J Mater Sci (2010) 45:5490–5494
DOI 10.1007/s10853-010-4606-1

Microstructure and martensitic transformation behavior of a constant-strain aged Ni–Mn–Ga–Ti magnetic shape memory alloy

**G. F. Dong · Z. Y. Gao · C. L. Tan ·
W. Cai · J. H. Sui**

Received: 7 December 2009 / Accepted: 6 May 2010 / Published online: 20 May 2010

Abstract The $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ ferromagnetic shape memory alloy has been aged under 2% constant-strain at various temperatures for 3 h, and the microstructure and martensitic transformation behaviors have been investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). It was found that after constant-strain aging, the amount of the Ni-rich precipitates with lenticular morphology is higher and the size of the second-phase particle is smaller when compared to that of the conventional aged samples. The martensitic transformation temperatures first decrease remarkably with the increase of aging temperature, and then increase when the aging temperature exceeds 973 K, which can be attributed to the change of the Ni-content in the matrix as well as the strengthening effect by fine Ni_3Ti precipitates.

Introduction

Since the large magnetic-field-induced strains (MFIS) up to 10% was confirmed, the Ni–Mn–Ga ferromagnetic shape memory alloys (FSMAs) have attached considerable attention as potential microactuators since their large recovery strain (about several percent) and high responding frequency(kHz) related to the field-induced martensite variants re-arrangement or magnetic-field-induced crystallographically reversible martensitic transformation [1–4]. However, the wide field of applications and the relatively poor ductility of Ni–Mn–Ga Heusler-type alloys have triggered a great deal of interest and many investigations have been proposed to solve this problem. As well known, the transformation behavior and the mechanical properties in Ni–Mn–Ga alloys can be affected by various thermomechanical treatments, such as thermal cycling, aging treatment, and annealing treatment [5–10]. Furthermore, the addition of the fourth element, such as Fe, Co, In, Nd, Sm, Gd, Y, and Dy, etc., also substantially affects phase transformation and mechanical behavior of Ni–Mn–Ga alloys [11–16]. In our previous article [17–19], the Ti-doping Ni–Mn–Ga shape memory alloys, obtained by substitution of Ti for Ga, were investigated with a focus on their basic properties including the microstructure, transformation behavior, magnetic property, and mechanical property.

It was found that the mechanical behavior of Ni–Mn–Ga alloy could be remarkably increased by forming small amounts of Ni_3Ti second phase through Ti-doping and aging treatment, as occurs in Ni–Co–Al and Ni–Al shape memory alloy. Also, the highest compressive strength of 1403 Mpa is obtained in alloy constant-strain aged at 873 K for 3 h, this is about 500 MPa higher than that of the conventional aging alloy [18]. In this study, we continue to investigate the constant-strain aging effect on a $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloy, and the main purpose is to identify the martensitic transformation behavior and microstructural changes produced by constant-strain aging treatment.

G. F. Dong (✉)
College of Physical Science and Technology, Dalian University,
116622 Dalian, China
e-mail: dgfu0451@163.com

Z. Y. Gao · W. Cai · J. H. Sui
National Key Laboratory Precision Hot Processing of Metals,
School of Materials Science and Engineering, Harbin Institute
of Technology, P.O. Box 405, 150001 Harbin, China

C. L. Tan
College of Applied Science, Harbin University of Science
and Technology, 150080 Harbin, China

Experimental

The nominal composition of the alloy $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ was prepared by the non-consumable arc-melting in an argon atmosphere using 99.97 mol% electrolytic Ni plate, 99.5 mol% electrolytic Mn plate, 99.99 mol% Ga, and 99.92 mol% sponge Ti. The obtained ingot was sealed into a quartz tube with a vacuum of 10^{-4} Torr and annealed at 1273 K for 5 h, followed by quenching into the ice-water to achieve the high chemical order. Spark cut samples were then constrained aged at 823, 873, 973, 1073 K for 3 h under a constant strain of about 2% (stress direction is perpendicular to the outside of the article), and quenched into icy-water.

The martensitic transformation characteristics were monitored by the Differential Scanning Calorimetry (PE Diamond DSC) in the temperature range of 200–400 K with a heating and cooling rate of 20 K/min. The microstructure and composition of the experimental alloys were examined using an Mx2600FE Scanning Electron Microscope (SEM) equipped with a microanalysis system and Philips CM-12 Transmission Electron Microscopy (TEM) operated at 120 kV. Samples for the SEM and TEM were electro-chemically polished in a solution of 20% perchloric acid and 80% ethanol at ambient temperature and by double-jet electropolishing in the case of TEM thin foils.

Results and discussion

Figure 1 shows the SEM image of the $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloys after the conventional aging treatment and constant-strain aging treatment, respectively. It can be seen that the microstructure of the alloys after aging treatment is characterized by the presence of dispersed phase particle with a average size of several microns, the particles are located not only at the grain boundaries but also inside the grains. Compared with the sample by conventional aging treatment, the amount of second particle in the sample after constant-strain aging treatment is notably more and the size is smaller, as shown in Fig. 1b. The nucleation and growth of aged precipitates can be affected by the external stress field. Under the external stress fields, the nucleation site increases and the precipitates grow preferentially along specific direction and are characterized by the lenticular morphology. The precipitates are expected to be coherent with the matrix. The growth of precipitates is hindered if the neighbor stress fields interact with each other, which results in the increase of the amount and the reduction of the size of the precipitates.

After solution treatment at 1273 K for 5 h, $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ shape memory alloy did not show any precipitates [17]. Figure 2 shows the microstructure of $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloys aged at various temperatures between 823 and 1073 K for 3 h under 2% constant-strain and conventional aging treatment after the solution treatment. The size of the precipitate increases with the increasing aging temperature. All the precipitates were confirmed to be a Ni_3Ti phase by electron diffraction and EDS [17, 18]. The bright-field image also shows the characteristic morphology of the precipitates. That is, the lenticular shape precipitates are observed along two directions under 2% constant-strain aged alloys, whereas less size of the precipitates are observed almost three directions in the conventional aging treatment alloys. It also should be note that some dislocations appear (indexed by arrows) when the aging temperature exceeds 973 K under 2% constant-strains aged alloys, indicating that the precipitates losing the coherence with the matrix. In addition, the dislocations are not observed in the conventional aging treatment alloys also precipitates losing the coherence and the matrix with increase aging temperate.

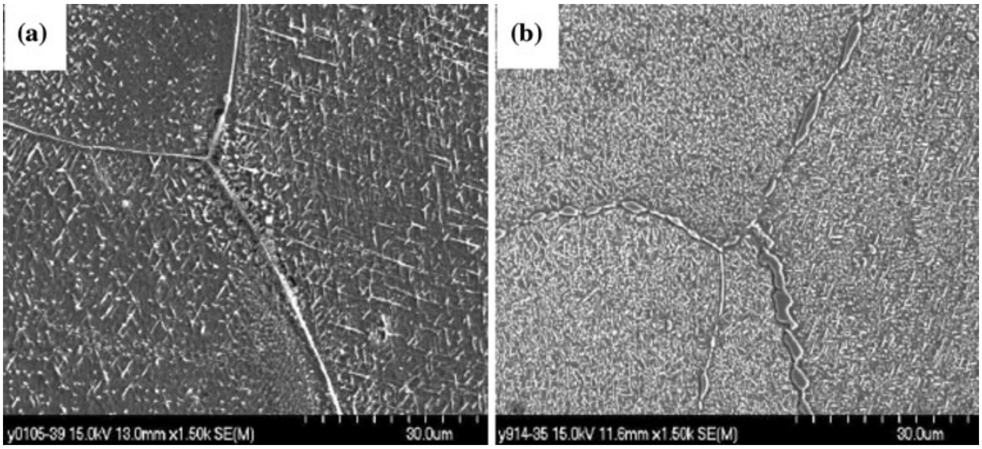
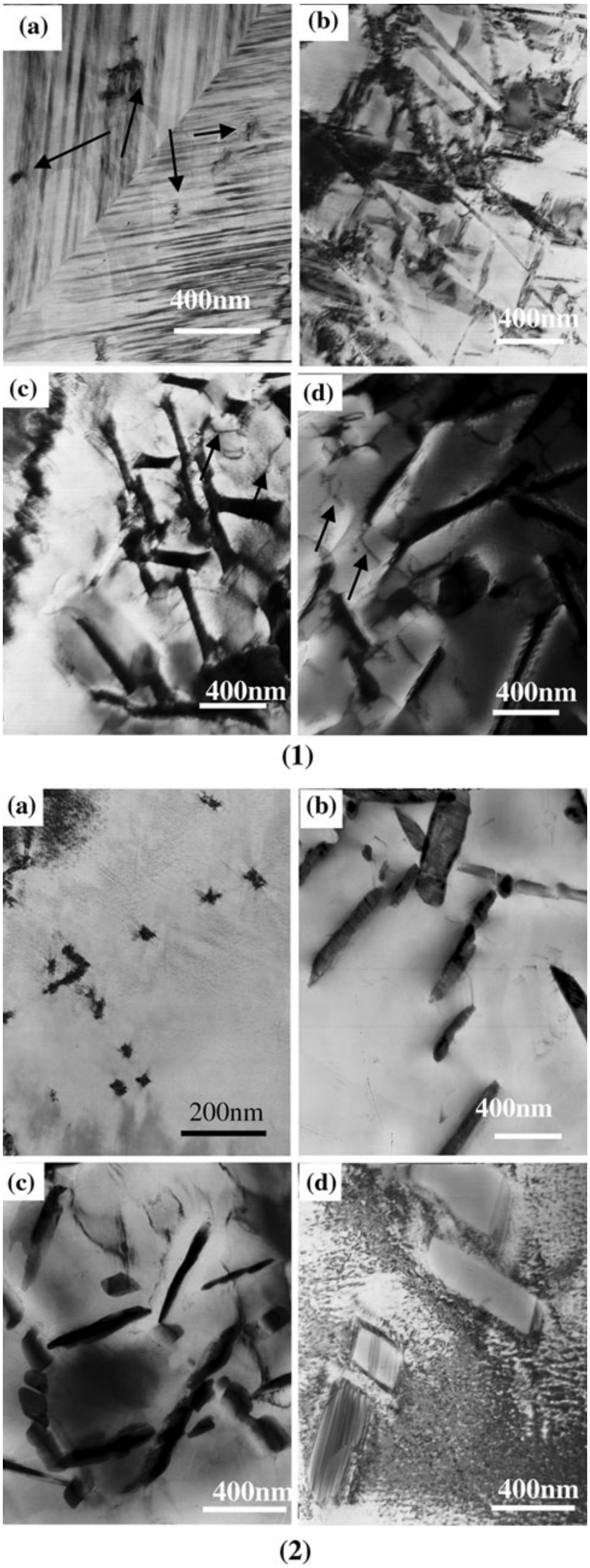


Fig. 1 SEM images of Ni53Mn23.5Ga18.5Ti5 alloys at 873 K for 3 h **a** without constraint strain **b** with 2% compression constant-strain



◀**Fig. 2** (*1*) TEM images of microstructure in the $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ aged at different temperature for 3 h under 2% constant compression strain; (*2*) TEM images of microstructure in the $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ free-aged at different temperature for 3 h **a** $T = 823$ K, **b** $T = 873$ K, **c** $T = 973$ K, **d** $T = 1073$ K

Figure 3 shows the DSC curves of both solution and aged by 2% constant-strains $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ samples. All measurements were conducted from cooling at high temperature. The peaks which appear during cooling and heating can be attributed to the first-order thermo-elastic martensitic transformation from BCC $L2_1$ parent phase to tetragonal martensite and reverse transformations, respectively.

Figure 4 shows the critical temperatures of the transformation determined from the DSC curves as a function of the aging temperature. Compared with the solution-treated sample, the transformation temperatures of aged $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloys first decrease then increase as aging temperature exceeds 973 K, resulting from the modified matrix composition due to precipitation that will be discussed in the following paragraph. The change of martensitic transformation temperatures appears to be much more pronounced in the constrained aged samples. From Fig. 4b, it seems that free aging by 3 h at 873 K causes a small decrease of martensitic transformation temperatures (less than 10 K), while the same treatment performed under 2% strain (Fig. 4a) shifts the martensitic transformation temperatures by about 160 K. This can be mainly contributed to the composition change of the matrix caused by the precipitation of the second phase. We can also seen that the temperature hysteresis increase with the increment of aging temperature since the coherent precipitates hinder the movement of the interfaces during the forward and reverse martensitic transformation.

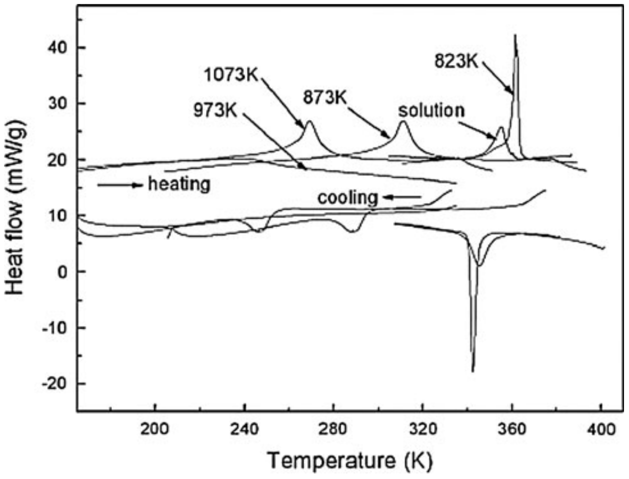
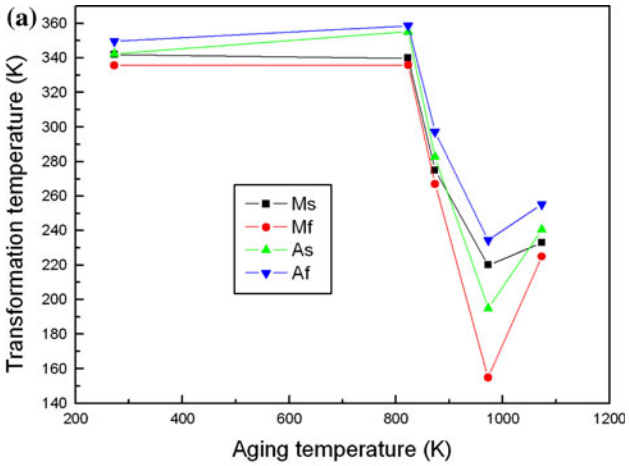


Fig. 3 DSC curves for Ni53Mn23.5Ga18.5Ti5 alloy aged at various temperature for 3 h under constant 2% compression strain



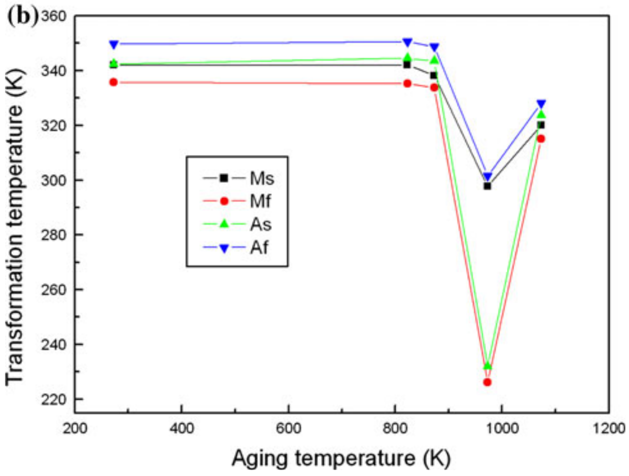
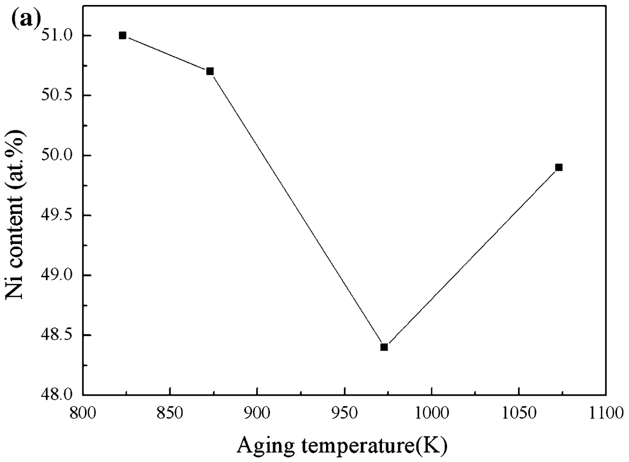


Fig. 4 The critical temperatures of the transformation as a function of the aging temperature for $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloy aged for 3 h **a** under constant 2% compression strain, **b** free-aging



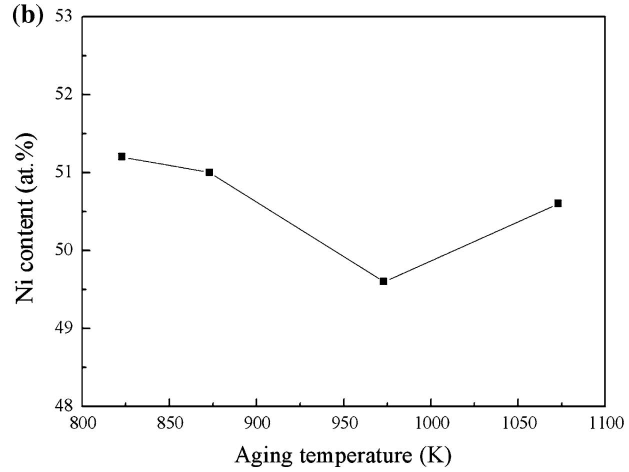


Fig. 5 Dependence of Ni content in matrix on the aging temperature of $Ni_{53}Mn_{23.5}Ga_{18.5}Ti_5$ alloy aged **a** under constant 2% compression strain, **b** free-aging

When the aging temperature exceeds 973 K, the precipitates increase in size and lose the coherence with the matrix, so the interface maybe easily move during heating and cooling, resulting in the decrease of the transformation hysteresis.

In order to correlate the martensite transformation behavior with structural change, the EDS under different aging treatment have been carried out, and the dependence of the Ni content in the matrix on the aging temperature is present in Fig. 5. It is noted that the Ni content in the matrix decreases with the aging temperature increasing, reaches the minimum value at 973 K and then slight increases when aging temperature exceeds 973 K, which can be attributed to the precipitation of Ni-rich second phase during aging. The change of Ni content in the matrix appears to be much more pronounced in the constrained aged samples. From Fig. 5b, it seems that free aging by 3 h at 973 K causes a small decrease of Ni content in the matrix (less than 3.4 at.%), while the same treatment performed under 2% strain (Fig. 5a) shifts the Ni content in the matrix by about 4.6 at.%.

The effect of the aging treatment on the transformation behavior can be explained as a combined effect of compositional change of the matrix and the precipitate hardening. It is generally accepted that the transformation temperature of Ni–Mn–Ga alloys is directly dependent on the Ni content [20]. When the aging temperature is lower than 973 K, the decrease of Ni content is responsible for the decrease of transformation temperatures. On the other hand, the fine precipitates may strengthen the matrix effectively, which results in the suppression of the shape change due to transformation and the subsequent decrease of transformation temperature. When the aging temperature is higher than 973 K, the Ni content in the matrix increases. The precipitate grows and loses coherence with the matrix. The dislocation shown in Fig. 2 may act as the nucleation site for the martensitic transformation. Therefore, the transformation temperatures increase with increasing the aging temperature to above 973 K.

Conclusions

This study investigated the microstructure and the martensitic transformation behavior of the constant-strain aged Ni–Mn–Ga–Ti alloys. It was found that as compared to that of the conventional aged samples, the microstructure of the constant-strain aged samples is characterized by much more and finer Ni-rich second particles. The martensitic transformation temperatures first decrease remarkably with the increase of aging temperature, and then increased when the aging temperature exceeds 973 K. The evolution of the martensitic transformation behavior can be related to the change of the Ni-content in the matrix as well as the strengthen effect by fine Ni_3Ti precipitates.

Acknowledgement This study is supported by the National Natural Science Foundation of China (Grant Nos. 50901026 and 50971052).

References

1. Ullakko K, Huang JK, Kanter C, Kokorin VV, O'Handley RC (1996) Appl Phys Lett 69:1966
2. Wuttig M, Liu L, Tsuchiya K, James RD (2000) J Appl Phys 87(9):4707
3. O'Handley RC, Murray SJ, Marioni M, Nembach H, Allen SM (1998) J Appl Phys 83(6):3263
4. Mullner P, Chernenko VA, Kostorz G (2004) J Appl Phys 95:1531
5. Hosoda H, Wakashima K, Sugimoto T, Miyazaki S (2002) Mater Trans 43:852–855
6. Khovailo VV, Kainuma R, Abe T, Oikawa K, Takagi T (2004) Scripta Mater 51:13
7. Kim JI, Liu Y, Miyazaki S (2004) Acta Mater 52:487
8. Xin Y, Li Y, Chai L, Xu HB (2004) Scripta Mater 54:1139
9. Seguí C, Cesari E, Font J, Muntasell J, Chernenko VA (2005) Scripta Mater 53:315
10. Otsuka K, Ren XB (2001) Mater Sci Eng A 312:207
11. Gao L, Cai W, Liu AL, Zhao LC (2006) J Alloy Compd 425:314
12. Tsuchiya K, Tsutsumi A, Ohtsuka H, Umemoto M (2004) Mater Sci Eng A 378:370
13. Nakanishi N, Mori T, Miura S, Murakami Y, Kachi S (1973) Philos Mag 28:277
14. Khan M, Dubenko I, Stadler S, ALi N (2004) J Phys Condens Matter 16:5259
15. Stadle S, Khan M, Mitchell J, Ali N, Gomes AM, Dubenko I, Takeuchi AY, Guimaraes AP (2006) Appl Phys Lett 88:192511
16. Gautam BR, Dubenko I, Mabon JC, Stadle S, Ali N (2009) J Alloys Compd 472:35
17. Dong GF, Cai W, Gao ZY, Sui JH (2008) Scripta Mater 58:647
18. Dong GF, Tan CL, Gao ZY, Feng Y, Cai W, Sui JH (2008) Scripta Mater 59:268
19. Gao ZY, Dong GF, Cai W, Sui JH, Feng Y, Li XH (2009) J Alloys Compd 481:44
20. Jiang CB, Feng G, Gong SK, Xu HB (2003) Mater Sci Eng A 342:231