

Formation of Metastable TbFe₅ Phase by Mechanical Alloying

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Bulk materials of TbFe₂ (giant magnetostrictive) and TbFe₃ were prepared by arc melting the constituent high pure elements under argon atmosphere. The two materials together were ball milled in toluene atmosphere for 70 h. The mixture is found to be predominantly amorphous after about 37 h of milling. The saturation-magnetization initially was found to increase and then found to decrease with milling time. The anisotropy of the material is seen to decrease as the milling time was increased, due to the formation of the amorphous phase. Differential scanning calorimetry (DSC) studies on the powders milled for 70 h showed two phase transitions, one at 90 °C and another one at 110 °C. Powder X-ray diffraction (XRD) of the annealed sample showed that a metastable phase formed at 90 °C and is found to be TbFe₅ phase and that the phase formed at 110 °C was TbFe₃. The average particle size calculated using the Sherrer's formula is found to be 30 nm.

Index Terms—Anisotropy, crystallization temperature, magnetic materials, magnetization process, particle size, rare-earth iron compounds.

I. INTRODUCTION

THE BINARY RFe₂ (R = rare earth) Laves phase compounds are known to possess large cubic magnetocrystalline anisotropy [1], [2] as well as the highest Curie temperatures amongst all R-Fe compounds. Koon *et al.* reviewed the anisotropy and other magnetic properties of these materials [3]. While several of the cubic RFe₂ compounds are known to possess very large magnetostriction, the RFe₃ compounds (hexagonal), have large magnetization and do not possess significant magnetostriction. Ball milling is usually considered as a means of facilitating solid-state reactions which occur across the welded interfaces of the powder particles when impacted by the grinding media. All such solid-state reactions involve the formation of product phases that displace the reactants. As this process is governed by the geometry and diffusion rates of the reactants and products, it requires relatively high temperatures to overcome the energy barrier. Mechanical milling minimizes the energy barrier of the products by increasing the reaction interface, through continuously welding and fracturing the powder particles at the nanometer scale. This allows chemical reactions to take place at temperatures close to the room temperature [4]. Therefore, it was our interest to see if it was possible to obtain metastable compounds by mechanical alloying a mixture of TbFe₂ and TbFe₃ that would have the characteristics of both structures. For this purpose, in this paper, Tb has been chosen as the rare earth due to its large magnetocrystalline anisotropy as well as a large magnetostriction. The structural and magnetic properties of ball-milled mixtures of TbFe₂ and TbFe₃ are presented in this paper.

II. EXPERIMENTAL DETAILS

TbFe₂ and TbFe₃ were prepared starting from 99.9% pure Tb and 99.95% pure Fe, in an arc furnace under argon atmosphere. The melting was done several times to ensure homogeneous mixing of the elements. The weight loss after the melting was found to be less than 0.5%. Both compounds were mixed in the weight ratio 1:1, and the mixture was ground in a mortar and pestle to obtain particles less than 1 mm in size. The mixture was then milled in a planetary ball mill operating at a speed of 250 rpm and employing a ball to powder ratio of 10:1. The powders were milled in Toluene medium. Test samples were taken after 25, 37, 48, 60, and 70 h of milling and X-ray diffraction (XRD) patterns for all the samples were obtained. Magnetization measurements were carried out using a Princeton Applied Research (PAR) (model number 155) vibrating sample magnetometer at 300 K. Differential scanning calorimetry (DSC) experiment was carried out on the powders milled for 70 h to determine crystallization temperatures. The experiment was done in nitrogen atmosphere and heating rate employed was 20 degrees per minute.

III. RESULTS AND DISCUSSIONS

Fig. 1 shows the powder XRD patterns of the TbFe₂ and TbFe₃. It is seen that TbFe₂ has formed in the cubic Laves phase structure and that TbFe₃ has formed in the hexagonal structure. The lattice parameters calculated are seen to match with the values reported in literature.

Fig. 2 shows the XRD patterns of the samples ball milled for 25, 37, 48, 60, and 70 h. It is seen from the figure that after 25 h of milling, the mixture became predominantly amorphous. It is interesting to note that the mixture of TbFe₂ and TbFe₃ becomes amorphous much easier than TbFe₂ alone, which has been reported to contain crystalline phase even after 80 h of

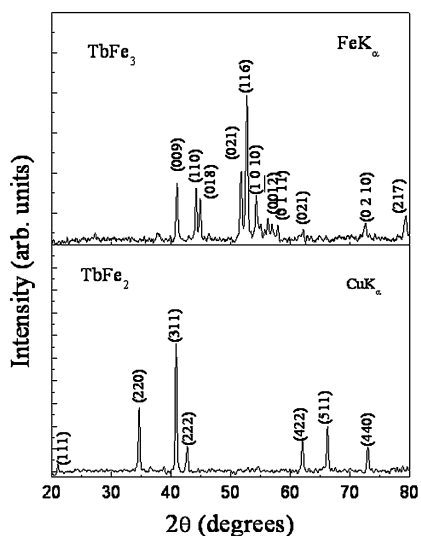


Fig. 1. Powder XRD patterns of ingots: (a) TbFe_2 ; (b) TbFe_3 .

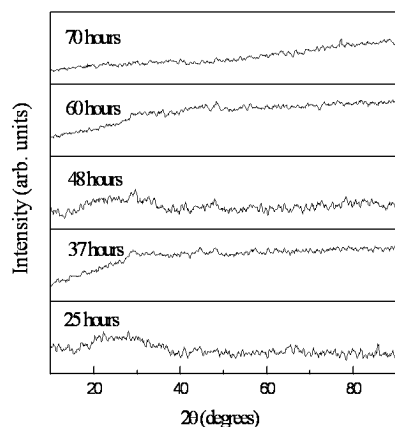


Fig. 2. XRD patterns of ball-milled samples.

milling [5]. After 70 h of milling, the mixture is seen to become amorphous.

Magnetization curves at 300 K for the ball-milled mixture are shown in Fig. 3. The magnetization value has not completely saturated in any of the samples.

The saturation-magnetization values were calculated from the Honda plots (M versus $1/H$) and are shown in Fig. 4. The initial increase in saturation-magnetization upon increasing the ball milling could be due to the formation of (low anisotropy) iron-rich phases as the metastable phases.

Further decrease in the saturation-magnetization could be due to the transformation of the crystalline phases to amorphous phases. Another possibility could be oxidation but there were no detectable amounts of oxides at least from the XRD patterns. Beyond 30 h, decrease in particle size could be dominating over the increase in the magnetization due to the iron-rich phase(s).

The magnetization curves also indicate a decrease in the anisotropy with increasing the milling time. It is also observed from Fig. 3 that the anisotropy decreases with the milling time. As both the starting constituents in the mixture are not magnetically hard, the aforementioned decrease in the anisotropy could be due to the formation of amorphous phase upon milling.

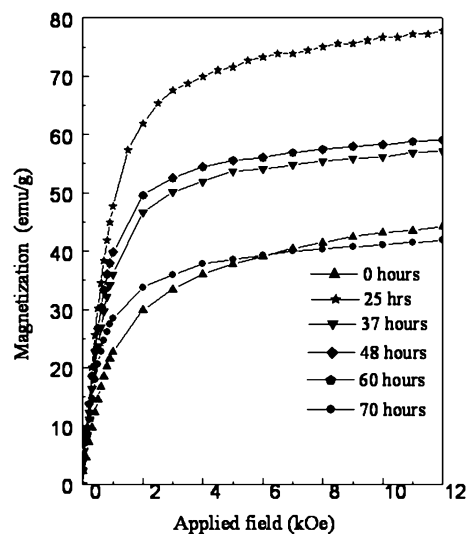


Fig. 3. Magnetization graphs for ball-milled samples.

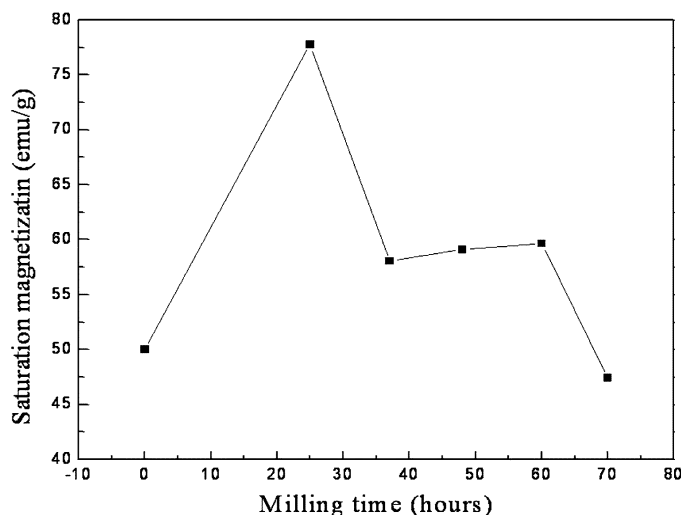


Fig. 4. Milling time versus saturation-magnetization of ball-milled samples.

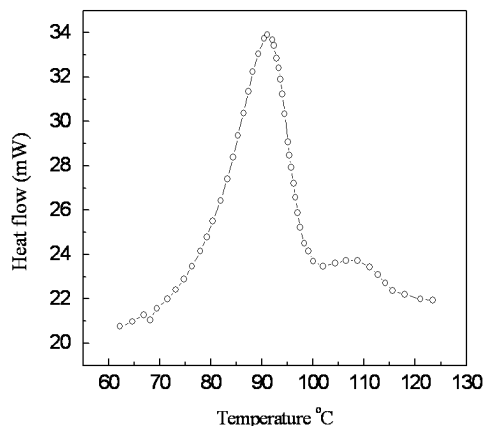


Fig. 5. DSC graph of ball-milled sample for 70 h.

The next step was to determine the crystallization temperature and also look for the formation of metastable phase(s). DSC experiment was carried out for this purpose and Fig. 5 shows DSC graph of the sample ball milled for 70 h. There are two

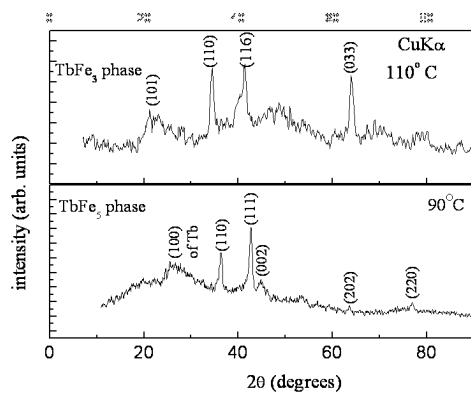


Fig. 6. XRD patterns of the annealed samples.

exothermic peaks one at 90 °C and the other at 110 °C are seen in the graph.

Thus the metastable phase formed is not sustained. The ball-milled samples were annealed at 90 °C and 110 °C for 3 h and XRD patterns were taken on the annealed samples and are shown in Fig. 6. It is found that the metastable phase which crystallized at 90 °C is TbFe₅ phase by matching the XRD pattern with that for the CaCu₅ structure [6], [7]. In addition, (100) peak corresponding to Tb also is seen.

The lattice parameters of the ball-milled sample annealed at 90 °C are found to be $a = 4.953 \text{ \AA}$ and $c = 4.017 \text{ \AA}$. The sample annealed at 110 °C is seen to be TbFe₃ compound and the lattice parameters are seen to match the reported values. Thus, the TbFe₅ phase is not stable even after the ball milling process. On the other hand, the rapidly solidified NdFe₅ has been reported to form along with Nd₂Fe₁₇ and iron and could not be stabilized at high temperatures [8]. The magnetization measurements for the samples annealed at 90 °C and 110 °C are shown in Fig. 7.

The saturation-magnetization of the TbFe₅ is found to be 56 emu/g and the saturation-magnetization value of the TbFe₃ is found to be 59 emu/g. The saturation-magnetization of TbFe₃ may be compared with that reported in literature for the crystalline TbFe₃ which is 61 emu/g [9]. The average particle size of the 70-h annealed sample was calculated using the Sherrer's formula and is found to be 30 nm.

IV. CONCLUSION

Structural and magnetic studies on ball-milled TbFe₂+TbFe₃ samples were carried out. The ball-milled samples have become amorphous after 70 h of milling. The magnetization is seen to decrease with increase of milling time. Annealing the ball-milled sample showed the formation of TbFe₅ at 90 °C and TbFe₃ at 110 °C. The average crystallite size of the 70-h annealed sample was found to be about 30 nm.

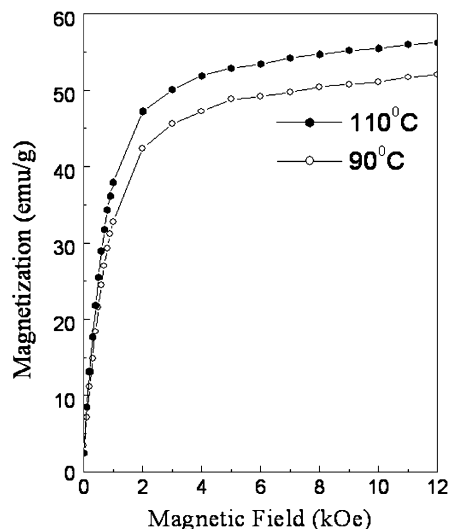


Fig. 7. Magnetization graphs of annealed samples at 90 °C and 110 °C.

ACKNOWLEDGMENT

S. Narayana Jammalamadaka would like to thank the Indian Institute of Technology Madras, Chennai, India, for the financial support.

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