Influence of magnetization on the reordering of nanostructured ball-milled Fe-40 at. % Al powders

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Deformation and nanocrystallization created by ball milling in Fe-40 at. % Al powders give rise to a progressive structural disorder and a spontaneous magnetization. Annealing tends to restore the structurally ordered paramagnetic state. The ordering-disordering process brings about a volume change clearly related to the saturation magnetization. This effect is associated with variation of the density of states at the Fermi level. The reordering temperature exhibits an anomalous field dependence, which can be explained considering the combined effect of directional magnetic order and structural order. [S0163-1829(98)51042-9]

Ordered Fe-Al alloys with Al content above 33 at. % are paramagnetic, however they evolve toward a ferromagnetic state as structural disorder increases. These Fe rich alloys have the $B2$-type ordered structure, where Fe atoms occupy the α sites and Al atoms and the rest of Fe atoms occupy randomly the β sites. It has been proposed[1,2] that the interaction between Fe atom pairs located at a_0 distance is antiferromagnetic, whereas it becomes ferromagnetic for a distance $(3/4)^{1/2}a_0$. However, the paramagnetic character of the equiatomic alloy seems to be in contradiction to this hypothesis. The induction of ferromagnetism by plastic deformation in bulk Fe-Al alloys has been thoroughly investigated by Takahashi and co-workers.[3,4] It has been shown that the appearance of spontaneous magnetization is associated with the rearrangement of the Fe atoms in the vicinity of the antiphase boundaries at the superlattice dislocations with [110] gliding planes. It is noteworthy that in plastically deformed DO_3 and $B2$ Fe-Al compounds there exists a strong uniaxial anisotropy of pair ordering origin.[3,4]

In order to get deeper insight on the microscopic mechanism governing the relation between the structural order-disorder and the corresponding magnetic disorder-order transformations some experiments have been carried out on ball milled Fe-40 at. % Al. Powders with this composition were ball milled[5,6] in a planetary mill (Fritsch Pulverisette 7) at 250 rpm for 0, 0.5, 1.5, 3, 6, 12, 23, and 72 h. 2 gr of powder were sealed under argon in agate vials ($V=12$ ml) together with 3 zirconia balls ($\varnothing=10$ mm) with a ball to powder weight ratio of 4. The powder samples were characterized by x-ray diffraction, vibrating sample magnetometry (VSM) and differential scanning calorimetry (DSC). Table I summarizes the dependence of the lattice constant, a_0, effective crystallite size, $\langle D \rangle$, microstrains, $\langle \epsilon^2 \rangle^{1/2}$, and long-range order parameter, LRO on the milling time. Figure 1(a) shows a close relation between the lattice parameter and the saturation magnetization at room temperature, M_S, for different milling times. The saturation magnetization was ob-

tained from the field dependence of the magnetization measurements. The classical law of approach to saturation, $M = M_S(1-a/H-b/H^2)+\chi H$, was used, where H is the applied field, χ is the field independent susceptibility, and a and b are coefficients which depend on the magnetic properties of the material. The milled powders were annealed for 1 h under vacuum, at temperatures 403, 523, 673, or 973 K. The temperatures were selected according to different regions obtained from DSC measurements. Table II illustrates the dependence of the relevant parameters on the annealing temperature. Figure 1(b) clearly shows the correlation between lattice parameter and magnetization during the structural reordering.

The DSC results (see Fig. 2) show that the structural reordering consists of two processes. They are characterized by the peaks around 420 and 680 K, respectively. Kinetics studies lead to approximate activation energies of 1.7 and 3.5 eV for each process. After milling for 72 h (disordered state), the sample is composed of nanosized grains with a high concentration of point defects and highly structurally disordered grain boundaries.[5,6] At this stage, both, boundaries and

TABLE I. Structural parameters of Fe-40 at. % Al powders ball milled for different times. Shown in brackets are the estimated statistical errors.

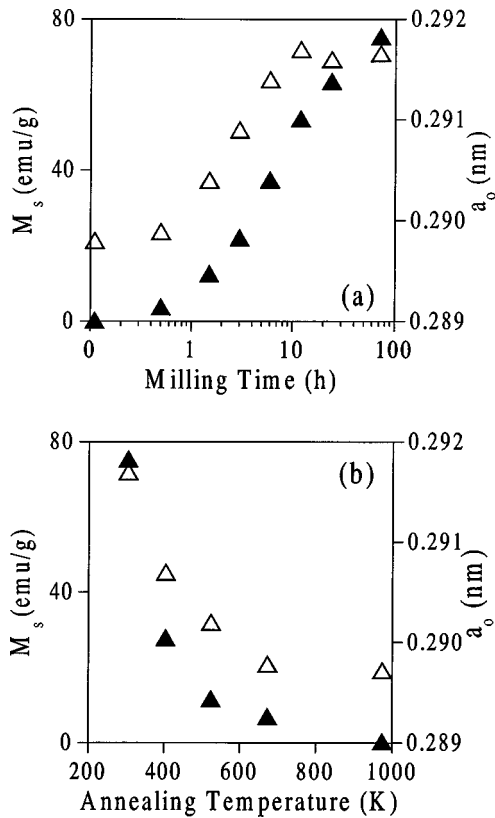| Milling Time (h)	a_0 (nm)	$\langle D \rangle$ (nm)	$\langle \epsilon^2 \rangle^{1/2}\ 10^3$	LRO
0	0.28980(2)	207(9)	0.56(3)	1.00(1)
0.5	0.28989(4)	43(3)	1.6(2)	0.97(2)
1.5	0.2904(8)	30(7)	4.3(1)	0.91(2)
3	0.2909(1)	25(3)	5.1(1)	0.85(2)
6	0.2914(2)	24(5)	5.4(1)	0.78(2)
12	0.2917(1)	23(5)	5.3(2)	0.71(2)
23	0.2919(1)	21(5)	5.3(2)	0.68(3)
72	0.2917(1)	13(2)	6.4(1)	0.66(5)

FIG. 1. Dependence of the room temperature saturation magnetization M_S, (full symbols) and the lattice parameter a_0 (empty symbols) on (a) milling time and (b) posterior annealing temperature for Fe-40 at. % Al powders.

grains are ferromagnetic.[7] According to Table II, the grain size does not show any remarkable variation after 1 h annealing at 403 K, therefore, the first DSC peak at $T = 420$ K, hereafter T_r (reordering temperature) should originate from annealing out the antisite defects and relaxation processes at the grain boundaries.[5,6] The lattice parameter decreases 50% and the saturation magnetization drops 65% with respect to the total change between the as-milled and the fully ordered state. Consequently, after annealing at 403 K, the ferromagnetic order is mainly restricted to the grain boundaries, which represent an important percentage of the sample volume. The second calorimetry peak at 680 K corresponds to the recrystallization of the alloy.[5,6]

The temperature dependence of the dc total susceptibility, M/H, for the sample milled for 72 h was measured, under vacuum or argon atmosphere, for different magnetic fields

TABLE II. Structural parameters of Fe-40 at. % Al powders ball milled for 72 h and annealed for 1 h at different temperatures. Shown in brackets are the estimated statistical errors.

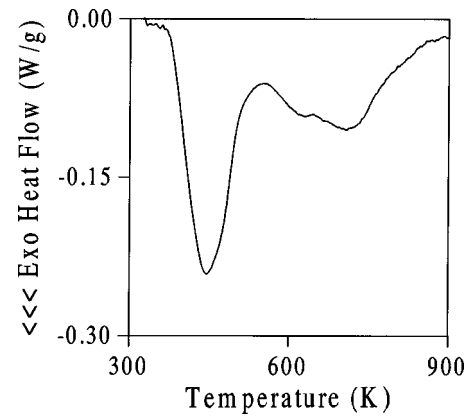| Anneal. Temp. (K)	a_0 (nm)	$\langle D \rangle$ (nm)	$\langle \epsilon^2 \rangle^{1/2} 10^3$	LRO
As-milled	0.2917(1)	13(2)	6.4(1)	0.66(5)
403	0.2907(1)	14(2)	5.4(1)	0.74(3)
523	0.2902(1)	18(3)	4.5(1)	0.97(2)
673	0.2898(1)	26(4)	1.1(2)	0.98(3)
973	0.28972(2)	49(3)	0.49(3)	1.00(1)

FIG. 2. DSC scan for the as-milled 72 h Fe-40 at. % Al powder at $\beta = 20$ K/min heating rate.

and at different heating rates. Figure 3(a) shows the temperature dependence of the dc susceptibility at different applied fields. The derivative of the susceptibility [Fig. 3(b)] exhibits, for low applied fields, two peaks in agreement with DSC measurements (Fig. 2). Thus it seems reasonable to assume that the two steps of the decrease of the susceptibility correspond to the two processes observed in DSC. However, it is noteworthy that the second peak of the derivative of the sus-
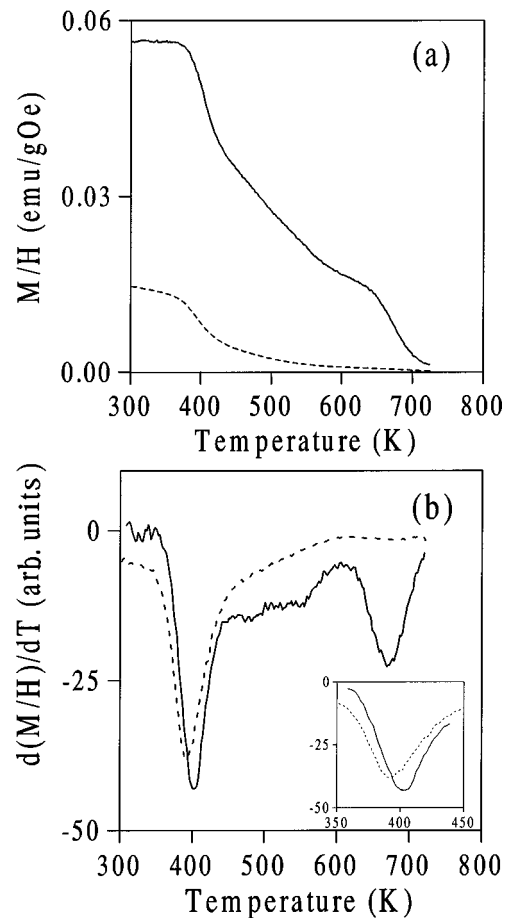

FIG. 3. Temperature dependence of (a) the dc susceptibility M/H, and (b) its derivative, $d(M/H)/dT$, for $H = 0.05$ kOe (solid line) and $H = 5$ kOe (dashed curve) for the as-milled 72 h Fe-40 at. % Al powder. Measurements were carried out at $\beta = 1.3$ K/min in vacuum. The inset shows an enlargement of the first peak.
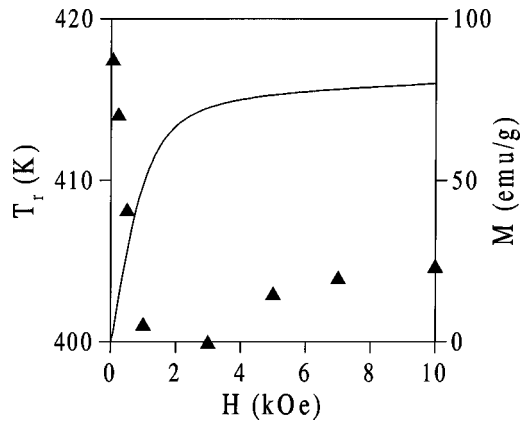
FIG. 4. Dependence of the reordering temperature T_r (symbols), measured at 3 K/min in argon, and initial magnetization curve (solid line) of the as-milled 72 h Fe-40 at. % Al powders.

ceptibility nearly disappears when heating in applied fields larger than the saturation field.[8] The extrapolation to zero field of the temperature at which derivative of the susceptibility has a peak corresponds with T_r observed in DSC. Thus we take $T_r(H)$ as the temperature at which the derivative of the susceptibility has a peak.

The reordering temperature $T_r(H)$ has been measured for different applied fields during the heating process and the results are shown in Fig. 4. For comparison, we have included the room temperature magnetization curve of the as-milled sample. A striking feature is exhibited by Fig. 4. When the field applied during heating is lower than the room-temperature saturation field, typically of 2.5–3 kOe, T_r decreases with the applied field. This decrease reaches about 20 K between 0.05 and 3 kOe. For higher applied fields, T_r slowly increases with the field. The total increase between 3 and 10 kOe is 4 K.

Since the magnetic field is expected to stabilize the ferromagnetic phase, which is associated with the structural disorder, an increase of the reordering transition is also expected. This behavior is, indeed, observed in the high-field regime. However, the decrease of T_r with the applied field at the low-field regime suggests that other effects should be taken into account. According to the magnetization curve shown in Fig. 4 the range of magnetic fields for which T_r decreases with increasing field corresponds to the range for which magnetization processes take place. The sign of the field dependence of T_r is reversed once the applied field becomes larger than the saturation field. Therefore, the results in Fig. 4 indicate that the applied field influences the reordering temperature in two ways:

(i) due to the magnetic free energy,[9] T_r should increase by an amount proportional to $\mu_B H/k_B$ where μ_B is the Bohr magneton and k_B the Boltzmann constant. For $H=10$ kOe this increase should be about 1 K, in qualitative agreement with the experimental results at high fields;

(ii) due to some effect associated with the magnetization process. The large decrease of the temperature, 20 K, cannot be quantitatively explained by strictly magnetic contributions of the applied field to the free energy.

From the experimental results reported here two important aspects should be discussed. First, we analyze the re-

markable correlation between lattice constant and magnetization shown in Figs. 1(a) and 1(b). Models developed to explain the induction of ferromagnetism by disordering ordered paramagnetic alloys invoke either the concept of distance dependent exchange interactions or the nearest-neighbor dependence of the magnetic moment.[1–4] Considering that the exchange dependence of the interatomic distances is of second order in metallic systems,[10,11] it seems reasonable to invoke a different argument. The results of Figs. 1(a) and 1(b) indicate as a reasonable cause of ferromagnetism the effects of the volume expansion-contraction have in the electronic band structure. Theoretical band-structure calculations have shown that band narrowing and Fermi-level shifts due to the expansion of the lattice increase the magnetic moment in Fe-50 at. % Al alloys.[12] Although disorder is also expected to affect the electronic band structure,[13] we propose that the lattice expansion induced by disordering has a sizable contribution on the appearance of ferromagnetism.

The second aspect is the apparent paradox shown in Fig. 4 at the low-field regime. According to this, moderate magnetic fields ease the reordering transition, which leads to the elimination of the ferromagnetic order. The following argument explains this apparent paradox. It is known that heating an alloy in applied magnetic fields gives rise to directional order.[14] This is the case in Fe-Al alloys, in which pair ordering anisotropy has been widely analyzed.[3] The preferred magnetization direction fluctuates from grain to grain in the as-milled sample as indicated by the magnetization curve (see Fig. 4). The mismatching of the magnetization directions at adjacent grains leads to a mismatching of the biasing effect of the magnetization on the reordering. In other words, the magnetization induces pair ordering locally, nevertheless the fluctuations of the magnetization provoke macroscopical disorder, thus hindering the full reordering, i.e., increasing T_r. As the field is increased the magnetization fluctuations decrease; consequently overall directionality of the pair ordering increases, hence it becomes easier to reorder the sample from a macroscopic point of view. When a saturating field is applied the magnetization is uniform through the whole sample and the biasing effect of the magnetization on the reordering process is also uniform everywhere thus promoting order. However, high fields tend to stabilize the magnetization, which is linked with disorder. Therefore, at high fields the field hinders again the reordering, hence T_r increases again.

In conclusion, we have studied the disordering (ball milling) and posterior ordering (annealing) in Fe-40 at. % Al powders. We have found that an important contribution to the magnetization of these materials comes from changes in the lattice parameter induced in the order-disorder transitions. This contribution is linked to the modifications in the electronic band structure induced by volume changes. The reordering temperature obtained from the derivative of the dc susceptibility has been found to depend strongly on the applied field. Due to directional ordering, the fluctuation of the local magnetization orientation causes the delay of the reordering transition. As this fluctuation decreases for intermediate applied fields, the reordering takes place easier as the

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