Magnetic Properties of Ni-Mn Base Polynary Alloys*

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The magnetic and electrical properties of Ni-Mn base polynary alloys have been measured. The specimens investigated are Ni-Mn-Me alloys (Me=V, Nb, Ta, Cr, Mo, W, Fe) containing less than about 24% Mn. The permeabilities depend remarkably on chemical composition and heat treatment. The alloy composition of 79.38% Ni, 8.51% Mn, 5.06% Fe, 3.02% Cr and 4.03% Mo when heated at 1150°C for 3 h and cooled from 650°C to room temperature exhibits a maximum performance. The highest initial permeability of 152.1 mH/m is obtained at the cooling rate of 240°C/h, while the cooling rate of 100°C/h yields the highest maximum permeability of 789.4 mH/m. In the latter the coercive force is 0.104 A/m, the magnetic hysteresis loss 9.2 J/m³/cycle (at a maximum induction of 0.2 T), the saturation induction 0.251 T, and the electrical resistivity 0.847 $\mu\Omega\text{m}$ at 20°C.

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I. Introduction

In previous work⁽¹⁾ the present author investigated the magnetic and electric properties in Ni-Mn alloys of the Ni₃Mn superlattice structure containing less than about 24% Mn. The ordering of the alloys was adjusted by appropriate heat treatments at temperatures below the order-disorder transformation point^{(2)~(4)} after the alloys were homogenized and purified in a high temperature hydrogen atmosphere. As the result, an Ni-Mn alloy containing 20.5% Mn was found to exhibit an initial permeability of 30.8 mH/m and a maximum permeability of 116.9 mH/m.

In order to improve the magnetic and electric properties of Ni-Mn alloys, the present author has studied the dependence of magnetic and electric properties on the composition and heat treatment for Ni-Mn base ternary, quaternary and quinary alloys with group Va and VIa elements and Fe which possess the same cubic structure as Ni-Mn binary alloys do.

II. Experimental

The starting materials used were the same grades of electrolytic Ni and electrolytic Mn as mentioned in previous work⁽¹⁾, and 99.8% pure V, Nb and Cr, and 99.9% pure Ta, Mo, W and Fe. The specimen preparation, heat treatments and measurements were carried out in the way similar to those described previously⁽¹⁾. Many different specimens of the ternary, quaternary and quinary alloys were prepared by addition of less than 9.7% V, less than 9.8% Nb, less than 14.6% Ta, less than 9.8% Cr, less than 12.6% Mo, less than 11.8% W and less than 24.2% Fe to high-permeability Ni-Mn binary alloys containing less than 24% Mn.

III. Results and Discussion

1. Ni-Mn base ternary alloys

Ni-Mn-Me alloys (Me=V, Nb, Ta, Cr, Mo, W or Fe) containing less than 24% Mn were furnace cooled to 650°C after homogenizing treatment by heating at 1150°C for 3 h in hydrogen atmosphere. These were then cooled to room temperature from 650°C at various cooling rates or further baked at various temperatures below the order-disorder transformation point. The magnetic and electrical properties of the alloys were measured at room temperature.

Figure 1 represents the cooling rate dependence of μ_0 and μ_m for four kinds of Ni-

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Fig. 1 Initial and maximum permeabilities vs cooling rate. After heating at 1150°C for 3 h, about 76% Ni-Mn-Fe alloys are cooled at various rates from 650°C to room temperature.

Mn-Fe alloys No. 24 (21.4% Mn, 3.07% Fe), No. 58 (19.53% Mn, 4.55% Fe), No. 67 (19.05% Mn, 5.03% Fe) and No. 79 (17.64% Mn, 6.48% Fe) which were cooled at various cooling rates from 650°C after the homogenizing treatment. As can be seen in the figure, both μ_0 and μ_m show generally a maximum at a cooling rate of 26°C/s. The highest values of μ_0 and μ_m are 55.3 mH/m for alloy No. 58 and 483.9 mH/m for alloy No. 67, respectively.

Figure 2 shows the dependence of μ_0 and μ_m on baking time for the same alloys as in Fig. 1 when they are baked at 380°C after cooling at a rate of 170°C/s from 650°C. In general, both μ_0 and μ_m exhibit a maximum against baking time and the maximum shifts toward shorter baking times with increase in

Fig. 2 Initial and maximum permeabilities vs baking time. After heating at 1150°C for 3 h, about 76% Ni-Mn-Fe alloys are cooled at the rate of 170°C/s from 650°C to room temperature and further baked at 380°C.

Fe content.

In Figs. 3 (a) and (b) are plotted the equi-value curves of the highest μ_0 and μ_m values against composition when each specimen is cooled to room temperature at six different rates of 170, 107, 26 and 9°C/s, and 100 and 10°C/h or further baked at various temperatures below the order-disorder transformation point after the homogenizing treatment. As can be seen from these figures, the values of μ_0 and μ_m are found to be extraordinarily high along the line of the composition $\text{Ni}_3(\text{Mn, Fe})$ which connects Ni_3Mn and Ni_3Fe . In the Ni-Mn system the highest values of $\mu_0 = 30.8$ mH/m and $\mu_m = 116.9$ mH/m are shown at 20.50% Mn, whereas with the addition of iron, these values generally increase rapidly to attain 55.3 mH/m at the composition of 75.92% Ni, 19.53% Mn and 4.55% Fe and 483.9 mH/m at the composition of 75.92% Ni, 19.05% Mn and 5.03% Fe,

Fig. 3 Highest initial and maximum permeabilities vs composition. After heating at 1150°C for 3 h, Ni-Mn-Fe alloys are cooled at various rates from 650°C to room temperature or further baked at various temperatures.

respectively. Moreover, with a further increase in iron content, μ_0 and μ_m rapidly decrease initially and then gradually along the line of $\text{Ni}_3(\text{Mn}, \text{Fe})$. Besides, the optimum cooling rate for the magnetic properties increases rapidly with the addition of iron to Ni-Mn alloys. In order to obtain the high permeability in Ni-Mn-Fe alloys containing more than about 2% Fe, it is considered necessary to cool those alloys at a rate larger than cooling in air as in the case of a Ni-Fe binary alloy (Permalloy) containing 78.5% Ni. This is likely to be due to acceleration of superlattice formation by the addition of Fe to Ni-Mn alloys.

Figure 4 indicates the cooling rate de-

Fig. 4 Initial and maximum permeabilities vs cooling rate. After heating at 1150°C for 3 h, about 80% Ni-Mn-Cr alloys are cooled at various rates from 650°C to room temperature.

pendence of μ_0 and μ_m after the homogenizing treatment for four kinds of Ni-Mn-Cr alloys No. 107 (19.52% Mn, 1.44% Cr), No. 118 (18.05% Mn, 1.97% Cr), No. 131 (17.04% Mn, 2.53% Cr) and No. 142 (16.51% Mn, 3.10% Cr). In the Cr-rich alloys, μ_0 and μ_m do not reach the highest values even if the alloys are subjected to cooling at such a very low rate as 0.75°C/h. Therefore, in order to maximize μ_0 and μ_m , it is necessary to bake the alloys at a temperature below the order-disorder transformation point after slow cooling from a high temperature.

Figure 5 illustrates the dependence of μ_0 and μ_m on baking time for the same alloys as in Fig. 4 when they are baked at 400°C after the homogenizing treatment and followed by cooling at a rate of 10°C/h from 650°C. The alloys show maximum values on the μ_0 or μ_m vs baking time curves and the maxima shift toward longer baking times with increasing Cr content. Since the optimum cooling rate

Fig. 5 Initial and maximum permeabilities vs baking time. After heating at 1150°C for 3 h, about 80% Ni-Mn-Cr alloys are cooled at the rate of 10°C/h from 650°C to room temperature and further baked at 400°C.

of these alloys is extremely small, it is required for the attainment of higher permeabilities of Ni-Mn-Cr alloys to bake the alloys for a long time at a temperature below the order-disorder transformation point after slow cooling from a high temperature. It may be concluded that the superlattice formation is suppressed by the Cr addition.

Figure 6 (a) and (b) show the equi-value curves of the highest values of μ_0 and μ_m vs composition at room temperature when the Ni-Mn-Cr alloys were cooled to room temperature at various rates after homogenizing or further baked at various temperatures, respectively. As shown in the figures, with increasing Cr content, μ_0 and μ_m increase with rapidity, and after passing through their maxima, diminish sharply. The highest values of μ_0 and μ_m were 49.3 mH/m for alloy No. 131 (80.43% Ni, 17.04% Mn and 2.53% Cr) and 320.5 mH/m for alloy No. 135 (79.33% Ni, 18.16% Mn and 2.51% Cr), respectively. These values are considerably greater than those measured with Ni-Mn binary alloys.

In Fig. 7 are plotted the highest values of

Fig. 6 Highest initial and maximum permeabilities vs composition. After heating at 1150°C for 3 h, Ni-Mn-Cr alloys are cooled at various rates from 650°C to room temperature or further baked at various temperatures.

Fig. 7 Highest initial permeability vs Mn content. After heating at 1150°C for 3 h, Ni-Mn-Me (Me: 2.5% V, 3.5% Nb, 5.0% Ta, 2.5% Cr, 4.0% Mo, 4.3% W or 4.5% Fe) ternary alloys are cooled at various rates from 650°C to room temperature or further baked at various temperatures.

μ_0 against Mn content for each of Ni-Mn ternary alloys with the addition of 2.5% V, 3.5% Nb, 5.0% Ta, 2.5% Mo, 4.0% W or 4.5% Fe when cooled at various rates from 650°C or further baked at various temperatures below the order-disorder transformation point after homogenizing. As can be seen from the figure, high initial permeability is generally obtained in the composition range of about 15–21% Mn and the highest value among the ternary alloy systems is 55.3 mH/m at 4.5% Fe. The high initial permeability can be realized by appropriate heat treatments near the composition Ni₃ (Mn, Me) where Me is V, Nb, Ta, Cr, Mo, W or Fe. Typical magnetic and electric properties of the ternary alloys are shown in Table 1, where W_h denotes the magnetic hysteresis loss, B_r the residual magnetic induction, H_c the coercive force, $4\pi I_{72}$ the magnetic induction at an effective magnetic field of 72 kA/m, and ρ the electrical resistivity. As shown in Table 1, the addition of each of the group Va and VIa elements or Fe to the Ni-Mn binary system increases permeability, $4\pi I_{72}$ and ρ . In the ternary alloys with V, Nb, Ta, Cr, Mo or W, the optimum heat treatment to obtain the highest permeability requires slow cooling from 650°C or further baking for a long time at a temperature below at the order-disorder transformation point, whereas in the ternary alloys with Fe rapid cooling is essential. This implies that the optimum heat treatment varies by the kind and content of the third element added.

2. Ni-Mn base quaternary and quinary alloys

As mentioned above, it has been found that very high permeabilities can be obtained by rapid cooling in Ni-Mn-Fe alloys, and that Ni-Mn-Cr and Ni-Mn-Mo alloys exhibit high permeabilities by baking for a long time at a temperature below the order-disorder transformation point after slow cooling. Therefore, it would be expected that Ni-Mn base quaternary or quinary alloys with a separate simultaneous addition of Cr and Mo might exhibit high permeabilities by slow cooling, e.g. furnace cooling, after homogenizing. Since this is technical importance, the magnetic

and electrical properties of these alloys have been measured in this investigation. The results show that the relation between heat treatment and magnetic and electrical properties for the Ni-Mn base quaternary and quinary alloys is almost similar to each other. Therefore, only the major results on the Ni-Mn base quaternary alloys are tabulated in Table 1, and the detailed data on the Ni-Mn base quinary alloys will be given in the following.

Figure 8 indicates the dependence of μ_0 and μ_m on cooling rate for Ni-Mn-Fe-Cr-Mo alloys No. 785 (4.63% Fe, 1.50% Cr, 1.57% Mo), No. 802 (5.15% Fe, 1.88% Cr, 3.06% Mo), No. 839 (5.06% Fe, 3.02% Cr, 4.03% Mo) and No. 921 (5.57% Fe, 1.93% Cr, 7.15% Mo) with composition of about 79% Ni and various contents of Fe, Cr and Mo, when cooled at various rates from 650°C after heating at 1150°C for 3 h under hydrogen atmosphere. Both μ_0 and μ_m indicate a maximum on each curve against the cooling rate and the cooling rate that corresponds to the maximum becomes gradually smaller with the addition of Cr

Fig. 8 Initial and maximum permeabilities vs cooling rate. After heating at 1150°C for 3 h, about 79% Ni-Mn-Fe-Cr-Mo alloys are cooled at various rates from 650°C to room temperature.

and Mo. The highest values of 152.1 mH/m in μ_0 and 808.3 mH/m in μ_m were obtained with alloy No. 839 containing 5.06% Fe, 3.02% Cr and 4.03% Mo, when cooled at a rate of 240 or 100°C/h, respectively.

Figure 9 also shows the effects of baking time for the same alloys as in Fig. 8 when they are cooled at a rate of 240°C/h from 650°C and further baked at 400°C. Generally the values of μ_0 and μ_m for alloys No. 785 and No. 802 containing smaller amounts of Cr and Mo decrease monotonously with increasing baking time, whereas those for alloys No. 839 and No. 921 containing larger amounts of Cr and Mo show a maximum against the baking time and the maxima shift to longer baking times with an increase in total Cr and Mo contents.

Figures 10 (a) and (b) show the equi-value curves of the highest values of μ_0 and μ_m measured at room temperature in each of the Ni-Mn-Fe-Cr-Mo alloys with about 2.9% Cr and about 4.1% Mo, respectively, when they are heated at 1150°C for 3 h and then cooled at various rates from 650°C to room temperature or further baked at various

Fig. 9 Initial and maximum permeabilities vs baking time. After heating at 1150°C for 3 h, about 79% Ni-Mn-Fe-Cr-Mo alloys are cooled at the rate of 240°C/h from 650°C to room temperature and further baked at 400°C.

Fig. 10 Highest initial and maximum permeabilities vs composition. After heating at 1150°C for 3 h, Ni-Mn-Fe-Cr-Mo alloys are cooled at various rates from 650°C to room temperature or further baked at various temperatures.

temperatures below the order-disorder transformation point. As is evident from these figures, with increasing Fe content, both μ_0 and μ_m increase rapidly, and after passing through their maxima, decrease gradually. From a number of the experiments whose results are not shown in these figures, it is understood that the composition range in which the highest values of μ_0 and μ_m can be obtained shifts to the iron-rich side with an increase in total Cr and Mo contents. As mentioned above, the highest values of μ_0

and μ_m for alloy No. 839 with 79.38% Ni, 8.51% Mn, 5.06% Fe, 3.02% Cr and 4.03% Mo are 152.1 and 808.3 mH/m, respectively, being considerably greater than the highest values of μ_0 and μ_m , 55.3 and 483.9 mH/m, as measured with Ni-Mn-Fe alloys. These values are compared with Supermalloy (Ni-Fe-Mo alloys).

Figure 11 shows the magnetization and magnetic hysteresis curves for alloy No. 839 which has the highest values of μ_m in the alloy system. The values of H_c and W_h at a maximum magnetic induction of 0.200 T are extremely small as 0.104 A/m and 9.2 J/m³/cycle, respectively and $4\pi I_{72}$ is 0.251 T and electrical resistivity 0.847 $\mu\Omega\text{m}$. Moreover, the magnetic and electric properties of representative alloys in the quinary alloy system are listed in Table 1. In general, with increasing Cr and Mo contents, the optimum cooling rates for the attainment of higher permeability in the Ni-Mn-Fe-Cr and Ni-Mn-Fe-Mo quaternary alloys and Ni-Mn-Fe-Cr-Mo quinary alloys become smaller, the permeabilities exhibited by these alloys are considerably higher than those in Ni-Mn-Fe ternary alloys, while $4\pi I_{72}$ decreases and ρ increases.

Fig. 11 Magnetization and hysteresis curves of alloy No. 839 cooled at 100°C/h from 650°C after heating at 1150°C for 3 h.

Thus it has been made clear that the high permeabilities of Ni-Mn base ternary, quaternary and quinary alloys prepared by the addition of group Va and VIa elements and Fe are obtained when the alloys are primary solid solutions with face-centered cubic lattice structure by purifying and homogenizing treatments at a high temperature in hydrogen atmosphere and then rapidly or slowly cooled, or further baked at temperature below the order-disorder transformation point. As reported in the previous investigations⁽⁵⁾⁽⁶⁾, the origin of the high permeabilities in these alloys has been considered that domain wall displacement can readily occur as the result of ordering due to appropriate heat treatments. These alloys can easily be wrought to sheet because of great ease in forging and hot- and cold-working. The ease of sheet manufacture should lead these alloys to possible commercial uses as soft magnetic materials in the weak direct and alternating magnetic fields.

IV. Conclusions

Ni-Mn base ternary, quaternary and quinary systems of less than about 24% Mn with group Va and VIa elements and Fe were prepared by melting in argon atmosphere. The specimens of these alloys were heated in hydrogen atmosphere at 1150°C for 3 h and then cooled from a temperature above the order-disorder transformation point at various cooling rates or further baked at different temperature below the order-disorder transformation point. Magnetic and electric properties of these alloys were measured at room temperature. The principal results are summarized as follows:

(1) Ni-Mn base ternary, quaternary and quinary systems with alloying elements V, Nb, Ta, Cr, Mo, W and Fe exhibit high permeabilities near the composition $\text{Ni}_3(\text{Mn}, \text{Me})$, where $\text{Me} = \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Mo}, \text{W}, \text{Fe}$, when subjected to heat treatment appropriate to the alloy compositions. Each of the ternary alloy systems with V, Nb, Ta, Cr, Mo or W exhibit the highest permeability when baked at temperature below the order-disorder transformation point after slow cooling from 650°C to room temperature, whereas the ternary

Table 1 Characteristics of typical Ni-Mn base polynary alloys.

Alloy Nos.	Composition (Rest Ni)		Cooling rate (°C/h)	Baking Temperature (°C)	μ_0 (mH/m)	μ_m (mH/m)	W_h (J/m ² /cycle)	B_c (T)	H_c (A/m)	B_m (T)	$4\pi I_{-2}$ (T)	ρ ($\mu\Omega$ m, 20°C)
	Mn(%)	Additional elements (%)										
—	20.50	—	10	—	30.8	90.5	—	—	—	—	0.165	—
—	20.50	—	10	400,	27.3	116.9	27.3	0.073	0.384	0.200	0.201	0.565
58	19.53	Fe 4.55	*26	—	55.3	302.9	—	—	—	—	—	—
67	19.05	Fe 5.03	*26	—	38.7	483.9	67.6	0.291	0.400	0.500	0.535	0.685
131	17.04	Cr 2.53	10	400,	49.3	225.3	—	—	—	—	—	—
135	18.16	Cr 2.51	10	400,	34.6	320.5	82.4	0.218	0.808	0.300	0.455	0.738
208	19.05	Mo 4.02	20	400,	28.8	433.7	268.2	0.383	1.144	0.700	0.801	0.588
213	19.74	Mo 4.06	20	400,	46.6	329.3	—	—	—	—	—	—
287	19.03	W 4.32	20	380,	19.1	240.1	103.6	0.320	0.680	0.500	0.623	0.587
287	19.03	W 4.32	20	400,	32.4	220.6	—	—	—	—	—	—
335	19.57	V 2.48	10	400,	40.5	335.6	—	—	—	—	—	—
335	19.57	V 2.48	10	400,	38.3	396.3	251.8	0.563	0.840	0.700	0.764	0.553
420	19.63	Nb 3.64	20	440,	42.4	605.9	256.7	0.525	0.840	0.700	0.818	0.504
420	19.63	Nb 3.64	20	440,	44.6	462.6	—	—	—	—	—	—
473	20.03	Ta 5.11	20	440,	15.8	342.5	242.8	0.420	0.672	0.700	0.714	0.527
473	20.03	Ta 5.11	20	440,	31.8	309.6	—	—	—	—	—	—
		Fe(%)	Cr(%)	Mn(%)								
598	16.30	4.02	1.90	—	800	—	—	—	—	—	0.296	0.723
613	13.52	4.08	3.34	—	240	—	—	—	—	0.200	0.214	0.750
634	11.04	5.10	4.82	—	240	—	10	0.161	0.256	0.200	0.255	0.832
657	7.30	6.11	6.68	—	240	—	200	—	—	—	0.207	0.857
701	13.20	5.17	—	4.82	8000	—	—	0.146	0.192	0.200	0.230	0.812
720	10.83	4.50	—	6.72	400	—	—	—	—	—	0.202	0.876
746	10.83	4.50	—	6.72	240	—	—	0.159	0.160	0.200	0.224	0.894
761	8.65	5.32	—	9.30	240	—	40	—	—	—	0.132	0.942
785	12.52	4.63	1.50	1.57	4600	—	—	0.173	0.424	0.200	0.380	0.823
839	8.51	5.06	3.02	4.03	240	—	—	—	—	—	0.158	0.851
839	8.51	5.06	3.02	4.03	240	—	3	0.120	0.120	0.200	0.207	0.850
839	8.51	5.06	3.02	4.03	100	—	—	0.116	0.104	0.200	0.251	0.847
921	6.56	5.57	1.93	7.15	25	—	—	—	—	—	0.081	0.908
954	6.44	8.25	4.07	5.16	50	—	—	—	—	—	0.195	0.916

* °C/s

alloy system produced by alloying Fe exhibits the highest permeability when rapidly cooled from 650°C.

(2) The optimum cooling rate to obtain the highest permeability in the quaternary and quinary alloy systems prepared by adding Cr and/or Mo is reduced with increasing Cr and Mo contents, and the permeabilities of these alloys remarkably are increased. The highest initial permeability μ_0 of 152.1 mH/m is exhibited by alloy No. 839 (79.38% Ni, 8.51% Mn, 5.06% Fe, 3.02% Cr, 4.03% Mo) when heated in hydrogen atmosphere at 1150°C for 3 h and then cooled at the rate of 240°C/h from 650°C. The same alloy exhibits maximum permeability μ_m of 808.3 mH/m when similarly heated and then cooled at the rate of 100°C/h from 650°C.

(3) The magnetic induction in an effective field of 72 kA/m becomes considerably larger in each of the Ni-Mn base ternary alloy systems prepared by alloying the elements V, Nb, Ta, Cr, Mo, W or Fe than Ni-Mn binary alloys, whereas it decreases in the Ni-Mn base quaternary and quinary alloy systems with addition of Cr and/or Mo. The electrical resistivity ρ in the above-mentioned alloy systems is comparatively large. In alloy No. 839 with the highest value of μ_m , $4\pi I_{72}$ is 0.251 T, and the coercive force and the magnetic hysteresis loss at a maximum magnetic induction of 0.200 T are 0.104 A/m

and 9.2 J/m³/cycle, respectively, the electrical resistivity being 0.847 $\mu\Omega\text{m}$ at 20°C.

(4) These alloys with the high permeability can readily be forged and hot- and cold-worked

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