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Thermoelastic martensitic transition and magnetic properties of the $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy in different structural states

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Abstract

Investigations of the temperature dependence of magnetization revealed that, in the ferromagnetic shape memory $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy, after formation of the nanocrystalline state by a severe plastic deformation method, neither ferromagnetic ordering nor a structural transition takes place. Subsequent annealing leads to the restoration of magnetic ordering. Also, on increasing the temperature of annealing restoration of the structural transition for the first time was observed. It was shown that the temperature of the thermoelastic martensitic transition depends on crystallite sizes. An intermartensitic transition in coarse grained $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy was discovered.

1. Introduction

Nowadays intermetallic Ni–Mn–Ga system alloys arouse much interest among researchers since in addition to the thermoelastic martensitic transition they possess ferromagnetic properties [1–4]. A number of works have shown that the martensitic transition in these alloys is accompanied by an effect of shape-memory and that it can occur in the ferromagnetic state. As a result, the structural transition in these alloys is sensitive to the presence of the external magnetic field and there can occur a reversible structural transition and shape-memory effect controlled by the magnetic field at a constant temperature [5–8]. A shape memory effect controlled by an external magnetic field can arise from a magneto-induced martensite to austenite structural transition at fixed temperature [6] or from magneto-induced reorientation of martensite variants when the sample dwells completely in the low-temperature phase. The

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temperatures of structural and magnetic transitions in these alloys are also sensitive to changes in the stoichiometric composition and insertion of impurity atoms [9, 10]. In particular, the replacement of atoms Mn for atoms Ni increases the temperature of the structural transition and decreases the Curie point. At a certain parity of Ni and Mn atoms, co-occurrence of the above-stated transitions is possible. Reasoning from the facts above one can conclude that a study of phase transitions in these alloys is of both practical and scientific interest. That is why the present paper considers the influence of the structural state on phase transitions in the alloy $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$. The temperature dependence of magnetization $\sigma(T)$, describing both magnetic and structural transitions, is used for this study.

2. Materials and experimental procedure

The coarse-grained (CG) alloy $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ was produced by the technique described in [6]. It is well known that the adding of Fe to Ni–Mn–Ga alloys improves their toughness, mechanical properties and therefore makes them more convenient for practical applications [22–24]. Fe-doping also increases the saturation magnetization and Curie point, and decreases the structural transition temperature [23, 24]. That is why this alloy was chosen for our studies. X-ray microanalysis on a JEOL JSM-840 scanning electron microscope showed high homogeneity in the composition of the ingots. For the formation of nanocrystalline (NC) structures, plates 6.0 mm in diameter and 0.5 mm thick were cut from the initial alloy by the electric-spark method and subjected to severe plastic deformation (SPD) at room temperature on Bridgman anvils under a pressure of 7 GPa. The rotation angle of the anvil's movable component is 10π. Intermediate structural states were obtained by annealing the NC samples at temperatures 623 K (2 h), 673 K (2 h), 773 K (30 min) and 1073 K (5 min) in a vacuum no worse than 10^{-3} Pa.

The microstructure of the CG sample was studied with an optical metallographic microscope (AXIOVERT-100A). The microstructure of the NC state was studied on a transmission electron microscope (JEM-2000EX). Curves of the temperature dependence of magnetization was recorded using an automatic vacuum magnetic microbalance [11]. The measurements of specific magnetization $\sigma(T)$ were performed during heating and cooling of the samples in the range 77–380 K in a field with magnetizing force 80 kA m^{-1}.

3. Results and discussion

Microstructure studies have revealed that the CG sample is a polycrystal with mean grain size of about 0.5 mm (figure 1 shows an image of the low-temperature phase at 283 K). Typical martensite plates are observed in the grains.

The disorientation of martensite plates in different grains shows that the grain boundaries are high angle. Figures 2 and 3 show electron microscopic images of the structure and electron diffraction patterns for the NC state and the state after annealing of the NC sample at 773 K, respectively. The NC structure comprises small size crystallites without distinct boundaries between them. We failed to reveal a fine boundary structure between the crystallites. However, it is seen they are characterized by a high density of defects. The evaluated mean crystallite size is 10 nm. The electron diffraction pattern presents a set of diffraction rings consisting of reflections strongly blurred by azimuth. This testifies both the essential internal stresses and the high-angle disorientations of the crystallographic axes of different crystallites with respect to each other. After annealing of the NC sample at 773 K, noticeable transformations occur in its structure. In particular, one can see distinct boundaries between crystallites (a mean

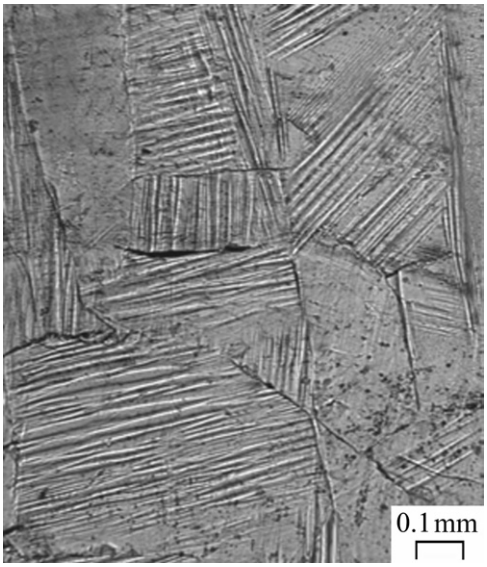

Figure 1. Microstructure of the coarse-grained $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy at 283 K.

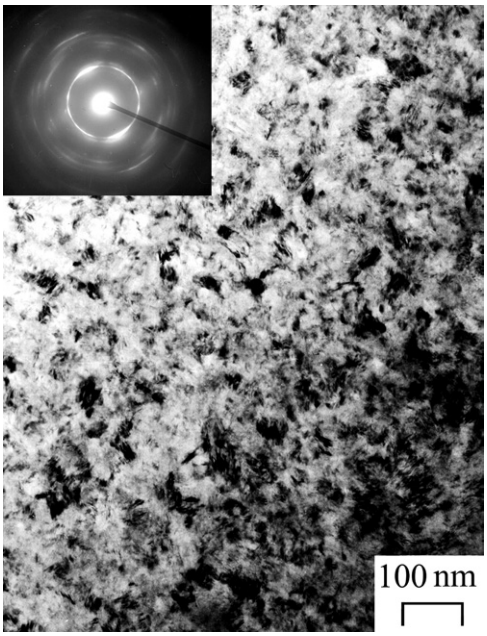

Figure 2. Microstructures and electron diffraction patterns of the nanocrystalline $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy.

size of 200 nm). The appearance of boundaries with a typical banded contrast in separate grains indicates that the recrystallization processes occurred during annealing. The presence of the colour contrast between different grains testifies to their disorientation. The reflections observed on the electron diffraction pattern are already distinct, that being evidence of the

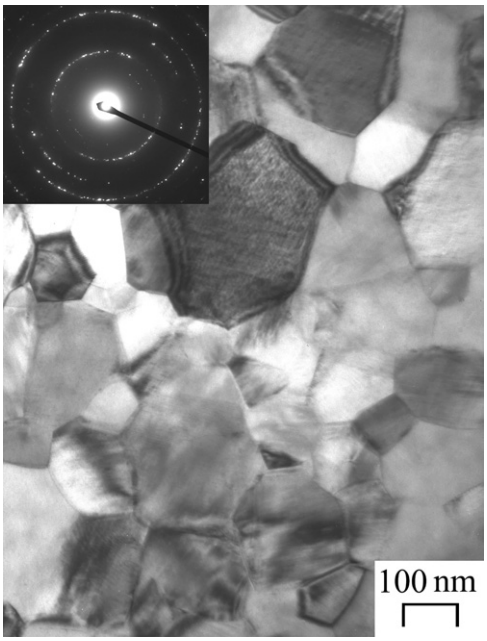

Figure 3. Microstructure and electron diffraction pattern of the nanocrystalline $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy annealed at 773 K.

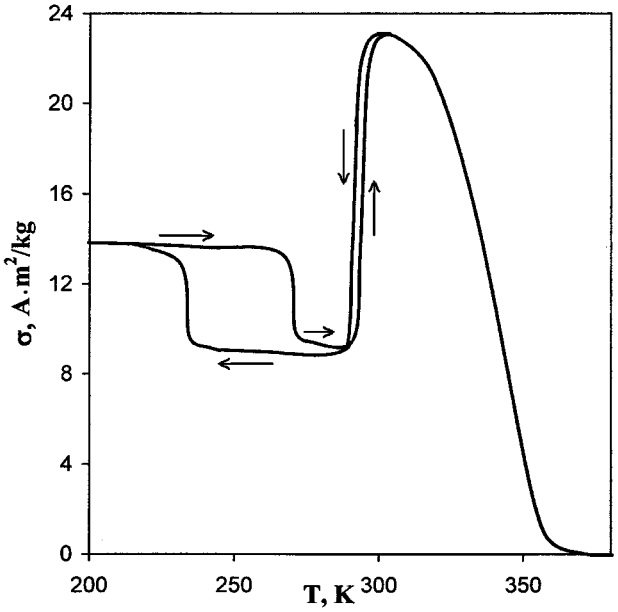

Figure 4. Temperature dependence of magnetization of the coarse-grained $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy measured in a field of $H = 80$ kA m^{-1}.

relief of internal stresses. For the states obtained after annealing the NC sample at 623, 673 and 1073 K, the mean crystallite size is equal to 100, 160 and 3000 nm, respectively.

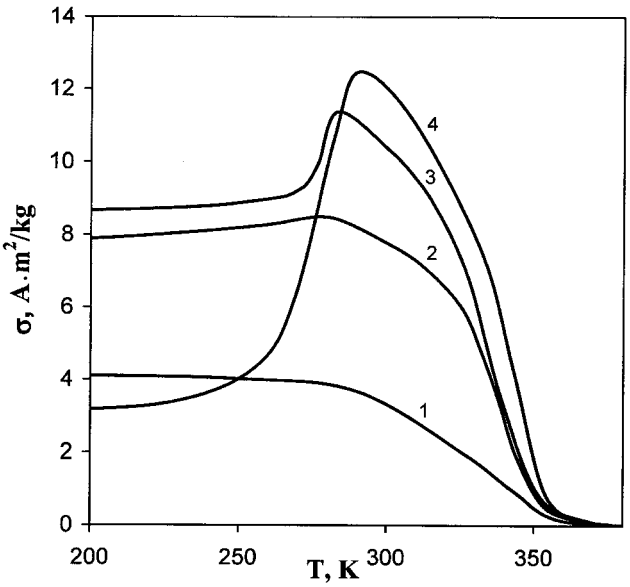

Figure 5. Temperature dependence of magnetization of the $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy measured in field of $H = 80$ kA m^{-1} in different structural states obtained by annealing the nanocrystalline sample at temperatures 623 (1), 673 (2), 773 (3) and 1073 K (4).

The $\sigma(T)$ dependence for the CG sample (figure 4) within the temperature range below 300 K is rather complex, which is attributed to the structural phase transformations occurring in the alloy under study. In particular, within the temperature range 220–300 K there are two dips in the curves corresponding to heating and cooling. Upon heating from 270 to 293 K the value of magnetization σ remains almost unchanged at the bottom of this dip. With increasing temperature above 293 K there occurs a sharp increase in σ, which achieves its maximum at about 300 K. Heating of the sample above 300 K leads to a decrease in σ, which becomes equal to zero at 357 K. The temperature at which the maximum $\sigma(T)$ is observed roughly indicates the ending of the low-temperature martensite phase transformation to high-temperature austenite phase. The hysteresis between the direct and reverse martensite–austenite transitions is less than 1 K. But the sharp downwards jump at 270 K during heating reverses upon cooling only in the range 242–220 K. Thus the second dip on the curve arises. Other researchers also observed the formation of a dip in the $\sigma(T)$ curve in some Ni–Mn–Ga system alloys while performing measurements in relatively weak magnetic fields [12–14, 25]. They explained its formation by the change in the period of modulation of the martensite phase (intermartensitic transition). In fact, different martensitic phases have different magnetic anisotropy constants [15]. Therefore we can see such behaviour (the formation of a dip) during measurements in low magnetic fields. The kind of intermartensitic transition in the alloy under study will be considered in detail in our next publications.

Neither structural transformations nor ferromagnetic properties are observed in NC $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$. This can be attributed to both the small size of the crystallites and the potential disordering of the studied composition during SPD. The fact that in the process of SPD there occurs disordering of the ordered compositions was considered in [16–18]. For example, complete disordering of the atomic structure was observed in the intermetallic alloy Ni_3Al subjected to severe plastic torsion straining under a pressure of 8 GPa [17]. Only after

annealing at 623 K does there occur partial ordering of the composition Ni_3Al. Note that annealing of the NC sample of the $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ alloy at temperatures below 623 K does not lead to restoration of ferromagnetic ordering. At the same time it is known that the value of magnetization in some ordering compositions, for example in Ni_3Mn, is evidence for the ordering factor [19]. Also no ferromagnetic ordering was observed in disordered Ni–Mn–Ga thin films [20]. That is why the considered NC composition $Ni_{2.14}Mn_{0.81}Fe_{0.05}Ga$ might be completely disordered.

Figure 5 shows the $\sigma(T)$ curves for states after annealing of the NC sample at temperatures 623 K (curve 1), 673 K (curve 2), 773 K (curve 3), 1073 K (curve 4). In figure 5 are shown only curves of heating because curves of cooling are almost the same, with hysteresis only of about 1 K between the temperatures of the direct and reverse structural transitions taking place. After annealing at 623 K there occurs a ferromagnetic order that might be connected with the beginning of the process of ordering during annealing in the composition under study. However, in this case the $\sigma(T)$ curve does not have any features indicating the occurrence of structural transformations, and its character is typical for conventional ferromagnets. After annealing at 673 K one can observe a growth of the magnetization value. At 278 K a flat maximum is observed in this curve. Annealing at 773 K leads to a further increase in the value of magnetization. Note that in this case the maximum $\sigma(T)$ is much more distinct and takes place at 283 K. The increase in the temperature of annealing of the NC sample shifts the maximum of the $\sigma(T)$ curve to the region of higher temperatures. For example, after annealing at 1073 K the maximum is observed at 290 K. The occurrence of maxima on the $\sigma(T)$ curves, corresponding to annealing at temperatures from 673 K and above, is evidently connected with the restoration of the martensite–austenite transition in these states. The assumption that the appearance of a maximum on curves 2, 3, 4 is attributed to the onset of martensite–austenite transition is confirmed by the fact that maxima are not observed when measurements of $\sigma(T)$ are performed in a magnetic field of higher strength (above 300 kA m^{-1}) and that is typical for Ni–Mn–Ga alloys. However, structural transitions in recrystallized states are more widespread, i.e. take place over a wider temperature range compared with the CG state. And even after annealing at 1073 K no intermartensitic modulation transition is observed. Consequently one can conclude that recrystallization of the NC state of the alloy under study provides processing materials with physical properties essentially distinguished from those in the CG state although the temperatures of their structural transitions are almost similar (in spite of the approximate similarity of temperatures of their structural transitions). The temperature dependence of the structural transitions is connected with the crystallite sizes. It is known that the martensitic transition occurs due to the movement of transformation dislocations being steps of martensite of an atomic size at interfaces. Consequently, the temperature of the martensitic transition depends on the size of the crystallites, since their boundaries, being barriers for the movement of dislocations, restrict the length of their free run [21]. A wider temperature range of the martensite–austenite transition in the states obtained by recrystallization of the NC sample is induced by non-uniformity of crystallite sizes in each individual state that initiates the non-simultaneous onset of the structural transition within the sample interior.

Acknowledgments

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References

[1] Webster P J, Ziebeck K R A, Town S L and Peak M S 1984 *Phil. Mag.* **49** 295
[2] Kanomata T, Shirakawa K and Kaneko T 1987 *J. Magn. Magn. Mater.* **65** 76
[3] Zheludev A *et al* 1995 *Phys. Rev.* B **51** 11310
[4] Worgull J, Petti E and Trivisonno J 1996 *Phys. Rev.* B **54** 15695
[5] Tickle R and James R D 1999 *J. Magn. Magn. Mater.* **195** 627
[6] Cherechukin A A, Dikshtein I E, Ermakova D I, Glebova A V, Koledov V V, Kosolapov D A, Shavrov V G, Tulaikova A A, Krasnoperov E P and Takagi T 2001 *Phys. Lett.* A **291** 175
[7] Ullakko K, Huang J K, Kantner C, O'Handley R C and Kokorin V V 1996 *Appl. Phys. Lett.* **69** 1966
[8] O'Handley R C, Murray S J, Marioni M, Nembach H and Allen S M 2000 *J. Appl. Phys.* **87** 4712
[9] Vasil'ev A, Bozhko A, Khovailo V, Dikshtein I, Shavrov V, Seletskii S and Buchelnikov V 1999 *J. Magn. Magn. Mater.* **196** 837
[10] Wirth S, Leithe-Jasper A, Vasil'ev A N and Coey J M D 1997 *J. Magn. Magn. Mater.* **167** L7
[11] Mulyukov Kh Ya, Sharipov I Z and Absalyamov S S 1998 *Instrum. Exp. Techn.* **41** 438
[12] Wang W H, Wu G H, Chen J L, Gao S X, Zhan W S, Wen G H and Zhang X X 2001 *Appl. Phys. Lett.* **79** 1148
[13] Wang W H, Liu Z H, Zhang J, Chen J L, Wu G H, Zhan W S, Chin T S, Wen G H and Zhang X X 2002 *Phys. Rev.* B **66** 052411
[14] Golub V O, Vovk A Ya, O'Connor C J, Kotov V V, Yakovenko P G and Ullakko K 2003 *J. Appl. Phys.* **93** 8504
[15] Sozinov A, Likhachev A A and Ullakko K 2002 *IEEE Trans. Magn.* **38** 2814
[16] Korznikova G, Korznikov A and Dimitrov O 2002 *Ann. Chim. Sci. Mater.* **27** 35
[17] Korznikov A V, Tram G, Dimitrov O, Korznikova G F, Idrisova S R and Pakiela Z 2001 *Acta Mater.* **49** 663
[18] Languillaume J, Chmelik F, Kapelski G, Bordeaux F, Nazarov A A, Canova G, Esling C, Valiev R Z and Baudelet B 1993 *Acta Metall. Mater.* **41** 2953
[19] Sharipov I Z, Mulyukov R R and Mulyukov Kh Ya 2003 *Phys. Met. Metallogr.* **95** 47
[20] Kim K W, Kudryavtsev Y V, Rhee J Y and Lee Y P 2004 *J. Magn. Magn. Mater.* **272–276** 1176
[21] Malygin G A 2000 *Solid State Phys.* **42** 1469
[22] Feng X, Fang D-M and Hwang K-C 2002 *Chin. Phys. Lett.* **19** 1547
[23] Liu Z H, Zhang M, Wang W Q, Wang W H, Chen J L, Wu G H, Meng F B, Liu H Y, Liu B D, Qu J P and Li Y X 2002 *J. Appl. Phys.* **92** 5006
[24] Wu G H, Wang W H, Chen J L, Ao L, Liu Z H, Zhan W S, Liang T and Xu H B 2002 *Appl. Phys. Lett.* **80** 634
[25] Khovailo V V, Oikawa K, Wedel C, Takagi T, Abe T and Sugiyama K 2004 *J. Phys.: Condens. Matter* **16** 1951