Investigation of superparamagnetic fine particles of ordered (B2 + D0₃) structure and ordered B2 structure with monoclinic α′-Mn

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Abstract

This investigation reports on optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and the superconducting quantum interference device (SQUID) magnetometer study of ferromagnetic fine particles formed in Fe–9Al–30Mn–x(C,Si) alloys overaged at 823 K from 2 days to 140 days. The results reveal that the ferromagnetic fine particles of the alloy overaged at 823 K for 140 days come as a result of the lamellar perovskite x-phase owing to a phase transition. Two structures are contained in the ferromagnetic fine particles, one is the the ferromagnetic spinel ordered (B2 + D0₃) structure, the other is the ordered B2 structure with monoclinic α′-Mn. The superconducting quantum interference device (SQUID) magnetometer test shows that a superparamagnetic behavior appears in the alloy if it is overaged at 823 K for 140 days. The zero-field-cooled (ZFC) magnetization measurement reveals that a spontaneous saturation magnetization at Tₛ = 0 K as well as a blocking temperature T_B = 30 K exists in the same sample. The results of the temperature dependence of susceptibility for the ZFC and FC (field-cooled under 100 Oe) data, with hysteresis saturation magnetization behavior, follow a superparamagnetic property. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The understanding the behavior of intermetallics is a challenging problem in materials science, especially in its technical application as well as its increasing attention in materials science from the viewpoint of fundamentals. Intermetallics have a greater variety of crystal structures than metallic elements. Intermetallic compounds that have useful physical properties can lead to functional materials like superconductors based on Nb₃Sn compounds, shape–memory alloys (NiTi), high permeability magnetic materials (NiFe) and permanent magnet alloys (Co₅Sm) [1,2]. Intermetallics crystallize in structures with ordered atom distributions in which atoms are preferentially surrounded by unlike atoms. The atom diffusion in an intermetallic compound is not due to random vacancy motion, but is the result of a complicated ordering atom nearest-neighbor (NN) jump sequence on its own sublattice that does not disturb the ordered arrangement of other atoms on their lattice sites [3–5].

In this paper, it is shown that the alloy Fe–9Al–30Mn–x(C,Si) overaged at 823 K for 140 days gives rise to ferromagnetic fine particles, which are intermetallic compounds. The measurement of the magnetic properties by SQUID, reveals that a super-soft magnetic property (similar to superparamagnetism) exists in the alloy overaged at 823 K for 140 days. In an attempt to characterize the soft magnetic phases present in the fine particle morphologies, the sample overaged at 823 K for 140 days was examined using optical microscopy, scanning electron microscopy...
3. Results and discussion

3.1. Metallographic features of lamellae and fine particle morphologies

The optical micrographs of the alloy in the solid solution and overaged for various times at 823 K are shown in Fig. 1(a–d). First, the micrograph of the alloy 1323 K solid solution treated for 1 h and quenched in water is shown in Fig. 1(a). Here the cellular precipitate structure can not be seen in the grain boundary or the bulk grain. In Fig. 1(b) shown after being overaged at 823 K for 2 days, a typical cellular precipitate phase around the grain boundary is clearly exposed as indicated by arrow shown in Fig. 1(b). A higher magnification photograph of the cellular precipitate phase is shown in Fig. 1(c). It reveals that around the grain boundary, the cellular precipitate phase includes both lamellar structures and embryo fine particle morphologies, as indicated by the arrows shown in Fig. 1(c). After being overaged at 823 K for 60 days, the fine particle morphologies are shown in Fig. 1(d), in which the fine particle morphologies arise from the lamellar perovskite k-phase owing to a phase transition. The lamellar morphologies consist of the γ, κ, B2 and D0₃ phases that has been reported elsewhere [6]. Figs. 2(a) and (b) are optical micrographs of the same alloy overaged at 823 K for 140 days. They reveal the lamellar structures as well as coarsened fine particle morphologies, respectively. Very complicated phases including antiphase boundary segments (APBs) exist in the fine particle morphologies shown in the optical micrograph (Fig. 2(a)). There are two kinds of structures present in the ferromagnetic fine particle morphologies, one is the spinel ordered (B2 + D0₃) structure, the other is an ordered B2 structure with monoclinic α’-Mn. This result will be verified later by TEM.

3.2. SEM observation and analysis

In Fig. 3(a–d), the typical lamellae and fine particle morphologies observed in the alloy overaged at 823 K for 140 days by SEM are shown. Careful analysis of the SEM micrograph in Fig. 3(a), reveals that the microstructures consist of three phases, i.e. the lamellar structures and the ferromagnetic fine particle morphologies, which are comprised of spinel and porous structures indicated by the arrows, respectively. Because the lamellar structures are being reported elsewhere [6], this paper will focus on the study of the spinel and porous structures by TEM. The corresponding SEM higher magnification photographs of spinel, porous, and lamellar phase transition to spinel ordered structures are shown in Figs. 3(b), (c) and (d), respectively. Fig. 3(e) shows the same alloy overaged at 823 K for 60 days, revealing that only lamellar and porous structures...
can be seen. In order to know whether or not a spinel ordered structure actually exists, a higher magnification micrograph of spinel structure showing in Fig. 3(f) must be obtained. This micrograph reveals that there is not any spinel ordered structure appearing in the micrograph. Therefore, by observing the different microstructures between the above two samples (aged at 140 days versus 60 days), it is safely deduced that varying aging times will induce different magnetic properties. The notation will be verified later in the experiment study by the SQUID magnetometer.

3.3. TEM observation and analysis

3.3.1. Fine particle morphologies — the ferromagnetic spinel ordered \((B_2 + D_{03})\) structure

Fig. 1. The optical micrographs of the alloy solid solution and after overaging at 823 K for given times. (a) 1323 K for 1 h solution treated and quenched in water, (b–c) overaged for 2 days, (d) overaged for 60 days, respectively. The cellular phase begins to precipitate along the grain boundary region shown in (b), and the cellular phase contains the lamellar structures and fine particle morphologies indicated by arrow shown in the higher magnification micrograph (c).

Fig. 2. The optical micrographs of same alloy overaged at 823 K for 140 days. (a) The fine particle morphologies; (b) the lamellar structures. A similar antiphase boundary segments (APBs) indicated by arrow show in (a).
Fig. 3. Scanning electron microscopy (SEM) micrographs of the alloy overaged at 823 K for 140 days, the microstructures of the sample consist of three phases. (a) Lamellae, and the fine particle morphologies which are comprised of spinel and porous structures. The corresponding higher magnification micrographs show the (b) spinel, (c) porous, and (d) lamellar phase transition to spinel structure, respectively. (e) The same alloy overaged at 823 K for 60 days showing only lamellar and porous morphologies can be seen, (f) the enlarger magnification of the fine spinel region, revealing the fine spinel particles can not be seen in the alloy overaged at 823 K for 60 days.

Figs. 4(a)–4(f) are a series of transmission electron microscopy (TEM) micrographs taken from the fine particle morphologies’ spinel structures of the alloys overaged at 823 K for 140 days. Their corresponding SEM micrograph is shown in Fig. 3(b). Fig. 4(a) is a typical selected area diffraction pattern (SADP) zone axis [\(\{133\}\)]\(_{B2 + D03}\)/[\(\{340\}\)]\(_{k}\) \((hkl = \text{ordered } B2 \text{ or } 2(hkl) = \text{ordered } D0_3; hkl = \kappa\text{-phase})\). Careful analysis of the SADP zone axis, reveals it as \((01 \{1\})_{B2}\) or \((02 \{2\})_{D03}/(0 \{0\}2)\). Fig. 4(b) is a dark field (DF) image for \(01 \{1\}_{B2}; 02 \{2\}_{D03}\) or \(0 \{0\}2\), reflections that corresponds to Fig. 4(a). Fig. 4(c) is a bright field (BF) image. From the TEM micrographs of Fig. 4(a–c) analysis, it can be safely inferred that the ferromagnetic spinel ordered \((B2 + D0_3)\) structure results from the lamellar perovskite \(\kappa\)-phase owing to a phase transition. For further confirmation that the ferromagnetic spinel phase is the ordered \((B2 + D0_3)\) structure, TEM micrographs taken from the same specimen are shown in Fig. 4(d–f). The SADP image taken from the local spinel ordered structure shown in Fig. 4(d) reveals the zone axis as \([\{121\}]_{B2 + D03}\). Fig. 4(e) is a dark field image formed using \(210\)\(_{B2}\) or \(420\)\(_{D03}\) reflections corresponding to Fig. 4(d). A spinous morphology, indicated by the arrow shown in Fig. 4(e), is the position in which the periodically fluctuating layer of smaller \(\kappa\)-phases, with a 45° direction decomposition from the lamellar perovskite \(\kappa\)-phase. The result has been confirmed by TEM, and reported elsewhere [6,13,24]. Fig. 4(f) is a bright-field image. Careful analysis of the BF and DF images (Fig. 4(e–f)), the phase transition mechanism indicates that the periodically fluctuating layer of smaller \(\kappa\)-phase.
decomposes along one of three elastically soft $<100>$ directions from the lamellar perovskite $\kappa$-phase. Subsequently, the ferromagnetic spinel ordered ($B_2 + D_0_3$) structure preferentially develops along the nearest-neighbor (NN) antiphase boundary segments (APBs) at the same time [6–8,13,24]. The NN is connected with $1/2 a_0 <111>$ APBs of ordered $B_2$ or $1/4 a_0 <111>$ APBs of ordered $D_0_3$, which is accordingly called the easy direction of magnetization of the soft magnetic materials [6–8,13,24].

3.3.2. Fine particle morphologies — the ordered $B_2$ structure with monoclinic $\alpha'$-Mn (porous structures)

Figs. 5(a)–5(f) are a series TEM micrographs taken from the porous structures shown in Fig. 3(c). For a confirmation of the ordered $B_2$ [(Fe/Mn)Al] structure’s existence in this region, the selected area diffraction pattern (SADP) demonstrates the zone axis of the ordered [111] $B_2$ structure shown in Fig. 5(a). Fig. 5(b) is the DF image formed using the ordered $\overline{1} 0_1$ reflection corresponding to Fig. 5(a). The Mn atom concentration at the antiphase boundary segment (APBs) of the ordered $B_2$ structure causes the $\alpha'$-Mn phase (monoclinic structure) to precipitate preferentially along the APBs of the ordered $B_2$ structure. The Mn-richness of the monoclinic $\alpha'$-Mn phase is verified by EDS spectra and shows that it preferentially precipitates along the APBs of the ordered $B_2$ structure as has been reported elsewhere [13]. The monoclinic $\alpha'$-Mn precipitates along the APBs of the ordered $B_2$ structure.

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Fig. 4. Transmission electron microscopy (TEM) micrographs of the alloy overaged at 823 K for 140 days, taken from the spinel structures of the fine particle morphologies, showing ferromagnetic spinel ordered ($B_2 + D_0_3$) structures result from lamellar perovskite $\kappa$-phase owing to a phase transition. (a) Selected area diffraction pattern (SADP) of the zone axis $[133]_{B_2 + D_0_3}$/[340] $\kappa$-phase; (b) dark field (DF) image for $01 \_1$ reflections; (c) bright field (BF) image, (d) SADP image taken from local spinel structure reveals the zone axis $[12\overline{1}]_{B_2 + D_0_3}$; (e) DF image formed using $2\overline{1} 0_1$ or $4\overline{2} 0_{100}$ reflections corresponding to (d), (f) BF image.

Fig. 5. TEM micrographs of the same specimen are taken from the porous structures which consist of the ordered B2 structure with monoclinic \( \alpha' \)-Mn. (a) Selected area diffraction pattern of the [111] ordered B2 zone axis, (b) \( \mathbf{0}_{h2} \) ordered B2 dark field image, (c) SADP demonstrates the monoclinic [T3 0] \( \alpha' \)-Mn zone axis, (d) DF image formed using the monoclinic 0 0 3 \( \alpha' \)-Mn reflection corresponding to (c), (e) high resolution TEM (HRTEM) image showing ordered B2 structure, (f) HRTEM image taken from the monoclinic \( \alpha' \)-Mn.

that also gives rise to the displacement fringe contrast (lattice-misfit strains) which is apparent in this dark-field image [9–13]. By careful analysis, the displacement fringe contrast revealed in the DF image is the result of the formation of a thin layer \( \alpha' \)-Mn phase along the APBs of the ordered B2 structure that strains the ordered B2 lattice.

After properly tilting the specimen and observing the same region, a different SADP is obtained as shown in Fig. 5(c). The crystallographic normal demonstrates the monoclinic [T3 0] \( \alpha' \)-Mn zone axis. This monoclinic \( \alpha' \)-Mn phase has lattice parameters of \( a = 6.6 \) Å; \( b = 7.9 \) Å; \( c = 6.4 \) Å and \( \beta = 109.4^\circ \). Fig. 5(d) is the dark field image using the monoclinic 0 0 3 \( \alpha' \)-Mn reflection corresponding to Fig. 5(c). From the DF image analysis, \( \delta \)-fringe layers exist in the monoclinic \( \alpha' \)-Mn phase [14,15]. The monoclinic \( \alpha' \)-Mn phase is also surrounded by the ordered B2 structure as revealed in this DF image. The monoclinic \( \alpha' \)-Mn phase transforms from the ordered B2 structure and shows that the fault fringes and antiphase boundary segments (APBs) exist in the ordered B2 structure. A high resolution TEM (HRTEM) image (Fig. 5(e)), taken from the same specimen, shows the presence of an ordered B2 structure with monoclinic \( \alpha' \)-Mn, and the glassy film (i.e. the faint wavy fringes) existence in the grain boundary as indicated by arrow (Fig. 5(e)). The glassy film transition is characterized by the constant value of susceptibility—
temperature ($\chi - T$) curve below blocking temperature ($T_B$) for the FC data at low magnetic fields as obtained by SQUID shown in Fig. 6 [16]. The bent lattice B2 planes along the interface of ordered B2 and monoclinic $\alpha'$-Mn can be clearly observed. Also, in the interface there are a number of edge dislocations, as indicated by arrow. Fig. 5(f) is a high resolution TEM image taken from the monoclinic $\alpha'$-Mn. By careful measurements of the lattice space, it is found that the d-spacing of the monoclinic $\alpha'$-Mn is 4.7 Å, therefore, the plane (Fig. 5(f)) can be reasonably inferred to be (011) $\alpha'$-Mn.

3.4. Superparamagnetic property

Superparamagnetism (SPM) characterizes small magnetic particles with very large magnetic moment. The particle is ferromagnetic when it is sufficiently small. It is no longer energetically favorable to form the domain structure that characterizes bulk ferromagnetism. The magnetic anisotropy of the ferromagnetic particle generates potential barriers, which at low temperatures prevent the magnetization vector from rotating to the direction of minimum energy in the applied magnetic field. Under these circumstances, such a particle is called ‘blocked’. As the temperature is gradually increased, the magnetization vector will be thermally agitated over the potential barriers, thus permitting the particle to rotate the magnetization vector to the direction of its thermal equilibrium. Under such a condition, the particle is then referred to as ‘unblocked’. The temperature below which the particle becomes blocked is called the ‘blocking temperature’ (i.e. the transition temperature between the ferrimagnetic and superparamagnetic state is called the blocking temperature).

Above the blocking temperature, the magnetization vector of the ferromagnetic particle rotates in a applied field in a way similar to that of a paramagnetic ion, and therefore the ferromagnetic particle is called superparamagnetic.

Fig. 6 shows the temperature dependence of the magnetic susceptibility ($\chi = M/H$) of the alloy overaged at 823 K for 140 days as measured by SQUID. The measured values displayed show both the zero-field-cooled (ZFC) data and the field-cooled (FC) data within a field of 100 Oe. In Fig. 6, it is found that the sharp peak in the susceptibility–temperature ($\chi - T$) curve occurs when blocking temperature is at 30 K ($T_B = 30$ K) for the ZFC data, and at the almost constant value of $\chi - T$ curve below this temperature ($T_B = 30$ K) for the FC data in a field of 100 Oe. These constitute the signature of a spin-glass transition [16]. The spin-glass transition is probably due to the dilute concentration of (Fe/Mn) and Si that is present in the nonmagnetic matrix. It is interesting to note that in Fig. 6 the $\chi - T$ curves — ZFC and FC do not coalesce above the blocking temperature ($T_B = 30$ K) until they reach room temperature at $T_R = 300$ K, and that the spontaneous saturation magnetization occurs at $T_S = 0$ K. Furthermore, the FC data lies above the ZFC data all the way out to room temperature. This magnetic property can be deduced in terms of the progressive unblocking of the ferromagnetic fine particles and their subsequent SPM contribution to the temperature-dependent part of $\chi - T$ curve. Careful analysis of the ZFC data in Fig. 6, indicates that at higher temperatures ($T > T_B$), the ZFC data for the $\chi - T$ curve progressively decreases as $1/T$, in accordance with the Curie–Weiss law: $\chi = C/(T - \theta)$ at low magnetic fields. Here $\theta$ is a constant, with the dimensions of the temperature for any one substance, and $\theta$ is equal to zero for those substances which obey Curie’s law. $C$ is the Curie constant per gram. Fig. 6 also shows the tendency of the ZFC data for $\chi - T$ curve to decrease as the temperature increases (i.e. the $\chi - T$ curve for the ZFC data decreases at $1/T$). This explains the fact that the fine particles are all unblocked at some low temperature ($T > T_B$). Finally, Fig. 6 reveals that the FC data always lies above the ZFC data. This result is explained as follows; Upon cooling the sample in a magnetic field (100 Oe), the SPM particles become trapped (i.e. blocked) in their higher-magnetized state and have not the thermal energy required to pass over the potential barriers to return to their lower-magnetized equilibrium configuration [16]. The ZFC and FC data measured by SQUID for the alloy overaged at 823 K for 60 days are shown in Fig. 7. The $\chi - T$ curve for the FC data measurements were also performed in a small magnetic field of 100 Oe. Fig. 7 gives an indication that the blocking temperature ($T_B$) for the sample is around 60 K. Above this temperature, the fine particles become

![Temperature dependence of the magnetic susceptibility (\(\chi - T\) curve) of the alloy overaged at 823 K for 140 days. The measurements were carried out both at zero-field-cooling (ZFC), and at field-cooling (FC) in a field of 100 Oe.](image)
unblocked and the system becomes SPM. The \( \chi - T \) curves of Fig. 6 show a feature that is different from that shown in Fig. 6. The blocking temperature of the ZFC data in Fig. 7 has shifted to a higher temperature (\( T_B = 60 \) K). Also, the ZFC and FC curves do not coalesce above the ZFC blocking temperature. By comparing Fig. 6 and Fig. 7, a great disparity in the susceptibility (\( \chi \)) and the blocking temperature (\( T_B \)) is found. The maximum value of susceptibility (\( \chi \)) of the field cooled (FC) data, for the sample overaged at 823 K for 140 days (Fig. 6) is about four times that of the FC data, for the sample overaged at 823 K for 60 days (Fig. 7). This is believed to be due to the effect of the structure induced by field cooling and the co-operative effect of fine particle magnetic moments that are operating in the system.

The corresponding optical micrographs and SEM micrographs for the above two samples are shown in Fig. 1(d), Fig. 2(a), and Fig. 3(b), Fig. 3(f), respectively. Careful analysis of the micrographs and its magnetic property reveals that as the fine particle morphologies in the micrograph become finer, the susceptibility and SPM behavior also improves. The above results confirm that the inter-particle interaction hindering rotation of particle magnetic moment is less if the volume fraction of SPM particles is large [17]. The change in the blocking temperatures for the above two samples (\( T_B = 30 \) K vs. \( T_B = 60 \) K) is primarily due to different fine particle sizes and fraction amounts in the fine particle metallic-micrographs as shown in Fig. 2(a) with Fig. 1(d) and Fig. 3(b) with Fig. 3(f), respectively. It has been widely accepted that the blocking temperature can be defined by the following equation [7,18]: 
\[
KV = 25\kappa_BT_B,
\]
therefore, 
\[
T_B = KV/(25\kappa_B),
\]
where, \( K \) is the anisotropy energy per unit volume, \( V \) is the volume of the single domain magnetic particle, \( \kappa_B \) is the Boltzmann’s constant, and \( T_B \) is the blocking temperature. Thus it can be seen that the blocking temperature is determined by the anisotropy energy (\( K \)) of the unit magnetic particle volume, and the size of the single domain magnetic particle (\( V \)). \( V \) equals \( 1/N_V \), where \( N_V \) is the number of magnetic fine particles per unit test volume (\( \text{Å}^{-3} \)). The anisotropy energy usually comes from the shape of the particle, the crystalline direction, and the strain within the single domain particle. According to the equation 
\[
T_B = KV/(25\kappa_B),
\]
it can be reasonably inferred that the change in the blocking temperatures (\( T_B \)) is predominantly due to the change in the volume (\( V \)) of the unit ferromagnetic fine particle size and anisotropy energy (\( K \)) per unit volume. Therefore, referring back to Fig. 6 and Fig. 7, it is revealed that the sample overaged at 823 K for 140 days (Fig. 6) shows a lower average blocking temperature (\( T_B = 30 \) K) and therefore a smaller anisotropy energy per unit volume and smaller size per single magnetic particle. In contrast, the sample overaged at 823 K for 60 days (Fig. 7) gives a higher average blocking temperature (\( T_B = 60 \) K) and thus larger anisotropy energy per unit volume and larger size per single magnetic particle (or very few magnetic particles per unit test volume). The changes in the ferromagnetic fine particle size mean that the number of fine particles in the two samples are different. In particular, the sample with a longer overaged time (140 days), has more fine particles than the shorter overaged time (60 days) sample. The notion is in exact agreement with the series of optical micrographs as shown in Fig. 1(d) with Fig. 2(a), and the SEM micrographs shown in Fig. 3(b) with Fig. 3(f). On the other hand, in the present study work, the ferromagnetic spinel ordered (\( \text{B}_2 + \text{D}_0_3 \)) fine particles can be found in greater amounts in the longer aged sample (overaged 140 days), but they disappear (or are very few) in the shorter aged sample (overaged 60 days) as shown by the SEM photograph (Fig. 3(f)).
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hysteresis losses. One special case in which the details of the magnetization loop can provide considerable metallurgical information is that of the alloy overaged at 823 K for 140 days which contains ‘superparamagnetic’ particles. These fine particles consist of the ferromagnetic spinel ordered (B2 + D0₃) structure shown in Fig. 3(b) with Fig. 4(d–f), and the ferromagnetic ordered B2 structure with monoclinic α’–Mn particle shown in Fig. 3(c) and Fig. 5(d–f). These are ferromagnetic particles that are sufficiently fine that the assembly is in thermal equilibrium within an applied field. This yields a non-hysteretic loop. All of the figures mentioned above clearly demonstrate the superparamagnetic nature of the alloy overaged at 823 K for 140 days [7,19–22]. The $M–H$ curves, measured at low temperatures (5, 50, and 150 K), of the alloy overaged at 823 K for 60 days are shown in Fig. 9. The hysteresis loops display a soft magnetic property and reveal an almost constant magnetization value for the magnetic moment per unit mass $39–38.7$ (emu g $^{-1}$) throughout the temperature range of about 5–150 K. By comparing Fig. 8 and Fig. 9, it is evident that the alloy overaged at 823 K for 140 days possesses superior ferromagnetism, a higher susceptibility ($\chi = M/H$), and a greatly increased soft magnetic property than that of the alloy overaged at 823 K for 60 days. By looking at the optical micrographs Fig. 1(d) with Fig. 2(a) and SEM micrographs Fig. 3(b) with Fig. 3(f) observations along with the magnetic property study, it is clearly revealed that the longer overaged alloy (at 823 K for 140 days) has much more the fine particle morphologies, and has achieved a higher saturation magnetization.

The saturation magnetization of ferromagnetic materials depends on the number of uncompensated spins in the magnetic atoms. Ferromagnetism this is the result of a net spontaneous magnetization which arises from the alignment of the net magnetic moments. It is also known that the ferromagnetism is owing essentially to the electron spins, and the electron spin imbalance in the ferromagnetic atoms is just the exchange forces [7], (i.e. the spin moments of neighboring magnetic atoms are aligned by exchange forces, and the exchange forces are responsible for the ferromagnetism as well). If the magnetic atoms are in sufficiently close contact with each other to favor parallel spins so that magnetic electrons can be exchanged between neighboring magnetic atoms, a cooperative phenomenon may occur which spontaneously aligns the spins of all the magnetic carriers in the lattice and binds their spin moments very strongly. This condition generates stronger nearest-neighbor (NN) exchange forces, and produces a stronger ferromagnetic exchange interaction for a spontaneous magnetization. This spontaneous magnetization characteristic of ferromagnetic materials is also coincident with this experiment as shown in Fig. 6. As seen here, the nearest-neighbor (NN) is connected with $1/2 a_0 < 111 >$ APBs of ordered B2 (or $1/4 a_0 < 111 >$ APBs of ordered D0₃), which is accordingly called the direction of easy magnetization of the soft magnetic materials. The exchange between electrons of neighboring magnetic atoms in ferromagnetic materials, (which causes the individual magnetic moments of all magnetic atoms in such materials to be aligned), is the principal contribution to the magnetic energy of a specimen. Therefore, such materials will possess a spontaneous magnetization at zero field (ZFC), for which the result

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Fig. 8. Magnetization ($M$) versus magnetic field ($H$) $M–H$ curves measured at low temperature 5, 50, and 150 K of the alloy overaged at 823 K for 140 days.

Fig. 9. Magnetization ($M$) versus magnetic field ($H$) $M–H$ curves measured at low temperature 5, 50, and 150 K of the alloy overaged at 823 K for 60 days.
is consistent with this experiment as shown in Fig. 6. as indicated by the ZFC data with a spontaneous magnetization at \( T_S = 0 \) K. The investigation of spontaneous magnetization can present interesting structural information about the materials in question. The position and density of magnetic domain walls as well as their special features can again be of great importance to the study of the structures of materials. Therefore, it is believed that the alloy overaged at 823 K for the longer time (140 days) induces fine particle morphologies which possess long range ordered structures. These structures can be regarded as large high anisotropy ferromagnetic phases whose existence in the fine particle morphologies are mainly responsible for the observed ferromagnetism [7,16–24]. However, according to the TEM observation, reveals that the ferromagnetic spinel ordered (B2 + D0₁) structure results from the lamellar perovskite \( \kappa \)-phase owing to a phase transition [13,24]. The phase transition mechanism of lamellar perovskite \( \kappa \)-phase is first decomposition along one of the three elastically soft <100> directions forming the periodically fluctuating layers of smaller \( \kappa \)-phase ([Fe,Mn]₃AlC). Subsequently the ferromagnetic spinel ordered (B2 + D0₁) structure preferentially develops along the nearest-neighbor (NN) antiphase boundary segment (APBs) at the same time. There exists a nearly 45° difference between the smaller \( \kappa \)-phases and the ferromagnetic spinel ordered (B2 + D0₁) structures [6,8,13,24]. Summarizing the above investigations, it can be concluded that the super-soft magnetic property of this alloy overaged at 823 K for 140 days is mainly attributable to the fine particle morphologies, which consist of the ferromagnetic spinel ordered (B2 + D0₁) structure and ordered B2 structure with monoclinic \( \alpha ' \)-Mn.

4. Conclusions

The superparamagnetic fine particles of the alloy overaged at 823 K for 140 days consist of the ferromagnetic spinel ordered (B2 + D0₁) structure, and ordered B2 structure with monoclinic \( \alpha ' \)-Mn. These ferromagnetic fine particles result from lamellar perovskite \( \kappa \)-phase owing to a phase transition.

TEM selected area diffraction pattern (SADP) reveals that the orientation relationship between the ferromagnetic spinel ordered (B2 + D0₁) structure and \( \kappa \)-phase can be demonstrated as \([0\overline{1} 1]_{B2}/(0\overline{2} 2)_{D01}/(0 0\overline{2})_{\kappa} ; [1 1 0]_{B2 + D01}/[3 4 0]_{\kappa} \).

Through SQUID magnetic measurements and SEM investigation, it is confirmed that the ZFC data for the \( \chi \sim T \) curve reveals a low blocking temperature (\( T_B \)) and many more the fine particles in the sample. This conclusion correlates with the equation: \( T_B = KV/ (25K_B) \). Also, the \( \chi \sim T \) curves appearing the ZFC and FC do not coalesce until they reach room temperature, and the FC data lies above the ZFC data all the way out to room temperature.

SQUID measurements reveal that at higher temperatures (\( T > T_B \)), the ZFC and FC data for the \( \chi \sim T \) curves decreases progressively as \( 1/T \) at low magnetic fields, exactly in accordance with the Curie–Weiss law: \( \chi = C/(T - \theta) \).

The results of temperature dependence of susceptibility (\( \chi \))-ZFC and FC (field-cooled under 100 Oe) data with hysteresis saturation magnetization measured by SQUID, of the alloy overaged at 823 K for 140 days, follow a superparamagnetic property.

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