EFFECT OF ORDERING ON THE FIELD INDUCED ANISOTROPY IN Ni-Mn ALLOYS AT LOW TEMPERATURE (*)

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Résumé. — La mise en ordre des atomes modifie de façon importante l'anisotropie obtenue en refroidissant sous champ des alliages Ni-Mn, près de la composition Ni_3Mn. Après un recuit de 2 heures à 400 °C produisant une faible mise en ordre, l'anisotropie uniaxiale à 4 °K est doublée ($K_u \approx 2 \times 10^4$ erg/cm^3) et l'anisotropie unidirectionnelle divisée par 10 ($K_d \approx 1 \times 10^4$ erg/cm^3), pour un échantillon à 27 % Mn. K_u (mesurée à 77 °K) est maximum pour un champ de mesure de 10 kG, après un recuit de 1 à 2 heures à 400 °C. La réduction de K_d avec l'ordre est probablement due à une réduction du caractère antiferromagnétique de certaines régions, associée à la diminution du nombre de paires Mn-Mn. L'apparition d'anisotropie uniaxiale est probablement liée à un changement, avec le degré d'ordre, dans la nature des configurations de spin antiferromagnétiques ou presque antiferromagnétiques permises dans une structure c.f.c.

Abstract. — Ordering dramatically modifies the anisotropy obtained by field cooling in Ni-Mn alloys near the Ni_3Mn composition. For one 27 % Mn sample, the uniaxial anisotropy at 4 °K doubled ($K_u \approx 2 \times 10^4$ erg/cc) and the unidirectional anisotropy decreased tenfold ($K_d \approx 1 \times 10^4$ erg/cc) after a two hour anneal at 400 °C to produce weak partial ordering. K_u (measured at 77 °K) is maximum for a measuring field of about 10 kOe and a 400 °C annealing time from 1-2 hours. The decrease in K_d with ordering is probably due to a reduction in the antiferromagnetic character of some regions as the number of Mn-Mn pairs is reduced. The appearance of uniaxial anisotropy may be related to a change in the nature of the allowed antiferromagnetic or nearly antiferromagnetic spin-configurations for the f.c.c. lattice with degree of order.

Extensive investigations by Kouvel and co-workers [1] have shown that disordered polycrystalline Ni-Mn alloys with 20 to 30 atomic percent Mn exhibit a very large *unidirectional* anisotropy

$$(K_d \approx 4 \times 10^4 \text{ erg/cc})$$

when cooled in a magnetic field to 4 °K, and that this anisotropy vanishes at some temperature between 20 and 80 °K, depending on composition. Satoh [2, 3] has recently reported that partial ordering of single crystal alloys results in a large field induced *uniaxial* anisotropy at 77 °K. The present study was initiated to see if similar effects occur for partially ordered polycrystals and, if so, to examine the transition from the Kouvel type behaviour to that found by Satoh as ordering progresses.

Polycrystal samples with 22-31 atomic percent Mn were prepared. After the initial casting, the ingots were cold-rolled to one-half the original cross section, annealed for several days at 1 000 °C, cold-rolled a second time, annealed again, and quenched in oil. Compositions were determined by atomic absorption spectro-photometry. Spherical samples (3 mm diam.) were prepared by the two-pipe lapidary method. After shaping, these samples were reannealed for several days and quenched in oil to obtain a disordered atomic arrangement. Partial ordering was accomplished by annealing at 400 °C. Below about 420 °C, ordering is believed to occur homogeneously [4]. An annealing temperature of 400 °C was chosen to reduce the annealing times to reasonable periods while retaining the simplest possible ordering process for later interpretation of the results. All heat treatments and quenching operations were done with the specimens sealed in evacuated silica tubes to avoid Mn loss and oxidation. Torque data were obtained with a conventional recording torque magnetometer at temperatures from 4.2 °K to room temperature and fields up to 20 kOe. Magnetization data were obtained on some samples using a Cioffi recording fluxmeter and vibrating sample magnetometer.

In general, the disordered (D. O.) samples showed the large unidirectional anisotropy reported by Kouvel [1]. Weak partial ordering was found to drastically modify the character of the torque for samples near the Ni_3Mn composition. The inset in figure 1

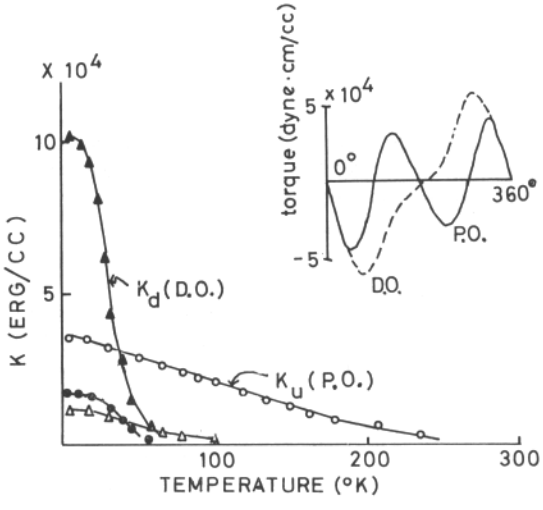

FIG. 1. — Effect of partial ordering on the induced anisotropy in 27 % Mn alloy. Insert : Torque curves for disordered (D. O.) sample (dotted curve) and partially ordered (D. O.) sample (solid curve) at 4.2 °K. Solid symbols (D. O.) ; Open symbols (P. O.) ; Circles : K_u ; Triangles : K_d.

shows typical torque curves at 4.2 °K for a disordered 27 % Mn alloy (quenched from 1 000 °C) and a companion sample which was subsequently annealed at 400 °C for two hours to produce weak partial ordering (P. O.). The short anneal drastically changes the character of the torque. Fourier analysis of the curves gives a ten-fold reduction in K_d and a two-fold

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increase in the uniaxial anisotropy constant K_u. The cooling field was 20 kOc and the measuring field was 12 kOe. The main part of the figure shows the temperature dependence of K_u and K_d for the two samples, as measured during warm-up. For the D. O. alloy, the unidirectional anisotropy decreases quite rapidly and vanishes at around 70 °K. K_u also vanishes at about the same temperature. The P. O. sample shows a drastically reduced K_d and a dominant uniaxial anisotropy which extend to much higher temperatures. K_u finally disappears at about 250 °K. Figure 2

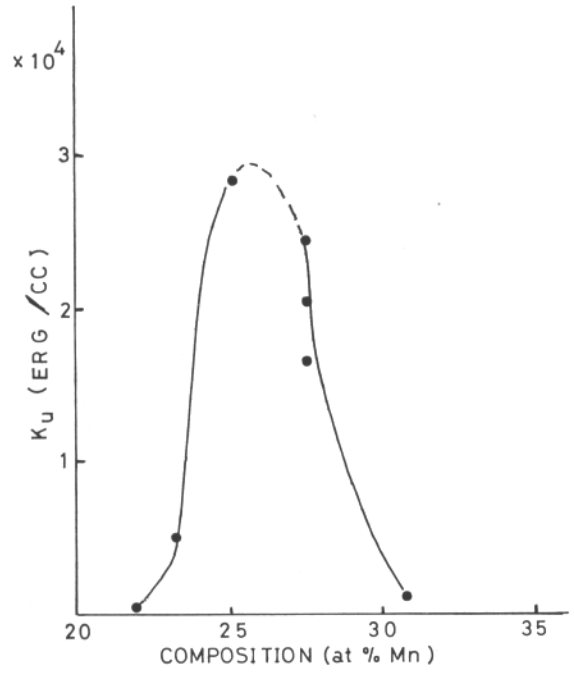

FIG. 2. — Composition dependence of K_u and K_d, as measured at 77 °K, for P. O. samples.

shows the composition dependence of K_u and K_d, as measured at 77 °K for samples which were initially quenched from 1 000 °C and then annealed for 2 hours at 400 °C. The largest K_u occurs near the Ni_3Mn composition. Data for the 22 % Mn sample at 4.2 °K showed no appreciable K_u (but large $K_d \approx 10^5$ erg/cc).

Figure 3 shows the dependence of K_u and K_d on measuring field for the weak P. O. (2 hours at 400 °C) 25 % Mn sample. K_u increases form near zero to a peak value at about 10 kOe and decreases slowly at higher field, if the data are taken for separate cooling runs or for successively smaller measuring fields. In addition, the torque curves, when measured at the lower fields (less than 7 kOe), become somewhat degraded, losing the clear uniaxial character. Once the degradation occurs, moreover, the original uniaxial curves cannot be completely recovered by returning to high field. These effects appear to be related to the field annealing behaviour. After the initial field-cooling, an annealing field at 90° to the easy-axis has no effect unless it is first cycled through zero (or below 7 kOe) before measuring the torque. Then, K_u decreases somewhat. This effect was first noted by Satoh [3], but he found that some waiting time at zero field was required in order to affect a change in the anisotropy. For a well homogenized sample,

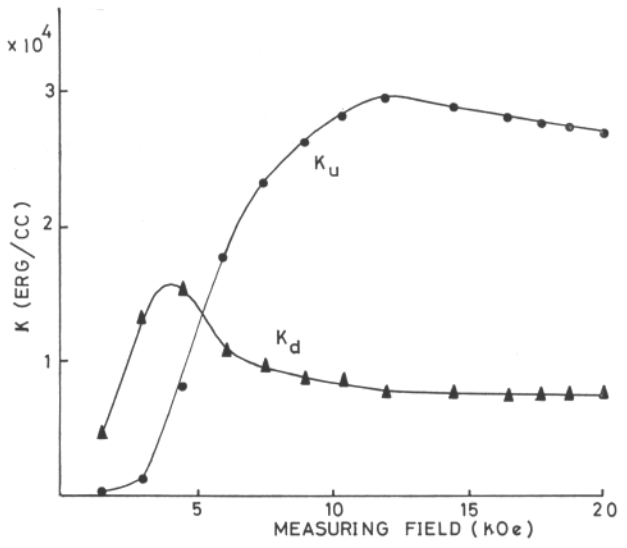

FIG. 3. — Dependence of K_u and K_d on measuring field at 77 °K for 25 % Mn P. O. sample.

annealed at 1 000 °C for one week prior to the initial quench, no waiting time was required in our study.

Figure 4 shows the dependence of K_u and K_d at 77 °K on the annealing time at 400 °C, when measured in about 18 kOe after cooling in a field of 20 kOe. The data show considerable scatter, particularly

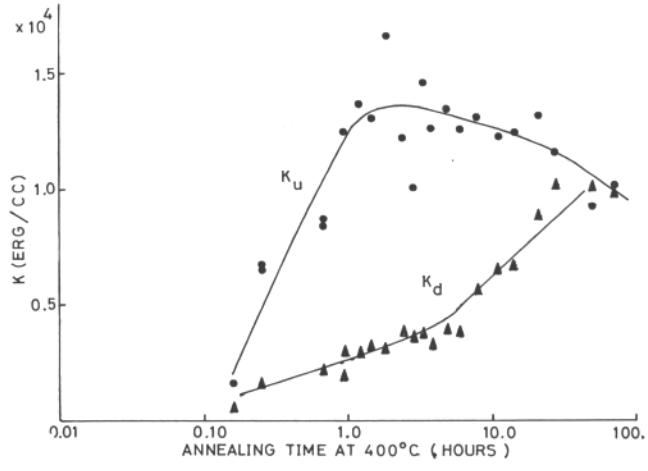

FIG. 4. — Dependence of K_u and K_d on annealing time at 400 °C for 27 % Mn sample.

for K_u, even though all the points are for a single sample (27 at % Mn) annealed in sucessive stages. Nevertheless, K_u shows a clear maximum after only 1-2 hours at 400 °C and begins to decrease for longer times. The unidirectional term, which is rather small during the first few hours of ordering, actually begins to increase quite rapidly as further ordering takes place. It should be emphasized that even for 100 hours, the ordering is far from complete. Marcinkowski and Brown [4] indicate that almost 1 000 hours at 425 °C are required for complete ordering. Magnetization data also show that the degree of order is very small for the present annealing treatments. The D. O. and P. O. (2 hr. at 400 °C) samples (27 % Mn)

show almost identical magnetization curves. At 77 °K, the curves are linear in applied field with

$$4\pi M \approx 2\,500 \text{ G} \quad \text{at} \quad 20 \text{ kOe}.$$

Kouvel has explained the unidirectional anisotropy at 4.2 °K in terms of exchange interactions between ferromagnetic and antiferromagnetic regions. The decrease in *this* K_d with ordering is probably due to a reduction in the antiferromagnetic character of some regions as the number of Mn-Mn pairs is reduced. The data in figure 4, however, show that the K_d at 77 °K actually begins to increase at some stage in the ordering process. This behaviour is not explained by the simple exchange anisotropy idea. The appearance of uniaxial anisotropy may be related to a change in the nature of the allowed antiferromagnetic or nearly antiferromagnetic spin-configurations for the f.c.c. lattice with degree of order. A preliminary analysis shows that the stable configuration during the initial stages of ordering is a non-colinear ferrimagnetic arrangement. As ordering progresses the configuration first changes to colinear ferrimagnetic and then to ferromagnetic. It is believed that the pseudo dipole interaction gives rise to a uniaxial anisotropy for the non-colinear ferrimagnetic arrangement. More detailed calculations are in progress. A complete analysis related to Ni-Mn and other magnetic f.c.c. alloys will be published by one of the authors (S. Chikazumi) at a later date.

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