HIGH FIELD MAGNETIZATION IN EQUILIBRIUM ORDERED NICKEL-MANGANESE ALLOYS*

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Summary

The equilibrium ordered states for 400°C and 500°C annealing in Ni-Mn alloys near the Ni_3Mn composition have been investigated. The results indicate distinctly different order configurations for the two temperatures. At 400°C, homogeneous long range order results, with a saturation magnetization which is relatively insensitive to composition. At 500°C, the data suggest that the ordering is inhomogeneous, with the nucleation and growth of stoichiometric Ni_3Mn clusters in a Mn- or Ni-rich matrix, depending on composition.

Introduction

One distinctive property of Ni-Mn alloys near the Ni_3Mn composition is, as first discovered by Kaya and Kussmann[1], that strong ferromagnetism appears with the development of Cu_3Au-type atomic order. In the perfectly ordered state, there are no antiferromagnetic Mn-Mn pairs and simple ferromagnetism results from the ferromagnetic Mn-Ni and Ni-Ni interactions. Previous work indicates that the magnetic state depends on, among other things, the annealing temperature. Based on magnetization data for a 22.7 at.% Mn alloy, Marcinkowski and Brown[2] proposed that short range order results from ordering at temperatures above 480°C and homogeneous long range order results from ordering below 400°C. More recent data, however, suggest that the order is inhomogeneous above 480°C. The nickel-manganese phase diagram proposed by Tsiuplakis and Kneller[3] shows the existence of many intermetallic compounds and two-phase regions. Domain observations by Lorentz microscopy and hysteresis measurements by Yokoyama and Satoh indicate that Mn content above 25 at.% and high annealing temperatures can result in inhomogeneous magnetic order.[4]

With this background, the present study was undertaken in an attempt to clarify the nature of the equilibrium magnetic order state in Ni_3Mn alloys. Magnetization data were obtained for a range of compositions from 22.1 to 32.1 at.% Mn for two annealing temperatures, 400°C and 500°C. Measurements were made at low fields (0-8 kOe) from 4K to room temperature. Additional data in fields up to 100 kOe were obtained at 300K. Neutron diffraction data were also obtained. The results indicate distinctly different equilibrium order configurations for 400°C and 500°C annealing. The lower temperature annealing results in homogeneous long range ferromagnetic order as proposed by Marcinkowski and Brown. The high temperature annealing results in the development of stoichiometric, long range order domains.

Experiment

The alloys were cast into ingots in an argon atmosphere after rf-induction melting. The ingots were homogenized by alternate cold-working and annealing. Compositions were determined by atomic absorption methods. Samples for measurement were spheres, approximately 3 mm in diameter. The alloys were put into a disordered state by sealing them in vacuo in quartz tubes (3 mm i.d. and 0.5 mm wall thickness), holding at 1000°C for three hours, and quenching in ice-water. Thermocouple measurements indicated that the time spent in the ordering temperature range of 600°C to 350°C during the quenching process was three seconds. Neutron diffraction did not detect the presence of any kind of atomic order for samples quenched in this manner.[5]

Samples of each composition (22.1, 24.6, 26.2, 29.0, and 32.1 at.% Mn) were ordered in two ways: (1) by holding at 400°C for eighty days or (2) holding at 500°C for fifty hours. These two temperatures were selected because of the differences in the magnetic and atomic order noted by Marcinkowski and Brown. The annealing times were estimated on the basis of a previous study[6] to produce equilibrium ordered states. Recent measurements indicate that the fifty hour estimate from Ref. 6 for equilibrium order at 500°C is too low. For an annealing time of 300 hours, the 8 kOe magnetization of the 26.2 at.% Mn sample increased by 20% over the value at 50 hours. Therefore, the 500°C annealing data discussed below may not be completely representative of equilibrium order. After quenching in ice water, magnetization data were obtained for the ten samples at 0 to 8 kOe and 4 to 300K. Measurements at 300K were made in fields up to 100 kOe.[7]

Results

Magnetization curves at room temperature for all samples in fields up to 100 kOe are presented in Fig. 1 for 400°C annealing and in Fig. 2 for 500°C annealing. With the exception of the 32.1 at.% Mn alloys, the 100 kOe magnetization is larger for the 400°C samples than for the 500°C samples. The difference decreases with increasing Mn content. The difference is larger for Mn below 25 at.% and is smaller for Mn above 25 at.%. The high field portions of the curves for the 500°C samples also appear to be closer to saturation, except for the 22.1 at.% Mn alloy.

The character of the magnetization curves for fields up to 8 kOe at temperatures down to 4K is quite similar to that shown in Figs. 1 and 2. The 4K moments are higher by about 10%, but the essential features do not change. The one exception is the 500°C, 22.1 at.% Mn sample, for which the magnetization increases drastically below 250K.

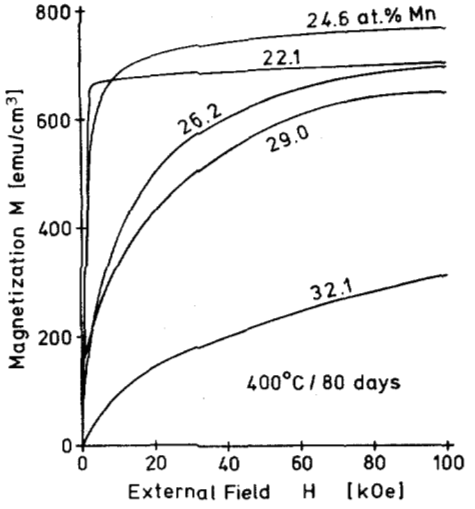

Fig. 1. Magnetization versus static field at 300K for the five alloy samples, which were annealed at 400°C for 80 days from an initially disordered state.

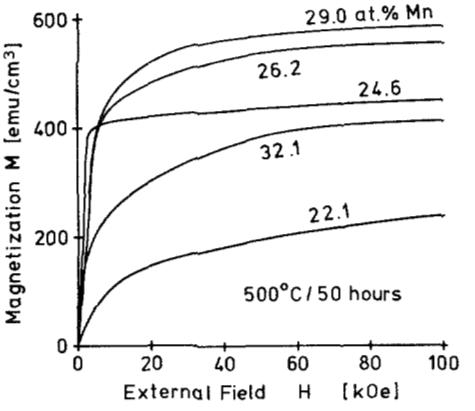

Fig. 2. Magnetization versus static field at 300K for the five alloy samples, which were annealed at 500°C for 50 hours from an initially disordered state.

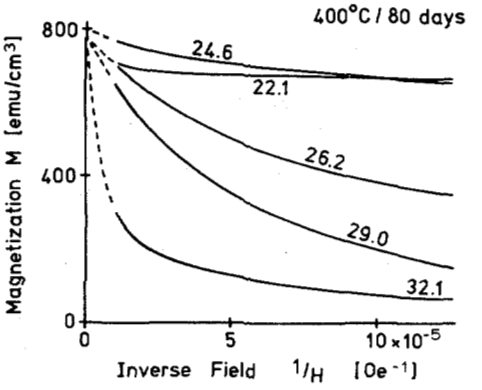

Fig. 3. Magnetization versus inverse static field at 300K for the five alloy samples, annealed at 400°C for 80 days from an initially disordered state. Composition in at.% Mn is shown for each curve.

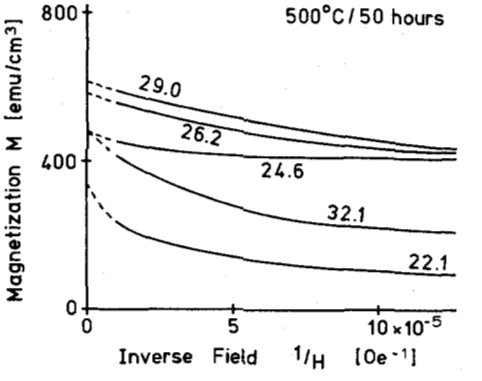

Fig. 4. Magnetization versus inverse static field at 300K for the five alloy samples, annealed at 500°C for 50 hours from an initially disordered state. Composition in at.% Mn is shown for each curve.

The magnetization data shown in Figs. 1 and 2 are presented versus inverse static field in Figs. 3 and 4, respectively. This presentation is convenient, in that the high field values and the extrapolated saturation values can be easily compared. The solid lines represent the actual measurements and the dotted lines represent estimated extrapolations.

For 400°C annealing, the moment at 100 kOe exhibits the well-known maximum in the vicinity of 25 at.% Mn, which was explained by the existence of a superlattice structure and resultant ferromagnetic order.[1] The extrapolated values suggest, however, that the saturation moment for 400°C equilibrium order is somewhat insensitive to composition. All curves, with the possible exception of the 32.1 at.% Mn sample, extrapolate to near 800 emu/cm^3.

For 500°C annealing, both the high field data and the extrapolations indicate a maximum moment in the 26-29 at.% Mn range. The estimated saturation values are all substantially below the levels for 400°C annealing. Because the order is not saturated at the 50-hour annealing time used for these samples, these data may not be completely representative of the equilibrium state.

Neutron diffraction[5] and x-ray data were also obtained. The 32.1 at.% Mn, 400°C sample was checked by powder x-ray diffraction for possible second phase content. Tsiuplakis and Kneller[3] reported the existence of a Ni_2Mn phase near this composition. The present powder x-ray data did not show any evidence of a Ni_2Mn phase. Only the fcc Ni_3Mn phase was detected. While Laue diffraction[3] does show evidence of subspots, divergent beam x-ray diffraction shows that these subspots originate from the mosaic structure of the alloy.[8] The 24.6 and 26.2 at.% Mn samples, annealed at 500°C, were checked by neutron diffraction for superlattice development. The data were taken on rod samples which were annealed in the same manner as the spheres used in the magnetic studies. These two samples revealed well defined superlattice peaks.

Discussion

The high field magnetization for 400°C annealing, as shown in Figs. 1 and 3, exhibits the well-known maximum in the vicinity of 25 at.% Mn. This is explained by the existence of a superlattice structure and resultant ferromagnetic order.[1] The extrapolated saturation values, indicated in Fig. 3, are near 800 emu/cm^3. This value is in good agreement with the theoretical value of 820 emu/cm^3 for 25 at.% Mn, calculated by assuming that (1) all moments are parallel, (2) the Shull and Wilkinson data[9] on the atomic moments, $\mu_{Mn} = 3.2\ \mu_B$ and $\mu_{Ni} = 0.3\ \mu_B$, are accurate, and (3) the lattice parameter is 3.59 Å. The maximum field of 100 kOe was insufficient to obtain precise extrapolated saturation moments. The data do suggest a shallow peak in saturation magnetization at 25 at.% Mn. Such behavior appears to be reasonable. For Mn above 25 at.% the excess Mn atoms tend to couple antiferromagnetically and the net moment decreases. For Mn below 25 at.% the relatively small moments of the Ni atoms also cause a reduction in the net moment.

The 400°C data show that the approach to saturation becomes harder for more Mn content. This indicates that the antiferromagnetic tendency, although overwhelmed by the ferromagnetic character, increases with Mn content. This result is consistent with both the Marcinkowski and Brown picture of homogeneous long range order at 400°C and the antiferromagnetic nature of Mn-Mn nearest neighbor interactions. As a result, the hardness to saturation (which may be taken as the slope of the magnetization versus inverse field curve at high field) will increase for Mn content above 25 at.%. For Mn content below 25 at.%, these considerations do not apply. The approach to saturation should be relatively easy and insensitive to small composition changes. Such expectations are confirmed by the data shown in Fig. 3. Previous Lorentz microscopy data[4] also confirm the drastic effect of excess Mn on the magnetization in Ni-Mn alloys.

For 500°C annealing, the atoms are more mobile than at 400°C. The lower free energy for atomically ordered regions is likely to lead to an inhomogeneous order development in the form of ferromagnetic clusters of microscopic dimensions. Such a possibility was examined by Kneller.[10] He estimated a cluster size on the order of 30 Å for 29.3 at.% Mn, annealed 20 hours at 480°C. A simplified cluster model was also used by Patton, et al., to qualitatively describe the order development at 500°C for a 26.2 at.% Mn alloy.[11]

These ordered clusters are likely to be of the stoichiometric Ni_3Mn composition. Sato[12] has suggested that, due to the magnetic contribution to the free energy, Mn atoms will tend to select Ni atoms as nearest neighbors, and that excess Mn atoms will be excluded from the Ni_3Mn order domain. These excess Mn atoms will tend to couple antiferromagnetically and will not contribute to the net moment. The tendency of the coercive force to increase with Mn content[4] may be due to these excess Mn atoms between order domains. Since the overall magnetization is mostly due to ferromagnetic Ni_3Mn clusters, the magnetization curves are somewhat more rectangular than those for 400°C annealing. The existence of stoichiometric order domains at 500°C may also be inferred from the phase diagram of Ref. 3.

The relatively small room temperature magnetization and the drastic increase in magnetization below 250K, for the 22.1 at.% Mn sample annealed at 500°C, may be due to a superparamagnetic-ferromagnetic transition. For the other compositions, this transition presumably occurs above room temperature. This implies that the magnetic interaction between the ordered Ni_3Mn clusters is related to the Mn concentration in the matrix.

It is noteworthy that the neutron diffraction data show well defined superlattice reflections for the 24.6 and 26.2 at.% Mn alloys annealed at 500°C. This suggests that the ordered Ni_3Mn clusters occupy a relatively large amount of the sample volume, on the order of 50 to 75% based on a comparison of Figs. 3 and 4. The observation that longer annealing times at 500°C lead to a further increase in the magnetization suggests that the stoichiometric order domains would occupy an even greater volume fraction at equilibrium.

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