Online available since 2007/May/15 at www.scientific.net

doi:10.4028/www.scientific.net/MSF.546-549.2241

Heusler Type CoNiGa Alloys with High Martensitic Transformation Temperature

Yunqing Ma[1,a], Chengbao Jiang[2,b], Yan Li[2,c], Cuiping Wang[1,d], Xingjun Liu[1,e]

[1]Department of Materials Science and Engineering, Xiamen University, Xiamen 361005, China

[2]Department of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100083, China

[a]myq@xmu.edu.cn, [b]jiangcb@buaa.edu.cn, [c]liyan2000@vip.sina.com, [d]wangcp@xmu.edu.cn, [e]lxj@xmu.edu.cn

Keywords: CoNiGa, high-temperature shape-memory alloy, Heusler, martensitic transformation

Abstract. A strong need exists to develop new kinds of high-temperature shape-memory alloys. In this study, two series of CoNiGa alloys with different compositions have been studied to investigate their potentials as high-temperature shape-memory alloys, with regard to their microstructure, crystal structure, and martensitic transformation behavior. Optical observations and X-ray diffractions confirmed that single martensite phase was present for low cobalt samples, and dual phases containing martensite and γ phase were present for high cobalt samples. It was also found that CoNiGa alloys in this study exhibit austenitic transformation temperatures higher than 340℃, showing their great potentials for developing as high-temperature shape-memory alloys.

Introduction

Shape-memory alloys (SMA) with high martensitic transformation temperature have attracted much attention in recent years for the application as new functional materials of actuators and sensors, which is often operated at the temperatures higher than 200℃ [1,2]. As candidates, Cu-based alloys, NiAl, NiTi (Hf, Zr) and NiTiPd alloys have been developed [3-7], but their thermal instability, poor working property or high cost limit their practical applications. The studies to explore new high-temperature shape-memory alloys (HTSMA) keep active.

Recently, Ni_2MnGa Heusler alloys, which possess a cubic $L2_1$ structure at high temperature and undergo a martensitic transformation to a tetragonal structure upon cooling, have been extensively explored as actuator materials [8-10]. Several papers revealed that a high martensitic transformation temperature (up to 350℃) exists in NiMnGa alloys with Ni or Mn content higher than the stoichiometric Ni_2MnGa, showing their potentials as HTSMA [11-13]. Our recent work revealed that single crystalline $Ni_{54}Mn_{25}Ga_{21}$ exhibits a large reversible strain (6.1%), a high martensitic transformation start temperature (M_s >200℃), and that 1000 thermal cycles have little influence on its microstructure, martensitic transformation behavior, as well as its shape-memory effect [14]. Its good thermal stability is thought to be resulted from the high degree of the self-accommodation of martensitic variants [15]. Though the brittleness of polycrystalline NiMnGa ternary alloys is a vital obstacle for its practical applications [16], it is exciting to find that a excellent thermal stability exists in Heusler structured alloys.

CoNiGa alloys exhibit similar structure as NiMnGa alloys [17]. Previous papers reported that some CoNiGa ribbons fabricated using melt-spinning method exhibit good ductility and are not broken even after bending to an angle of 180º, indicating that CoNiGa alloys bear superior plasticity to NiMnGa alloys [18]. In addition, another merit of CoNiGa alloys is the avoidance of the highly volatile element Mn during the melting of ingots, which will make it more accurate to control the ingot composition. So in this paper, several CoNiGa alloys with different compositions have been studied to investigate their potentials as high-temperature shape-memory alloys, with regards to their microstructure, crystal structure and martensitic transformation behavior.

Experimental

Two series of CoNiGa alloys (high cobalt and low cobalt, as respectively listed in Table 1) were prepared from the metallic elements Co (99.9%), Ni (99.95%), and Ga (99.99%) by the arc-melter in argon atmosphere. Each button was re-melted four times to ensure homogeneity. Homogenization treatment was performed for all buttons by sealing them under vacuum in quartz ampoules and annealing at 1100℃ for 24 h, followed by water quenching.

The phase structures of the alloys were identified by X ray diffractometer with Cu K_α radiation. The phase transformation temperatures were determined by differential scanning calorimetry (DSC) (NETZSCH DSC 404 C), with the cooling and heating rate of 10℃/min. The microstructures of the alloys were examined by optical microscope modeled Leica DMI-5000M.

Table 1 Two series of CoNiGa alloys studied

Series	No.	Composition [at.%]
Low cobalt	B1	$Co_{43.5}Ni_{25}Ga_{30}$
	B2	$Co_{43.1}Ni_{25}Ga_{30}$
High cobalt	A1	$Co_{48.7}Ni_{26.1}Ga_{25.2}$
	A2	$Co_{48}Ni_{26.8}Ga_{25.2}$
	A3	$Co_{48}Ni_{26.1}Ga_{25.9}$
	Am	$Co_{63.5}Ni_{35.3}Ga_{25}$

Results and Discussion

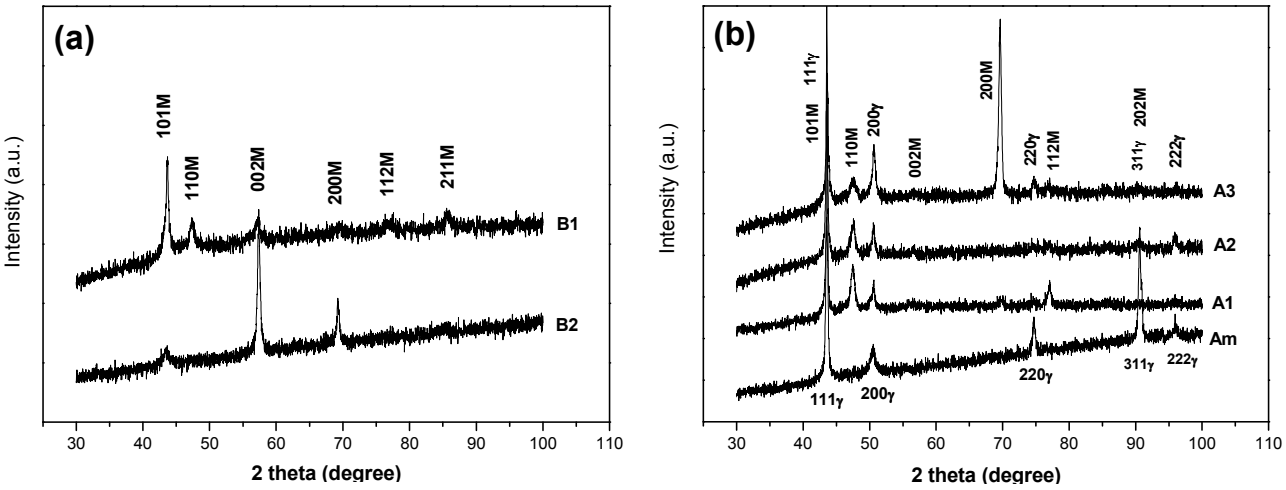

Fig. 1 X-ray diffraction patterns of (a) low cobalt samples, (b) high cobalt samples

Figure 1 shows the X-ray diffraction patterns of the studied alloys. For low cobalt samples, all the peaks could be indexed by the single tetragonal structure, indicating all the two low cobalt samples consist of single martensite phase, as indexed in Fig. 1(a). The lattice parameters of the martensitic phase are calculated to be a=b=2.71 Å，c=3.22 Å，c/a=1.19, which are closed to the previous results [17]. For A1, A2 and A3 of high cobalt samples, except the diffraction peaks of tetragonal structured martensite, three additional peaks appeared. The positions of the three additional peaks keep almost unchanged with the change of composition, implying that a new phase was formed. The new phase was confirmed as γ (face-centered cubic) phase with the main diffraction peaks of (111), (200), (220), (311), and (222), as shown in Fig. 2(b). The lattice parameter of the γ phase is a = 3.590 Å. As for the Am ($Co_{63.5}Ni_{35.3}Ga_{25}$) sample with the highest Co content, only the peaks of γ phase were identified from the X-ray diffraction pattern.

Optical metallographs of typical microstructures were shown in Fig. 2. Two low cobalt samples exhibit rather similar pure martensite structures, as typically shown in Fig. 2(a) of $Co_{43.1}Ni_{25}Ga_{30}$. The straight lamellar martensitic twins with a spacing of about 20～50μm indicate configurations of

typical self-accommodation arrangement. The interfaces among twin variants are straight and clear, implying well characteristics of thermoelasticity. As for the high cobalt samples, dual phases were present, as typically shown in Fig. 2(b) of $Co_{48.7}Ni_{26.1}Ga_{25.2}$. The characteristic of the microstructure consists of the martensitic twins with lamellar configuration and the white γ phase. With the highest Co content sample of $Co_{63.5}Ni_{35.3}Ga_{25}$, though no martensitic phase could be monitored from the X-ray diffraction, small particles of martensite with lamellar shape was clearly observed among the big γ grains at high magnification (Fig. 2(c)). Their minor amount, small size and highly dispersed state account for the absence of their peaks on X-ray diffraction patterns. For the Heusler type intermetallics with high brittleness, the introduce of the γ phase with face-centered cubic structure implies the greatly improvement of their polycrystalline plasticity [16]. At the same time, as γ phase does not participate in the reversible martensitic transformation, its size, shape and distribution configuration possibly have important effects on the martensitic transformation and the reorientation of martensitic variants, especially for $Co_{63.5}Ni_{35.3}Ga_{25}$ with little amount of martensitic phase.

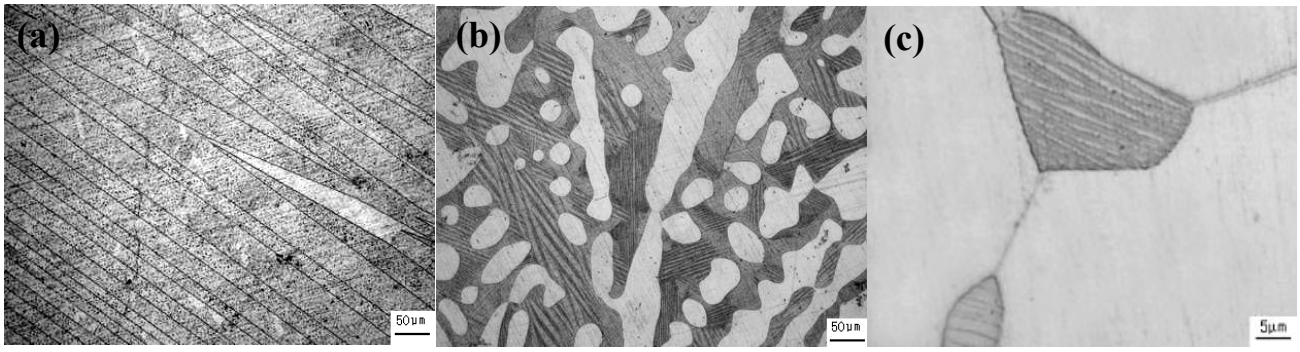

Fig. 2 Optical images of (a) $Co_{43.1}Ni_{25}Ga_{30}$; (b) $Co_{48.7}Ni_{26.1}Ga_{25.2}$; (c) $Co_{63.5}Ni_{35.3}Ga_{25}$

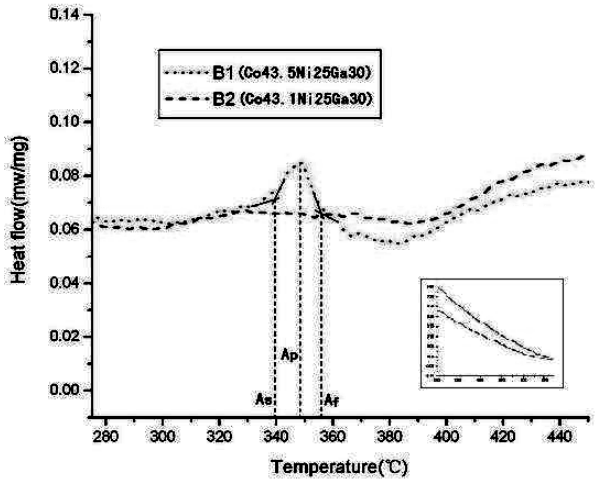

Fig. 3 Heating DSC curves of low cobalt samples, with the insert of cooling curves

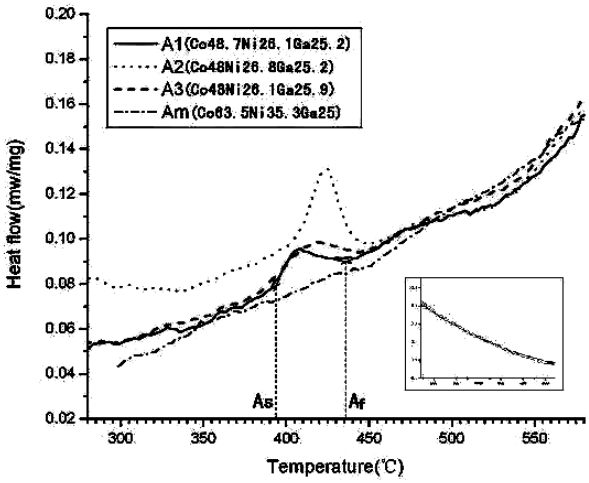

Fig. 4 Heating DSC curves of high cobalt samples, with the insert of cooling curves

DSC measurements were performed for all specimens. Fig. 3 shows the heating DSC curves of low cobalt samples. For B1 ($Co_{43.5}Ni_{25}Ga_{30}$), there is a clear endothermic peak appeared on the heating DSC curve, which is associated with the reverse martensitic transformation from tetragonal martensite to cubic austenite, where the austenite transformation starting temperature A_s and finishing temperature A_f are 340 and 356℃, respectively. It should be mentioned that the latent heat of the reverse martensitic transformation (1.6 J/g) is very small, which is only one fifth of that (8.4 J/g) of Ni_2MnGa alloys [15]. For B2 ($Co_{43.1}Ni_{25}Ga_{30}$) sample, although single martensitic phase was confirmed at room temperature by the X-ray diffraction and optical observations, no endothermic peaks corresponding to its reverse martensitic transformation could be monitored from the heating DSC curve. Additionally, no exothermic peaks could be detected on the cooling curves for both B1 and B2 samples, as indicated in the insert of Fig. 3. The possible reasons were likely come from two

aspects. One is the stabilization of the martensite phase. Another one may be the little latent heat associated with the phase transformation, which may be beyond the sensitivity of the DSC equipment. More studies should be conducted on this item.

Similar to the low cobalt samples, endothermic peaks corresponding to the reverse martensitic transformations from tetragonal martensite to cubic austenite could be seen on the heating curves for high cobalt samples of A1 ($Co_{48.7}Ni_{26.1}Ga_{25.2}$), A2 ($Co_{48}Ni_{26.8}Ga_{25.2}$) and A3 ($Co_{48}Ni_{26.1}Ga_{25.9}$), but none on the cooling curves, as shown in Fig. 4. A_s and A_f temperatures of these three alloys are all around 395 and 435℃, which are high enough for use as HTSMA. For Am ($Co_{63.5}Ni_{35.3}Ga_{25}$) sample, though the small pieces of matensitic phase with lamellar shape could be observed from optical microscope, no peaks were monitored both for heating and cooling DSC curves. The main reason might be the small amount of martensite phase and the surrounding γ phase, which will hamper the phase transformation of the martensite.

Summary

1. Through composition adjustment, the austenitic transformation temperatures of CoNiGa alloys were successfully raised to above 340℃, showing their potentials as HTSMA, in spite of the single martensitic phase or dual phases they present at room temperature.
2. More works should be conducted to make it clear why CoNiGa alloys with high austenitic transformation temperatures exhibit no reversible martensitic transformation, although their microstructures showed good accommodations of martensitic twins.

References

[1] K. Otsuka and X.B. Ren: Intermetallics Vol. 7 (1999), p. 511

[2] K. Otsuka and C.M. Wayman: *Shape memory materials* (Cambridge University Press, Cambridge 1998).

[3] H.B. Xu: Mater. Sci. Forum Vol. 394-395 (2002), p. 375

[4] J.H. Yang and C.M. Wayman: Intermetallics Vol. 2 (1994), p. 111

[5] Y.Q. Ma, C.B. Jiang CB, L.F. Deng and H.B.Xu: J. Mater. Sci. Tech. Vol. 19 (2003), p. 431

[6] J.V. Humbeeck: J. Eng. Mater. Tech. Vol.121 (1999), p. 98

[7] D. Golberg, Y. Xu, Y. Murakami, S. Morito et al.: Scripta Metall. Mater. Vol. 30 (1994), p. 1349

[8] K. Ullakko, J.K. Huang, C. Kantner, et al.: Appl. Phys. Lett. Vol. 69 (1996), p.1966

[9] C.B. Jiang, G. Feng and H.B. Xu: Appl. Phys. Lett. Vol. 80 (2002), p. 1619

[10] J. Pons, V.A. Chernenko, R. Santamarta and E. Cesari: Acta Mater. Vol. 48 (2000), p. 3027

[11] V.A. Chernenko, E. Cesari, V.V. Kokorin et al.: Scripta Metall. Mater. Vol. 33 (1995), p. 1239

[12] Y. Li, Y. Xin, C.B. Jiang and H.B. Xu: Scripta Mater. Vol. 51 (2004), p. 849

[13] X. Jin, M. Marioni, D. Bono, S.M. Allen, et al.: J. Appl. Phys. Vol. 91 (2002), p. 8222

[14] H.B. Xu, Y.Q. Ma and C.B. Jiang: Appl. Phys. Lett. Vol. 82 (2003), p. 3206

[15] Y.Q. Ma, C.B. Jiang, G. Feng and H.B. Xu: Scripta Mater. Vol. 48 (2003), p. 365

[16] Y.Q. Ma, L.H. Xu, Y. Li, C.B. Jiang, H.B. Xu and Y.K. Lee: Z. Metallkd. Vol. 96 (2005), p. 843

[17] V.A. Chernenko, J. Pons, E. Cesari and A.E. Perekos: Mater. Sci. Eng. A Vol. 378 (2004), p. 357

[18] M. Sato, T. Okazaki, Y. Furuya and M. Wutting: Mater. Trans. Vol. 44 (2003), p. 372

Progress in Light Metals, Aerospace Materials and Superconductors
10.4028/www.scientific.net/MSF.546-549

Heusler Type CoNiGa Alloys with High Martensitic Transformation Temperature
10.4028/www.scientific.net/MSF.546-549.2241

DOI References
[1] K. Otsuka and X.B. Ren: Intermetallics Vol. 7 (1999), p. 511
doi:10.1016/S0966-9795(98)00070-3
[3] H.B. Xu: Mater. Sci. Forum Vol. 394-395 (2002), p. 375
doi:10.4028/www.scientific.net/MSF.394-395.375
[4] J.H. Yang and C.M. Wayman: Intermetallics Vol. 2 (1994), p. 111
doi:10.1016/0966-9795(94)90005-1
[7] D. Golberg, Y. Xu, Y. Murakami, S. Morito et al.: Scripta Metall. Mater. Vol. 30 (1994), p. 1349
doi:10.1016/0956-716X(94)90271-2
[8] K. Ullakko, J.K. Huang, C. Kantner, et al.: Appl. Phys. Lett. Vol. 69 (1996), p.1966
doi:10.1063/1.117637
[9] C.B. Jiang, G. Feng and H.B. Xu: Appl. Phys. Lett. Vol. 80 (2002), p. 1619
doi:10.1063/1.1445267
[11] V.A. Chernenko, E. Cesari, V.V. Kokorin et al.: Scripta Metall. Mater. Vol. 33 (1995), p. 1239
doi:10.1016/0956-716X(95)00370-B
[13] X. Jin, M. Marioni, D. Bono, S.M. Allen, et al.: J. Appl. Phys. Vol. 91 (2002), p. 8222
doi:10.1063/1.1453943
[17] V.A. Chernenko, J. Pons, E. Cesari and A.E. Perekos: Mater. Sci. Eng. A Vol. 378 (2004), p. 357
doi:10.1016/j.msea.2003.10.361