compare the differences in evolved microstructure via solidification and solid state phase transformation under equilibrium and non-equilibrium processing conditions.

3. Results and discussion

Structural analysis reveals that the alloy under near--equilibrium solidification conditions consists of α -Fe and Fe_2B equilibrium phases in agreement with the equilibrium binary Fe-B phase diagram [9]. However, the alloy under relatively rapid solidification conditions by suction casting into a Cu mold leads to formation of so--called non-equilibrium Fe_3B phases in addition to α -Fe and Fe_2B equilibrium phases, Fig. 1a. The number and the relative fraction of these phases observed in the solidification microstructures promptly change by solid state phase transformation when they are subjected to ball milling, Fig. 1b. It is evident from XRD analysis that initially observed Fe₂B and Fe₃B intermetallic phases tend to disappear even at 1 h milling time and eventually lead to the stabilization of α -Fe nanoparticles by further milling. Moreover, longer milling time (i.e., 60 h) would also give rise to probable formation of amorphous phase in addition to stabilization of α -Fe nanoparticles.



Fig. 1. XRD pattern of (a) starting powder (0 h) 30 and 60 h which indicate the disappearance of Fe_3B and Fe_2B phases, (b) XRD pattern of as cast, suction (nonequilibrium), equilibrium, 0 h, and 2 h milling powder.

The existence of an amorphous phase could be detected by X-ray diffraction in which broad peak was observed at low angle of diffractograms, as shown in inset of Fig. 1b, and also by isochronal differential scanning calorimetry (DSC) thermograms where a characteristic endothermic heat event of the glass transition followed by exothermic heat release events due to crystallization from amorphous precursor was detected on heating, Fig. 2.

Besides, it is evident from DSC thermograms that two successive endothermic heat events at ≈ 725 °C and ≈ 900 °C on heating correspond to magnetic ordering (the Curie point) and $\alpha \rightarrow \gamma$ phase transformation, respectively, which confirm the existence and stabilization of magnetic α -Fe nanoparticles by milling of Fe₈₀B₂₀ alloy.



Fig. 2. DSC thermograms of $Fe_{80}B_{20}$ alloy showing phase transformations and invariant reactions on heating.

These experimental evidences imply that the high energy ball milling of $Fe_{80}B_{20}$ alloy results in the formation of nanoalloy particles in which α -Fe nanocrystalline phase appears to be embedded in amorphous matrix. However, detailed TEM studies would be required for further clarification of the formation of this nanocomposite structure.

SEM analyses have revealed that nanocomposite nanoparticles start to form after 5 h of milling time and the particle size of nanocomposite powder is in the range of 35–100 nm. However, the average size of nanoparticles achieved after 5 h milling does not show significant variations with further milling time but their morphology changes from spherical to plate-like shape by amalgamation of these particles, Fig. 3.



Fig. 3. SEM micrographs of milled $Fe_{80}B_{20}$ particles at (a) 0 h, (b) 5 h, (c) 30 h, and (d) 60 h milling time.



Fig. 4. Magnetization curves of milled $Fe_{80}B_{20}$ particles at various milling time.

The effect of milling time on the magnetic behavior of the Fe₈₀B₂₀ nanoalloy particles can be perceived in Fig. 4 where the room temperature hysteresis loops, saturation magnetizations, and coercivities are presented. Saturation magnetization values of nanoalloy particles monotonically decrease with increasing milling time, which can be attributed to the increase in fractions of nanoscale particles. However, significant improvement of the coercivity by milling would be ascribed to vanishing of intermetallic phases along with the enhancement of magnetic α -Fe nanocrystalline phase.

4. Conclusions

 $Fe_{80}B_{20}$ crystalline/amorphous nanocomposite powders have been synthesized by using surfactant-assisted high-energy ball milling. The particle size of nanoalloy powder is in the range of 35–100 nm and their morphology changes from spherical to plate-like shape by amalgamation of these particles with increasing milling time. Magnetic behavior of the $Fe_{80}B_{20}$ nanoalloy particles would be attributed to the fraction of nanoscale particles and enrichment of magnetic α -Fe nanocrystalline phase by milling.

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