Original Article

Effect of milling time on the microstructure and magnetic properties of amorphous Ti$_{50}$Fe$_{50}$ alloys prepared by mechanical alloying

Yongbo Xu$^a$, Shengfeng Zhou$^{b,*}$, Bangquan Liao$^a$, Shuzhen Zhao$^a$, Xiaoqin Dai$^a$, Dongchu Chen$^{c,*}$

$^a$ Laser Technology Institute, Tianjin Polytechnic University, Tianjin, 300387, PR China
$^b$ Institute of Advanced Wear & Corrosion Resistance and Functional Materials, Jinan University, Guangzhou, 510632, PR China
$^c$ School of Materials Science and Energy Engineering, Foshan University, Foshan, Guangdong, 52800, PR China

Abstract

The effect of milling time on the microstructural evolution and magnetic properties of Ti$_{50}$Fe$_{50}$ alloys prepared by mechanical alloying were investigated. The results showed that the powder size was decreased sharply and then stabilized. Correspondingly, the milled powders experienced a transition from the lamellar shape to the spherical shape due to severe plastic deformation as well as the competition of cold welding and fracturing when the milling time was increased. Compared with the detailed composition primary powder (composed of Ti and α-Fe phases), the nanocrystalline Ti and α-Fe phase gradually disappeared and the amorphous phase were formed in the Ti$_{50}$Fe$_{50}$ alloys after milling for 40 h. When the milling time was increased to 60–90 h, the nanocrystalline disappeared and the complete amorphization of the milled Ti$_{50}$Fe$_{50}$ alloys occurred. However, a small amount of the nanocrystalline TiFe was formed except for a large of amorphous phase in Ti$_{50}$Fe$_{50}$ alloys for 100 h. Meanwhile, the formation of paramagnetic amorphous/nanocrystalline Ti and TiFe phase resulted in the saturation magnetization and coercive of the milled Ti$_{50}$Fe$_{50}$ alloys were decreased. Therefore, they exhibited excellent soft magnetic (0–90 h) and paramagnetic properties (100 h).

© 2019 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

* Corresponding authors.
E-mails: zhousf1228@163.com (S. Zhou), chendc@fosu.edu.cn (D. Chen).

https://doi.org/10.1016/j.jmrt.2019.07.001
2238-7856© 2019 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

Titanium and titanium alloys, as important structural materials, are widely used in the fields of biomedical engineering, aerospace and new energy due to their excellent biocompatibility, corrosion resistance, higher strength and lower young’s modulus [1]. However, the high cost because of the addition of noble metals (such as Au, Nb and Ta) and the serious human health problems caused by the introduction of toxic elements (such as V and Al) in titanium alloy limit the application [2,3]. In order to overcome these disadvantages, a large number of non-toxic and low-cost elements, such as Cu [4], Sn [5] and Fe [6], were added into titanium alloys and gradually developed into a new Ti alloy systems.

Due to low cost and abundant resources in nature, Fe added into Ti alloys not only stabilizes the β-Ti phase, but plays a role in solid-solution strengthening, resulting in an improvement in mechanical properties [7]. Therefore, TiFe alloys have been attracted extensive attention. For example, Chu et al. [8] found that the tensile strength (916 MPa) and plasticity (13%) of TiFe alloys were greatly improved by the addition of Fe in Ti alloys, due to the formation of β-Ti phases in TiFe alloys and the precipitation of fine α phase in β phase. Nazari et al. [9] prepared a novel TiFe alloy coating by laser melting the low-cost materials (titanium swarf and iron powder) on the Ti substrate. The results showed that the TiO2, TiC, Fe2O3 and Fe2C fine dendritic structures were formed, and the microhardness of the coating was up to 800 HV. Zhang et al. [6] found that the yield strength (2028 MPa), fracture strength (2627 MPa) and plasticity (7.5%) of Ti72Fe28 alloy are much higher than those of other (Ti0.72Fe0.28)100-xTa,x alloys due to the formation of fine β-Ti and TiFe eutectic structure in Ti72Fe28 alloy. In addition, Chu et al. [10] and Zadorzhnyy et al. [11] found that the TiFe alloys can be used as hydrogen storage material because the TiFe phase in TiFe alloys tended to react with hydrogen. Therefore, it is very significant to study the formation mechanism of TiFe alloys prepared by different methods and the effect of the structural evolution on their properties.

Generally, the preparation methods of TiFe alloys mainly includes melt-spinning [12], powder metallurgy [13,14] casting [15] and mechanical alloying (MA) [11]. Compared with other preparation processes, MA has been widely used to prepare various nanocrystalline, metastable crystal, quasicrystal and amorphous alloy due to its advantages, such as wide selecting suitable materials, lower preparation cost, easier control, material savings and mass production [11]. Among these materials prepared by MA, amorphous alloys, as a new type of materials which have unique structural characteristics of long-range disorder and short-range order, have excellent corrosion and wear resistance, high hardness and excellent magnetic properties. Therefore, they exhibit extensive application prospects in the fields of national defense, marine, biome medicine and electronic information [10,16,17]. In this paper, the nanocrystalline/amorphous and completely amorphous Ti50Fe50 alloys were synthesized by mechanical alloying and the effect of milling time on the microstructure and magnetic properties were studied.

2. Experimental

2.1. Preparation methods

The mixture of pure Fe powder (99.99%, 20 µm) and pure Ti powder (99.9%, 60 µm) with a ratio 1:1 was used as original materials for mechanical alloying. The stainless steel balls with the diameter of 8 mm was used as milling media. The mixture and balls with the ration of 1:10 were enclosed into stainless steel vials. Subsequently, the TJ-2L planetary ball mill (Techin, China) was employed to prepare samples. The rotation speed was 900 rpm and the milling time was extended to 40–100 h based on our research [18]. Moreover, the operation was paused for 10 min to avoid rising temperature in vial.

2.2. Characterization of structure and magnetism

The microstructure of mixture powders and milled samples were analyzed by scanning electron microscopy (SEM, FEI Nova Nano SEM 400). Phase constituents were characterized by X-ray diffraction (XRD, D/MAX-2500, Cu Kα (λ = 0.15406 nm), 40 kV, 40 mA). The grain size, lattice parameters and microstrain were calculated through Rietveld refinements. The powder particles size distribution was measured by laser scattering particle size analyzer (HORIBA LA-300). The thermal stability of milled powders was characterized by Differential scanning calorimeter (DSC, SDT Q600) with a heating rate of 20 °C/min under argon atmosphere at 300–1473 K. The magnetic properties were examined by superconducting quantum interference magnetometer (SQIUD) with a maximum applied magnetic field of 20,000 Oe at room temperature.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows SEM images of primary Ti powder and Fe powder without milling, respectively. The primary Ti powder presents polygonal shape with a particle size of 60 µm (Fig. 1a) and the primary Fe powder is irregular flocculent with a particle size of 20 µm (Fig. 1b). The XRD patterns of primary Fe powder and primary Ti powder are shown in Fig. 2. Obviously, the strongest peak is located at 44.7° and other two weaker peaks are identified as bcc α-Fe phase in primary Fe powder. While the primary Ti powder consists of hcp Ti phase, whose strongest peak is located at 40.2°.

Fig. 3 shows the XRD patterns of Ti50Fe50 powders after milling for 40–100 h. It can be seen that the widths of all diffraction peaks are dramatically increased, but the intensities are decreased and even disappear except for nanocrystalline α-Fe (2.53 ± 0.07 nm) at 44.6° and 82.1° and α-Ti (3.62 ± 0.09 nm) at 40.3°. The diffraction peaks shift to smaller angle for α-Fe, while shift to larger angle for α-Ti after milling for 40 h compared to primary powders (Fig. 2). After milling time for 60 h, the width of diffraction pattern is further increased and all crystals disappear. Therefore, the formation of com-
The amorphous phase is obtained when the milling time is increased to 60–90 h. The reduction of diffraction intensity, the increase of the diffraction width and the disappearance of the diffraction peaks are related to the formation of solid solution [19], nanocrystalline and disordered amorphous Ti-rich [20]. The formation mechanism can be explained as follows: (i) The negative enthalpy of mixing of TiFe (ΔH = -17 kJ/mol) [21] provides thermodynamic driving force for atoms to diffuse with each other. Therefore, the mutual solubility between Fe and Ti atoms occurs and the diffraction peaks of nanocrystalline and amorphous are overlapped after milling for 40 h. (ii) The atomic radius of Ti (0.145 nm) is larger than that of Fe (0.127 nm), which leads to Ti atoms rapidly diffusing into α-Fe. Generally, the solid solubility of Ti in α-Fe is 4 at. % at equilibrium. As a result, the microstrain is generated in Ti₅₀Fe₅₀ alloy due to the formation of vacancies, dislocations and grain boundaries during MA, resulting in lattice distortion and reducing diffusion distance. Therefore, an unstable supersaturation solid solution α-Fe is formed, leading to the broadening and shift of the diffraction peaks. When the milling is increased to 60 h, the supersaturated solid solution can transform into metastable disordered amorphous phase, which further broadens the width of the diffraction peak. However, when the time continues to increase, the amorphous phase is changed into crystalline intermetallic TiFe. (iii) The Gibbs free energy of the amorphous phase is lower than that of the crystalline phase, which is more beneficial for the formation of the amorphous phase. However, the appearance of a weak nanocrystalline TiFe (14.75 ± 0.4 nm) diffraction peak at 43.3° is caused by the crystallization of amorphous TiFe after milling for 100 h.

The DSC results of complete amorphous Ti₅₀Fe₅₀ alloy are shown in Fig. 4. Obviously, there are two exothermic peaks in

![Fig. 1 – SEM patterns of (a) primary Ti, (b) primary Fe powders.](image_url)

![Fig. 2 – The XRD pattern of primary Fe and Ti powders.](image_url)

![Fig. 3 – XRD patterns of milled Ti₅₀Fe₅₀ alloys under different milling time.](image_url)

![Fig. 4 – DSC patterns of milled Ti₅₀Fe₅₀ alloys after milling for 60 h and 90 h.](image_url)
the DSC curve after milling for 60 h, i.e., the first peak (740.8 K) and second peak (1030.9 K). The former is caused by structural relaxation in powder due to the formation of a large amount of stress, while the latter is consistent with the crystallization due to the rearrangement of constituent atoms [20]. However, when the milling time continues to 90 h, a crystallization peak appears at a lower angle (1015.5 K) because the much more stable TiFe phase is formed above crystallizing temperature Tx (951 K).

Fig. 5a is the particle size distribution of Ti50Fe50 powders after milling for 60 h, 90 h and 100 h. The results show that the average particle size for 60 h (27.2 μm) is generally increased to 37.5 μm (100 h), and that for 90 h (29.9 μm) tends to become more uniformed. The median particle diameter (Dm) and specific surface of Ti50Fe50 powders after the different milling time (Fig. 5b) further indicate that the particle size increases slowly from 24.6 μm to 35.2 μm. This is because the competition of cold welding and fracture generally reach the dynamic balance at 60–90 h, but the cold welding occurs again when the milling is increased to 100 h.

Fig. 6a shows the microstructure of Ti50Fe50 powders after milling for 5 h. Comparing to Fig. 1a and b, the milled powders present a flat and laminar structure after being compressed both balls and between balls and vial wall, due to the excellent ductility of Fe and Ti elements [22]. As the time increases, higher microstrain energy and kinetic energy are produced due to the severe plastic deformation and the collisions of balls or ball and vial during MA. Therefore, the temperature in vials is increased and then accelerates the mutual diffusion between atoms [22]. As a result, some lamellar powders are further agglomerated to form the irregular lump microstructures (Fig. 6a–c), while the others are welded on the surface of the balls and vial wall. Additionally, the powders stripped from the welding structure are rewelded to form the incomplete welding or fracture microstructure.

To further analyze the microstructure of Ti50Fe50 powders during MA, the schematic diagram of the microstructure evolution of Ti50Fe50 powders is shown in Fig. 7. At the early milling time, the cold welding is dominant although the powders experience the competition of cold welding, fracturing and rewelding, which leads to the milled powders to be sharply aggregated (Fig. 7a). Thus, the particle size of milled powders is larger than that of the primary powders. With the increasing of milling time, the morphology of Ti50Fe50 powders transforms from irregular microstructure to subspherical or rod-like shape (Fig. 6b and d). Meanwhile, the brittleness of powder particles increases because of the appearance of amorphous phase so that the particle size is decreased (Fig. 6a) [23]. Continuing to milling from 20h to 90h, the particle size continues to decrease and tends to be stable, the morphology of milled powders tends to be more spherical shape because the amorphous phase with smaller Gibbs energy is formed (Fig. 6d and e). This is consistent with the result in Fig. 7b. After milling for 100 h, a small amount of powder particles is rewelded (Fig. 6f and Fig. 7c), resulting in an increase in particle size. However, the formation of large amounts of smaller powders results in homogeneous distribution of milled powders.

### 3.2 Magnetism of Ti50Fe50 alloy

Fig. 8a shows the hysteresis loops of Ti50Fe50 alloys after three different milling time. The results show that all curves present the sigmoidal shape and not reach the completely saturate state at applied field as high as 20,000 Oe. Especially for 100 h, the saturation magnetization (Ms) and remanence (Mr) of Ti50Fe50 alloy is less than 1 emu/g and 0.02 emu/g, respectively, which is expected as paramagnetic material [24,25]. However, when the milling time is 60–90 h, the magnetization (Ms) of Ti50Fe50 alloys has relatively narrow hysteresis loops and lower coercivity (Hc), indicating that the alloy exhibits the excellent soft magnetic characteristics.

The relationship of the saturation magnetization (Ms) and coercivity (Hc) of Ti50Fe50 alloys with the increase of milling time as given in Fig. 8b. As the milling time increases, the Ms and Hc of Ti50Fe50 alloys are decreased from the maximum 14.7 emu/g and 99.9 Oe (60 h) to the minimum 0.9 emu/g and 8.2 Oe and (100 h), respectively. These values are far less than those of our previous results [18]. This further shows that the magnetic transformation of milled Ti50Fe50 alloys from excellent soft magnetics (<90 h) to paramagnetic (100 h). The relationship of remanence-to-saturation ration (Mr/Ms) versus milling time (Fig. 8c) is also corresponding to the mentioned above results.

Generally, the decrease of the saturation magnetization (Ms) is closely related to the variation of chemical composition, the environment of magnetic atoms and the electronic structure of materials [24]. For Ti50Fe50 alloys, the addition of non-ferromagnetic element Ti decreases the content of ferromagnetic element Fe, the electronic interaction between Fe and Ti is weaken, i.e., the d–d electron orbital hybridization significantly inhibits the magnetic moment of Fe because of the charge transfer from Ti atoms with lower electronegativity to 3d orbitals of Fe [26,27]. Therefore, the saturation magnetization (Ms) of Ti50Fe50 alloy is reduced. In addition, the ferromagnetic atoms Fe is gradually dissolved into the paramagnetic phase Ti-rich phase. Meanwhile, the non-ferromagnetic atoms Ti interacts with α-Fe as the increase of milling time from 40 h to 100 h, the more paramagnetic amorphous phases (40–100 h) and a small amount of paramagnetic nanocrystalline TiFe (100 h) are formed (Fig. 3). Thus, the saturation magnetization (Ms) is further reduced because the magnetic dipole moment of Fe atoms is reduced [28].

The variation of coercivity (Hc) is decided by magnetic domain motion, exchange interaction, magnetic anisotropy, demagnetizing effects, surface state and structure of materials. These factors are influenced by microstrain, grain size, dislocation densities and grain boundaries of crystalline alloys, but are affected by the residual stresses, free volumes and microstructure of amorphous alloys [24,29,30]. When the milling time is 40 h, the formation of these nanocrystal defects leads to reduce the Hc because the powder particles experience the sever plastic deformation [24]. However, when the milling is 60–90 h, the balance of fracturing and cold welding is established, the particles size tends to more homogeneous and a completely amorphous phase is formed. Therefore, the long-range disorder and short-range order microstructure of amorphous phase induce the magnetic domain to present
Fig. 5 – (a) The particles size distribution of milled Ti$_{50}$Fe$_{50}$ alloys, (b) The effect of milling time on the median particles diameter ($D_{50}$) and specific surface.

Fig. 6 – SEM images of milled Ti$_{50}$Fe$_{50}$ alloys for (a) 5 h, (b) 15 h, (c) 20 h, (d) 60 h, (e) 90 h, (f) 100 h.

disorder characteristic. Moreover, the free volume in amorphous is easy to generate unstable clusters, which is collapsed to relax the stress, resulting in the magnetic domain walls are pinned. The stress considered as the pinning centers can also pin the magnetic domain walls and then hind the movement of the magnetic domain walls, leading to a difficulty
Fig. 7 – The schematic diagram of microstructure evolution of Ti$_{50}$Fe$_{50}$ alloys during mechanical alloying.

Fig. 8 – (a) Hysteresis loops, (b) the variation of saturation magnetization and coercivity with the milling time and (c) remanence-to-saturation ratio ($M_r/M_S$) as a function of milling time of milled Ti$_{50}$Fe$_{50}$ alloys for 60 h, 90 h and 100 h.

In reverse. In addition, the exchange interaction between Fe atoms is weaken due to the large free volume, the dissolution of Fe element, the interaction of demagnetizing effect, gaps and porosities between the partial powder particles, further reducing the $H_C$ of Ti$_{50}$Fe$_{50}$ alloy.

4. Conclusions

During mechanical alloying, Ti atoms and Fe atoms in Ti$_{50}$Fe$_{50}$ alloy powder can interact with each other to form supersaturated solid solution α-Fe and α-Ti, respectively, before the formation of a completely amorphous. When the milling time is increased to 60–90 h, the particles size tends to be constant, the milled morphology exhibits the spherical shape and the completely amorphous phase can be formed. However, the crystallization of the partial amorphous phase can occur after milling for 100 h. The saturation magnetization ($M_S$) and coercivity ($H_C$) of alloys are decreased due to the severe plastic deformation and the formation of paramagnetic amorphous or nanocrystalline phase.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51471084), the Outstanding Youth Foundation of Jiangxi Province (201628CB23039) and the Natural Science Foundation of Tianjin (17JCZDJC40500), the key Project of Department of Edu-
cation of Guangdong Province (2016GCZX008), and the Project of Engineering Research Center of Foshan (20172010018).

REFERENCES