Non-ferromagnetic Elinvar-Type Alloys in the Mn-Ni-Ti and Mn-Ni-Zr Systems*

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Young's modulus at high temperatures, thermal expansion, rigidity modulus, hardness and tensile strength at room temperature have been measured for Mn-Ni-Ti and Mn-Ni-Zr alloys subjected to various heat-treatments and cold-working. The Young's modulus vs temperature curves of the annealed ternary alloys indicate marked changes that are associated with the phase transformation and the antiferromagnetic to paramagnetic transformation. The temperature coefficient of Young's modulus at room temperature is largely affected by annealing, cold-working and reheating after cold-working and also composition. The temperature coefficient vs composition curves has a positive maximum, revealing the Elinvar characteristics. Young's modulus, hardness and tensile strength at room temperature of the Mn-Ni binary alloys increase with addition of Ti or Zr.

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I. Introduction

We have reported in details on the experimental results of annealed Mn-Ni alloys⁽¹⁾. Those alloys show the antiferromagnetic to paramagnetic transformation in the region where the γ phase of a *fcc* structure and a very small amount of the α phase of a *fcc* structure coexist. Accompanied by the transformation, the Elinvar characteristics appear in a wide composition range and vary in a complex way by cold-working and various heat-treatments. The recent work on the effect of additions of the third elements to the Mn-Ni alloys has confirmed that the Elinvar characteristic will appear over a wide composition range and these alloys are nonmagnetic⁽²⁾⁽³⁾. The mechanical properties of the binary and ternary alloys are relatively low; 90~150 GPa in Young's modulus, 150~300 in Vickers hardness and 300~700 MPa in tensile strength, making the alloys disadvantageous for practical application. Throughout the previous experiments, the additives which raised the Young's modulus of binary alloys are molybdenum and wolfram⁽³⁾

of group VIB elements and niobium and tantalum⁽⁴⁾ of group VB elements of the periodic table having relatively large atomic radii. To further improve the Young's modulus and other mechanical properties of the binary alloys, the changes in the various properties with addition of titanium or zirconium in group IVB whose atomic radius is nearly the same as the above elements were studied.

II. Experimental

The starting materials of the alloys are 99.8% electrolytic manganese, 99.82% electrolytic nickel and sponge-like titanium and zirconium. The former two elements have been described in the previous work⁽¹⁾. These were rendered to the rod-shaped pieces of 10 mm diameter by melting and casting, then reduced to a 2 mm diameter by forging at high temperatures and drawing at room temperature. Finally rods 110 mm in length were cut from them as specimens with a 90% cold reduction in area. No well-defined ternary phase diagrams have been established for Mn-Ni-Ti and Mn-Ni-Zr system in the literature. Therefore, the melting points of the ternary alloys were at first determined. The specimens in the annealed state were prepared by heating for 2 h at temperatures 100°C lower than the melting point and by cooling at the rate of 100°C/h. The samples in the quenched state were ob-

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tained by water-quenching from the annealing temperature. In addition to the processes of cold-work and water-quench, the specimens were reheated at an appropriate temperature between 200 and 800°C for 2 h and cooled at 100°C/h. The composition ranges of the specimens studied were 65~85% manganese, 15~30% nickel and 0~15% titanium for the Mn-Ni-Ti system and 55~85% manganese, 15~30% nickel and 0~25% zirconium for the Mn-Ni-Zr system.

The various phases of the alloys were observed by X-ray analysis. The values of Young's modulus were calculated from the measured values of resonance frequency (500~900 Hz) using the vibrator-controlled oscillator system⁽⁵⁾ and the density, and its temperature coefficients were also calculated from the values of Young's modulus and thermal expansion coefficient, respectively. The magnetic properties were measured in magnetic fields of up to 800 kA/m using a magnetic balance, and the electrical resistivity measurements were made by the four-terminal method. To get the values of hardness and tensile strength, the micro-Vickers hardness tester and an Instron-type testing machine were used, respectively.

III. Results and Discussion

1. Temperature dependence of Young's modulus, magnetic susceptibility and electrical resistivity

Figure 1 shows the Young's modulus E vs temperature curves for several Mn-Ni-Ti and Mn-Ni-Zr alloys in the annealed state. In almost all alloys the changes in E with temperature are reversible and take a clear-cut minimum and maximum in each curve. The results of X-ray analysis have revealed that the minima on the E - T curve that appear at the low and high temperature side corresponds to the tetragonal (α) to cubic (γ) phase transformation and the antiferromagnetic to paramagnetic transformation (T_N : Néel points), respectively.

The variation in E with temperature is very small in the neighborhood of the minimum and the maximum on the E - T curve, thus showing the Elinvar properties. But these

Fig. 1 Young's modulus vs. temperature curves of Mn-Ni based alloys in the annealed state.

characteristics disappear gradually as the contents of the alloying elements increased. It has been considered that the phenomena occurs by either the shift of the phase transformation point to the low or high temperature side, or the antiferromagnetic to paramagnetic transformation by the addition of the alloying elements.

Figure 2 shows the temperature dependence of magnetic susceptibility χ_θ and specific electrical resistivity ρ of a Mn-Ni-Zr alloy. The two curves are reversible in the same manner during heating and cooling, each indicating a distinct anomaly point marked with T_N .

2. Temperature coefficient of Young's modulus at ordinary temperatures

Figure 3 are plotted the equi-value curves of the mean temperature coefficients of Young's modulus e at 0~40°C as a function of composition for ternary Mn-Ni-Ti and Mn-Ni-Zr alloys in the annealed state. For both alloys, the positive e values fall on a narrow area

Fig. 2 Temperature dependence of magnetic susceptibility and electrical resistivity of Mn-22.10%Ni-9.85%Zr alloy in the annealed state.

Fig. 3 Temperature coefficients of Young's modulus at 0~40°C for Mn-Ni-Ti or Mn-Ni-Zr alloys in the annealed state.

centered on the composition line of 20%Ni and change gradually to negative values with increasing titanium or zirconium content. The range of positive e values is wider in the case of zirconium than titanium addition.

Figure 4 shows the relation between e and the additives for a Mn-22%Ni alloy subjected to cold-working or slow-cooling after reheating at 400°C for 2 h. In the case of zirconium addition, for any conditions of cold-working or reheating, the e value shows a gradual increase at first with increasing zirconium content. After passing through a small maximum, the e shows a somewhat steep decrease and the

Fig. 4 Effect of additional elements on the temperature coefficient of Young's modulus of Mn-22%Ni alloy in both states of cold-working and subsequent reheating at 400°C.

rate of decrement in the reheated state is larger than in the cold-worked state. On the other hand, in the case of titanium addition, the e value linearly decreases from the beginning, and the rate of decrement in the reheated state is also large. The amount of the additives which gives rise to the zero e value is 3~5% for titanium and 8~9% for zirconium. In both cases, the region of positive e values becomes slightly narrow compared to that in the annealed state.

The workability is greatly affected by additives: the workability limits are 5% in the case of titanium and 8% in the case of zirconium. The reason why such a limitation on the workability occurs is that in the ternary alloys the intermetallic compounds† of the additives and manganese or nickel are formed which are very brittle. Because of the brittleness, the alloys cannot be worked at elevated temperatures.

Figure 5 shows the effect of additives on e of a Mn-22%Ni alloy which was water-quenched or reheated at 400°C after water-

† X-ray diffraction analysis confirmed the intermetallic compounds to be Mn_2Ti and MnTi for the Mn-Ni-Ti system⁽⁶⁾ and Mn_2Zr for the Mn-Ni-Zr system⁽⁷⁾, but other compounds possibly exist in some degree.

Fig. 5 Effect of additional elements on the temperature coefficient of Young's modulus of Mn-22%Ni alloy in both states of water-quenching and subsequent reheating at 400°C.

quenching. In the case of zirconium addition, both curves are similar in shape to those of Fig. 4, except for the large maximum of the temperature coefficient. On the contrary, in the case of titanium addition the e decreases linearly with increasing titanium content in both the water-quenched and reheated states and the decreasing tendency is quite opposite to the case of Fig. 4. These various changes of e are thought to be caused by the fact that the Néel point and the $\alpha \rightleftharpoons \gamma$ phase transformation point shifts in a complicated manner with composition, cold-working and heat-treatment.

To know the dependences of e on cold reduction rate and cooling rate after annealing for the ternary Mn-22.10%Ni-2.16%Ti, Mn-20.27%Ni-2.10%Ti, Mn-19.29%Ni-2.18%Zr and Mn-24.18%Ni-5.25%Zr alloys in the annealed state, the experiments were carried out. In the case of cold-working, the value of e vary markedly even for a few per cent of reduction rate in cross-sectional area; the value of e changes from positive to negative sign or *vice versa*. However, the e remains nearly unchanged with a further increase in reduction rate. This is due to the gradual change in fiber

structure of the alloy by cold-working after annealing, and if the arrangement of the fiber structure is made in a definite direction, e will not undergo any change. In the Mn-Ni-Ti and Mn-Ni-Zr alloys, the fiber structure in a 90% cold-worked state takes mainly the $\langle 111 \rangle$ direction. The e value becomes larger in positive or negative sign with increasing cooling rate, in the order of the slow-cooled < air-cooled < water-quenched states. It is shown by the e measurements that Mn-Ni-Ti and Mn-Ni-Zr alloys with almost zero temperature coefficients of Young's modulus at room temperature can be obtained by a proper choice of the cold-reduction rate and heat-treatment.

Figure 6 shows a typical Elinvar-type temperature dependence of E at $-60 \sim 80^\circ\text{C}$ for several ternary alloys subjected to slow-cooling at a rate of 100°C/h after heating at 100°C below the melting point for 2 h and reheating at 400 or 600°C for 2 h after 90% cold-working or water-quenching from the annealing temperature. As seen from the figure, all the curves agree well with each other during heating and cooling, and the temperature dependence of E is very small.

3. Young's modulus, hardness and tensile strength at ordinary temperature

When the third elements are added, the E

Fig. 6 Temperature dependence of Young's modulus for Mn-Ni-Ti and Mn-Ni-Zr alloys in the states of annealing and reheating for 2 h after cold-working or water-quenching.

values of Mn-Ni alloys become generally small in both of the cold-worked and water-quenched states, but the values are increased in the course of reheating. The equi-value curves of E vs composition at room temperature for Mn-Ni-Ti and Mn-Ni-Zr alloys reheated at 400°C for 2 h after water-quenching are shown in Fig. 7. In the case of Mn-Ni-Ti alloys, E increases gradually with increasing titanium content, and the E value is normally as low as 100 GPa in the composition range where the Elinvar characteristics appear. The Young's modulus of Mn-Ni-Zr alloys subjected to the same heat-treatment increases with increasing zirconium content, and the rate of increment is larger than in the case of titanium addition. The E reaches a value nearly equal to common materials of 140~160 GPa in the composition range where the Elinvar characteristics come into existence. Figure 8 shows the effect of the alloying elements on E , Vickers hardness H_v at room temperature for a Mn-22%Ni alloy which was water-quenched and reheated at 400°C for 2 h, and also on tensile strength σ_t at room temperature for the same alloy which was cold-worked and reheated at 600°C for 2 h. As illustrated in the figure, E shows a relatively steep increase at first and then a gradual increase with increasing content of either additive, indicating no marked discrepancy

Fig. 7 Young's modulus at room temperature for Mn-Ni-Ti or Mn-Ni-Zr alloys in the state of reheating at 400°C for 2 h after water-quenching.

Fig. 8 Effect of additional elements on the Young's modulus, E , Vickers hardness H_v and tensile strength, σ_t for Mn-22%Ni alloy.

between the two curves by the different heat-treatments. In the case of Mn-Ni-Zr alloys, the value of H_v continues to increase monotonically with increasing zirconium content, while with increasing titanium content, the H_v rises sharply up to a value of ca. 850 at 5% of titanium, beyond which it remains nearly constant. The σ_t of ternary Mn-Ni-Ti and Mn-Ni-Zr alloys becomes larger than that of the binary alloys during cold-working or reheating after cold working, but no marked increment in σ_t during water quenching and the subsequent heat treatment can be observed. It is evident that the σ_t increases markedly by the addition of only about 2% of Ti or Zr to the binary alloys, after which it rises slowly with increasing additive content and there are no remarkable differences in σ_t by the heat-treatments or additives as in the case of E .

As mentioned above, the E value obtained in this study is higher than that of ternary alloys with Cr, W and Mo⁽³⁾ and is almost equal to ternary alloys with V, Nb and Ta⁽⁴⁾. It seems likely that the increment in Young's modulus is caused by solid solution hardening owing to the relatively large atomic radius of the alloying elements. The large additions of the additives result in an increase in hardness or

Table 1 Young's modulus E and its temperature coefficient e , rigidity modulus G and its temperature coefficient g , linear thermal expansion coefficient α_l , Vickers hardness Hv and tensile strength σ_t for some Mn-Ni base alloys in the states of annealing and cold-working, water-quenching and reheating.

Composition (%)			Basal treatment	Reheating temp. (°C)	$E/GPa,$	$e/^\circ C^{-1},$	$G/GPa,$	$g/^\circ C^{-1},$	$\alpha_l/^\circ C^{-1},$	Hv 20°C	$\sigma_t/MPa,$
Ni	Ti	Zr			20°C	0~40°C	20°C	0~40°C	0~40°C		20°C
20.27	2.10	—	ann.	—	95.0	-0.5 $\times 10^{-5}$	42.3	-0.7 $\times 10^{-5}$	23.0 $\times 10^{-6}$	160	370
22.15	5.22	—	c.w.	—	122.1	+0.7	45.1	+0.5	23.1	250	—
22.10	3.09	—	c.w.	400	110.3	+1.5	43.8	+1.3	23.1	260	780
18.35	2.11	—	c.w.	600	118.5	-0.2	44.7	-0.5	23.1	245	765
22.10	2.16	—	w.q.	—	92.6	0.0	42.0	-0.2	23.1	160	530
22.10	3.09	—	w.q.	400	98.5	0.0	42.6	-0.1	23.1	180	545
22.10	3.09	—	w.q.	600	103.7	+0.3	43.1	+0.2	23.2	200	555
24.18	—	5.25	ann.	—	145.2	+1.5	47.5	+1.4	23.1	150	505
24.30	—	8.26	c.w.	—	169.0	+1.8	50.1	+1.6	23.4	360	865
22.33	—	8.45	c.w.	400	175.8	+0.5	50.8	+0.2	23.2	340	845
19.29	—	2.18	c.w.	600	110.6	-1.7	43.9	-1.8	23.5	350	800
24.34	—	3.71	w.q.	—	125.2	-0.5	45.5	-0.9	23.2	150	475
22.42	—	11.87	w.q.	400	172.1	-1.2	50.5	-1.5	22.5	230	—
21.15	—	4.50	w.q.	600	120.4	-2.0	44.9	-2.2	23.3	170	500

ann: the state of annealing

c.w.: the state of 90% cold-working

w.q.: the state of water-quenching

Young's modulus as a result of the disappearance of the γ phase and the coexistence of the α -Mn phase and the intermetallic compound phase. Thus both the workability and the Elinvar characteristics of the alloys are deteriorated, although the values of Hv and E become considerably larger.

As a consequence, the results of measurements at room temperature for the representative Elinvar-type alloys in the ternary Mn-Ni-Ti and Mn-Ni-Zr systems are listed in Table 1. The Elinvar characteristics are found to appear in a certain composition range in the respective states of annealing, cold-working, water-quenching or reheating after cold-working or water-quenching.

Futhermore, the effects of cold-working and heat-treatments on the rigidity modulus G and its temperature coefficient g in the annealed state are nearly similar to those observed for E and e , respectively. The hardness of the alloys changes from Vickers hardness 160 to 850 with composition, cold-working, water-quenching, and reheating after cold-working or water-quenching. In contrast to the binary alloys, those alloys are hardened by the addi-

tion only few per cent of titanium or zirconium. The tensile strength increases steeply by addition of the third elements, and the rate of increment is slightly larger in the case of zirconium than titanium additions. Various treatments such as cold-working or reheating after cold-working can develop a high value of the order of 750~850 MPa in tensile strength.

In sum, the addition of titanium or zirconium to the Mn-Ni binary alloys exhibit the Elinvar characteristics over a certain composition range. The ternary alloys are nonmagnetic and have a high modulus of elasticity. These results suggest the suitability of the alloys for use as structural materials of precision instruments such as tuning forks and hair springs of watches.

IV. Conclusions

Measurements of Young's modulus at $-150\sim 400^\circ C$ and of thermal expansion, rigidity modulus, density, hardness and tensile strength at room temperature have been carried out for binary Mn-Ni alloys, with titanium or zirconium as third elements, subjected to various heat treatments and cold working.

(1) In the Young's modulus vs temperature curves at $-150\sim 400^{\circ}\text{C}$ for the ternary alloys cooled at 100°C/h after heating at 100°C below the melting point for 2 h, a minimum and a maximum were clearly observed. The temperature at which this minimum appears on the low temperature side corresponds to the tetragonal (α) to cubic (γ) phase transformation, and the one on the high temperature side originates from the antiferromagnetic to paramagnetic transformations.

(2) The temperature coefficient of Young's modulus at ordinary temperatures varies markedly depending on annealing, cold-working, and reheating after cold-working and also on composition. Generally, the Elinvar characteristics are found to appear distinctly in a relatively narrow composition range where a positive temperature coefficient of Young's modulus is present.

(3) Young's modulus for the ternary alloys at room temperature shows generally a low value in the state of water-quenching or cold-working, but it increases by a reheating treatment. Particularly, a high value of $140\sim 160$ GPa can be obtained in the Mn-Ni-Zr system.

(4) The changes in rigidity modulus and its temperature coefficient at ordinary temperatures for the ternary alloys with composition, cold-working, and heat-treatment are similar to those in Young's modulus and its temperature coefficient.

(5) The hardness of the Mn-Ni system becomes higher by the addition of titanium and zirconium, and varies in a complex manner from Vickers hardness 160 to 850 depending on cold-working and various heat-treatments.

(6) The tensile strength of the Mn-Ni system in the annealed state are raised by addition of titanium and zirconium, and attains such a high value as 750 to 850 MPa by cold-working and heat-treatment after cold-working.

(7) The nonferromagnetic Mn-Ni-Ti and Mn-Ni-Zr alloys studied exhibit excellent Elinvar characteristics and have a relatively high value of Young's modulus. These alloys can thus be used as suitable materials for special precision instruments.

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