Nonferromagnetic Elinvar-Type Alloys in the Mn–Ni–Co System*

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Measurements of Young's modulus at $-150 \sim 400^\circ\text{C}$ and of rigidity modulus, thermal expansion and hardness at room temperature have been carried for Mn–Ni–Co alloys subjected to cold working and varying heat treatments. An anomalous variation associated with antiferromagnetic transformation was observed in the Young's modulus vs temperature curves for the ternary alloys which had been slowly cooled after heating at 950°C for 1 hr. The temperature coefficient of Young's modulus is highly dependent on the metallurgical processing history, i.e. annealing, cold working and reheating after cold working or water quenching as well as the alloy composition. The existence of a positive large maximum in the temperature coefficient of Young's modulus vs composition curves demonstrates the Elinvar characteristics of the ternary alloys. The behaviors of the rigidity modulus and its temperature coefficient are very similar to those of the Young's modulus and its temperature coefficient. The hardness of the alloys varies in a complex manner within the order of $100 \sim 800$ in Vickers hardness. The corrosion resistivity of the alloys is very satisfactory.

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I. Introduction

Mn–Ni alloys in the annealed state exhibit the $fcc \rightleftharpoons fct$ phase transformation and the accompanying paramagnetic $\rightleftharpoons$ antiferromagnetic transformation in the α phase region where the γ phase of the fcc structure exists. These transformations have a remarkable effect on the elastic modulus of the alloys, and some of the anomalous variations in elasticity with temperature have been explained as representation of the Elinvar characteristics⁽¹⁾. In previous work we have reported that the Elinvar characteristics of Mn–Ni binary alloys are affected in a complex manner not only by the alloy composition but also by cold working and heat treatment. The Elinvar properties of the binary alloys are also found to depend significantly on the third elements added. Mn–Ni–Cr⁽²⁾ and Mn–Ni–Fe⁽³⁾ ternary alloys, in which the Elinvar characteristics have already been found over a wide range of compositions, are nonferromagnetic over most of their composition ranges and show a considerable increase in corrosion resistivity as compared with Mn–Ni binary alloys. This result would provide important information on their practical applications.

Extensive work on the effects of alloying of third elements on Mn–Ni alloys has been carried out at our laboratory, and the experimental results on Mn–Ni alloys with Co as the third element are presented in this paper.

II. Experimental Procedure

The alloying elements were electrolytic Mn, electro-

lytic Ni and electrolytic Co. The former two were the same as those used for the binary alloys⁽¹⁾ and the latter was the same as that used for a study of Mn–Cu–Co alloys⁽⁴⁾. The methods for specimen preparation, heat treatment and measurement were identical with those for Mn–Ni binary alloys⁽¹⁾, except for the annealing temperature. The uncertainty of the Mn–Ni–Co ternary phase diagram in question makes it impossible to decide the annealing temperature from its solidus as the standard, so that the annealing temperature of 950°C has been uniformly employed throughout the present work. The specimens used were 50 kinds of alloys with compositions of $40.0 \sim 95.0\%$ Mn, $0 \sim 40.0\%$ Ni and $0 \sim 40.0\%$ Co. The temperature coefficient of Young's modulus was derived from calculations of the measured values for the resonance frequency ($590 \sim 830$ Hz) and the thermal expansion coefficient.

III. Results and Discussion

The experimental results are shown in Figs. 1 ~ 13 and Tables 1 ~ 4. The measured data on the thermal expansion coefficient necessary for calculation of the temperature coefficient of Young's modulus are listed in the tables. Figure 1 shows the temperature dependence of Young's modulus E for several kinds of the Mn–Ni–Co alloys in the annealed state. The temperature dependence of E is reversible in all cases, revealing a pronounced minimum and maximum in E vs temperature curves. The fact that the variation in E with temperature is very small in the vicinity of the minimum and the maximum reflects the appearance of the Elinvar characteristics. As has been reported by Hicks⁽⁵⁾, the anomalous variation of E is thought to relate to the $fct \rightleftharpoons fcc$ phase transformation and the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation. In Fig. 2 the temperature coefficient of Young's modulus e at $0 \sim 40^\circ\text{C}$, is plotted as an equi-value curve against composition for the ternary alloys in the an-

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Fig. 1 Temperature dependence of Young's moduli for several Mn-Ni-Co alloys in the state of annealing.

Fig. 2 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of annealing.

nealed state. The values of e are in general negative, but the Elinvar characteristics are revealed in a small composition range near Mn-18%Ni-2%Co where the values of e are positive. However, the range of the positive e values disappears almost completely when the Co content exceeds 5%, and the alloys containing less than 10%Co exhibit relatively low temperature coefficients of the order of $e = -20 \times 10^{-5}$.

It seems very likely that the temperature coefficient of Young's modulus is affected not only by annealing

Fig. 3 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of 96% cold working.

Fig. 4 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of reheating at 200°C after cold working.

but also by cold working or quenching. The relationship between e and composition for the specimens subjected to 96% cold working is represented by the equi-value curves in Fig. 3. The figure shows that the composition range of the positive e values is considerably extended as compared with that in the annealed state, and that the transformation temperature is lowered to the neighborhood of room temperature by cold working. Figure 4 shows the values of e in the state of slow cooling after 96% cold working and subsequent reheating at 200°C for 1 hr. In the figure the composition dependence of e undergoes a variation nearly similar to that in the state of cold working and the range of the positive e values is relatively narrow.

Fig. 5 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of reheating at 400°C after cold working.

Fig. 6 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of reheating at 600°C after cold working.

The composition dependence of e in the states of slow cooling after 96% cold working and subsequent reheating at 400 and 600°C for 1 hr are shown in Figs. 5 and 6, respectively. It is shown in these figures that the

Fig. 7 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of water quenching.

Fig. 8 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of reheating at 200°C after water quenching.

Fig. 9 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of reheating at 400°C after water quenching.

Fig. 10 Temperature coefficients of Young's moduli at 0 ~ 40°C for Mn-Ni-Co alloys in the state of reheating at 600°C after water quenching.

ranges of the positive e values become narrower gradually with rise in reheating temperature. This tendency is probably due to the reason that the transformation temperature moves gradually toward the higher temperature side. Figure 7 shows the results of measurements in the state of water quenching after heating at 950°C for 1 hr. The composition range of the positive e values is considerably narrower than that in the state of cold working and rather resembles that in the state of annealing. Figures 8, 9 and 10 show the composition dependences of e in the state of slow cooling after quenching and subsequent reheating at 200, 400 and 600°C for 1 hr, respectively. The composition dependences of e in the state of reheating at 200 and 400°C behave in a way nearly similar to that in the quenched state, while in the state of reheating at 600°C the range of the positive e values is further reduced.

In order to obtain a better understanding of the effects of the reduction rate, quenching temperature and cooling rate after heating on e in the annealed state, experiments were performed on the ternary alloys of Mn-10.02% Ni-10.08% Co, Mn-15.04% Ni-4.06% Co, Mn-10.01% Ni-5.05% Co and Mn-13.03% Ni-2.02% Co. In the case of cold working, the e shows a drastic change from a positive to a negative value or from a negative to a positive value with increase in sectional reduction rate. Similarly, the value of e in the state of water quenching undergoes a marked variation with quenching temperature. When the same specimens were heated at 950°C and cooled to room temperature at various rates, the values of e are greatly changed with cooling rate as have been observed for the cases of cold working and water quenching. The above results show evidently that the alloys having the near-zero temperature coefficient of Young's modulus can be obtained by proper choice of the reduction rate, water quenching temperature and cooling rate.

Figure 11 shows the temperature dependence of E in the temperature range of -50 ~ 80°C for several kinds of the ternary alloys in the state of 96% cold working after heating at 950°C for 1 hr and in the state of reheating at 200, 400 and 600°C for 1 hr after

Fig. 11 Temperature dependence of Young's moduli for Mn-Ni-Co alloys in the states of cold working and reheating for 1 hr at 200, 400 and 600°C after cold working.

Fig. 12 Temperature dependence of Young's moduli for Mn-Ni-Co alloys in the states of water quenching and reheating for 1 hr at 200, 400 and 600°C after water quenching.

cold working. All the E vs temperature curves exhibit a very small minimum or maximum, and the curves on heating and cooling show a good agreement with each other. Figure 12 shows the temperature dependence for several of the ternary alloys in the state of water quenching after heating at 950°C for 1 hr and in the state of reheating at 200, 400 and 600°C for 1 hr. Under any of these conditions, E shows a close agreement on heating and cooling as in the case of heating after cold working and is quite stable against temperature. Because these ternary alloys possess excellent Elinvar characteristics and have very low quadratic parameters, they would be very promising materials for immediate practical applications.

Fig. 13 Corrosion resistivity in Mn-Ni-Co alloys: The hatched area shows the range of high corrosion resistivity.

Table 1 Changes in corrosion resistivity of Mn-Ni-Co alloys in areas A and B of Fig. 13. (mg/cm²/day)

Alloys	After 40 weeks	After 81 weeks
Mn-30Ni-10Co(A)	0.05	0.08
Mn-10Ni-10Co(B)	0.09	0.22

In an effort to examine the corrosion resistivity of Mn-Ni-Co alloys, the specimens were immersed in brine water with the same concentration as sea-water for a period of 81 weeks, and the extent of general corrosion was qualitatively investigated. The experimental results are shown in Fig. 13 and Table 1. As shown in the table, the composition range A (*c.f.* Fig. 13) enclosed with about 15 ~ 40%Ni and less than about 25%Co in the ternary system exhibits relatively high corrosion resistivity, without showing no marked difference in the amount of corrosion after 40- and 81-week immersions. In other domains the corrosion resistivity decreases sharply with increase in Mn and Co contents or with the lapse of the immersion time.

Tables 2 ~ 4 summarize the results of measurements of Young's modulus, rigidity modulus G and its temperature coefficient g , thermal expansion coefficient, hardness at room temperature for typical Elinvar-type alloys in the Mn-Ni-Co system. The effects of heat treatments and cold working on G and g are found to be quite similar to those on E and e , respectively. The hardness of the ternary alloys is of the high order of magnitude in the composition range at which Mn occupies more than 90%, but in other composition ranges the hardness undergoes a complicated variation between 120 and 777 in Vickers hardness with composition, heat treatment and cold working.

The ternary alloys of less than 40%Ni, less than 20%Co and 60 ~ 95% Mn exhibit the Elinvar characteristics over a wide composition range. These alloys are also characterized by the low quadratic parameters and the nonferromagnetic nature. With these considerations, the ternary alloys would be materials highly suitable for use in precision instruments such as tuning forks and hair springs of watches.

IV. Conclusions

Measurements of Young's modulus at low and high temperatures and of thermal expansivity, rigidity modulus, density and hardness at room temperature have been carried out for Mn-Ni-Co ternary alloys subjected to various heat treatments and cold working. The results obtained are as follows:

(1) In the state of cooling at a rate of 100°C/hr after heating at 950°C for 1 hr, a minimum and a maximum are shown in each of the Young's modulus vs temperature curves at -150 ~ 400°C for the compositions of 60 ~ 95% Mn, 1 ~ 40% Ni and 0 ~ 20% Co. This anomalous variation appears to be associated

Table 2 Young's modulus E and its temperature coefficient e , rigidity modulus G and its temperature coefficient g , thermal expansion α and Vickers hardness Hv for Mn-Ni-Co alloys in the annealed state at 950°C for 1 hr.

Composition(%)			E ($\times 10^5$ kg/ cm ² , 20°C)	e ($\times 10^{-5}$, 0~40°C)	G ($\times 10^5$ kg/ cm ² , 20°C)	g ($\times 10^{-5}$, 0~40°C)	α ($\times 10^{-6}$, 0~40°C)	Hv (20°C)
Mn	Ni	Co						
76.88	20.10	3.02	12.45	-1.46	4.48	-1.66	21.85	125
79.90	16.04	4.06	12.42	-0.13	4.72	-0.75	21.13	150
81.91	16.08	2.01	12.40	+1.55	4.70	+1.26	21.80	150

Table 3 Young's modulus E and its temperature coefficient e , rigidity modulus G and its temperature coefficient g , thermal expansion α and Vickers hardness Hv for Mn-Ni-Co alloys in the cold worked and reheated states.

Composition (%)			E ($\times 10^5 \text{ kg/cm}^2$, 20°C)	e ($\times 10^{-5}$, 0~40°C)	G ($\times 10^5 \text{ kg/cm}^2$, 20°C)	g ($\times 10^{-5}$, 0~40°C)	α ($\times 10^{-6}$, 0~40°C)	Hv (20°C)
Mn	Ni	Co						
96% cold worked after annealing								
75.85	20.12	4.03	12.73	-1.11	5.14	-1.35	21.70	238
77.28	10.02	12.70	9.86	+0.06	4.55	+0.06	19.90	263
84.90	5.01	10.09	12.10	-0.25	4.76	-0.56	21.22	280
Reheated at 200°C for 1 hr after cold working								
75.85	20.12	4.03	12.53	-0.43	5.10	-0.75	21.65	240
76.81	15.16	8.03	12.20	-0.32	5.08	-0.51	20.44	245
78.28	10.02	11.70	9.80	+1.72	4.54	+1.63	19.80	261
84.90	5.01	10.09	11.97	-0.75	4.75	-0.88	21.05	260
Reheated at 400°C for 1 hr after cold working								
75.85	20.12	4.03	12.54	-0.11	5.11	-0.25	21.67	242
76.81	15.16	8.03	12.20	-1.22	5.09	-3.74	20.33	240
79.90	10.02	10.08	9.80	+1.80	4.54	+1.12	20.36	262
84.94	10.01	5.05	9.60	+1.00	4.53	+0.56	21.50	222
Reheated at 600°C for 1 hr after cold working								
76.86	20.13	3.01	12.50	+0.40	5.10	+0.57	21.81	195
82.07	15.10	2.83	16.33	+1.16	5.51	+1.05	21.24	513

Table 4 Young's modulus E and its temperature coefficient e , rigidity modulus G and its temperature coefficient g , thermal expansion α and Vickers hardness Hv for Mn-Ni-Co alloys in the water quenched and reheated states.

Composition (%)			E ($\times 10^5 \text{ kg/cm}^2$, 20°C)	e ($\times 10^{-5}$, 0~40°C)	G ($\times 10^5 \text{ kg/cm}^2$, 20°C)	g ($\times 10^{-5}$, 0~40°C)	α ($\times 10^{-6}$, 0~40°C)	Hv (20°C)
Mn	Ni	Co						
Water quenched from 950°C after annealing								
78.88	20.05	1.07	13.19	+0.53	4.86	+0.43	22.37	156
86.87	9.10	4.03	11.37	-0.47	5.08	-0.50	22.01	282
Reheated at 200°C for 1 hr after water quenching								
78.88	20.05	1.07	12.98	+0.98	4.63	+0.65	22.31	136
81.16	15.04	3.80	12.82	-0.22	4.79	-0.63	21.50	177
Reheated at 400°C for 1 hr after water quenching								
82.94	15.06	2.00	12.37	+0.50	4.46	+0.33	21.96	120
Reheated at 600°C for 1 hr after water quenching								
78.88	20.05	1.07	10.09	+0.52	4.96	-0.37	22.44	261
82.94	15.06	2.00	11.39	-0.21	5.08	-0.40	22.03	285

with the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation. The Young's modulus at room temperature shows no marked difference by the states of annealing, cold working and water quenching, but its value has the tendency to increase in some measure with increasing Co content.

(2) The temperature coefficient of Young's modulus in the vicinity of temperature is greatly changed by annealing, cold working, water quenching and reheating after water quenching. The value is also highly dependent on composition. In general, the temperature coefficient of Young's modulus exhibits a positive large maximum value against composition, reflecting the presence of the Elinvar characteristics.

(3) The variations in rigidity modulus at room

temperature and its temperature coefficient in the vicinity of room temperature with heat treatment, cold working and composition are very similar to those for the Young's modulus and its temperature coefficient.

(4) The values for the thermal expansion coefficient in the vicinity of room temperature against composition and the variety of processing show similar results to those observed for Mn-Ni binary alloys.

(5) The variations in hardness of the ternary alloys with composition, cold working and heat treatments occur within the order of 100~800 Vickers hardness in a complicated manner.

(6) Nonferromagnetic Mn-Ni-Co alloys in the

composition range of less than 40%Ni, less than 20% Co and 60 ~ 95% Mn exhibit clearly the Elinvar characteristics and are relatively high in corrosion resistivity. Therefore, these ternary alloys are considered as being suitable for use in precision instruments and gauges.

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