Comparison of long- and short-range magnetic-order development in Ni_3Mn†

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The magnetic-order development in polycrystalline Ni-Mn alloys near the Ni_3Mn composition has been studied as a function of atomic ordering during anneal at both 500°C (short range) and 400°C (long range) after an initial quench from 1000°C. The data were analyzed using a simple Langevin superparamagnetism model to obtain a qualitative description of the magnetic-cluster-growth kinetics in each case. For annealing at 500°C, the clusters seem to "pop in" during the initial 5-min anneal, remain at constant concentration up to 3–5 h, and then decrease in concentration. The cluster moment increases smoothly, with a roughly exponential time dependence and a time constant of about 20 h. For annealing at 400°C, the behavior is reversed. The moment remains constant for annealing times up to 200 h. The concentration increases continuously and evidences no saturation at the 200-h time limit of the present data.

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INTRODUCTION

Nickel-manganese alloys near the Ni_3Mn composition show large changes in the magnetic properties with degree of short-range and long-range order.[1,2] Kneller[1] originally reported the superparamagnetic character of the alloy after annealing for 20 h at 480 °C, and estimated cluster sizes to be about 30 Å. Marcinkowski and Brown[2] later made a systematic study of the annealing-induced atomic order in Ni_3Mn. Their data indicated that at about 480 °C and above, only short-range atomic order (SRO) results and that the SRO saturates at times on the order of 10 h. Below about 420 °C, the ordering is primarily long range with Ni atoms generally favoring corner sites and Mn atoms favoring face-centered sites in the fcc lattice. These results indicate that the superparamagnetic behavior of Kneller relates to SRO-induced magnetic clusters.

A recent study of the cluster growth processes during short-range-order development[3] indicates a cluster moment (or size) which increases with an exponential time dependence and time constant of about 5—10 h. The clusters seem to "pop in" abruptly during the initial 5-min anneal at 500 °C; thereafter the cluster concentration decreases to about one-half the initial value.

The objective of the present study was to perform a similar set of room-temperature measurements for sequential annealing at 400 °C and analyze these data in terms of the simple Langevin superparamagnetic cluster model as in Ref. 3. In this way, a qualitative picture of the cluster growth processes for LRO atomic ordering (within the context of the Marcinkowski-Brown results) could be obtained, for comparison with the processes for SRO development.

EXPERIMENT

Two series of alloys near the Ni_3Mn composition were used. As described in Ref. 3, the 500 °C annealing study utilized three 3-mm spherical samples with 25 (±0.5) at.% Mn. The annealing study at 400 °C was done on one 3-mm sphere with 29 (±0.7) at.% Mn. The spheres were all ground from 5-mm cubes diced from well-homogenized ingots using a two-pipe lapidary method. After the initial casting of the ingots in an argon atmosphere, the bars were cold rolled, sealed in evacuated quartz tubes, and heat treated at 1000 °C several times before the final cold roll to ~6—7-mm square cross section prior to dicing. The spheres were finally sealed in evacuated quartz and held at 1000 °C for 24 h, followed by an oil quench. The sequential annealings at 400 and 500 °C were done with individual samples in evacuated quartz tubes. Quenching was done by removing the tubes from the furnace and stirring them in oil.

The magnetization measurements were made at room temperature, in fields up to 10 kOe, with a Princeton Applied Research vibrating sample magnetometer. Calibration was based on a pure nickel sample and an assumed nickel moment of 54.39 emu/g.[4] Typical magnetization data are shown in Figs. 1 and 2, respectively, for the 500 and 400 °C annealing sequences.

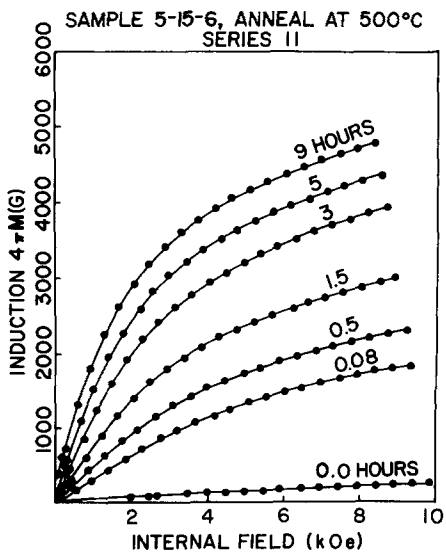

FIG. 1. Magnetic induction $4\pi M$ versus internal field at room temperature with annealing time at 500 °C as a parameter, for a 25 at.% Mn alloy sample, following an initial quench from 1000 °C to room temperature.

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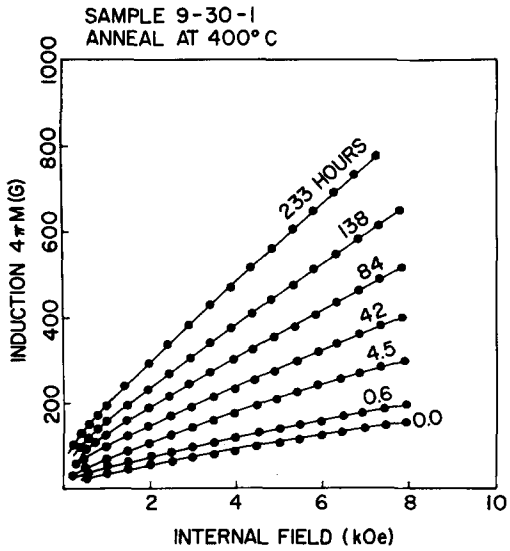

FIG. 2. Magnetic induction $4\pi M$ versus internal field at room temperature with annealing time at 400 °C as a parameter, for a 29 at.% Mn alloy sample, following an initial quench from 1000 °C to room temperature.

Figure 1 shows the evolution of the magnetization versus field behavior for one 25 at. % Mn sample due to sequential heat treatments at 500 °C. The magnetization increase with annealing time is quite rapid and the curvature increases substantially. The small remanence is presumably due to the appearance of a small nickel-rich surface layer with continued annealing in combination with demagnetization effects as the field for measurement is decreased. The data were obtained as a function of decreasing external field. Data were obtained up to 32 h cumulative anneal.

Figure 2 shows similar results for annealing of the 29 at. % alloy at 400 °C. The data shown extend up to a cumulative anneal time of 233 h. As a function of annealing time, the magnetization gradually increases, but the response is much slower than at 500 °C and the curvature does not change appreciably. A small remanence develops which is presumably due to the same causes as for 500 °C annealing.

These results show that the magnetic-order development for annealing at 400 and 500 °C is quite different. For 400 °C, the increase in magnetization is quite slow. The curvature of the magnetization field curve is small and does not increase appreciably. For 500 °C, the opposite statements are true. The increase in moment is quite rapid. (This may be due, in part, to the smaller Mn content.) The curvature also increases substantially. These results may be qualitatively related to cluster growth processes during annealing.

ANALYSIS

For the purposes of comparison, the room-temperature magnetization data were analyzed using the simple Langevin superparamagnetism model, and neglecting cluster distribution effects, cluster interactions, or other contributions to the average magnetization. For Langevin superparamagnetism, the magnetization M (emu/cm^3) versus internal field H is given

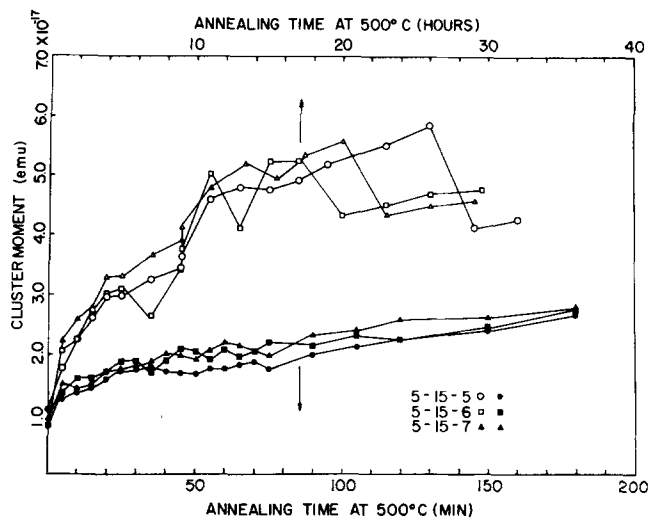

FIG. 3. Cluster moment versus annealing time at 500 °C for Ni-Mn alloy (~25 at.% Mn) following an initial quench from 1000 °C.

by

$$M = N\mu \mathcal{L}(\mu H/kT), \tag{1}$$

where N is the cluster concentration (cm^{-3}), μ is the cluster moment (emu), $\mathcal{L}(x)$ denotes the Langevin function

$$\mathcal{L}(x) = \coth(x) - 1/x, \tag{2}$$

k is Boltzman's constant, and T is the temperature (°K). The limits of $H \gg kT/\mu$ and $H = 0$ yield two simple working equations:

$$M_\infty = N\mu, \tag{3}$$

$$\chi_{initial} = N\mu^2/3kT. \tag{4}$$

The magnetization data of M versus H can be used to obtain the initial susceptibility $\chi_{initial}$ and estimates of the extrapolated infinite field magnetization M_∞. These two quantities can be used in turn to estimate the cluster moment and density.

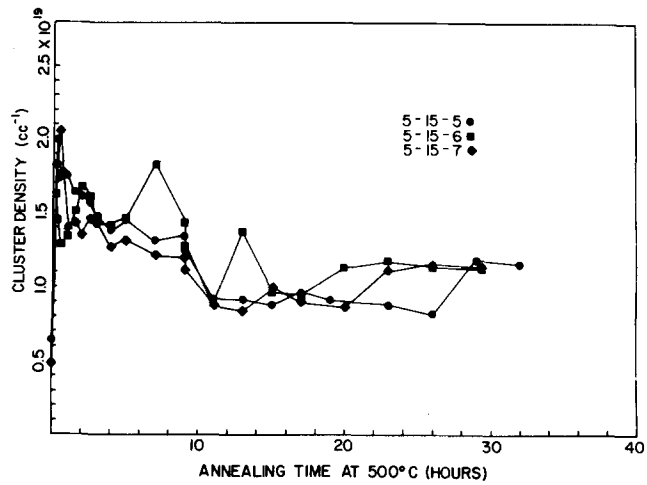

FIG. 4. Cluster density versus annealing time at 500 °C for Ni-Mn alloy (~25 at.% Mn) following an initial quench from 1000 °C.

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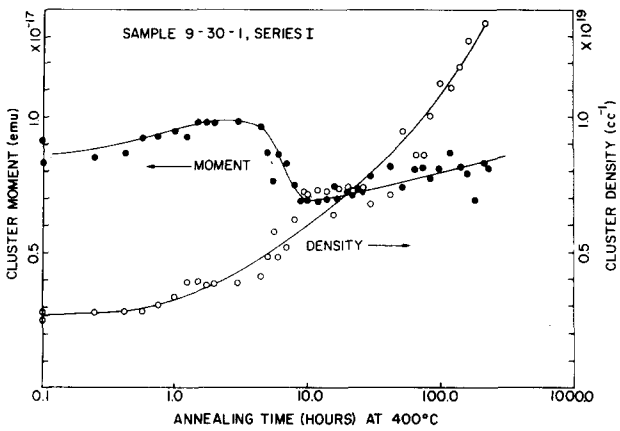

FIG. 5. Cluster moment and density versus annealing time at 400 °C for Ni-Mn alloy (~at.% Mn) following an initial quench from 1000 °C.

Results for cluster moment and density for annealing at 500 °C are shown in Figs. 3 and 4, respectively, for three samples of the same nominal 25 at. % composition. Figure 3 shows that the cluster moment associated with short-range-order domains starts at a small value ($\mu \approx 1.0\times10^{-17}$ emu) and increases roughly exponentially with a time constant of 10—20 h for this alloy. At the Kneller limit of 20 h (and a slightly higher temperature than Kneller's), the moment has essentially saturated. The data indicate a possible decrease in μ at 30 h, but the scatter is too large to really tell. The initial cluster moment is probably related to the fact that the initial quench resulted in samples which were not completely disordered atomically, but contained some residual SRO due to the nonzero quench time.

Figure 4 shows the associated cluster concentration for annealing at 500 °C. The results indicate that the cluster formation occurs almost exclusively during the initial 5-min anneal. Once the clusters "pop in", there is a slow and gradual reduction in cluster concentration until the concentration stabilizes at about 1.0×10^{19} cm^{-3}. This gradual decrease in concentration may be tentatively related to the increase in moment. As μ increases, some clusters coalesce or merge and reduce the effective cluster concentration.

The results for annealing at 400 °C, for one sample of nominal 29 at. % Mn (±0.7%), are shown in Fig. 5. The right axis denotes the cluster moment and the left axis denotes the cluster concentration. For annealing at 400 °C, the time scale for order development is considerably longer than at 500 °C. The anneals were extended to over 200 h. Figure 5 clearly shows that the magnetic-cluster kinetics associated with LRO development are significantly different from those connected with SRO. In fact, the dependence of moment and concentration on anneal time appear to be reversed. For LRO development, the cluster moment remains essentially constant with anneal time. Additional clusters do not "pop in", as for SRO. The exception to this is the small increase and then decrease at 5—10 h. The cluster concentration, on the other hand, shows a significant increase with annealing time. At 250 h, the limit of the present data, there is no evidence of impending saturation.

DISCUSSION

The data for magnetic-order development in nominal Ni_3Mn at 400 and 500 °C annealing temperatures clearly show that the processes are quite different. The analysis, in terms of a simple Langevin superparamagnetism model, expresses these differences in terms of specific evolutions for magnetic cluster moments and concentrations.

It is to be emphasized tha the results in Figs. 3—5 are only qualitative. Insofar as the model for analysis neglects the interactions between clusters, the cluster moments are overestimated and the cluster concentrations are underestimated. Preliminary low-temperature data for the 25 at. % composition and annealing at 500 °C indicate superparamagnetic Curie temperatures which range from about + 100 °K (for the disordered alloy) to −100 °K (for anneals of several hours) to 0 °K (20 or 30 h). Therefore, the correction factor due to interactions is on the order of 3. Since the tendency is known, the data in Figs. 3 and 4 can be interpreted on that basis.

Low-temperature data for the 400 °C annealing on the 29 at. % Mn alloy is limited to one annealing time.[5] The superparamagnetic Curie temperature was observed to increase from 145 °K for the alloy quenched from 1000 °C to about 250 °K after a 20-min anneal at 400 °C. Thus the correction factor for interactions would be on the order of 6—10 (smaller moments and larger concentrations). Since the magnetization data in Fig. 2 show no overwhelming evidence that the Curie temperature is above 300 °K for extended anneal times, it is reasonable to assume tha this correction factor remains relatively constant. Apart from a vertical scale adjustment, Fig. 5 is qualitatively representative of the cluster moment and concentration dependence on annealing time.

One final point concerning the comparison between the magnetic-order development at 400 and 500 °C has been raised by Guttman.[6,7] The present knowledge of the magnetic-order phase diagram for Ni_3Mn is inadequate to make unambiguous assignments of SRO to 500 °C and LRO to 400 °C. The early Marcinkowski and Brown result[2] placed an upper temperature limit of 420 °C on the single-phase LRO region, and a lower temperature limit of 480 °C on the single-phase SRO region. Reference 7 reports new data on the long-range-order parameter for a 26.8 at. % Mn alloy, annealed for several days at temperatures from about 370 to 559 °C. The x-ray analysis reveals an extensive two-phase field between the disordered and ordered forms. From the perspective of these new results, it is clear that 400 °C annealing cannot be simply associated with LRO development and 500 °C annealing cannot be simply associated with SRO development. As Guttman points out, a thorough study of the phase diagram is needed before

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definitive statements can be made about single-phase regions for atomic ordering.

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