Nonferromagnetic Elinvar-Type Alloys in the Mn-Ni-Mo 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 out with Mn-Ni-Mo alloys subjected to cold working and heat treatment. The ternary alloys slowly cooled after annealing for 1 hr at 950°C show an anomalous temperature dependence to be associated with the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation. Young's modulus at room temperature do not show any significant variations in both the cold worked and annealed states, but this value tends to increase with increasing manganese or molybdenum concentration. The temperature coefficient of Young's modulus show a wide variation from a negative to a positive value by annealing, water quenching, cold working, and reheating after water quenching or cold working, with a strong composition dependence. The variations in rigidity modulus and its temperature coefficient with heat treatment, cold reduction rate and composition are very similar to those in Young's modulus and its temperature coefficient. The vickers hardness of the alloys varies in a complex manner between about 100 to 650 by the various treatments and compositions. The corrosion resistivity of Mn-Ni-Mo alloys is relatively good.

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I. Introduction

It has been shown in a previous paper⁽¹⁾ that the Invar property appears in Mn-Ni alloys due to the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation within the composition range in which face-centered cubic γ phase exists. The Elinvar property has been known to exhibit a wide range of variations by cold working or heat treatment. Further studies on the effects of Cr⁽²⁾, Fe⁽³⁾ and Co⁽⁴⁾ additions on the qualitative properties of the binary alloys have revealed that the Elinvar property occurs in a wide composition range and also that the corrosion resistivity of the ternary alloys is improved to an extent unobtainable with the binary alloys. This paper concerns recent experimental work on the Elinvar property of ternary Mn-Ni-Mo alloys.

II. Experimental

The alloys used in this work were prepared from electrolytic Mn, electrolytic Ni and electrolytic Mo, of which the former two had the same purities as those described previously⁽¹⁾ and the latter was of the same purity as used for the experiments of Mn-Cu-Mo alloys⁽⁵⁾. The details of specimen preparation, heat treatment and cold working have been previously described for similar experiments on the binary alloys. The absence of the phase diagram of ternary Mn-Ni-Mo alloys made it impossible to determine the annealing temperature from the solidus and consequently annealing was performed at an arbitrary temperature of 950°C throughout this work. 50 specimens used

were in the composition range of 40.0–95.0%Mn, 0–40.0%Ni and 0–25.0%Mo. The temperature coefficients were calculated from the measured values of the resonance frequency (500–800 Hz) and the thermal expansion coefficient.

III. Results and Discussion

The experimental results are shown in Figs. 1–13 and Tables 1–3. Figure 1 represents the temperature dependence of Young's modulus E for several Mn-Ni-Mo alloys in the annealed state. In all cases the temperature dependence of E is reversible and exhibits a sharp minimum and maximum around which the variation of E with temperature is very small indicating the appearance of the Elinvar property. In the vicinity of the minimum E , the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation is expected to take place. Figure 2 shows the equi-value curves for the composition dependence of the temperature coefficient of Young's modulus, e , at $0\text{--}40^{\circ}\text{C}$ for the ternary alloys in the annealed state. The values of e are generally in negative sign. However, there exist the values in positive sign over a small range of compositions near Mn-15%Ni-5%Mo, showing that the Elinvar property occurs.

Figure 3 shows the composition dependence of e for the ternary alloys in a 96% cold worked condition. It is evident from the curves in the figure that the composition range with positive values of e becomes much wider than in the annealed state. Figure 4 shows the variation of e when the alloys were cold-worked to 96% reduction, reheated for 1 hr at 400°C and then cooled slowly. The composition dependence of the e values shows a variation similar to that in the cold worked state. However, in the case of reheating at 600 or 800°C for 1 hr, the composition range with positive values of e becomes considerably narrower as shown in Figs. 5 and 6. This is considered due to the decreased effect of cold working with the rise of the reheating temperature involved.

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Figure 7 shows the results of e measurements when the alloys were annealed at 950°C for 1 hr and subsequently quenched into water. The composition range with positive values of e is known to become considerably narrower than that in the cold worked state. The values of e for the alloys which were water quenched, slowly cooled and reheated at 400, 600 and 800°C for 1 hr are shown in Figs. 8, 9 and 10, respectively. The results plotted in these figures indicate

clearly that in all the states involved, the variation of e with composition is nearly identical with one another but differs considerably from that in the case of reheating after cold working.

With the intent of clarifying the dependence of e on the cold work reduction, quenching temperature and cooling rate after annealing, experimental work was performed on alloys of Mn-20.16% Ni-5.15% Mo, Mn-8.97% Ni-11.30% Mo and Mn-13.08% Ni-

Table 1 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-Mo alloys annealed 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	Mo						
74.69	20.16	5.15	10.85	-1.25	4.73	-2.32	21.50	130
74.80	15.10	10.10	12.72	-1.55	5.33	-2.26	20.85	189
80.00	8.97	11.03	12.05	+0.05	5.10	+1.10	20.25	380

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-Mo alloys in the cold worked and reheated states.

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	Mo						
96% cold worked after annealing								
66.39	15.11	18.50	11.68	-1.21	4.99	-2.23	20.36	290
79.90	7.50	12.60	12.88	-0.60	5.35	-1.55	19.80	365
Reheated at 400°C for 1 hr after cold working								
69.10	20.36	10.54	11.90	-1.35	5.05	-1.96	20.73	292
83.42	11.33	5.25	13.63	-1.67	5.60	-1.88	21.45	380
Reheated at 600°C for 1 hr after cold working								
74.80	15.10	10.10	16.25	-2.25	6.41	-3.96	20.22	365
80.50	15.70	3.80	16.21	+0.53	6.37	+0.98	21.46	303
Reheated at 800°C for 1 hr after cold working								
72.49	12.50	15.01	14.16	+0.79	5.75	+1.35	18.86	258
80.19	15.11	4.70	13.36	-1.22	5.52	-2.47	21.44	226

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-Mo alloys in the water quenched and reheated states.

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	Mo						
Water quenched from 950°C after annealing								
74.80	15.10	10.10	13.00	-1.25	5.40	-4.05	20.01	190
80.07	9.30	10.55	14.55	+0.18	5.90	+0.65	20.33	260
Reheated at 400°C for 1 hr after water quenching								
75.29	20.16	4.55	12.25	-0.27	5.17	-0.89	21.38	150
87.38	5.10	7.52	16.65	+0.66	6.67	+1.34	21.27	627
Reheated at 600°C for 1 hr after water quenching								
75.79	19.11	5.10	14.60	-0.76	5.91	-1.00	21.76	406
77.40	16.10	6.50	12.90	+1.23	5.37	+0.66	21.10	170
Reheated at 800°C for 1 hr after water quenching								
74.80	15.10	10.10	13.32	+1.15	5.51	+1.60	20.70	206
81.43	12.46	6.11	15.65	-0.77	6.18	-1.90	21.40	522

Fig. 1 Temperature dependence of Young's modulus of several Mn-Ni-Mo alloys in the annealed state.

Fig. 2 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys in the annealed state.

Fig. 3 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys 96% cold worked.

Fig. 4 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys in the state of reheating at 400°C after cold working.

Fig. 5 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys in the state of reheating at 600°C after cold working.

Fig. 6 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys in the state of reheating at 800°C after cold working.

Fig. 7 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys in the water quenched state.

Fig. 8 Temperature coefficients of Young's modulus at 0-40°C for Mn-Ni-Mo alloys in the state of reheating at 400°C after water quenching.

Fig. 9 Temperature coefficients of Young's modulus at 0–40°C for Mn–Ni–Mo alloys in the state of reheating at 600°C after water quenching.

Fig. 10 Temperature coefficients of Young's modulus at 0–40°C for Mn–Ni–Mo alloys in the state of reheating at 800°C after water quenching.

Fig. 11 Temperature dependence of Young's modulus for Mn–Ni–Mo alloys in the state of cold working and reheating for 1 hr at 400, 600 and 800°C after cold working.

Fig. 12 Temperature dependence of Young's modulus for Mn–Ni–Mo alloys in the state of water quenching and reheating for 1 hr at 400, 600 and 800°C after water quenching.

Fig. 13 Corrosion resistivity in Mn–Ni–Mo alloy: the hatched region is the range of large corrosion resistivity.

Table 4 Corrosion variation in Mn–Ni–Mo alloys in regions A and B of Fig. 13 (mg/cm²/day).

Alloys	After 40 weeks	After 81 weeks
Mn–25Ni–10Mo (A)	0.04	0.05
Mn–10Ni–10Mo (B)	0.10	0.18

5.11%Mo. The results show that there is a wide range of variation in e from positive to negative values and *vice versa* as the rate of the sectional reduction is increased. When the alloys were quenched into water or cooled down to room temperature at various rates from the annealing temperature of 950°C, the values of e exhibit a remarkable variation with quenching temperature and cooling rate, respectively. It can be assumed, therefore, that the ternary alloys having nearly zero temperature coefficient of Young's modulus at room temperature can be obtained by selecting the cold work reduction, the quenching temperature and the cooling rate. Figure 11 shows that the temperature dependence of E for the alloys subjected to the various treatments is very small and reversible in the temperature range of –50–80°C. Figure 12 shows the temperature dependence of E for the alloys in the state of water quenching after annealing at 950°C and in the state of reheating for 1 hr at 400, 600 and 800°C after water quenching. As can be seen in the figure, only a very small variation of E with temperature is observed.

In order to examine the corrosion resistivity of Mn–Ni–Mo alloys, the specimens were immersed in brine solution with nearly the same salt concentration as sea water for 81 weeks and the rates of total corrosion were measured qualitatively. The experimental results are given in Figs. 13 and Table 4. In this alloy system the corrosion resistivity is relatively high over the hatched region A enclosed with approximately 15–40%Ni and below approximately 20%Mo in the figure. In this region the amount of corrosion shows no significant variation with time, e.g., the exposure of 40 or 81 weeks. In the rest of the composition range the corrosion resistivity shows a tendency to decrease rapidly with increasing time or increasing Mn or Mo concentration.

Room-temperature measurement results of the representative Elinvar alloys in the Mn–Ni–Mo system

are listed in Tables 1-3, from which a definite conclusion can be drawn that the Elinvar property appears over a wide range of composition in all of the annealed, cold worked, and reheated states. The effects of heat treatment and cold working on the rigidity modulus G and its temperature coefficient g in the annealed state are very similar to those on E and e . The hardness of the alloys exhibits the dependence on composition, heat treatment and cold working which varies in a complex manner between Vickers hardness 130 and 627.

Ternary Mn-Ni-Mo alloys with compositions of less than 40%Ni, 0-25%Mo and 60-95%Mn reveal the Elinvar property by proper heat treatment and cold working and are nonmagnetic. Consequently, it can be concluded that these alloys are suitable for applications as structural materials of precision instruments such as tuning forks and clock hair springs.

IV. Conclusions

Measurements of the Young's modulus from low to high temperatures and of the thermal expansion, rigidity modulus, density of states and hardness at room temperature have been performed with ternary Mn-Ni-Mo alloys of 60-95%Mn, 0-40%Ni and 0-25%Mo subjected to a variety of heat treatment and cold working. The results obtained are as follows:

(1) There appear a minimum and a maximum in Young's modulus on each of the Young's modulus vs temperature curves for Mn-Ni-Mo alloys which were cooled at a rate of 100°C/hr after annealing at 950°C for 1 hr. The temperature where the minimum occurs seems to be associated with the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation. Generally, the Young's

modulus at room temperature does not show much difference by the condition of heat treatment or cold working, but the value has the tendency to increase as the Mn or Mo concentration is increased.

(2) The temperature coefficient of Young's modulus in the vicinity of room temperature differs greatly by annealing, cold working, quenching, and re-annealing after cold working or quenching, with a strong composition dependence. In general the composition range where the temperature coefficient in positive sign exist is considerably broad and exhibits the Elinvar property.

(3) The variations in rigidity modulus and its temperature coefficient at room temperature with heat treatment, cold work reduction rate and composition are quite similar to those in Young's modulus and its temperature coefficient.

(4) The dependence of hardness on heat treatment, cold working and composition varies in a complex manner between Vickers hardness 100 and 650.

(5) Nonmagnetic Mn-Ni-Mo alloys of less than 40%Ni, less than 25%Mo and 60-95%Mn exhibit a pronounced Elinvar property and have good corrosion resistivity. Therefore, these alloys are suitable for uses as structural materials of precision instruments.

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