On a New High-Magnetic Permeability Alloy "Nimalloy" in the Nickel and Manganese System*

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After cooling at various rates from 900°C or the subsequent heating at various temperatures below the order-disorder transformation temperature, the magnetic properties of ferromagnetic nickel-manganese alloys have been measured at room temperature with the ring-form specimens punched out from the plates, and the relation between magnetic permeability and order-disorder transformation of Ni_3Mn (23.78 wt% Mn) has been investigated. It has been found that the initial and maximum permeabilities become larger as the cooling rate decreases or the subsequent heating temperature increases: the initial permeability vs. composition curve shows only one maximum, and the maximum permeability vs. composition curve, two maxima. The alloy containing 21.91% manganese shows the highest initial permeability of 6860 when heated at 380°C for 50 hr after cooling at a rate of 10°C/hr from 900°C and the alloy with the composition of 22.00% manganese attains the highest maximum permeability of 20,400 when heat treated similarly: the former has a magnetic hysteresis loss of 18.3 erg/cm³/cycle ($B_{\text{max}}=2000$ G), a coercive force of 0.031 Oe and a specific electrical resistivity of 60.7 $\mu\Omega\text{-cm}$ at 20°C. Moreover, these alloys can be forged and rolled more readily than Permalloy and are therefore named "Nimalloy" because they are the alloys of nickel and manganese.

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I. Introduction

One of the present authors has made, with other collaborators, a study on the relation between magnetic properties and magnetostriction or superlattice formation in ferromagnetic alloys, and found that there is a close relation between them. As a consequence of the study, he discovered a new alloy high in permeability comparable with Sendust (Fe-Si-Al alloy)⁽¹⁾ and Alperm (Fe-Al alloy)⁽²⁾.

Directing attention to the existence of order-disorder transformation of Ni₃Mn in nickel-manganese alloys, the authors have recently studied on the relation between degree of order and magnetic properties in the alloys.

A large number of studies^{(4)~(8)} have been carried out on the phase diagrams of nickel-manganese alloys since Zemczuzny, Urasow and Rykowski⁽³⁾ initiated their work in 1908. As related to the phase diagrams on the nickel-rich side, Kaya and Kussmann⁽⁹⁾ were the first to measure in greater detail the variation of the electrical and magnetic properties of nickel alloys containing 15~40% manganese after various heat treatments, and explained that a ferromagnetic superlattice Ni₃Mn would be formed in nickel alloys either by slow cooling from high temperatures or by heating for a long time at temperatures below 500°C after rapid cooling. The ordered phase was later confirmed by means of X-ray and neutron diffraction techniques by Dehlinger and other workers^{(10)~(13)}. The magnetic transformation points indicated in Fig. 1⁽¹⁴⁾ are those obtained by Kaya and Kussmann⁽⁹⁾ and also by Köster and Rauscher⁽¹⁵⁾, while the order-disorder transformation temperatures

are those derived from thermal analysis and the variation in modulus of elasticity by Köster and Rauscher⁽⁵⁾.

The order-disorder transformation temperatures shown

Fig. 1 Equilibrium diagram of Ni-Mn alloys.

Table 1 Results of chemical analysis of metals used.

	Co (%)	Fe (%)	Mn (%)	Si (%)	Cu (%)	Pb (%)	C (%)	P (%)	S (%)
Electrolytic Ni	0.180	0.003	0.000	0.000 ⁴	0.001 ⁸	0.000	0.002	—	0.000 ³
“ Mn	—	0.010	—	0.100	—	—	0.005	Trace	0.043

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in Fig. 1 concerns with the long-range order. Recently, Marcinkowski and other workers^{(15)~(16)} have also made clear that there exists the short-range order in nickel-manganese alloys at relatively high temperatures.

As for the magnetic permeability, Gumlich, Steinhaus, Kussmann and Scharnow⁽¹⁷⁾ obtained an initial permeability of 2,380 and a coercive force of 0.12 Oe in a nickel alloy containing 17% manganese by slow cooling from 900°C, while the maximum permeability obtained by Jaffee⁽¹⁸⁾ was 5,300 in a Ni₃Mn alloy heated at 380°C for a long time. And no detailed and systematic studies on the relation between superlattice Ni₃Mn and magnetic permeability have heretofore been carried out. In view of this, the authors have investigated the relation of magnetic properties vs. cooling rate for the alloys within the range of the Ni₃Mn phase as reported in the

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following.

II. Samples and Experimental Methods

Electrolytic nickel and electrolytic manganese were used as materials, with the chemical composition shown in Table 1.

For sample preparation (700 g in total weight), nickel was placed in an alumina crucible and its surface was covered with an appropriate flux to prevent oxidation, and melted by a high frequency electric induction furnace. Then, manganese was added to the melt and mixed thoroughly to make a homogeneous alloy. It was cast into an iron mould 30 mm in square and 90 mm in length, and the ingot was forged to an about 80 mm thick plate. Further, the plate was rolled at 1000°C to a thickness of about 1 mm and then cold-rolled to a thin plate of 0.3mm-thickness, from which a ring-form specimen 35 mm in inner diameter and 46mm in outer diameter was punched out. Finally, five sheets of the ring-form plates thus prepared were laminated to become equiangular with each other in the rolling direction. After heating in vacuum at 900°C for 1 hr, they were cooled to room temperature at various rates or further heated at various temperatures within the range of order-disorder transformation. The specimens within the composition range of 0~35.56% manganese numbered 53 kinds. The magnetizing coil and search coil were coiled round the five laminated plates and the magnetic properties were measured by the ballistic method.

On the other hand, a part of the above-mentioned ingot was cut out and made into a cylindrical rod of about 5 mm diameter. The diameter of the rod was then reduced to about 2 mm by using a swaging hammer at room temperature, from which a rod about 100 mm in length was cut out. The rod heat-treated in the same way as for the above-mentioned ring-form plate was used for the measurement of magnetization at an effective field of 900 Oe and of electric resistance. The electric resistance was measured by a potentiometer method, and its mean temperature coefficient was obtained over 0°~40°C.

III. Experimental Results and Considerations

The results of measurements are given in Figs. 2~5. In Figs. 2 and 3 are shown the observed values of the initial permeability μ_0 and the maximum permeability μ_m in nickel-manganese alloys which were heated at 900°C for 1 hr and then cooled to room temperature at six different rates of 170°C/sec, 240°C/hr, 100°C/hr, 10°C/hr, 5°C/hr and 3°C/hr.

As can be seen from the figures, μ_0 would gradually increase with increasing manganese content and then decrease after passing through a maximum. The maximum is considerably small at the cooling rate of 170°C/sec, but it increases rapidly with decreasing cooling rate and the position shifts to the manganese-rich side. When the cooling rate becomes extremely small, however, the maximum decreases again. The maximum value of μ_0 is 5,090 at the cooling rate of 5°C/hr with the com-

position of 21.80% manganese. With the exception of a case at the cooling rate of 170°C/sec, the maximum permeability vs. concentration curves has two maxima; Either of the maxima increases gradually with decreasing cooling rate and the position of the first maximum shifts

Fig. 2 Initial permeabilities of Ni-Mn alloys cooled to room temperature at various rates after heating at 900°C for 1 hr.

Fig. 3 Maximum permeabilities of Ni-Mn alloys cooled to room temperature at various rates after heating at 900°C for 1 hr.

to the manganese-low side and that of the second maximum to the manganese-rich side. However, even in this case, the two maxima decrease again as the cooling rate becomes extremely small in a way similar to the initial permeability. The maximum value of μ_m is 12,490 at the cooling rate of 5°C/hr with the composition of 21.80% manganese.

Next, Fig. 4 shows the relation between the intrinsic magnetic induction $4\pi I$ and the manganese content at an effective magnetic field of 900 Oe for the rod specimens mentioned above. The values of $4\pi I$ is known to increase with increasing manganese content when cooled rapidly at the rate of 170°C/sec and to attain a maximum at about 8% manganese, but thereafter it gradually decreases initially and then rapidly. And it becomes nonmagnetic at manganese contents of more than about 23% manganese. At the slower cooling rate, $4\pi I$ indicates a gradual decrease up to about 22% manganese with increasing manganese content. At more than about 22% manganese, the second maximum appears at about

24% manganese (Ni_3Mn) and at the slow cooling rates of 10°C/hr , 5°C/hr and 3°C/hr , among which the trend is most remarkable at 3°C/hr where the maximum value reaches 5,045 G. As is evident from the results of other workers, this can be attributed to the advance of super-

Fig. 4 Intrinsic magnetic induction at an effective field of 900 Oe in Ni-Mn alloys cooled to room temperature at various rates after heating at 900°C for 1 hr.

lattice formation with decreasing cooling rate.

The above-cited specimens cooled at the various rates were further heated at varying temperatures below the order-disorder transformation temperature, and the values of μ_0 and μ_m were measured at room temperature. Among these specimens, the values of μ_0 and μ_m against the manganese composition in those heated at 300° , 350° , 380° , 400° , 450° and 480°C for 50 hr after cooling at the rate of 10°C/hr are shown in Figs. 5 and

Fig. 5 Initial permeabilities of Ni-Mn alloys heated at various temperatures for 50 hr after cooling at a rate of 10°C/hr from 900°C .

6. In general the μ_0 and μ_m vs. composition curves closely resemble those obtained by changing the above cooling rates. In other words, the raising of the heating temperature and the lowering of the cooling rate reveal a similar effect to each other, which is considered a

natural phenomenon in alloys with the order-disorder transformation. The highest values of μ_0 and μ_m are 6,860 in a 21.91% manganese alloy heated at 380°C for 50 hr and 20,400 in a 22.00% manganese alloy similarly heat-treated, respectively, both values being considerably

Fig. 6 Maximum permeabilities of Ni-Mn alloys heated at various temperatures for 50 hr after cooling at a rate of 10°C/hr from 900°C .

Fig. 7 Intrinsic magnetic induction at an effective field of 900 Oe in Ni-Mn alloys baked at various temperatures for 50 hr after cooling at a rate of 10°C/hr from 900°C .

high compared with those in the alloys subjected only to cooling.

Fig. 7 shows the relation between $4\pi I$ and composition measured at the effective field of 900 Oe for the specimens which were further heated at the various temperatures below the order-disorder transformation temperature after cooling at 10°C/hr . This $4\pi I$ vs. concentration curve is closely analogous with that in Fig. 4 obtained from the specimen only subjected to cooling at the various rates. This is also considered to be a natural consequence in so far as the alloys have the order-disorder transformation, in the same way as for μ_0 and μ_m . In this case, the maximum value of $4\pi I$ is 6,054 in a 22.72% manganese alloy heated at 450°C for 50 hr, showing a fairly high value compared with 5,045 G in a 24% manganese alloy cooled at the rate of 3°C/hr . Moreover, the reason why $4\pi I$ is small in the case of heating at

480°C than at 450°C might be attributed to the partial decrease in degree of the long-range order due to the fact that the temperature of 480°C lies in the proximity of the order-disorder transformation temperature.

Comparison of Figs. 2~7 shows that the maximum

hysteresis curve might be attributed to the fact that the alloy consists of a mixture of long-range and short-range ordered phases.

In short, by appropriate heat treatment, the ferro-magnetic nickel-manganese alloys under study give rise

Table 2 Magnetic and electric properties of typical Ni-Mn alloys variously heat-treated.

Alloy No.	Mn (%)	Cooling rate (°C/hr)	Baking	μ_0	μ_m	$B(G)$ for μ_m	$\frac{Wh}{cm^3/cycle}$	$Br(G)$	$Hc(Oe)$	$4\pi I(G)$ $H=900$ Oe	$\frac{\sigma}{(\mu\Omega\text{-cm, } 20^\circ C)}$	α ($\times 10^{-3}$, $0^\circ \sim 40^\circ C$)	Density (g/cm ³)
			Temperature, time				for $B_m=2000$ G						
5	12.13	5	—	1130	6820	1241	83.9	1635	0.130	6233	31.9	2.02	8.58
20	19.00	240	—	2310	6590	153	8.5*	410*	0.030*	1910	53.3	1.38	—
21	19.12	100	—	3490	7450	254	111.8	614	0.030	2430	53.1	1.38	8.44
22	19.21	10	450°C, 50 hr	3180	8480	210	30.8	687	0.051	2210	53.1	1.38	—
23	19.33	10	—	2330	10330	450	33.8	916	0.042	2740	53.3	1.34	—
32	21.47	10	—	4240	8400	148	4.2*	140*	0.020*	1256	60.1	0.68	—
33	33	10	300°C, 50 hr	5090	9100	630	9.0*	337*	0.025*	—	59.8	0.72	—
35	21.80	5	—	5090	12490	626	18.5	876	0.027	2760	60.5	0.94	8.42
36	36	3	—	3500	7800	2082	24.5	700	0.058	3231	57.8	0.92	—
36	21.91	10	350°C, 50 hr	6520	14670	908	10.6*	347*	0.034*	1760	61.2	0.99	—
37	37	10	380°C, 50 hr	6860	18000	891	18.3	954	0.031	2790	60.7	0.93	—
37	22.00	10	380°C, 50 hr	5880	20400	908	19.3	1052	0.027	2804	60.7	0.93	8.40
43	43	10	400°C, 50 hr	5380	14700	960	20.4	1075	0.030	3675	59.1	1.02	—
43	23.24	5	—	330	4010	—	2405.0	1512	3.570	3813	58.2	1.20	—

* For $B_{max}=1,000$ G

permeabilities fall into the composition range of less than about 22% manganese, where the maximum value of permeability is inconsistent with Ni_3Mn which corresponds to the maximum value of $4\pi I$ and the permeability itself is extremely small at the Ni_3Mn composition. This indicates the relation between permeability and order-disorder transformation in which the permeability decreases all the more when the degree of order increases considerably. The phenomenon bears a close resemblance to the cases of Permalloy (Fe-Ni alloy)⁽¹⁹⁾, Sendust (Fe-Si-Al alloy)⁽¹⁾ and Alperm (Fe-Al alloy)⁽²⁾.

Typical magnetic properties of nickel-manganese alloys in the present experiments are listed in Table 2, where Wh is the hysteresis loss ($B_{max}=2,000$ G) and considerably small in value, σ the specific electrical resistivity, and α its temperature coefficient. The fact that the value of σ is fairly large is advantageous as a high-permeability alloy.

In Fig. 8 are shown magnetization and hysteresis curves

Fig. 8 Hysteresis curves obtained at the maximum induction of 2,000 G in No.36 and No. 43 alloys.

for No. 36 alloy which has the highest initial permeability and is small in hysteresis loss and for No. 43 alloy which is high in coercive force but is the Perminvar type. The cause of formation of this Perminvar-type

to high permeability and in addition can more readily be forged and rolled either at room temperature or at high temperatures than commercial Permalloy alloys. The authors, therefore, named these alloys "Nimalloy" because they are the alloys of nickel and manganese.

IV. Summary

Specimens punched out in a ring form were prepared from 53 kinds of ferromagnetic nickel-manganese alloys containing 0~35.56% manganese. After heating at 900°C for 1 hr, the specimens were cooled to room temperature at various rates or further heated at different temperatures below the order-disorder transformation temperature. The magnetic properties, and electric resistance and its temperature coefficient of the specimens were measured at room temperature, with the results summarized as follows:

(1) The initial permeability becomes larger gradually with increasing manganese content and then decreases rapidly after passing through a maximum. The maximum shows a rapid increase with decreasing cooling rate or with rising heating temperature below the order-disorder transformation temperature, and then decreases after passing through a maximum. The highest value of the initial permeability is 5,090 at a cooling rate of 5°C/hr with 21.80% manganese when cooled from 900°C. When heated at various temperatures for different times after cooling at the rate of 10°C/hr and heated at 380°C for 50 hr, the value is 6,860.

(2) The maximum permeability vs. concentration curve has in general two maxima, either of which increases gradually with decreasing cooling rate or with raising heating temperature until it attains a maximum and then decreases. The maximum value is 12,490 in the 21.80% manganese alloy cooled from 900°C at 5°C/hr and when heated at a variety of temperature for different times, it is 20,400 in the 22.00% manganese alloy heated at 380°C for 50 hr.

(3) The intrinsic magnetic induction at an effective

(19) G. W. Elmen: J. Franklin Inst., 207 (1929), 582.

field of 900 Oe increases with decreasing cooling rate or increasing heating temperature, and the rate of increase is greater with increasing manganese content. Moreover, the value indicates a maximum at about 8% manganese and give rise to a second maximum at about 24% manganese (Ni_{13}Mn) only by slow cooling or heating at higher temperatures below the order-disorder transformation temperature. The second maximum reaches 6,054 when heated at 450°C for 50 hr after cooling at 10°C/hr.

(4) The minimum values of the hysteresis loss and the coercive force against a maximum induction of 2,000 G are as low as 18.3 erg/cm³/cycle in the 21.91% manganese alloy and 0.027 Oe in the 21.80% manganese alloy.

(5) The specific electrical resistivity of the 21.91%

manganese alloy which shows excellent magnetic properties when heated at 380°C for 50 hr after slow cooling from 900°C at 10°C/hr has a high value of 60.7 $\mu\Omega$ -cm (20°C) and its temperature coefficient is 0.93×10^{-3} (0° ~ 40°C).

(6) These nickel-manganese alloys are not only distinguished in magnetic properties but also can be more readily forged and rolled than Permalloy, which are named "Nimalloy".

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