Effect of aging and ball milling on the phase transformation of Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_{8-x}$Zr$_x$ alloys

B. Tian $^{a,b,*}$, Y.X. Tong $^{a,b}$, F. Chen $^{a,b}$, L. Li $^{a,b}$, Y.F. Zheng $^{a,b,c}$

$^a$ Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, China
$^b$ Center for Biomedical Materials and Engineering, Harbin Engineering University, Harbin 150001, China
$^c$ Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

**Abstract**

This study investigated phase transformation of Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_{8-x}$Zr$_x$ ($x = 0, 4, 8$) alloys after aging and ball milling. For the Cu$_4$Zr$_4$ and Zr$_8$ dual phase alloys, aging has enhanced magnetic susceptibility and magnetic exchange of the matrix, resulting in an increase of the Curie temperature of austenitic matrix. The decrease of martensitic transformation temperatures for the Cu$_4$Zr$_4$ alloy and the increase of martensitic transformation temperatures for the Zr$_8$ alloy after aging should be related to the dissolution and precipitation of the second phase in the matrix, respectively. Ball milling is effective to smash the Cu$_4$Zr$_4$ and Zr$_8$ alloys to fine particles, but cannot fracture the Cu$_8$ alloy to particles, indicating an inherent high ductility and strength of the Cu$_8$ alloy. Therefore, the macroscopic brittleness of the polycrystalline Cu$_8$ alloy was mainly caused by the weak grain boundaries. For the Cu$_4$Zr$_4$ and Zr$_8$ particles, the martensitic transformation and Curie transition of austenitic matrix disappeared and the Curie transition of second phase remained after ball milling. After post-annealing at 800 °C, the Curie transition of austenite was recovered due to the restoration of atomic order, but the martensitic transformation cannot be retrieved which might be caused by the grain refinement of the austenitic matrix after ball milling.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Ni–Mn–Ga ferromagnetic shape memory alloys (FSMAs) have been extensively investigated in the past few years due to their large magnetic field induced strain (MFIS) [1–3]. The MFIS mainly originates from the martensitic twin variants reorientation via twin boundary motion under a magnetic field, which is closely related to the martensitic structure. Therefore, the martensitic transformation is critical for the performance of MFIS. In addition, the superelasticity and shape memory effect of SMAs (including the conventional Ni–Ti SMA and magnetic-response Ni–Mn–Ga FSMA) is also fundamentally based on the martensitic transformation [4]. Transformation temperature, hysteresis and interval etc. are critical characters of the martensitic transformation for applications of SMAs. As is known, most of Ni–Mn–Ga alloys often exhibit a narrow transformation hysteresis (<20 °C) [5,6]. Doping a fourth element or introducing a second γ phase in the Ni–Mn–Ga alloys has been found to increase the transformation hysteresis [7,8]. Recently, in our group, Zr has been added in a single phase Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_8$ alloy and it was found that the alloy transformed from a single martensite to a dual phase containing martensitic/austenitic matrix and Zr-rich second γ phase [9]. The transformation hysteresis was largely decreased for the dual phase Zr-doped Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_8$ alloys, as compared to the single phase Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_8$ alloy, which was attributed to the martensitic structure change of the matrix [9]. For the dual phase SMAs, aging treatments often influence the precipitation of second phase and change the composition of matrix, resulting in a change of martensitic transformation temperatures [10,11]. In our recent study, it has been found that the martensitic transformation temperature and transformation enthalpy of the Zr-doped Ni$_{46}$Mn$_{33}$Ga$_{17}$Cu$_4$ dual phase alloys was increased and decreased, respectively, after aging and with increasing aging temperature [12]. However, the effect of aging on the phase transformation of the dual phase Zr-doped Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_8$ alloys still remains unknown. Additionally, for the Zr-doped Ni$_{50}$Mn$_{25}$Ga$_{17}$Cu$_8$ dual phase...
alloys, the intergranular fracture dominates during mechanical deformation and leads to a severe brittleness [9]. Ball milling was often employed to crush the brittle FSMAs and making use of the FSMAs powders to prepare composites or sinter bulks [13–15]. Undoubtedly, the phase transformation of the powders is critical for the property of subsequent bulk materials. Based on the above analysis, in this article, the Zr-doped Ni_{50}Mn_{25}Ga_{17}Cu_{8} alloys are further aged and ball milled, and then the effect of aging and ball milling on the phase transformation behavior of the alloys was systematically investigated.

2. Experimental details

The Ni_{50}Mn_{25}Ga_{17}Cu_{8-x}Zr_{x} (x = 0, 4, 8) polycrystalline ingots were prepared by arc-melting high purity elements of Ni, Mn, Ga, Cu, and Zr under an argon atmosphere [9]. Then the as-cast ingots were annealed at 1173 K for 12 h in vacuum quartz tubes for homogeneity. Following Ref. [9], the alloys for x = 0, 4, and 8 are denoted as Cu_{8}, Cu_{4}Zr_{4}, and Zr_{8}, respectively. The dual phase Cu_{4}Zr_{4} and Zr_{8} alloys were sealed in vacuumed quartz tubes and aged at 400 °C and 600 °C for 10 h. For ball milling, the bulk Cu_{8}, Cu_{4}Zr_{4}, and Zr_{8} alloys were mechanically crushed to a size of <3 mm and then ball milled for 0.5 h in a QM-3A vibration ball mill with hardened steel vial and balls in a ball-to-powder ratio of 10:1. The acetone was added as the milling medium and the milling speed was 1400 rpm/min. Finally the as-milled powders were annealed at 800 °C for 2 h in vacuum. The microstructure of the samples was observed using Olympus–311U optical microscope and FEI Quanta200 scanning electron microscope (SEM) equipped with an energy dispersive spectrometry (EDS) analyzer. The martensitic transformation and Curie transition of the samples were determined by measuring the temperature dependence of low-field ac magnetic susceptibility in a field of 50 Oe, in which the ac-susceptibility was measured by using mutual inductance bridge and phase-locked amplifier. X-ray diffraction (XRD) was carried out for phase identification at room temperature using a Panalytical Xpert PRO diffractometer with Cu Kα radiation. The martensitic transformation of some samples was also characterized using a Perkin–Elmer Diamond differential scanning calorimeter (DSC) with a heating/cooling rate of 20 °C/min.

3. Results and discussion

Fig. 1 (a) shows the susceptibility-temperature curves of the Cu_{4}Zr_{4} and aged alloys. It is seen that the three alloys exhibit a similar transformation behavior upon heating/cooling, and the susceptibility of the alloy has been largely enhanced with increasing the aging temperature. The critical phase transformation temperatures have been indicated on the curve of the 600 °C aged sample. Upon heating, the sudden increase of susceptibility at ~361 K is the Curie transition of austenitic matrix [9]. The decrease of susceptibility from ~281 (M_{s}) to 231 K (M_{f}) corresponds to the martensitic transformation, the middle temperature of the martensitic transformation curve (the point with the largest slope) at ~267 K, which corresponds to the transformation peak temperature in the DSC results, has been characterized as the martensitic transformation temperature (T_{M}). M_{s} and M_{f} represent the martensitic transformation start temperature and finish temperature, respectively. On continue cooling, the susceptibility increase at ~200 K is the Curie transition of the Zr-rich second γ phase [16]. Upon heating, the increase of susceptibility from ~245 (A_{s}) to 291 K (A_{f}) stands for the reverse martensitic transformation, and in the same way the middle temperature of the reverse martensitic transformation curve at ~274 K is indicated as the austenitic transformation temperature (T_{A}). A_{s} and A_{f} represent the austenitic transformation start temperature and finish temperature, respectively.

It can be found that the Curie transition of austenite and the martensitic transformation have been progressively enhanced, whereas the Curie transition of second γ phase was gradually weakened, with increasing the aging temperature. This indirectly demonstrates that the volume fraction of matrix could be increased and that of the second phase was decreased to some extent during aging, meaning partial dissolution of the second phase in the matrix. In addition, the T_{M} has been found to be increased clearly with the increase of aging temperature, which means the enhancement of magnetic exchange of the alloys. For the original bulk alloy, the sudden drop of susceptibility after the Curie transition of austenite on cooling was attributed to the stress-induced magnetocrystalline anisotropy (the stress here mainly refers to the internal stress caused by quenching) [17,18]. This susceptibility drop became much gentler with increasing the aging temperature to 600 °C, indicating that the stress-induced magnetocrystalline anisotropy has been greatly decreased. This further means that the internal stress originating from quenching has been reduced after aging at 600 °C, similar to the effect of annealing on the internal stress caused by ball milling in the Ni–Mn–Ga particles [18]. The internal stress is
mainly related to the defects, lattice distortion or local atomic disorder, so the reduction of internal stress also indicates the improvement of overall atomic order and lattice integrity, which should be responsible for the enhancement of magnetic susceptibility and magnetic exchange of the aged alloy. In addition, the transformation intervals (\(M_t - M_f, A_s - A_f\)) are greatly enlarged after aging and the \(T_M\) and \(T_A\) are decreased that is also verified by DSC measurement results shown in the inset of the figure. For the FSMAs, the transformation temperatures and transformation intervals are sensitive to the alloy composition \([6,8]\), therefore the change of transformation temperatures and interval further indicates the composition change of the alloy after aging, which is caused by the partial dissolution of second phase in the matrix. Fig. 1(b) is the room temperature XRD patterns for the Cu4Zr4 and aged alloys. The Cu4Zr4 alloy can be indexed to be a mixture of austenite, martensite and second \(\gamma\) phase \([9]\). After aging at 400 °C and 600 °C, it can be seen that the aging treatment does not introduce new phase. This further confirms that the effect of aging on phase transformation of the Cu4Zr4 alloy should be attributed to the partial dissolution of second phase in the matrix and the improvement of the lattice order, as analyzed in the above results. Fig. 2(a) shows the susceptibility measurement results of the Zr8 and aged alloys. The susceptibility of the alloy is enhanced and the Curie temperature of austenite is increased after aging, which is quite similar to the results of Cu4Zr4 alloy. In addition, the stress-induced magnetocrystalline anisotropy is also progressively decreased with increasing the aging temperature. The main difference between these two alloys is that the transformation temperatures (\(T_M\) and \(T_A\)) are increased (the DSC measurements also show the similar results, as shown in the inset of Fig. 2(a)) and the Curie transition of second phase seems to be slightly enhanced after aging. It has been reported in our previous study that the martensitic transformation temperatures of the dual phase Cu2Zr2 and Zr4 alloys were increased progressively with increasing aging temperature due to the precipitation of second phase \([12]\). The XRD result shown in Fig. 2(b) does not show any trace of new phase for the aged Zr8 alloy. Thus, it is possible to infer that the further precipitation of the second phase may happen in the Zr8 alloy after aging. Based on the above results, it is simply concluded that the second \(\gamma\) phase could further precipitate in the present Zr8 alloy and Cu2Zr2 and Zr4 alloys \([12]\) but dissolve in the present Cu4Zr4 alloy after aging. The second \(\gamma\) phase is Zr-rich, and therefore the evolution of the second phase during aging should closely depend on the specific Zr content, on which the further investigation is still in progress. The ball milling is effective to crush the single phase Cu4 alloy and dual phase Cu2Zr2 and Zr4 alloys to fine particles \([16]\). However, for the present Cu8, Cu4Zr4 and Zr8 alloys, the results are different, to be specific, the dual phase Cu4Zr4 and Zr8 alloys are easy to be milled to small particles, but the Cu8 alloy is difficult to be fractured by ball milling, as shown in the micrographs of Fig. 3. For comparison, the optical micrographs of the original bulk alloys are also given for the Cu8, Cu4Zr4 and Zr8, as shown in Fig. 3(a, c and e), respectively. It is seen that the alloy has transformed from a single martensite to a dual phase containing second phase after addition of Zr, and the volume fraction of the second phase increased with increasing the Zr content. Fig. 3(b, d and f) present the SEM images of the Cu8, Cu4Zr4 and Zr8 alloys after ball milling, respectively. The Cu4Zr4 and Zr8 alloys have been crushed to fine particles with a size of \(<40 \mu m\) by the ball milling. However, the Cu8 alloy seemingly cannot be effectively fractured to particles using the same milling procedure, and the alloy exhibits a large sheet with a size at around 200–500 μm that is comparable to the grain size of the bulk alloy. In addition, some large bulks containing several grains can also be found, as shown in the inset of Fig. 3(b), in which the ongoing intergranular cracking indicated by an arrow can be seen. This means that the Cu8 alloy presents a high intrinsic ductility for the single grains and the presence of brittleness reflected on the mechanical testing results \([9]\) should be caused by the weak grain boundaries of the polycrystalline alloy. The reported high plasticity and strength in the drop-cast Cu8 alloy is in agreement with our present results \([7]\). Additionally, it is noted that the general particle size of Zr8 seems to be smaller than that of the Cu4Zr4, which should be caused by that the amount of the small size second phase in the Zr8 is more than that in the Cu4Zr4 alloy \([16]\). Fig. 4(a–c) shows the EDS results of the as-milled Cu8 sheets, Cu4Zr4 and Zr8 particles, respectively. There are no contaminations of Fe or Cr \([19]\) originating from the steel balls or vial. Yet the O contamination can be found in the three milled samples, which was commonly thought to be caused by the slight oxidation of Mn on the particle surface after ball milling \([19]\). However, the O contamination in the Cu8 alloy sheets is much severer than that in the Cu4Zr4 and Zr8 particles, indicating a high oxidation of Cu8 sheet surface. The microstructure results have demonstrated that the Cu8 alloy has an inherent high ductility and strength and is difficult to be fractured to small size, which certainly increased the mutual friction energy between the alloy and milling balls and vial and elevated the temperature on the contacting surface, thus resulting in a severer oxidation of the Cu8 alloy.

Fig. 2. (a) Susceptibility-temperature curves of Zr8, 400 °C and 600 °C aged alloys. Inset is the DSC curves of Zr8, 400 °C and 600 °C aged alloys. (b) XRD patterns of Zr8, 400 °C and 600 °C aged alloys.
The Cu4Zr4 and Zr8 particles were annealed and characterized for phase transformation, as shown in Fig. 5. Fig. 5(a and c) shows the susceptibility measurement results of the Cu4Zr4 and Zr8 particles, respectively. For comparison the susceptibility-temperature curve of the original bulk alloy is also included in the figure. For both Cu4Zr4 and Zr8, the Curie transition of austenite and martensitic transformation of the alloy disappeared after ball milling, but the Curie transition of second phase still remained, which is consistent with the results in the dual phase Cu2Zr2 particles [16]. The disappearance of Curie transition of austenite and martensitic transformation is attributed to the atomic disorder of the matrix caused by ball milling [18]. The presence of Curie transition of the second phase is due to that the structure of the hard second phase is not destructed by the ball milling. The XRD results shown in Fig. 5(b and d) for the Cu4Zr4 and Zr8 particles, respectively, in which both milled particles are indexed to be a mixture of the disordered fcc structure matrix and the bcc structure second phase. After annealing, the Curie transition of austenite for the both particles is recovered but the martensitic transformation still disappears. The XRD results show that the structure of matrix has almost recovered to the state of original bulk alloy for both particles. Therefore, the recovery of Curie transition of the austenite should be attributed to the reversion of the atomic order after annealing [18]. The unrecovered martensitic transformation for the two particles after annealing should be mainly related to the grain refinement of the matrix particles caused by ball milling [16]. Additionally, it is also noted that the Curie transition of the second phase is found to be seriously weakened after annealing, as compared to the as-milled sample and original bulk alloy, which could be attributed to the effect of annealing on the precipitation of second phase, as referred to the above aging treatment on the second phase in the bulk alloys.

4. Conclusions

The effect of aging and ball milling on the phase transformation of Zr-doped Ni50Mn25Ga17Cu8 alloys is studied. The Cu4Zr4 and Zr8 dual phase alloys present a phase transformation sequence of Curie
Fig. 4. EDS results of (a) Cu8, (b) Cu4Zr4 and (c) Zr8 alloys after ball milling.

Fig. 5. Susceptibility-temperature curves of bulk alloy, as-milled powder and 800 °C annealed powder for (a) Cu4Zr4 and (c) Zr8. XRD patterns of bulk alloy, as-milled powder and 800 °C annealed powder for (b) Cu4Zr4 and (d) Zr8.
transition of austenite, martensitic transformation and Curie temperature of second phase upon cooling. After aging, the Curie transition temperature of austenite increases and the susceptibility of the whole alloy is enhanced with increasing aging temperature for both alloys. The martensitic transformation temperatures decrease and increase for the Cu4Zr4 and Zr8 alloys, respectively.

Ball milling is effective in crushing the Cu4Zr4 and Zr8 alloys to fine particles but is difficult to mill the Cu8 alloy to particles. The martensitic transformation and Curie transition of austenite disappear after ball milling for the dual phase alloys. The 800 °C annealing treatment can restore the Curie transition of austenite but cannot retrieve the martensitic transformation of the Cu4Zr4 and Zr8 particles.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (51201044), the Natural Science Foundation of Heilongjiang Province (ZD201012, E201229), the Project of Harbin Foundation of China (51201044), the Natural Science Foundation of Harbin Engineering University, and the Fundamental Research Funds for the Central Universities, China (HEUCF201403011).

References