Intermetallics 100 (2018) 188–192

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Effect of Co, Cu, Nb, Ti, V on magnetostriction and mechanical properties of TbDyFe alloys

Naijuan Wang[a], Yuan Liu[a,b,*], Huawei Zhang[a,b], Xiang Chen[a,b], Yanxiang Li[a,b]

[a] School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China
[b] Key Laboratory for Advanced Materials Processing Technology, Ministry of Education, PR China

A R T I C L E I N F O

Keywords:
TbDyFe alloys
Mixing enthalpy
Microstructure
Micro-hardness
Magnetostriction

A B S T R A C T

The previous studies have revealed that addition of different elements in TbDyFe alloys have different influences on its microstructure, mechanical and magnetic properties. According to the effects, one can classify elements into different groups. This paper aims to explain the differences by the enthalpy of mixing between the atomic pairs. Various alloys of the type $Tb_{0.3}Dy_{0.7}Fe_2$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Cu_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Nb_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Ti_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}V_{0.1}$ were prepared by an arc melting under a high-purity argon atmosphere. The effects of Co, Cu, Nb, Ti, V addition on the microstructure, mechanical properties and magnetic properties of TbDyFe alloys were studied systematically. The results showed that according to the different mixing enthalpy between different atom-pairs, the elements added in TbDyFe alloy could be classified into two different groups. One had a more negative mixing enthalpy with the rare earth element Tb (Dy), such as Co, Cu, which were prone to form phases with rare earth elements; the others possessed a more negative enthalpy of mixing with Fe, such as Nb, Ti, V, which were conducive to react with Fe. With Co, Cu element addition, the alloys exhibited dendritic morphology. While the alloys demonstrated the second phase precipitation morphology with addition of Nb/Ti/V elements. Compared to the $Tb_{0.3}Dy_{0.7}Fe_2$ alloy, the $REFe_3$ phase appeared in the alloys with addition of Co/Cu element. The $NbFe_2$/Fe_2Ti/FeV phase precipitated in the alloys with Nb/Ti/V addition, respectively. But the formation of $REFe_3$ phase was effectively suppressed due to the addition of Nb/Ti/V elements. The presence of both $REFe_3$ phases and $NbFe_2$/Fe_2Ti/FeV paramagnetic phases all reduced the magnetostriction of $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}M_{0.1}$ (M = Co, Cu, Nb, Ti, V) alloys compared to the $Tb_{0.3}Dy_{0.7}Fe_2$ alloys.

1. Introduction

Giant magnetostrictive Terfenol-D alloys are some of the most important functional magnetic materials [1]. The potential of these magnetic materials are now being employed in variety of applications, such as sensors, precision machinery, magnetomechanical transducers, and adaptive vibration-control systems [2–5]. The Terfenol-D alloys possess high magnetostrictive coefficients at room temperature accompanied with low magnetocrystalline anisotropy constants [6], however, its intrinsic brittleness greatly limits the applications of this material [7].

Previous studies have focused on improving the magnetostrictive and mechanical properties by alloying with elements. J. Arout Chelvane et al. [8] studied the effects of Ti addition on the microstructure and magnetic properties of Tb-Dy-Fe alloys. The study shows that the addition of Ti in TbDyFe alloy diminishing the formation of pro-peritectic $(Dy,Tb)Fe_3$ phases, which improves the magnetostriction. The effect of Nb and Zr addition on the microstructural features and magnetic properties of $Tb_{0.3}Dy_{0.7}Fe_{1.95}$ was studied by Mithun Palit et al. [9]. The researches show that the Nb addition results in the formation of $NbFe_2$ as the primary phase while Zr addition results in the depletion of $(Tb,Dy)Fe_3$ phase owing to the substitution of Zr for rare earths in the main phase. A significant improvement in magnetostriction was obtained for the alloy with a low concentration of Zr or Nb compared to the parent alloy (x = 0). Moreover, some research has been reported on the substitution of other 3 d metals such as Ni, Co, and Mn for Fe in $Tb_xDy_{1-x}Fe_2$ compounds in order to improve their magnetostrictive properties [10]. The results reveal that large magnetostriction in polycrystalline materials with the addition of Co element can be retained in a wide temperature range from −80 to 100 °C. Hongping Zhang et al. [11] studied the effect of V on microstructure and magnetic properties of polycrystal Tb-Dy-Fe alloy. The results indicate that the grains of the alloy have been broken down, the Laves phase has spread all over the microstructure and the Fe-rich phase has been increased by

* Corresponding author. School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China.
E-mail address: yuanliu@tsinghua.edu.cn (Y. Liu).

https://doi.org/10.1016/j.intermet.2018.06.015
Received 27 January 2018; Received in revised form 10 June 2018; Accepted 23 June 2018
Available online 03 July 2018

the addition of V. The addition of V changed the point of anisotropy compensation of the alloys to higher Tb content, improved the magnetostrictive properties significantly.

All of the above studies have pointed out the influence of alloying on magnetic properties of TbDyFe alloy. However, better understanding of the microstructures of TbDyFeM (M is the fourth component) alloy is still limited and urgent. In recent years, a new alloy-design concept, termed as high entropy alloys (HEAs), was proposed [12]. High entropy alloys (HEAs), typically defined as the alloys composing of multiple principal elements in equal or near equal atomic percent (at.%) ranging from 5 to 35 at.%, are attracting much attention in the field of advanced metallic materials [13–16]. The study by Yiping Lu et al. [17] confirms that HEAs provide an easy way to design/locate advanced materials for their microstructure and phase composition using mixing enthalpy. TbDyFeM (M is the fourth component) is a quaternary high entropy alloy. Based on the inspiration of research in HEAs, the phase formation classified by mixing enthalpy and its influences on the microstructure and magnetostriction properties of TbDyFe alloys were studied systematically in the paper.

2. Experimental

The alloys of $Tb_{0.3}Dy_{0.7}Fe_2$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Cu_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Nb_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Ti_{0.1}$, $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}V_{0.1}$ were prepared by an arc melting under a high-purity argon atmosphere. The alloys were prepared from materials of the following purities: Tb, Dy (99.99 wt%), Fe, Cu (99.95 wt%). To compensate the volatility of rare-earths, the starting compositions were 2 at% richer in rare-earths in order to result in the correct stoichiometry. The ingots were re-melted at least 5 times to improve their chemical homogeneity. The phase constitutions of the alloys were identified by X-ray diffraction (XRD) on a D8-Advance diffraction meter (Cu Kα radiation, λ = 0.154 nm) at a scanning rate of 6 min^{-1}. The XRD profiles were fitted by JADE 5.0 XRD analytical software (Materials Data, Inc., Livermore, CA) to eliminate the Kα2 radiation. The microstructure and chemical composition as well as fracture morphology were characterized by means of field emission scanning electron microscopy (FESEM) (Zeiss MERLIN-VP-COMPACT) equipped with an energy dispersive X-ray (EDX) (Oxford INCA) analyzer and with a JEOL JXA-8230 electron probe microanalyzer (EPMA). The micro-Vickers hardness measurements were conducted by an FM-800 microhardness tester under a load of 25 gf or 10 gf applied for 20 s. The static measurement of magnetostriction was tested by standard strain gauge with the sample size of $4 \times 4 \times 6\,cm^3$.

3. Results and discussion

3.1. Microstructure

Previous studies show that the enthalpy of mixing between the atom pairs can explain the phase formation trend in the alloy. The more negative mixing enthalpy means the larger binding force between atomic pairs, which is inclined to form intermetallic compound [17]. However, the more positive mixing enthalpy means the less miscibility of the different elements in the liquid alloy, which leads to separation or segregation of different elements in alloy [18].

Table 1 shows the mixing enthalpy between the different atom-pairs in alloys TbDyFeM (M = Co, Cu, Nb, Ti, V). The mixing enthalpy of the rare earth elements Tb(Dy) and the Fe element is −3 kJ/mol. Both the mixing enthalpy of Tb(Dy) and Co or Tb(Dy) and Cu are all −23 kJ/mol. The mixing enthalpy of Fe and Nb, Fe and Ti, Fe and V are −16 kJ/mol, −17 kJ/mol, −7 kJ/mol, respectively. According to the classification, the elements can be classified into two different groups. One has a more negative mixing enthalpy with the rare earth element Tb(Dy), such as Co, Cu, which is prone to form phases with rare earth elements; the others possess a more negative enthalpy of mixing with Fe, such as Nb, Ti, V, which is inclined to react with Fe.

Table 1
Mixing enthalpy of different atom-pairs ΔH_{AB}^{mix} (kJ/mol) calculated by Miedema's approach [19].

	Co	Cu	Nb	Ti	V	Fe
Tb(Dy)	−23	−23	28	14	15	−3
Fe	−1	13	−16	−17	−7	

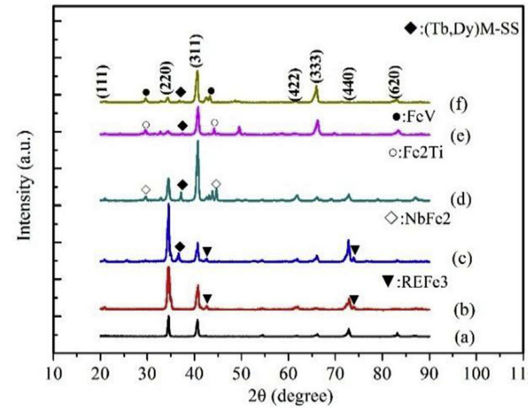

Fig. 1. X-ray diffraction patterns of alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$; (b) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$; (c) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Cu_{0.1}$; (d) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Nb_{0.1}$; (e) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Ti_{0.1}$; (f) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}V_{0.1}$.

In order to analyze the structure of these high entropy magnetic alloys, XRD patterns of the alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$, (b) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$, (c) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Cu_{0.1}$, (d) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Nb_{0.1}$, (e) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Ti_{0.1}$, and (f) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}V_{0.1}$ were obtained and shown in Fig. 1. The alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$ is the standard ratio of commercially Terfenol-D alloys. It serves as a comparative sample for the study of other alloys. This XRD analysis revealed that the alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$ is composed of single $REFe_2$ phase. Compared to the alloy (a), there are other phases present in the alloys with the addition of Co, Cu, Nb, Ti, V elements where the components can also be determined from BSEM and EPMA analysis as described in a later section. There are $REFe_3$ phases appeared in the alloy (b) and (c) with the addition of Co or Cu. Besides the precipitation of rare earth-rich phases (Tb,Dy)M, there is also $NbFe_2$, Fe_2Ti, FeV phases appeared in the alloy (d), (e) and (f), respectively.

Fig. 2 shows the BSEM images of the alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$, (b) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$, (c) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Cu_{0.1}$, (d) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Nb_{0.1}$, (e) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Ti_{0.1}$, and (f) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}V_{0.1}$. It is obvious that the alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$ is composed of gray matrix phases and white precipitation phases. The alloy (b) and (c) consist of gray matrix phases, gray-black dendrite phases and white precipitation phases. The alloy (d)-(f) include gray matrix phases, black second phases, and white precipitation phases. As can be seen from the microstructure, compared with the alloy (a), the first type of alloy (b) and (c) with the addition of Co and Cu are composed of interdendritic and dendritic phase morphology. While there are second precipitation phases dispersed in the second kinds of alloy (d)-(f), with the addition of Nb, Ti, V element.

Fig. 3 exhibits the element distribution analysis conducted by EPMA for alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$, (b) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$, (c) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Cu_{0.1}$, (d) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Nb_{0.1}$, (e) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Ti_{0.1}$, and (f) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}V_{0.1}$. The results clearly clarify that the element distributes homogeneously in all the alloy gray matrix $REFe_2$ phase. The white phases precipitated in alloy (a) $Tb_{0.3}Dy_{0.7}Fe_2$ is (Tb,Dy)-rich phases. The white (Tb,Dy)Co rare earth-rich phases and gray-black $(Tb,Dy)(Fe,Co)_3$ phases can be observed in alloy (b) $(Tb_{0.3}Dy_{0.7})_{0.3}Fe_{0.6}Co_{0.1}$. The white (Tb,Dy)Cu phases and gray-black $(Tb,Dy)Fe_3$ phases are discovered in alloy (c). The black second precipitation phases shown in alloy (d)-(f) are $NbFe_2$,