

Magnetic properties of ball-milled TbFe₂ and TbFe₂B

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Abstract. The magnetic properties of ball-milled TbFe₂ and TbFe₂B were studied by magnetization measurements. X-ray diffraction studies on TbFe₂B showed that boron occupied interstitial position in the crystal structure, just as hydrogen did. The value of the saturation magnetization of TbFe₂B was found to be smaller than that of TbFe₂. This is explained on the basis of a charge transfer between the boron atoms and the 3d band of Fe. The anisotropy of TbFe₂B was found to be large compared to that of TbFe₂. X-ray diffractograms for the ball milled samples showed that after 80 h of milling, a predominantly amorphous phase was obtained. TbFe₂B was found to undergo easy amorphization compared to TbFe₂. Magnetization of TbFe₂ was found to decrease rapidly with initial milling hours and was found to be constant with further hours of milling. TbFe₂B exhibited an anomalous behaviour with an increase in moment with milling hours and this may be due to the segregation of α -Fe.

Keywords. Amorphous materials; intermetallic compounds; magnetic materials; magnetic properties.

1. Introduction

The RFe₂ (R = rare earth) Laves phase compounds are known to possess large cubic anisotropy (Clark *et al* 1972) and highest Curie temperature (T_C) of all RT₂ compounds (T = transition metal). RFe₂ compounds crystallize in cubic MgCu₂ (C15) type structure. These compounds are known to exhibit diverse magnetic properties due to the competing effects of exchange interaction and crystalline electric field effects. Koon *et al* (1991) reviewed the anisotropy and other magnetic properties in these materials. Dhilsha and Rama Rao (1990) reported single particle excitations in Co substituted Ho_{0.85}Tb_{0.15}Fe₂, through electrical resistivity measurements. Low temperature magnetization studies on Ni substituted Dy_{0.73}Tb_{0.27}Fe₂ and Ho_{0.85}Tb_{0.15}Fe₂ have revealed domain wall pinning (Senthil Kumar *et al* 1995). Annapoorni *et al* (1989, 1990) investigated the effect of hydrogen on the structural, magnetic and electrical properties of Dy_{0.73}Tb_{0.27}Fe₂ and Ho_{0.85}Tb_{0.15}Fe₂. They observed the solubility of hydrogen through isotherms, compensation temperatures near T_C that decreased with increasing hydrogen concentration (Annapoorni *et al* 1989) and reported a metal–semiconductor transition induced by hydrogen (Annapoorni *et al* 1990). The modifications of the magnetic properties due to hydrogenation have been understood as due to the transfer of charges from the 3d band of Fe to hydrogen (Annapoorni and Rama Rao 1990). Kishore *et al* (1998) observed spin flip meta-magnetism and domain wall pinning resulting from the modification of magnetoelastic

properties in hydrogenated Dy_{0.73}Tb_{0.27}Fe_{2-x}Co_x compounds. Lee *et al* (2000) measured magneto-optical equatorial spectra of polycrystalline RFe₂ and derived half-diagonal conductivities.

In recent years, structural and magnetic properties of ball-milled RFe₂ compounds have been investigated. ⁵⁷Fe Mossbauer, magnetization and a.c. susceptibility studies on ball milled YFe₂ showed significant changes in magnetic properties and these have been attributed to the systematic disordering of the crystal structure and subsequent reduction in ordering temperature with milling time (Larica *et al* 1998). In addition, the formation of disordered distribution of magnetic moments (spin glass/asperomagnetic behaviour etc) has been reported. ^{155,157}Gd NMR studies on the ball-milled GdFe₂ and GdCo₂ have shown a broadening of the spectrum due to the transferred hyperfine interaction from the segregation of elemental particles upon milling (Tribuzy *et al* 1999). Modder *et al* (1999) studied the structural and magnetic properties of ball-milled GdX₂ (X = Al, Mg, Pt, Ir, Rh) Laves phase compounds. Geshev *et al* (1997) reported a significant increase in coercivity in TbFe₂ upon ball milling. In this paper, we report the effect of the addition of boron on the magnetic properties of TbFe₂ and also the magnetic properties of the above compounds as a function of reduction in particle size.

2. Experimental

TbFe₂ and TbFe₂B were prepared by arc melting the high pure elements (Tb and B, 99.9% purity; Fe, 99.95% purity). The ingots were melted several times to obtain a homo-

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geneous mixture. In all the compounds, the weight loss after melting was less than 0.5%. The ingots were annealed in vacuum at 950°C for 7 days and were then furnace cooled to room temperature. Powder X-ray diffraction studies were carried out on the compounds employing $\text{FeK}\alpha$ radiation for structural characterization.

Ball milling was carried out using a planetary ball mill (FRITSCH) at a speed of 300 rpm and a ball-to-powder weight ratio of 15 : 1. The milling was carried out in toluene for 80 h employing tungsten carbide balls of 10/20 mm diameter. The magnetization measurements were carried out using a PAR vibrating sample magnetometer up to a field of 10 kOe.

3. Results and discussion

Figures 1 (a) and (b) show the XRD patterns of TbFe_2 and TbFe_2B , respectively. Both the compounds formed in cubic Laves phase structure. The lattice parameter of TbFe_2 is found to be 7.340 Å, which is in agreement with that reported in literature.

The XRD pattern of TbFe_2B indicates two sets of peaks corresponding to two lattices with MgCu_2 structure. These have been indexed, one corresponding to a lattice (lattice I) with a lattice parameter of 8.017 Å and the other set corresponding to a further expanded lattice (lattice II) with a lattice parameter of 8.268 Å. Ren *et al*

(2002) reported that boron in $\text{Dy}_{0.7}\text{Pr}_{0.3}(\text{Fe}_{1-x}\text{B}_x)_2$ ($x = 0.1-0.3$) occupies Fe sites, with a decrease in lattice parameter with increasing boron concentration. The effect of boron in $\text{Tb}_{0.7}\text{Pr}_{0.3}(\text{Fe}_{1-x}\text{B}_x)_2$ ($x = 0.05-0.35$) has been studied by Ren *et al* (2001). They have shown that the lattice expands when boron occupies the interstitial sites for concentration up to $x = 0.1$ and for further increase in boron concentration the lattice contracts due to the occupancy of boron in lattice at the Fe sites. However, in the present case of TbFe_2B there is only a lattice expansion and therefore, the probability that boron occupies the interstitial sites could be more than that for the occupation at the substitutional site. This situation may be likened to the case of hydrogen occupying the interstitial sites. However, while hydrogen preferentially occupies the tetrahedral site formed by two Tb atoms and two iron atoms, boron may prefer to occupy the site formed by three iron atoms and a Tb atom. This could expand the lattice more than in the case of hydrogenated compounds. This combined with the fact that boron atom is bigger than hydrogen, might be responsible for the lattice I itself to be an expanded lattice.

Figures 2 (a) and (b) show the magnetization curves of TbFe_2 and TbFe_2B , respectively at 12 K. Both the magnetization values did not saturate up to a field of 10 kOe. It is seen that the magnetization decreases with the introduction of B in TbFe_2 . In TbFe_2 , the Tb and Fe moments

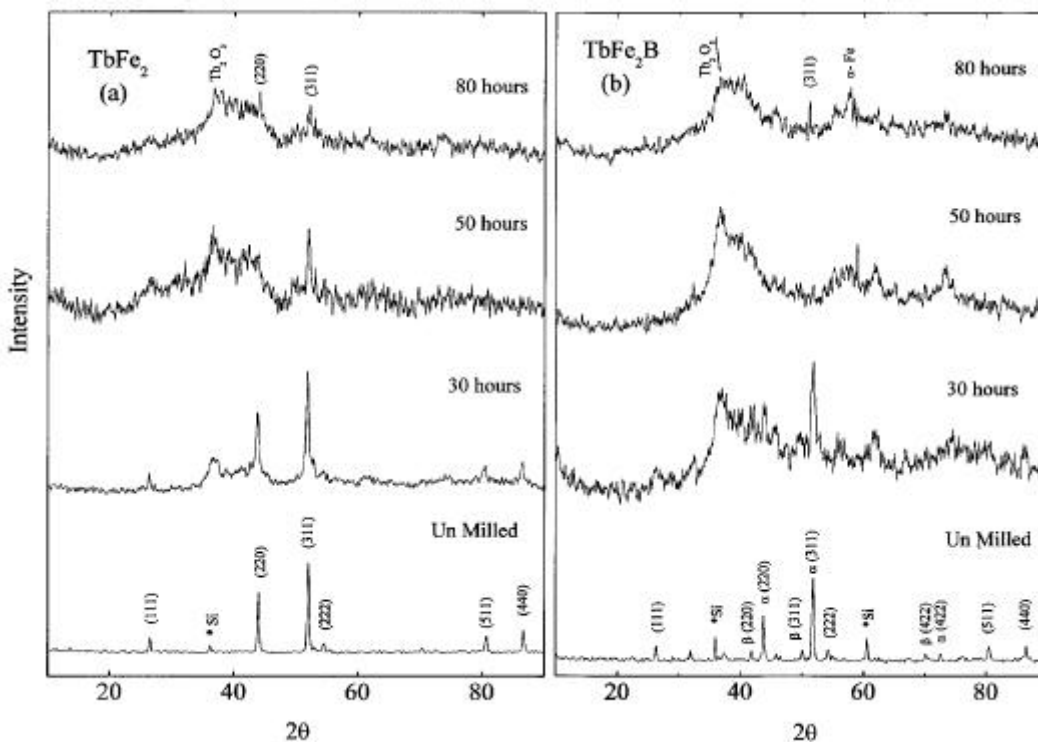


Figure 1. (a) X-ray diffraction patterns of unmilled and ball milled TbFe_2 and (b) X-ray diffraction patterns of unmilled and ball milled TbFe_2B , peaks indexed as 'α' correspond to lattice I and those peaks indexed as 'β' correspond to lattice II.

are antiparallel and the net magnetic moment is dominated by the Tb moment. The magnetic moment per iron atom has been reported to be $1.64 \mu_B$. As in the case of hydrogenated compounds, the addition of boron may cause the depletion of the 3d band of Fe thereby increasing the Fe moment and hence a decrease in the net magnetic moment of the alloy. However, while hydrogen causes a fanning of the Tb moments leading to a decrease in the anisotropy, with the addition of boron, the anisotropy is seen to increase. This again, may be due to the affinity of boron for iron, causing the anisotropy of the iron sublattice to increase, adding to the anisotropy of the Tb sublattice.

The ball-milled samples of $TbFe_2$ and $TbFe_2B$ were analysed using XRD, after various milling times (figures 1 (a), (b)). The intensities of the peaks for both the compounds are seen to decrease with the increase of milling time. The XRD pattern for $TbFe_2$ taken after 80 h of milling shows a predominantly amorphous phase along with the $MgCu_2$ type crystalline phase. In fact, the development of amorphous phase is seen after 50 h of milling. In addition to the $MgCu_2$ and amorphous phases, Tb_2O_3 phase is seen to develop. This could have been picked up from the air molecules present in the vial used for ball milling,

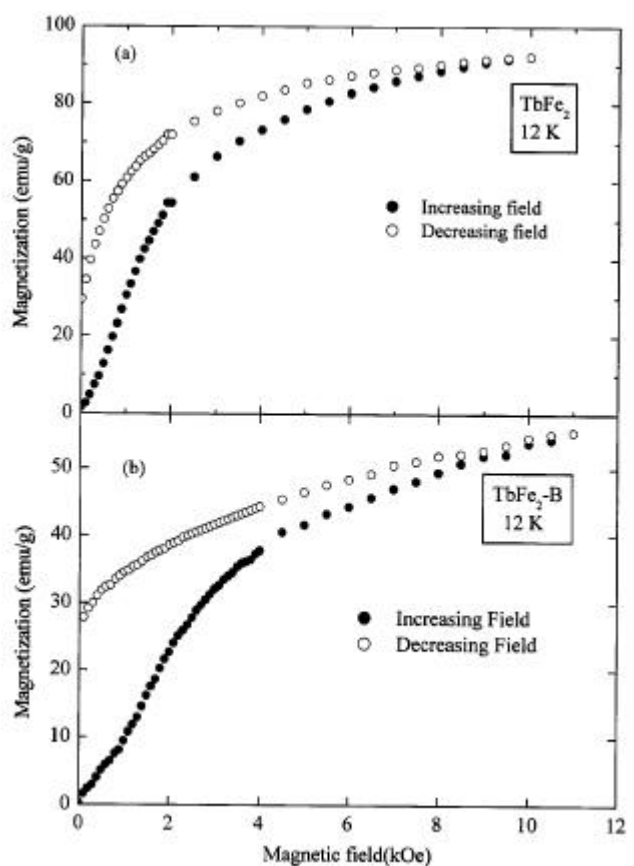


Figure 2. Magnetization curves of (a) $TbFe_2$ and (b) $TbFe_2B$, at 12 K.

even though the milling was carried out in toluene medium, due to the small size of the particles leading to a large effective surface area. Tang *et al* (1997), in fact, reported the formation of oxides of Dy and Tb when $Dy_{0.7}Tb_{0.3}Fe_{1.97}$ was ball-milled in ethanol or argon medium. The XRD pattern of $TbFe_2B$ after 80 h of milling shows reflections corresponding to terbium oxide, an amorphous phase and α -Fe, in addition to the $MgCu_2$ phase. The amorphous phase in this material is seen to form after < 30 h of milling, in contrast to $TbFe_2$.

Figure 3 shows the magnetization curves at 12 K, of ball milled $TbFe_2$ at various stages of milling. The magnetization does not saturate up to a field of 1 Tesla, irrespective of the particle size. However, the magnetization at 10 kOe decreases rapidly for the material ball milled for 30 h, compared to the starting material. The magnetization is found not to change much subsequently. Inset shows the variation of magnetization at 10 kOe as a function of milling time. The decrease in the magnetic moment can be understood as follows: the Fe moments that are suppressed in the alloy, from the elemental value might have been recovered due to the localization upon reduction in the particle size. Since Fe and Tb moments are anti-parallel there is a net decrease in the magnetic moment of ball-milled $TbFe_2$. Of course, it is assumed that the Tb moments are not affected as they are localized. In addition, the reduction in particle size causes disordering at the surfaces that may also cause a reduction in magnetization. Tang *et al* (1997) reported similar observations in Dy–Tb–Fe alloy.

The magnetization curves of $TbFe_2B$ at 12 K (figure 4) are interesting in the sense that the magnetization decreases with milling up to 30 h and subsequently increases (see inset). The decrease can be attributed to the localization of Fe moments, causing a net decrease in the magnetization due to anti-ferromagnetic ordering of Fe and Tb moments. Rhombohedral distortion in the cubic

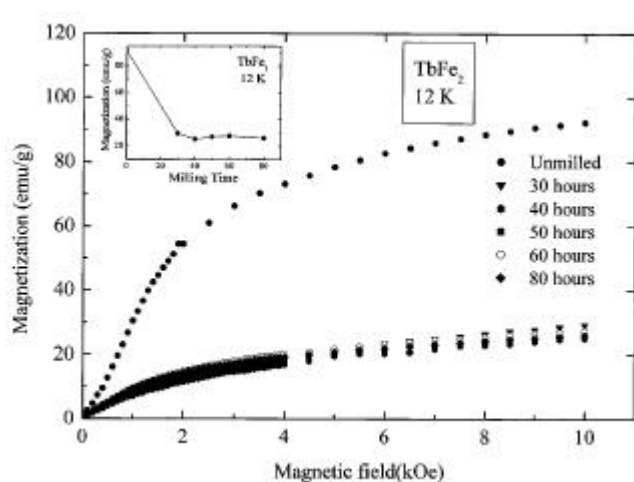


Figure 3. Magnetization curves of ball milled $TbFe_2$ at 12 K.

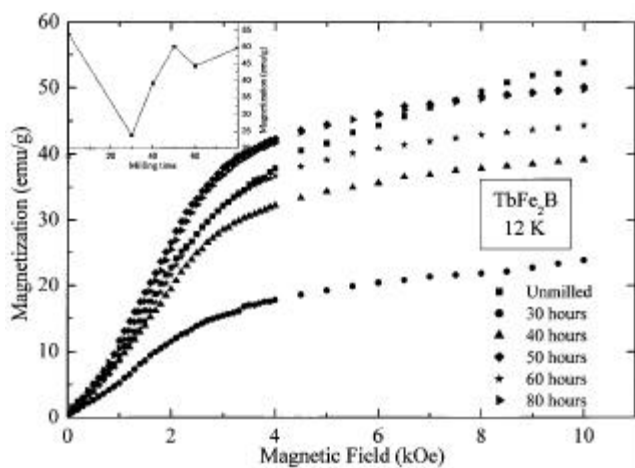


Figure 4. Magnetization curves of ball milled TbFe_2B at 12 K.

Laves phase compounds due to magnetoelastic interactions has been reviewed by Clark (1980). The milling could enhance the already enhanced rhombohedral distortion due to the addition of boron. The increased distortion could in turn lead to the separation of $\alpha\text{-Fe}$. Therefore, the increase in the magnetic moment with increasing milling time beyond 30 h could be due to the separation of $\alpha\text{-Fe}$ upon ball milling.

Figure 5 shows the magnetization curves up to a field of 2 kOe and at 12 K, of ball milled TbFe_2B at various stages of milling and discontinuous increase of magnetization is seen in all the compounds. Such a phenomenon, termed as spin flip metamagnetism, is encountered in several rare earth iron intermetallic systems with pronounced localized and uniaxial anisotropy (Gignoux and Schmitt 1995). Kishore *et al* (1998) observed this phenomenon for the first time in hydrogenated $\text{RFe}_{2-x}\text{Co}_x$ compounds. They attributed the metamagnetism as due to

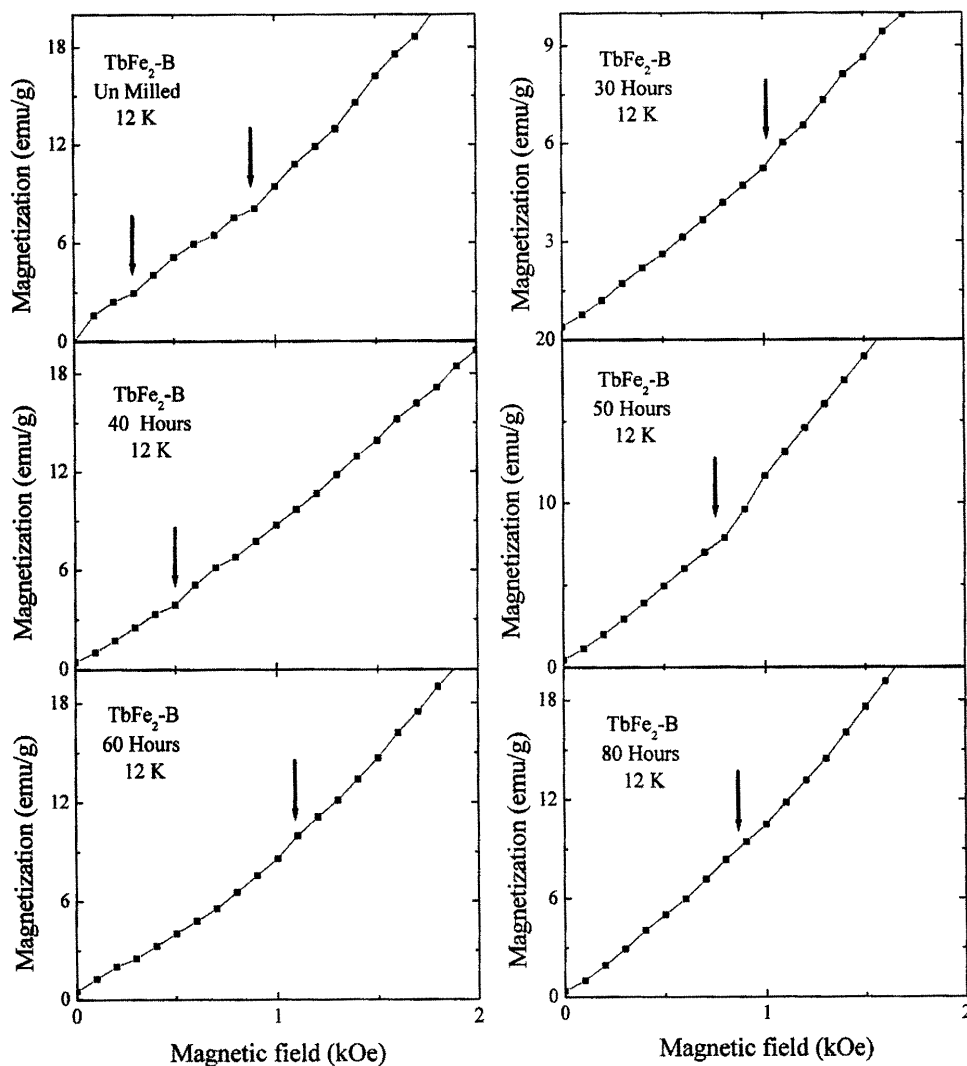


Figure 5. Magnetization curves of ball milled TbFe_2B at 12 K shown up to a field of 2 kOe.

the localization of anisotropy as a result of the ordering of hydrogen with periodicity incommensurate to the periodicity of the main lattice, in the already rhombohedrally distorted lattice. A similar effect, though to a smaller magnitude, could be responsible for the observed behaviour of magnetization in $TbFe_2B$. In the present case, the discontinuous changes in magnetization is more pronounced and extends up to 2 kOe in the unmilled compound and is less pronounced and shifted towards lower fields, in the milled compounds. This is of course, to be expected due to the amorphous nature of the compound, after milling.

4. Conclusions

The decrease in magnetization of $TbFe_2$ with the introduction of boron has been explained on the basis of the depletion of 3d band. The severe milling of $TbFe_2$ and $TbFe_2B$ show the development of predominant amorphous phases in both the compounds, after 80 h of milling. The magnetization of ball milled $TbFe_2$ decreases rapidly up to 30 h of milling and remains constant with further milling as has been attributed to the localization of Fe moments with decrease in particle size. Magnetization of ball-milled $TbFe_2B$ decreases up to 30 h of milling and increases with further milling. The initial decrease may be attributed to the localization of the Fe moments and the subsequent increase is due to the separation of α -Fe due to the inherent rhombohedral distortion which is further enhanced by boron during milling. Spin-flip metamagnetism is observed in 12 K magnetization curves of ball-milled $TbFe_2B$ up to a field of 2 kOe.

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