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Equiatomic Transition Metal Alloys of Manganese

III. The Tetragonal NiMn Phase

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Measurements have been made of the variation with composition of lattice parameters, density and magnetic susceptibility of the low temperature NiMn phase which has the tetragonal CuAuI-type structure. These are discussed and compared with similar measurements on the PtMn and IrMn phases with the same type of structure.

Studies [1-2] of the PtMn and IrMn phases with the ordered CuAuI-type structure have established sharp changes in the slope of the lattice parameters a, c, c/a, and U as a function of composition in the equiatomic region, which have been attributed to the different sizes of the Pt and Mn atoms, respectively Ir and Mn atoms. The low temperature NiMn phase with the same type of structure [3-5] provides an interesting comparison since here the Ni atoms are smaller than the Mn atoms, whereas the Pt and Ir atoms are larger.

The CuAuI-type structure of the low temperature NiMn phase has definitely been confirmed by Kasper and Kouvel [5] by X-rays (FeK-radiation) and by neutron diffraction, and the Ni—Mn phase diagram has been carefully established by Coles and Hume-Rothery,[4] who showed that the NiMn phase has a range of homogeneity extending for several atomic % on either side of the equiatomic composition.

EXPERIMENTAL

The alloys were prepared from 99.9 + % "spec-pure" nickel powder (Johnson, Matthey & Co., Ltd.) and electrolytic 99.9 + % pure manganese (Johnson, Matthey & Co., Ltd.) by heating accurately weighed quantities of the components in evacuated, sealed silica tubes for 3 days at 950°C. The sintered powders were ground and reannealed

for 10 days at 640°C and finally quenched in water without shattering the silica tubes. The compositions of 18 alloys studied were determined by chemical analysis.*

X-Ray diffraction, density and magnetic susceptibility measurements were carried out as described in the preceding paper.[2]

RESULTS AND DISCUSSION

The range of composition of the NiMn phase, estimated by the disappearing phase method on the Guinier X-ray photographs and from the variation in the unit cell dimensions shown in Fig. 1, extends from about 47.5 to about 54.8 atomic % Ni. The comparison (Fig. 2) of pycnometrically determined densities with those calculated from the X-ray data, shows that the solid solution of the NiMn phase is substitutional on both sides of the equiatomic composition.

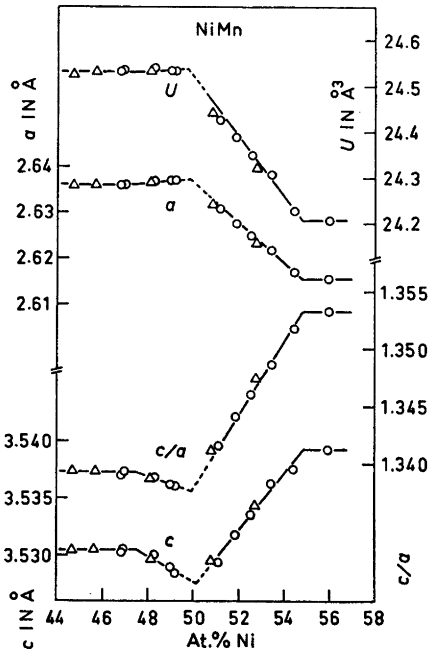

Fig. 1. Variation in lattice constants, axial ratio, and unit cell volume of the NiMn phase as a function of composition. (Average values of the lattice dimensions obtained from Guinier and Unicam photograph data are shown for alloy series I (O) and values obtained by the Guinier camera are shown for series II (△).)

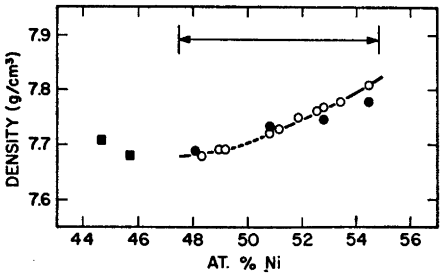

Fig. 2. Observed (●) densities of the NiMn phase and those calculated from the X-ray data on the basis of substitutional solid solution (O), both as a function of composition. The observed densities (■) of 2 two-phase alloys are also included.

* We thank Dr. J. C. Chaston under whose supervision the analyses were performed at the Research Laboratories, Johnson, Matthey and Co., Ltd., Wembley.

A. Lattice parameters

The lattice parameters of NiMn as a function of composition show similar features to those found for the PtMn and IrMn phases, notably a change of slope at 50 atomic % where a maximum occurs in a and a minimum in c. The sharp changes in slope of the lattice parameter curves of PtMn and IrMn in the equiatomic region have been qualitatively attributed to size effects.[1,2] If this is correct, we should now be able to provide quantitative evidence for it from data obtained on those alloys, and compare it with NiMn where Mn is the larger component. Specifically we have suggested: (i) That the expansion of a as the concentration of the larger component increases towards 50 atomic %, results from the close intralayer contacts that occur between these atoms as they are introduced into alternate layers parallel to the basal plane, filling these at 50 atomic % (Fig. 3). (ii) That the expansion of c when the concentration of the larger component increases beyond 50 atomic % results from close interlayer contacts between the larger atoms, because these atoms then enter the other layers parallel to the basal plane (Fig. 3). (iii) The contraction of c in (i) and of a in (ii) is regarded as trivially complementary to the compulsory expansions, in order to keep the cell volume and hence energy from increasing excessively. Finally we recognized that the size effects outlined in (i), (ii), and (iii) may be modified by other inter- or intralayer interactions between the unlike atoms ($A-B$ interactions), and that these may differ from one system to another.

From (i), assuming full CuAuI-type ordering, we recognize the a parameter at the equiatomic composition ($a_{0.5}$) as giving the apparent diameter of the larger component, D_L, since in the AuCuI-type structure close contacts between these atoms lie along [100] and [010] of the primitive cell containing two atoms (Fig. 3). Furthermore, since the actual distribution of the larger atoms in the alternate layers is random at compositions less than 50 atomic %, we expect the a parameter to follow approximately a Vegard's law relationship between D_S (diameter of smaller component) and D_L *over the range 0—50 atomic % of the larger component*, and not over the range 0—100 atomic % as in a normal random solid solution between two components.

Secondly, with full CuAuI-type ordering, the interlayer interatomic distance, d, at 50 atomic % is $(D_L + D_S)/2 = d_{0.5}$. As the distribution of

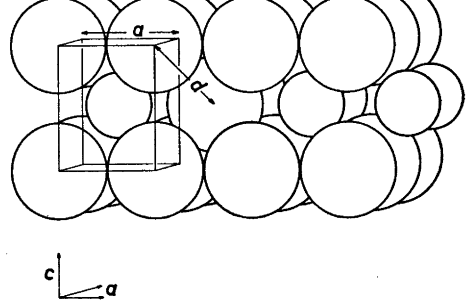

Fig. 3. Pictorial view of atomic arrangement in CuAuI-type structure. Intralayer interatomic distance a. Interlayer interatomic distance d.

the larger component in the second layer is also random at compositions above 50 atomic %, we would expect from (ii) that d would increase initially approximately according to a Vegard's law relationship from $(D_L + D_S)/2$ at 50 atomic % to D_L at 100 atomic % of the larger component, *i.e.* from D_S to D_L over a range from 0 to 100 atomic %, and not from 0 to 50 atomic % as in the case of the intralayer interatomic distance above.

The requirements can be tested from the experimental data. We expect a to vary as an approximately linear function of x, the atomic fraction of the larger component, and in proportion to $2(D_L-D_S)$. The interlayer interatomic distance, d, should also vary linearly with x, but in proportion to (D_L-D_S). Thus below 50 atomic % of the larger component, a expressed as $(a_{0.5}-a_x)/2(D_L-D_S)$ and above 50 atomic %, d expressed as $(d_x-d_{0.5})/(D_L-D_S)$ should be *a unique function of* x for the three phases, but a above 50 atomic % and d below this composition may be any function of x since the intra- or interlayer separations of the larger component no longer necessarily control their values. Fig. 4 indicates that these conditions are satisfied well enough for PtMn and IrMn to confirm our hypothesis that the sharp changes of slope of the lattice parameter-composition curves in the equiatomic region are due to size effects. In the case of NiMn there is no quantitative agreement with expectations and it is apparent that other effects such as Ni—Mn interactions, must exert a strong influence on the course of the lattice parameter variation; secondly that the diameter of Ni which we have taken

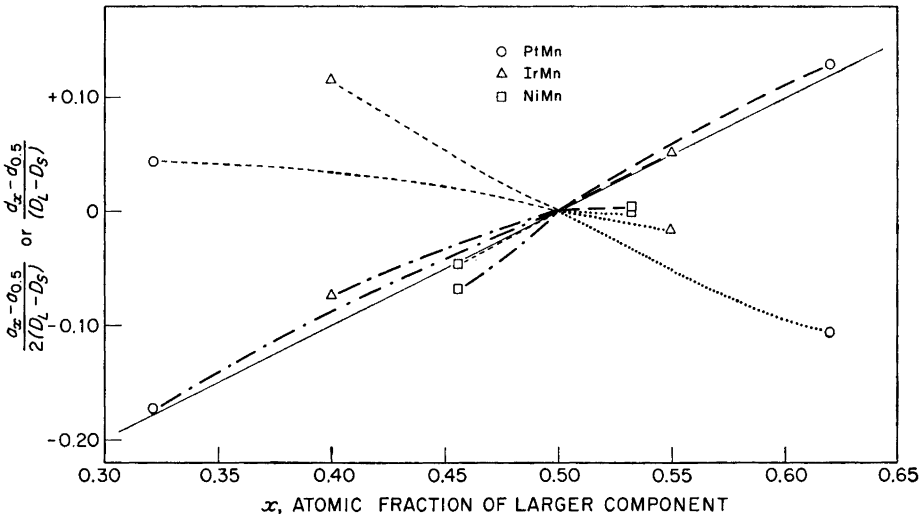

Fig. 4. See text for description.

1) — · — $(a_x-a_{0.5})/2(D_L-D_S)$ for alloys with < 50 atomic % of the larger component.
2) · · · $(a_x-a_{0.5})/2(D_L-D_S)$ for alloys with > 50 atomic % of the larger component.
3) — — $(d_x-d_{0.5})/(D_L-D_S)$ for alloys with > 50 atomic % of the larger component.
4) ----- $(d_x-d_{0.5})/(D_L-D_S)$ for alloys with < 50 atomic % of the larger component.
——— Variation expected for 1 and 3 of the Vegard's law relationships postulated in the text are followed.

from the pure metal, may be larger than its apparent size in the low temperature NiMn phase.

B. Magnetic properties

The magnetic susceptibility of alloys in the NiMn solid solution range is shown in Figs. 5a and b. Measurements extended to 1150°K by the Faraday method show that the Néel temperature of the antiferromagnetic alloys does not occur before the transition to the high temperature disordered NiMn phase. The PtMn, IrMn, and NiMn phases with the CuAuI-type structure show two characteristic types of behaviour:

(1) Antiferromagnetism with a high Néel temperature and (presumably) ferromagnetism with a much lower Curie temperature (apparently below 90°K for NiMn) is found as follows:

in NiMn with less than about 49 atomic % Ni
in NiMn with more than 49 atomic % Ni, when quenched from 640°C
in IrMn over the whole composition range
in PtMn with less than about 50 atomic % Pt.

Our neutron diffraction studies on PtMn containing less than 50 atomic % Pt (Andresen *et al.*[6]) indicate antiferromagnetic coupling within (001) planes of Mn atoms with spins aligned along [001] and arranged ferromagnetically along [001]; chemically random and magnetically aligned or random Mn arrangement in mixed Pt—Mn layers. The weak ferromagnetism below 280—295°K (in PtMn) appears to result from spin canting (*cf.* Moriya [7]).

(2) Antiferromagnetism with a similar high Néel temperature, followed by a sigmoid $1/\chi$ *versus* T relationship where $1/\chi$ decreases with decreasing T("X change"), and finally a change to ferromagnetism (presumably) at low temperatures is found as follows:

in NiMn with more than about 49 atomic % Ni when the alloys are annealed down from about 725°K
in PtMn containing more than about 50 atomic % Pt.

Our neutron diffraction studies of PtMn with more than 50 atomic % Pt, and those Kasper and Kouvel on NiMn (50.6 atomic % Ni) indicate antiferromagnetic coupling within (001) Mn planes with spins aligned within the layers and arranged ferromagnetically along [001]. The interesting feature of the the PtMn and NiMn data is that the temperature at which the X change occurs is fairly independent of composition in both systems, and of the degree of order in PtMn, whereas the Curie temperature of PtMn is increased notably by increased Pt content or by partial interlayer disorder (which has the same effect of increasing the Pt content of the Mn layer).

We presume that there is a change in spin direction with composition in antiferromagnetic NiMn (as in PtMn) in the region of 49—50 atomic % Ni and we will examine this by neutron diffraction. From powder neutron diffraction experiments on PtMn, however, we are not able to determine the cause of the increase in susceptibility at the X change in the 300—500°K temperature region on cooling, or to establish whether the weak ferromagnetism encountered at low temperatures results from spin canting.

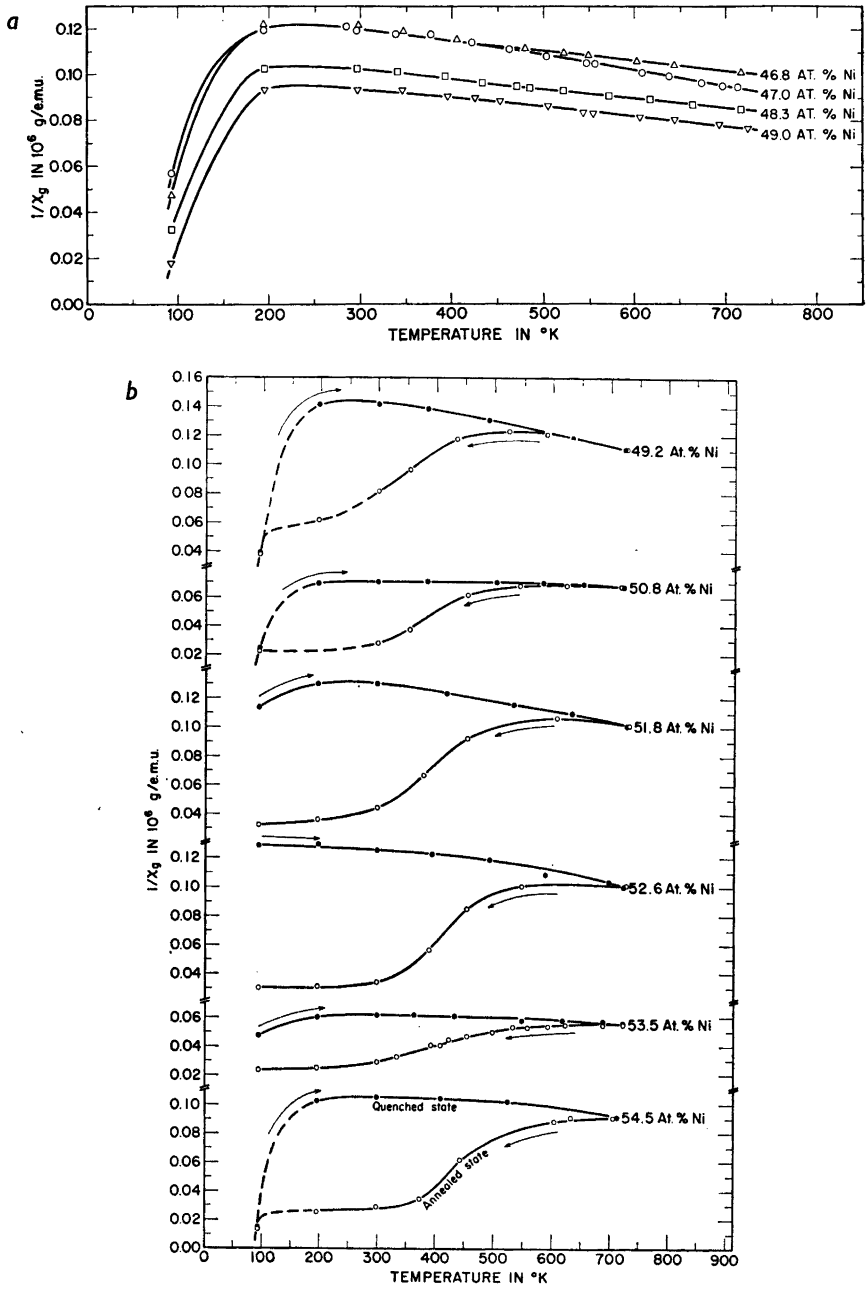

Fig. 5. The reciprocal magnetic susceptibility of the NiMn phase as a function of temperature for alloys with composition (*a*) < 49.0 atomic % Ni, (*b*) > 49.0 atomic % Ni.

Experiments on PtMn have indicated (i) that the temperature of the X change is essentially independent of both Pt content, and decrease of primary AuCuI-type ordering, and (ii) no evidence from X-ray diffraction of secondary ordering of excess Pt in the Mn layer, so the X change cannot be attributed to the loss of long range order, as in the case of pyrrhotite [8] which shows very similar thermomagnetic behaviour to Pt-rich PtMn samples. Since, however, experiments on NiMn show that the X effect can be quenched out, it is presumed to result primarily from some chemical process, rather than from a purely magnetic process. (Perhaps the effect can also be quenched out in PtMn alloys, if quenching is carried out from a comparable temperature of 1200°K which is at the same fraction of the melting point.) Nevertheless, although local short range ordering of Ni or Pt in the Mn layer onto next nearest neighbour sites would give local ferrimagnetic regions due to displacement of Mn atoms of like spin direction, the overall picture would be one of antiphase domain character, giving no net increase in χ.

Since the magnitude of χ resulting from the X change (*i.e.* below it) in both PtMn and NiMn is essentially independent of Pt or Ni content after the initial excess of these components over 50 atomic % has been established, it seems unlikely that the effect can be attributed to the presence of moments on these atoms, or to impurities. Furthermore, the high Néel temperature and the magnitude of the effect rule out the possibility of loss of antiferromagnetic spin coupling in the Mn layers as a cause of the increase in χ. Therefore, it seems that the X change results from a change in the direction of the aligned spins within the (001) plane, brought about by short range ordering of Pt or Mn in the Mn layer. Prevention of the development of short range order in NiMn by quenching would then prevent the change of spin direction. High temperature neutron diffraction results above and below the X change in the Pt-rich PtMn preclude a change of spin direction other than in the (001) plane. Similar variations of χ have been observed in FeS at about 410°K where the aligned spin direction changes from perpendicular to [001] to parallel to [001] over a range of temperature on cooling, with (in this case) a resultant decrease in χ (Haraldsen,[9] Hirahara and Murakami,[10] Andresen [11]).

CONCLUSIONS

The NiMn phase shows notable changes in slope of the lattice parameter composition curves at the equiatomic composition, similar to the PtMn and IrMn phases. Such changes result from size effects and the ordered distribution of components on alternate layers along [001], but in the case of NiMn, compared to PtMn and IrMn, other interactions besides size effects appear to exert a noticeable influence on the lattice parameter variation. NiMn is antiferromagnetic at high temperatures and probably weakly ferromagnetic at temperatures below those of the present measurements. Samples with more than 50 atomic % Ni when annealed slowly down from 725°K exhibit an increase of χ in the range from 500° to 300°K, which may result from a change in the direction of the aligned spins within the basal plane.

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