Atomic-size effect on the microstructural properties of Ni$_2$FeGa

Huai-Ruo Zhang a,b,⇑, Guang-Heng Wu a

a Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
b National Institute for Nanotechnology, Edmonton, 11421 Saskatchewan Drive, Canada T6G 2M9

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Abstract

The microstructural properties of melt-spun ribbon of the ferromagnetic shape-memory Heusler alloy Ni$_2$FeGa have been investigated by transmission electron microscopy. Two kinds of micromodulated structures, Fe-rich and Ga-rich, have been established. The Fe-rich micromodulated structure is formed by Fe atoms partially replacing Ga atoms on $\{3\ 5\ 0\}$ planes in the L$_2$$_1$ structure. The Ga-rich micromodulated structure concerns Ga atoms partially replacing Fe atoms on $\{3\ +\ n,\ 5\ +\ n,\ 0\}$($n \geq 0$) planes. The Fe-rich and Ga-rich micromodulated structures originate from spinodal decomposition of the Fe and Ga compositions, which is closely related to the difference of atomic sizes of Ni, Fe and Ga.

Keywords: Spinodal decomposition; Structural modulation; Order–disorder phenomena; Heusler alloy; Transmission electron microscopy

1. Introduction

Since the first discovery of the ferromagnetic and thermomagnetic properties of the Heusler alloy Ni$_2$MnGa [1], ferromagnetic shape-memory alloys (FSMAs) have attracted much attention due to their potential application as smart materials. Many kinds of $X_2YZ$-type magnetic Heusler alloys, such as Ni$_2$MnAl [3,4], Co$_2$NiGa [5,6] and Mn$_2$NiGa [7,8], exhibit next-nearest-neighbor chemical ordering, forming the L$_2$$_1$ crystal structure [2]. Derivatives of these alloys have been developed as FSMAs. In recent years, Ni–Fe–Ga alloys with compositions close to the stoichiometric Heusler alloy Ni$_2$FeGa have attracted much attention as promising FSMAs [9–16]. An alternative, the melt-spinning technique was used to avoid the formation of $\gamma$ phase and to obtain the ferromagnetic L$_2$$_1$ Ni$_2$FeGa phase [10]. However, this non-equilibrium solidification method may give rise to a rich variety of microstructures in the L$_2$$_1$ matrix, which has been observed in previous work [16]. But the origin and properties of these microstructures are not very well known for the Ni$_2$FeGa alloy. Investigation of the microstructural properties of Ni$_2$FeGa ribbon is very important to understand the martensitic transformation (MT) as well as the related physical properties and the metallurgical processing of the Ni–Fe–Ga system. In this work, various transmission electron microscopy (TEM) methods have been employed to study the microstructures of Ni$_2$FeGa ribbon at room temperature. Ga-rich and Fe-rich micromodulated structures have been established by analysing electron diffraction patterns (EDPs) and high-resolution transmission electron microscopy (HRTEM) images. It is found that the atomic-size differences play a very important role in the spinodal decomposition of Fe and Ga compositions.

⇑ Corresponding author at: National Institute for Nanotechnology, Edmonton, 11421 Saskatchewan Drive, Canada T6G 2M9. Tel.: +1 780 6411667.
E-mail address: Huairuo.Zhang@nrc-cnrc.gc.ca (H.-R. Zhang).

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2. Experimental

Precursor ingots were synthesized by melting high-purity Ni, Fe and Ga with stoichiometric Ni$_2$FeGa composition in an induction furnace under argon atmosphere. The ribbon samples were prepared by spinning the melt of the ingot onto a copper wheel rotating at high speed. The prepared ribbons usually have a width of 6 mm and a thickness of 5–30 μm. In order to avoid stresses which may promote the MT of the thermoelastic materials, introduced into the TEM samples by grinding, 5 μm thick ribbons were selected for ion-milling in a Gatan precision ion polishing system (PIPS). The TEM microchemical and crystal-structure analyses were performed in a TEM/STEM facility at an accelerating voltage of 200 kV. Additional experimental details on the sample preparation and characterization of physical properties have been reported in Ref. [10].

3. Results and discussion

3.1. Order–disorder structure of the Ni$_2$FeGa Heusler alloy

Although the next-nearest-neighbor ordered L$_2$$_1$ structure was established in as-prepared Ni$_2$FeGa ribbon by powder X-ray diffraction (XRD) [10], various locally disordered micromodulated structures can still be observed in the L$_2$$_1$ matrix by means of TEM characterization [16]. As shown in Fig. 1, the Ni$_2$FeGa L$_2$$_1$ structural unit cell is composed of alternating Ni–Fe and Ni–Ga bcc subunits. Theoretically, there are three most-favored microstructures that can be formed in the disordered regions due to the non-equilibrium solidification: (i) the Ni atoms remain on their Ni-sublattice positions, but the Fe and Ga sublattices are randomly occupied, resulting in a CsCl-type B$_2$ structure without the (1 1 1) superlattice reflection; (ii) Fe or Ga sublattice positions are occupied by Ni atoms, resulting in local DO$_3$-type Ni$_3$Ga or Ni$_3$Fe unit cells which contribute to the (1 1 1) reflection; (iii) the Ni, Fe and Ga atoms randomly occupy all lattice positions, resulting in the disordered bcc A$_2$ structure without the (1 1 1) superlattice refection. The XRD reflections of these three kinds of disordered structures coincide with those of the ordered L$_2$$_1$ structure and cannot be distinguished. By utilizing EDPs and TEM micrograph methods, however, a rich variety of micromodulated structures has been observed in the Ni–Fe–Ga alloys, which throw light on these local disordered structures [16].

3.2. Micromodulated structure with well-defined EDP satellites

Fig. 2a shows a typical [0 0 1] zone axis EDP frequently observed in the Ni–Fe–Ga alloys. Besides the well-known diffuse streaks which emanate from the Bragg diffraction spots along the (1 1 0)$^*$ reciprocal directions and which are observed in most of the alloys with tweed structures [19–22], there are two sets of satellites surrounding the main diffraction spots at the equivalent positions $G = 0.44a^* + 0.76b^*$ (indicated by the numbers 1 and 2 near the origin), where $a^*$ and $b^*$ are reciprocal lattice vectors of the L$_2$$_1$ structure. The intensity of the second-order diffraction of the satellites is substantially decreased and can be well identified in the region far away from the origin, indicated by the numbers 3 and 4. This suggests that micromodulated structures exist in the alloy. Another feature of this EDP is the short diffuse streak composed of closely spaced weak diffraction spots emanating from the Bragg diffractions, indicated by the number 5. This diffuse streak feature is also superposed on the satellites (indicated by the number 6). The diffraction-contrast imaging technique was further employed to identify the microstructures giving rise to the satellites and streaks. In Fig. 2b, the well-known tweed structure, giving rise to (1 1 0)$^*$ streaks, is clearly revealed by the bright-field TEM micrograph imaged using a small object aperture shown by a circle in Fig. 2a to just select the direct beam. Center dark-field TEM microscopy was performed to reveal the microstructures giving rise to satellites. Fig. 2c, imaged using both the satellites 1 and 2, reveals bright clusters seemingly dispersed randomly in the matrix. Fig. 2d–f, imaged using the satellites 1, 2 and 6 respectively, also reveals similar bright clusters. Moreover, due to the dramatic decrease of the interference of inelastic scattering around the Bragg diffraction at high scattering angle, the dark-field image of...
satellite 6, which has equivalent position as satellite 1, clearly reveals the long-period modulated structure (dark fringes) giving rise to the short diffuse streak indicated by the number 5. The dark-field image of satellite 2, which has stronger diffraction intensity than satellite 1, reveals the wave-like structure, which is composed of clusters and not parallel to $h_{220}$/Cl reciprocal directions.

Systematical specimen tilting was performed to study the microstructures giving rise to the satellites. The tilting was started from the [0 0 1] zone axis (Fig. 3a) along three different directions:

(i) Tilting 54.74° around the $<2 2 0>^*$ reciprocal direction to the [1 1 1] zone axis. The intersection angle of the two sets of satellites is increased with increasing tilting angle (Fig. 3b).

(ii) Tilting ±25.24° around the $<2 2 0>^*$ reciprocal direction to the [1 1 3] and [1 1 3] zone axes (Fig. 3c–e).

(iii) Tilting 45° around the $<0 4 0>^*$ reciprocal direction to the [1 0 1] zone axis (Fig. 3f).

A string of spots appears along the $<3 3 1>^*$ reciprocal directions. Some spots such as the ones numbered 1 and 2 and illustrated by the parallelograms in Fig. 3e and f belong to double diffraction spots. The intensity of the L2$_1$ structural (1 1 1) superlattice diffraction spot (as indicated in Fig. 3f) arising from the micromodulated structure region is less than that from the average structure region due to the decrease of the ordering. Based on the systematically tilted EDPs a schematic reciprocal unit cell can be reconstructed by adding two streaks into the L2$_1$ reciprocal unit cell, as shown in Fig. 3g, which interprets well the string of diffraction spots along the $<3 3 1>^*$ reciprocal directions. These streaks have eight equivalent positions and form at most four sets of satellites along the [0 0 1] zone axis, as shown in Fig. 3h.

HRTEM was also performed to study the details of the micromodulated structure. Fig. 4a shows a typical [0 0 1] zone axis HRTEM image with complex modulation contrast. The corresponding fast Fourier transformation (FFT) image in Fig. 4b clearly presents two sets of satellites numbered 1 and 2. Modulation waves $q_1$ and $q_2$ with 7.7 Å period are clearly revealed by inverse fast Fourier transformation (IFFT) using the satellites 1 and 2, respectively, as shown in Fig. 4c and d. Simple numerical superposition of Fig. 4c and d or IFFT using both satellites 1 and 2 can produce the same image Fig. 4e, which presents a similar modulation pattern as the experimental HRTEM image Fig. 4a. The modulation waves $q_1$ and $q_2$ can coexist or solely exist in local regions. As shown in Fig. 4f, with the two insets corresponding to the FFT image of the left bottom and right top areas of the low-magnification HRTEM image, respectively, there is clear evidence of the coexistence and non-coexistence of the waves $q_1$ and $q_2$.  

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**Fig. 2.** (a) Typical [0 0 1] zone axis EDP showing the satellites and the imaging conditions of the following micrographs. (b) Bright-field micrograph taken using the direct beam shown by a small circle in (a) to reveal the tweed structures. Central dark-field micrographs taken by selecting (c) both satellites 1 and 2, (d) satellite 1, (e) satellite 6 and (f) satellite 2.
3.3. Multimodulated structure with paired diffuse scattering streaks

Fig. 5a shows another striking feature observed in the Ni$_2$FeGa Heusler alloy. Besides one set of satellites which is mentioned above (indicated by a black arrowhead), there are paired diffuse streaks symmetric on both sides of each main diffraction spot and perpendicular to the (1 1 0)\(^{\perp}\) directions at \(G \pm 0.16(1 1 0)\(^{\perp}\) with scattering intensity higher on the low-angle side than on the high-angle side. In addition, as indicated by the white arrowheads in Fig. 5a, the streaks are seemingly composed of some weak satellites. Five satellites can be well identified by line profile analysis of the streak between two Bragg diffractions (Fig. 5b), which suggests that a multimodulated structure has formed in the alloy. Systematical specimen tilting was...
further performed to study the microstructures giving rise to the paired diffuse streaks. The tilting was started from the [0 0 1] zone axis around the \( \{220\}^* \), \( \{220\}^* \) and \( \{404\}^* \) three reciprocal directions. Fig. 5c–e shows patterns tilted around the \( \{220\}^* \) reciprocal direction. Slightly off the [0 0 1] zone axis the central row streaks at both sides of the \( \langle 110 \rangle^* \) direction, as well as the high-angle-side streak of the paired streaks in other rows, are invisible. Meanwhile the scattering intensity of the diffuse streaks decreases with increasing tilting angle off the [0 0 1] zone axis. Fig. 5f and g shows patterns tilted around the \( \langle 220 \rangle^* \) and the \( \langle 404 \rangle^* \) direction, respectively. The diffuse streaks persist in the \( \langle \zeta \zeta \eta \rangle^* \) reciprocal direction regardless the direction of tilting. Based on the systematically tilted EDPs a schematic reciprocal unit cell can be reconstructed by adding two sheets of diffuse planes into the \( L_{21} \) reciprocal unit cell, as shown in Fig. 5h, which interprets well the diffuse streaks along the \( \langle \zeta \zeta \eta \rangle^* \) reciprocal directions. The paired diffuse planes have two equivalent positions and form at most two sets of paired streaks along the \( \langle 110 \rangle^* \) directions along the [0 0 1] zone axis, as shown in Fig. 5i.

Paired diffuse streaks phenomena have been reported in Ta–W–O system [23], in which the paired diffuse streaks present a little bit stronger scattering at the high-angle side and in which the absence of diffuse scattering between the paired diffuse streaks was interpreted in terms of the Warren atomic-size effect [24]. According to this effect, asymmetric diffuse scattering around a fundamental Bragg diffraction is the result of a random binary solid solution consisting of atoms with appreciably different sizes. When the atom with larger scattering power is smaller in size, the diffuse scattering around a fundamental diffraction will be low at the low-angle side and high at the high-angle side. On the other hand, when the atom with larger scattering power is also larger in size, the diffuse scattering around a fundamental diffraction will be high on the low-angle side and low on the high-angle side [24,25]. Moreover, only when the scattering power of the two species is made identical, the feature of paired diffuse streaks can be clearly visible [23,25]. In addition, it is reported by Welberry [25], who employed the Monte Carlo method to simulate the effect of multi-site correlations on the diffraction pattern of a disordered alloy consisting of atoms with different sizes on a simple square lattice, that the two sets of paired diffuse streaks formed around each fundamental Bragg diffraction along two perpendicular directions are absent along the rows of Bragg diffractions passing through the origin \( (0\ 0\ 0) \). In Ni–Fe–Ga alloys, the Ga atom has both the largest scattering power and the largest size, having the largest size difference with the Ni atom. The intensity of the diffuse streaks along the row of Bragg diffractions passing though the origin \( (0\ 0\ 0) \) is weaker than those of neighboring rows and disappears after slight tilting, which suggests that the streaks of this row result from double diffraction and that...
they are forbidden. The phenomena of the paired diffuse streaks in Ni$_2$FeGa are in agreement with Welberry’s theoretical simulation, which suggests the paired diffuse scattering features of Ni$_2$FeGa possibly result from Warren atomic-size effect and correlate to the atomic-displacement modulation. In the highly ordered L2$_1$ structure of Ni$_2$FeGa, all atoms with different radii occupy their sublattice positions with a balance without lattice distortion. However, local partial disorder will introduce local lattice distortion due to atomic displacement from the average position. If the Fe and Ga atoms are considered as solute atoms in a Ni solvent, pseudo-binary Ni–Fe and Ni–Ga solid solutions can be assumed to exist in the local disordered area. In the former solid solution a Fe atom has a slightly smaller scattering power and it is slightly larger in size than a Ni atom, which could possibly produce diffuse scattering which is large at high-angle side and small at the low-angle side but difficult to observe. In contrast with this, a Ga atom has an appreciably larger scattering power and is also bigger than a Ni atom, which could very likely lead to large diffuse scattering at the low-angle side and small scattering at the high-angle side. The paired diffuse scattering streaks reveal the Ga-rich microstructure in Ni$_2$FeGa ribbon. In addition, the weak satellites superposed on the streaks suggest a multimodulation of the Ga composition. The static displacement of atoms of the

Fig. 5. (a) [0 0 1] zone axis EDP showing the paired diffuse scattering streaks between the fundamental Bragg diffraction along the (1 1 0)$^*$ reciprocal direction. (b) Line profile of the streak intensity from A to B shown in (a). Systematical tilting from the [0 0 1] zone axis around the (e–g) (2 2 0)$^*$ and (f) (0 4 0)$^*$ reciprocal directions to reveal the distribution of the diffuse streaks in reciprocal space. (b) Reconstructed reciprocal unit cell schematically showing the diffuse sheets giving rise to diffuse streaks in reciprocal planes. (i) Schematic diagram showing the two equivalent positions of paired diffuse scattering streaks observed along the [0 0 1] zone axis.
Ga-rich modulated structure produces a correlated atomic displacement along the \( \langle 110 \rangle \) directions, which results in the paired diffuse scattering streaks along the \( \langle 110 \rangle^* \) directions.

Diffraction contrast microscopy was further performed to reveal the microstructures giving rise to the paired diffuse streaks. Fig. 6a shows a bright-field micrograph taken with a diffraction condition about 16.6° off the \([0 0 1]\) zone axis, in the same position in which Fig. 5e was taken. The right-part image clearly reveals a wave-like structure which is not apparent in the \([0 0 1]\) zone axis imaging condition. Fig. 6b presents another micrograph showing the typical feature of a wave-like structure with a wave vector of around 10 nm. The wave-like contrast suggests a spinodal decomposition, i.e. chemical-composition modulation in this region, which is in strong agreement with the above analysis of diffuse scattering streaks resulting from Ga-component modulation. In addition to the apparent spinodal decomposition structure, a novel micromodulated structure has also been observed, which can illustrate intuitively the paired diffuse scattering streaks. Fig. 7a shows a diffraction pattern with apparent satellites superposed on the paired diffuse streaks, as well as the well-defined satellite (indicated by a black arrowhead) which has been discussed in Section 3.2. Fig. 7b has been taken using a small object aperture to exclude the interference of the strong fundamental diffractions. The corresponding FFT in the right-bottom inset corresponds well with the selected diffraction beams shown in Fig. 7a. The needle-shaped microstructures with an atomic width oriented along certain directions reveal an unambiguous picture of multimodulated microstructures. The measurement of modulation wave vectors including modulation periods and modulation directions of the needle-shaped microstructures corresponds well with the satellites superposed on the paired diffuse streaks. Fig. 7c shows a high-magnification micrograph of the interweaved needle-shaped microstructures. The corresponding FFT image reveals that the intensity of one of the streaks is much stronger than that of another one. Comparison of Fig. 7c and d proves that the needle structures are strongly related to the paired diffuse streaks and the weak satellites superposed on the streaks.

3.4. Model of the modulated structures

3.4.1. Ga-rich multimodulated structure

The contrast of the micrographs in Fig. 7 suggests that the needle structures of atomic width are the distortion centers which are rich in Ga atoms. The orientations of the needle structures throw light on the preferred position of Ga atoms in the local disordered region, and evidence the correlated atomic displacements as well. An atomic model can be employed to illustrate the distortion displacement modulation (coupled with chemical modulation). Fig. 8a shows a \([0 0 1]\) zone axis atomic projection of \( \text{L}_2 \) structure of \( \text{Ni}_2\text{FeGa} \), which is composed of pure Ni-atom columns (fractional coordinates \( z = 1/4, 3/4 \)), \( \text{Fe} + \text{Ga} \) (\( \text{Fe}: z = 0; \text{Ga}: z = 1/2 \)) and \( \text{Ga} + \text{Fe} \) (\( \text{Ga}: z = 0; \text{Fe}: z = 1/2 \)) atomic columns. A two-dimensional atomic plane of \( \text{Fe} \) and \( \text{Ga} \) can be obtained by just considering the first atomic plane at \( z = 0 \), as shown in Fig. 8b. The three lines \( \text{L}_1, \text{L}_2 \) and \( \text{L}_3 \), on \((5 3 0), (6 4 0) \) and \((7 5 0) \) planes, respectively, connect \( \text{Fe} \) atoms with different distances. The angles between these three lines and the reference line \( \text{L}_0 \) (\( \langle 110 \rangle \) direction) of the lattice are in good agreement with the scattering angles of the satellites superposed on the paired diffuse streaks. If the \( \text{Fe} \) atoms along the lines are replaced or partially replaced by Ga atoms, distortion centers will be produced at the replacement positions. Fig. 8b presents the...
chemical modulation periods $q_1$, $q_2$ and $q_3$ corresponding to the reciprocal length of the satellites superposed on the streaks. As illustration in Fig. 8b, the modulation period lengths are inversely proportional to the distance of the replacement centers, which is constrained by the balance of the distortion strain. The chemical modulation of Ga atoms with different modulation wave vectors in the local disordered region results in the multimodulated structures with paired diffuse scattering streaks.

3.4.2. Fe-rich modulated structure

The Ga-rich multimodulated structure was revealed by the needle structures as well as the diffuse scattering streaks due to atomic-size effect, which raises a question which positions are occupied by the Fe atoms absent in the Ga-rich region. Is it possible for the excess Fe atoms to replace the Ga atoms in the Fe-rich region? Theoretically, the Fe atom has a larger solubility in Ni solvent than a Ga atom due to the more similar physical properties of Ni and Fe atoms. Well-defined satellites were frequently observed accompanied by paired diffuse streaks in equivalent positions very close to the start point of the diffuse streaks, as indicated by the black arrowhead in Figs. 5a and 7a, which suggests a certain correlation between these two modulated structures. In Fig. 8c the line L1, on (5 3 0) plane, connects two Ga atoms and the angle between L1 and L0 is the same as in Fig. 8b. If the Ga atoms along the line are replaced or partially replaced by Fe atoms, taking account of the distortion effect, the modulation wave vector $q$ corresponds well to the well-defined satellites. On the other hand, from the point of view of the Warren size effect, Ni and Fe atoms have small differences both in scattering power and in size, and cannot produce visible diffuse scattering streaks. In addition, the small size difference of Ni and Fe atoms makes it easy for the excess Fe atoms to occupy a position on crystallographic planes that is most favorable in energy and to form a

![Fig. 7. (a) A diffraction pattern with apparent satellites superposed on the paired diffuse streaks, as well as the well-defined satellite indicated by the black arrowhead. The white circle illustrates the object-aperture size used to image the following diffraction contrast images. (b) The multimodulated structure composed of short needle structures and the corresponding FFT. (c and d) The interweaved and non-interweaved needle structures and the corresponding FFTs, respectively.](image-url)
constant modulated structure. In contrast, the large size difference between Ni and Ga atoms makes it difficult for the excess Ga atoms to find a favorable position on the crystallographic planes which results in a multimodulated structure. One could imagine that the Ga atoms tend to be excluded from the L2₁ structure of Ni₂FeGa so that a Fe-rich region is formed, which well interprets the EDPs experimental observation that well-defined satellites are more frequently observed than paired diffuse streaks. However, it should be noted that the two types of modulation structures are normally fine clusters dispersed in the L2₁ matrix, which makes it difficult to differentiate them by energy dispersive spectrometry (EDS). The partial replacement of Fe atoms by Ga atoms or Ga atoms by Fe atoms in the Ga-rich and Fe-rich regions locally lowers the atomic order from the L2₁ structure of Ni₂FeGa to that of the B₂ structure of NiGa or NiFe. This results in a decrease of the intensity of the (1 1 1) reflection, which has been observed in the [1 1 0] zone axis EDPs. It should be noted that the modulation of the chemical composition results in a local MT temperature variable, which will be reported in a future paper.

4. Conclusions

The non-equilibrium solidification of Ni₂FeGa melt-spun ribbon leads to a rich variety of micromodulated structures. The local spinodal decomposition produces Fe-rich and Ga-rich micromodulated structures interweaved in the average Ni₂FeGa structure. The Fe-rich microstructure originates from Fe atoms that partially replace Ga atoms on {3 5 0} planes in the Ni₂FeGa structure, which gives rise to a chemically modulated structure with well-defined satellites in the diffraction patterns. The Ga-rich microstructure originates from Ga atoms that partially replace Fe atoms on several planes {3 + n, 5 + n, 0}(n ≥ 0), which gives rise to a multimodulated structure with multi-site correlated atomic distortion displacements along the (1 1 0) directions due to the large size difference between Ga and Ni atoms. The distortion displacement modulation is coupled with the chemical-composition modulation, and the large difference between Ga and Ni atoms in scattering power and in size gives rise to the Warren atomic-size effect, resulting in paired diffuse scattering streaks between the fundamental Bragg diffractions, with the diffuse-scattering intensity high at the low-angle side and low at the high-angle side.

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