Elinvar Properties of Mn-Pt Alloys*

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Measurements of thermal expansion, Young's modulus, magnetic susceptibility and electrical resistivity at $-150\sim 500^{\circ}\text{C}$, and hardness and density at room temperature have been made for annealed Mn-Pt alloys. It has been found that Mn-10.05~40.21% Pt alloys cooled slowly after heating at 1100°C for 4 h have distinct anomalies in the vicinity of the antiferromagnetic Néel point in the Young's modulus vs temperature curves. The curve of composition vs temperature coefficient of Young's modulus at room temperature exhibit a large positive maximum at the concentration of 30.10% Pt, showing the existence of the Elinvar characteristics in the Mn-Pt alloy system.

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I. Introduction

The temperature dependences of the elastic moduli in binary Mn-Cu⁽¹⁾, Mn-Ni⁽²⁾, Mn-Ge⁽³⁾ alloys and their ternary alloys⁽⁴⁾ have been measured. In these measurements, the Elinvar characteristics have been shown in the vicinity of the antiferromagnetic to paramagnetic transition point for alloys within the composition range of γ phase region. Subsequently, a comprehensive study of the temperature variation of elasticity for Mn-base alloys having the γ phase at room temperatures is in progress.

Figure 1 shows an equilibrium diagram of Mn-Pt binary alloys proposed by Raub and Mahler⁽⁵⁾. It is clear that Mn-Pt alloys containing 7 to 57 wt% of platinum have the $(\alpha+\gamma')$ or the γ' phase, and the presence of the Elinvar characteristics are expected in these composition range. This paper describes the experimental results mainly on the Elinvar characteristics for the Mn-Pt alloys containing the $(\alpha+\gamma')$ or γ' phase.

Fig. 1 Equilibrium diagram of Mn-Pt alloys.

II. Experimental

The starting materials used were electrolytic manganese and 99.99% metallic platinum and weighed out to be 15 g. The chemical analysis of the former is listed in Table 1. Specimens used for this investigation had eleven different compositions. The electrolytic manganese was first melted in an alumina crucible using the Tammann furnace while blowing argon gas onto the metal surface. The platinum was then added to the melt and

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Table 1 Chemical impurities of manganese used.

Elements	Fe	Ni	Al	Si	C	P	S
%	0.007	0.000	0.000	0.008	0.007	trace	0.003

the mixture was homogenized completely by stirring. The forgeable molten alloys containing about 10–45% Pt were sucked into quartz tubes 3.5 mm in I.D. and reduced to rods of 2 mm diameter by 67.3% cold swaging. On the other hand, the non-forgeable molten alloys containing about 0–10% Pt and more than about 45% Pt were sucked into quartz tubes 3 mm in I.D.

Prior to measurements, the rod specimens were further heated for 4 h at 1100°C in argon atmosphere and cooled at the rate of 100°C/h.

Thermal expansivity of the annealed specimens was measured in the temperature range of $-150 \sim 500^\circ\text{C}$ with vertical⁽⁶⁾ and horizontal-type dilatometers, and the density was determined by the method of weighing in water at room temperature. The Young's modulus and their temperature coefficients were calculated using the resonant frequencies (800~1200 Hz) of the specimens at $-150 \sim 500^\circ\text{C}$ as measured with the vibrator-controlled oscillator⁽⁷⁾ and the measured values of the thermal expansivity and density at room temperature. Hardness measurement was made at room temperature under a load of 500 g using the micro-Vickers hardness tester. Electrical resistivity measurement was carried out by the four-terminal potentiometric method, and the magnetic susceptibility measurement was performed in magnetic fields up to 800 kA/m by a magnetic balance.

III. Results and Discussion

The experimental results are given in Figs. 2~6 and in Table 2.

1. Thermal expansion

Figure 2 show the thermal expansion curves for Mn-Pt alloys in the annealed state. The heating curves are in approximate agreement with the cooling curves, showing the reversible variation in length

Fig. 2 Linear thermal expansion curves of Mn-Pt alloys in the annealed state.

with temperature. Each of the expansion curves for the alloys containing 10.05~40.21% Pt shows an anomaly marked with T_N .

2. Young's modulus

Figure 3 shows the temperature dependence of Young's modulus E for Mn-Pt alloys in the annealed state. This variation is reversible in all cases and in the range $-100 \sim 300^\circ\text{C}$ a minimum and a maximum of E are shown on each of the curves for the alloys containing 10.05~40.21% Pt. The alloys are known to exhibit the Elinvar characteristics in the vicinity of these minimum and maximum E values. The temperatures T_N marked with arrows are almost coincident with the anomalous changes of the thermal expansion curves of Fig. 2. However, the reason for the appearance of another maximum and minimum at a temperature below the anomalous transi-

Fig. 3 Temperature dependence of Young's modulus for Mn-Pt alloys in the annealed state.

tion points in the alloys containing 20.10~40.21% Pt cannot be explained by the equilibrium phase diagram shown in Fig. 1.

To find out the effect of cold working or water quenching on the Elinvar characteristics, experiments were carried out for a Mn-30.10% Pt alloy. The results are shown in Fig. 4. In both cases of water quenching and cold working, the variations in E with temperature differed remarkably either by heating or by cooling. This seems mainly due to the precipitation of the α or the γ' phase from the γ phase by heating after quenching or to the removal of internal strains by heating after cold working⁽⁸⁾.

Fig. 4 Temperature dependence of Young's modulus after water quenching or cold working for a Mn-30.10% Pt alloy.

3. Magnetic susceptibility and electrical resistivity

Figure 5 shows the measured values of magnetic susceptibility χ_g and specific electrical resistivity ρ . The χ_g vs temperature curves are reversible by heating and cooling, where the transition points marked with T_N except for the Mn-5.03% Pt alloy are observed.

The ρ vs temperature curve of the Mn-30.10% Pt alloy also shows a pronounced transition point as in the case of the χ_g vs temperature curves. These transition points agree well with those of the thermal expansion curves and the E vs temperature curves, and seem to correspond to the antiferromagnetic to paramagnetic transition points (Néel points). The values of T_N obtained are plotted in Fig. 1. T_N show a tendency to gradually increase with Pt content as a result of the decrement of the α phase in the $(\alpha + \gamma')$ phase.

In practical application, the Elinvar characteristics are generally evaluated by the value of the mean temperature coefficient of Young's modulus, e at 0~40°C. The e value are estimated from the Young's modulus vs temperature curve in Fig. 3, using the equation

$$e = \frac{1}{E} \cdot \frac{\Delta E}{\Delta T} \quad (1)$$

The e values calculated are shown in Fig. 6.

Fig. 5 Temperature dependence of magnetic susceptibility and electrical resistivity for Mn-Pt alloys in the annealed state.

Fig. 6 Young's modulus E and its temperature coefficient e , linear coefficient of thermal expansion α_l , Vickers hardness H_v and density D for Mn-Pt alloys in the annealed state.

The linear coefficients of thermal expansion α_l at 0~40°C, the values of E , hardness H_v and densities D at ordinary temperatures for the Mn-Pt alloys in the annealed state are also shown in the same figure. Here α_l is defined as

$$\alpha_l = \frac{1}{l} \cdot \frac{\Delta l}{\Delta T} \quad (2)$$

The values of e are positive over a very wide range of composition from 21.0 to 44.5% Pt, and the alloy Mn-30.10% Pt exhibits a maximum value of $+54.50 \times 10^{-5}$. The E and H_v in each of the curves show minimum values which correspond to the maximum in e , and the α_l shows a broad maximum in the vicinity of the concentration of 30% Pt. The D increases monotonically with Pt content. Measurement results at ordinary temperatures

for the typical Mn-Pt alloy are listed in Table 2.

In sum, Mn-Pt binary alloys exhibit the Elinvar characteristics over a certain composition range. The alloys are nonferromagnetic and have a relatively high modulus of elasticity. These results suggest the suitability of the alloys for use as structural material of precision instruments such as tuning forks and hair springs of watches.

IV. Conclusions

Measurements of expansivity, Young's modulus, magnetic susceptibility and electrical resistivity at low and high temperatures and of hardness and density at ordinary temperatures have been carried out for annealed Mn-Pt alloys containing up to 50.01% Pt. The results obtained are summarized as follows:

(1) An anomaly which corresponds apparently to the antiferromagnetic to paramagnetic transition point (Néel point) appears in the expansivity curves of Mn alloys containing 10.05~40.21% Pt.

(2) The Young's modulus plotted as a function of temperature for the alloys 10.05~40.21% Pt exhibits a maximum or a minimum typical of the Elinvar characteristics. Each of these curves has an anomaly corresponding to the antiferromagnetic Néel point.

(3) The temperature coefficients of Young's modulus are greatly affected by cold working or quenching.

(4) The composition dependence of Young's modulus and hardness for the annealed alloys at ordinary temperatures shows a minimum at about 30% Pt, respectively. The density increase monotonically with Pt content. The mean thermal expansion coefficient at 0~

Table 2 Young's modulus E and its temperature coefficient e , linear coefficient of thermal expansion α_l , Vickers hardness H_v and density D for Mn-Pt alloys.

Pt contents (%)	E /GPa, 20°C	e ($\times 10^{-5}$ /°C, 0~40°C)	α_l ($\times 10^{-6}$ /°C, 0~40°C)	H_v (20°C)	D (Mg/m ³ , 20°C)
22.50	151.9	+22.50	25.10	630	10.50
30.10	147.0	+54.50	25.28	190	11.50
45.25	174.4	-1.10	24.47	190	13.80

40°C shows a small maximum with Pt concentration.

(5) The magnetic susceptibility and electrical resistivity vs temperature curves at $-150\sim 500^{\circ}\text{C}$ show the antiferromagnetic transition point of Mn-Pt alloys.

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