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Development and intrinsic properties of hexagonal ferromagnetic (Zr,Ti)Fe_2

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Nanocrystalline $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ ($x = 0$-0.4) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ ($y = 0$-0.35) with high saturation magnetization have been fabricated by the melt-spinning technique. Nanocrystalline $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ consists of the hexagonal C14 Laves phase (Ti,Zr)Fe_2. Fe addition decreases the lattice parameter *a* and shrinks the cell volume. The antiferromagnetic Fe-Fe interactions may decrease with the increase of x, leading to a significant enhancement of saturation polarization (J_s) and Curie temperature (T_c). The magnetocrystalline anisotropy constant K also increases with increasing x. Excessive Fe addition ($x > 0.25$) may induce structural disorder which lowers the J_s and T_c. Nanocrystalline $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ is composed of hexagonal (Ti,Zr)Fe_2 and Fe-rich amorphous phases with relatively high J_s. The lattice parameters *a*, *c* and cell volume *V* are almost unchanged with the increase of y for $y \geq 0.16$. Simultaneously, the T_c of (Ti,Zr)Fe_2 remains unchanged, indicating that B does not enter this lattice but takes part in forming the amorphous phase, in good agreement with the X-ray diffraction results. The volume fraction of the amorphous phase increases with the increase of B content and results in a large enhancement of J_s up to 10.8 kG. Further B addition ($y > 0.30$) decreases J_s, possibly due to the decrease of the J_s of the amorphous phase. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868696]

The magnetic properties of the C14 Laves phase $TiFe_2$ with the hexagonal structure show strong composition dependence due to the existence of the energetic near-degeneracy of an antiferromagnetic (AF) and ferromagnetic (FM) ground state.[1,2] The Ti-Fe alloy has a wide homogeneity range at 1300 °C,[3,4] leading to the appearance of a composition variation at room temperature for $TiFe_2$. Between $x = 0$ and $x = 0.7$, $TiFe_{2+x}$ may be AF and FM.[5,6] Stoichiometric $TiFe_2$ is AF, while Fe-rich $TiFe_2$ shows FM. So far, much work has been done on how the alloy composition affects basic magnetism of microcrystalline Ti-Fe alloys. Little attention has been paid to studying the effect of element addition on nanostructure and intrinsic properties of nanocrystalline Ti-Fe. A high quench rate is favorable to keep the high-temperature metastable phase to room temperature. In this work, we added 25 at. % Zr in order to decrease the fraction of AF alignment of intralayer Fe. We fabricated nanocrystalline $Zr_{0.25}Ti_{0.75}Fe_{2+x}$ ($x = 0$-0.4) and $Zr_{0.25}Ti_{0.75-y}B_yFe_{2.25}$ ($y = 0$-0.16) by melt spinning and investigate the effects of Fe and B content on intrinsic properties. All the samples exhibit FM. Fe and B additions lead to a large improvement of Curie temperature and saturation magnetization.

Ingots of $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ ($x = 0$, 0.15, 0.25, 0.40) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ ($y = 0$, 0.16, 0.30, 0.35) were arc melted from high-purity elements in an argon atmosphere. The ribbons were made by ejecting molten alloys in a quartz tube onto the surface of a copper wheel with a speed of 15 m/s. The ribbons are about 2 mm wide and 50 μm thick. The phase components were examined by Rigaku D/Max-B X-ray diffraction (XRD) with Co K_α radiation. The nanostructure was observed by the Tecnai Osiris Transmission Electron Microscope (TEM). The hysteresis loops were measured by a superconducting quantum interference device (SQUID) magnetometer at fields up to 7 T. Intrinsic properties: saturation magnetization, magnetocrystalline anisotropy constant, anisotropy field were determined by fitting the high-field part of hysteresis loops using the law-of-approach to saturation. Thermomagnetic curves were obtained using a Physical Property Measurement System (PPMS) vibrating sample magnetometer (VSM). The applied field is parallel to the long direction of the ribbon.

Figures 1(a) and 1(b) show XRD patterns of nanocrystalline $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ ($x = 0$, 0.40) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ ($y = 0.16$, 0.30). All the diffraction peaks were indexed to the hexagonal C14 structure. The $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ consists of the C14 structure except that here is an obvious shift of diffraction peaks for the $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ due to Fe addition. This implies a change of lattice parameters. The diffraction peaks for the $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ did not shift, indicating that the lattice parameters remain unchanged. A halo peak between 35° and 55° appears in the $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$, implying the existence of an amorphous phase. The relative intensity of the halo peak increases with the increase of B content suggesting that the volume fraction of the amorphous phase increases with increasing y. The $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ is composed of the crystalline (Ti,Zr)Fe_2 and amorphous phases. Figures 1(c) and 1(d) show B and Fe content dependence of cell

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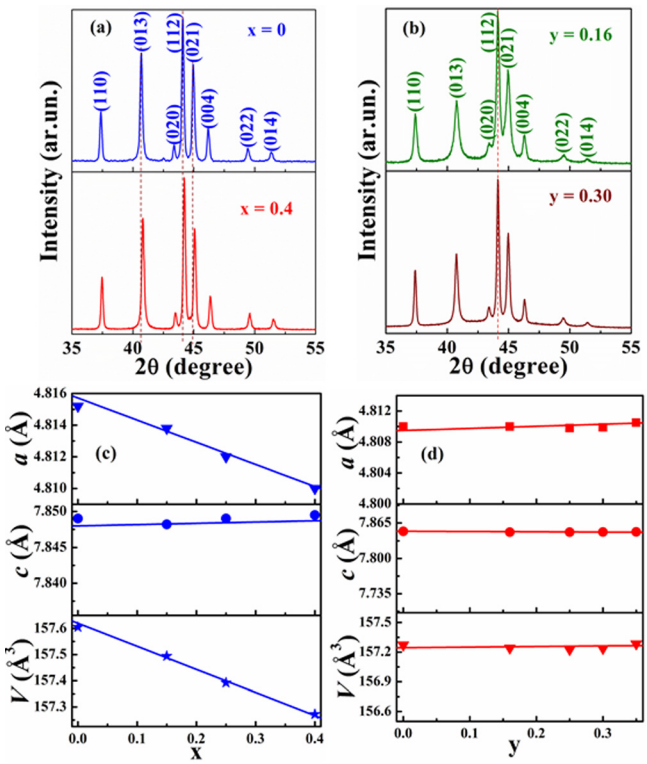

FIG. 1. XRD patterns of (a) $Ti_{0.75}Zr_{0.25}Fe_{2+x}$(x = 0, 0.4), (b) $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$(y = 0.16, 0.30). And corresponding (c) x and (d) y dependence of cell parameters (*a*, *c*, *V*).

parameters (*a*, *c*, *V*). Fe addition leads to no change of *c*, a decrease of *a*, and thus a decrease of *V*. It is believed that extra Fe (R_{Fe} = 126 pm) replaces some amount of Ti (R_{Ti} = 147 pm) or Zr (R_{zr} = 160 pm), leading to the shrinkage of the cell volume. Occupancy site of extra Fe needs to be further investigated. B addition results in a slight increase of *a*, *c*, *V* of the crystalline phase. The lattice parameters of the crystalline phase are almost unchanged with y and close to those of the x = 0.25 shown in Fig. 1(c). The composition of the crystalline phase is presumably $Ti_{0.75}Zr_{0.25}Fe_{2.25}$.

Figure 2 shows thermomagnetic curves for the x = 0, 0.25 and y = 0.3. The Curie temperature (T_c) was determined from the peak position of the dM/dT vs T plot shown in the inset. The M(T) curves of the x = 0 and 0.25 only have one ferro-paramagnetic transition from the magnetic (Ti,Zr)Fe_2. $TiFe_2$ is an antiferromagnet with T_N = 270 K.[7] Replacement

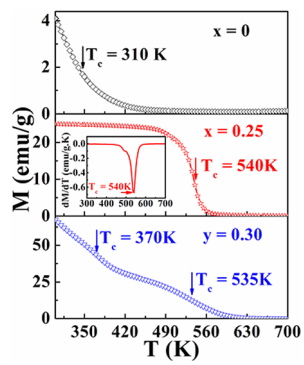

FIG. 2. M(T) curves of $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ (x = 0, 0.25) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ (y = 0.30).

of Ti by Zr to form $Ti_{0.75}Zr_{0.25}Fe_2$ yields a ferromagnet with T_c = 315 K. This trend is consistent with the ferromagnetism of the nearly isostructural (C15) laves phase $ZrFe_2$. Addition of excess Fe to form $Ti_{0.75}Zr_{0.25}Fe_{2.25}$ also increases T_c to 540 K. This is likely the result of increased number of ferromagnetic Fe-Fe bonds. There are two ferro- paramagnetic transitions in the M(T) curves of the y = 0.30 which correspond to the amorphous and crystalline phases. The T_c of the crystalline phase is almost the same as that for x = 0.25 which is consistent with a composition of the crystalline phase being $Ti_{0.75}Zr_{0.25}Fe_{2.25}$.

Figure 3 shows the TEM images of the x = 0.25, 0.40 and y = 0.30 samples. The nanostructure exhibits strong dependence on alloy composition. The composition of the grains for x = 0.25 and 0.40 checked by Energy-dispersive X-ray spectroscopy (EDX) are close to $Ti_{0.75}Zr_{0.25}Fe_{2.25}$ and $Ti_{0.75}Zr_{0.25}Fe_{2.4}$, respectively. The mean grain size for x = 0.25 is much larger than that for x = 0.40. Excessive Fe addition induces the appearance of many bands indicated by red arrows. High-resolution images (not shown here) show that they are planar defects. The TEM image of the y = 0.30 sample consists of grains and gray area indicated by yellow circles corresponding to the amorphous phase. No B was detected in the grains of the x = 0.30 sample. It was estimated that the composition of the amorphous phase for y = 0.30 is $Zr_{0.25}B_{0.75}Fe_{2.63}$ and its concentration is 40 at. %. The concentrations of the amorphous phase for y = 0.16 and 0.35 are 21.3 and 47 at. %, respectively. The B content and amorphous phase increase are consistent with the XRD results.

Figure 4 shows typical hysteresis loops of nanocrystalline $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ (x = 0-0.4) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ (y = 0-0.35) and deduced intrinsic properties. Fe addition increases J_s and T_c possibly due to the decrease of AF Fe-Fe interactions. Excessive Fe addition may induce the formation of structural disorder including planar defects, and thus lowers J_s and T_c. The K value increases first, which may be related to the decrease of lattice parameter a. Up to a maximum value at x = 0.15, and then slightly decreases possibly due to the increase of structural disorder such as planar defects. B addition leads to the formation of a large amount of amorphous phase which may have a high saturation

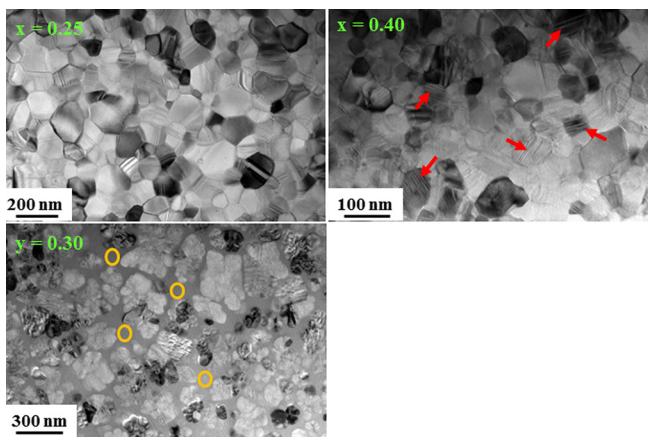

FIG. 3. TEM images of $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ (x = 0.25, 0.40) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ (y = 0.30).

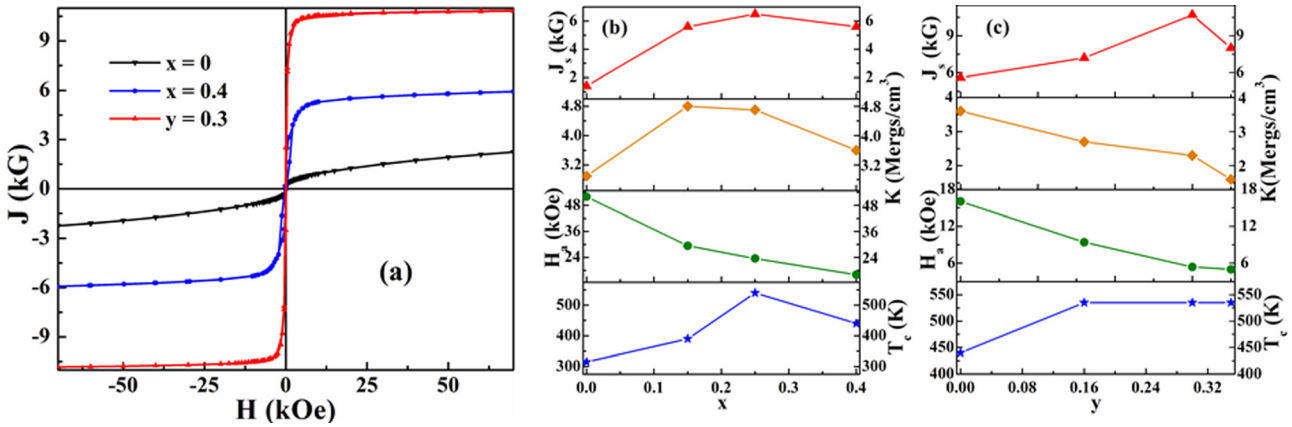

FIG. 4. Hysteresis loops of $Ti_{0.75}Zr_{0.25}Fe_{2+x}$ ($x = 0$, 0.4) and $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ ($y = 0.30$) (a). And x (b) and y (c) dependence of deduced intrinsic properties (J_s, K, H_a, and T_c).

magnetization. Therefore, J_s of the $Ti_{0.75-y}B_yZr_{0.25}Fe_{2.4}$ increases rapidly with the increase of B content. K decreases continuously with y due to the formation of soft magnetic amorphous phase. The T_c of the crystalline phase is independent of B content, indicating B hardly enters the crystalline phase. Further B addition ($y > 0.30$) results in a decrease of J_s due possibly to the decrease of magnetization of the amorphous phase. The magnetocrystalline anisotropy field of the $(Ti,Zr)Fe_2$ decreases with the increase of Fe or B content because of the big increase of saturation magnetization.

Strongly ferromagnetic $(Ti,Zr)Fe_2$ with high T_c has been synthesized. The cell volume V of the $(Ti,Zr)Fe_2$ decreases with increasing x. Fe addition significantly increases J_s, T_c, and slightly decreases K, H_a. Excessive Fe addition may induce the formation of structural disorder, which decreases J_s and T_c. The V of the $(Ti,Zr)Fe_2$ expands at first with the increase of B content, then remains unchanged. B addition increases J_s, but decreases K and H_a. The increase of J_s is believed to arise from the increase of the content of amorphous phase with high magnetization.

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[1]J. KÖble and M. Huth, Phys. Rev. B **66**, 144414 (2002).
[2]E. F. Wassermann, B. Rellinghaus, T. Roessel, and W. Pepperhoff, J. Magn. Magn. Mater. **190**, 289 (1998).
[3]W. Brückner, K. Kleinstück, and G. E. R. Schulze, Phys. Status Solidi **23**, 475 (1967).
[4]Y. Murakami, H. Kimura, and Y. Nishimura, The Japan Institute of Metals and Materials **21**, 665 (1957).
[5]E. Piegger and R. S. Craig, J. Chem. Phys. **39**, 137 (1963).
[6]W. Brückner, R. Perthel, K. Kleinstück, and G. E. R. Schulze, Phys. Status Solidi **29**, 211 (1968).
[7]T. Nakamichi, J. Phys. Soc. Jpn. **25**, 1189 (1968).