Antiferromagnetic Elinvar-Type Alloys in the Mn-Cu-W System*

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The Young's modulus at $-150\sim 400^{\circ}\text{C}$ and the elastic modulus, thermal expansion and hardness at room temperature have been measured for Mn-Cu-W alloys subjected to cold working and various heat treatments. It is shown that an anomaly associated with the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation appears on the Young's modulus vs temperature curves of the ternary alloys slow-cooled after heating at 900°C for 1 hr. The Young's modulus at room temperature is at a little variance between the states of annealing, cold working and water quenching, but its value has a tendency to increase with increase in Mn or W content. The temperature coefficient of Young's modulus differs greatly by the processes of annealing, cold working, water quenching and reheating after cold working or water quenching; the value undergoes a remarkable variation with composition, also. The presence of a large positive maximum on each of the temperature coefficient of Young's modulus vs composition curves indicates the Elinvar characteristics of the ternary alloys. The rigidity modulus and its temperature coefficient at room temperature show a very similar variation to that of Young's modulus and its temperature coefficient for the composition, heat treatment and cold working. In general the hardness of the ternary alloys undergoes a complicated variation within the range of $100\sim 660$ by cold working, water quenching and heat treatment after cold working or water quenching as well as with composition. The corrosion resistivity is fairly good.

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I. Introduction

The present authors⁽¹⁾ have previously reported that in the composition range of α phase where the γ phase of the *fcc* structure is embraced, Mn-Cu alloys in the annealed state reveal the Elinvar characteristics with an anomaly that is associated with the antiferromagnetic $\rightleftharpoons$ paramagnetic transformation, and that the characteristics of the ternary alloys are greatly changed by cold working and various heat treatments. Subsequent work on the effect of addition of Cr⁽²⁾, Ni⁽³⁾, Fe⁽⁴⁾, Co⁽⁵⁾ or Mo⁽⁶⁾ on the properties of this binary system has made it clear that these additions cause the Elinvar properties to appear over a wide composition range with improvement in corrosion resistivity. Studies on the changes in the properties of Mn-Cu alloys by the addition of other third elements are now in progress. The purpose of this paper is to present the results by the addition of W.

II. Experimental Procedure

The alloys used were prepared from electrolytic

Mn, electrolytic Cu and briquet W; the purities of the former two were the same as for the binary alloys⁽¹⁾ and the chemical impurities of the latter is tabulated in Table 1. Except for the annealing temperature, the methods for specimen preparation, heat treatments and measurements followed those for the binary alloys. Since the determination of the annealing temperature from its solidus as the standard was not feasible for lack of a definite phase diagram for the Mn-Cu-W system, the annealing temperature of 900°C was employed throughout the present study. The specimens used were 20 alloys with compositions of $30.0\sim 95.0\%$ Mn, $0.1\sim 70.0\%$ Cu and $0\sim 40.0\%$ W. The temperature coefficient of Young's modulus was calculated from the measured resonance frequency ($470\sim 880$ Hz) and the thermal expansion coefficient.

III. Results and Discussion

The experimental results are summarized in Figs. 1~16 and Tables 2~5. Figure 1 shows the temperature dependence of Young's modulus E for various Mn-Cu-W alloys in the annealed state. As shown in the figures, the temperature dependence of E is reversible in all cases, indicating obviously a minimum and

Table 1 Chemical impurities contained in briquet tungsten used.

Impurities	Fe	Sn	Mn	Cu	P	S	As	C	SiO ₂ +CaO
(%)	0.088	0.006	0.001	Trace	0.002	0.002	0.001	Trace	0.047

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Fig. 1 Temperature dependence of Young's modulus of several Mn-Cu-W alloys in the state of annealing.

Fig. 2 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of annealing.

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

a maximum on each of the curves. The small temperature dependence of E in the neighbourhood of the minimum and the maximum represents the Elinvar characteristics of the ternary alloys. Since these anomalous behaviors appear only in the α phase alloy, the temperature that corresponds to the minimum seems to be the Néel point. Figure 2 shows the equi-value curves for the composition dependence of the temperature coefficient of Young's modulus, e ,

at 0~40°C for the ternary alloys in the annealed state. In general e takes a negative value, but the presence of the positive values in a narrow composition range near Mn-55% Cu-3% W reveals the Elinvar characteristics.

In Fig. 3 are drawn the equi-value curves for the composition dependence of e in the specimens subjected to 96% cold working. As can be seen from the figure, both the composition range for the positive e values and the positive maximum value are considerably larger than those in the annealed state. Figure 4 shows e in the state of slow cooling after 96% cold working and reheating at 200°C for 1 hr, where the variation of e with composition approximates that in the state of cold working. However, in the state of slow cooling after 96% cold working and reheating at 400°C for 1 hr, the region of the positive e values becomes much wider as a whole as shown in Fig. 5. Figures 6 and 7 show the composition dependences of e in the states of slow cooling after cold working and reheating at 600 and 800°C for 1 hr, respectively. For the former, the range of the positive e values almost disappears; the variation of e for the latter closely resembles that in the state of annealing and the range of the positive e values is greatly reduced. This is due to the weakened effect of cold working as the result of raising of the reheating temperature.

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

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

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

Fig. 7 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of reheating at 800°C after cold working.

Figures 8 and 9 indicate the results of measurements in the state of water quenching after heating at 900°C for 1 hr and in the state of reheating at 200°C after water quenching, respectively. As compared to the states of cold working and of reheating at 200°C after cold working, the composition range which embraces the positive e values in all cases becomes widened and the maximum value of e increases considerably. In these cases another small region of the positive e values which has not been observed in the state of cold working and of reheating at 200°C after cold working appears near the composition of Mn-ca.57% Cu-ca.2% W. As shown in Fig. 10, in the state of reheating at 400°C after water quenching, the composition range of positive e values are still as wide as in the state of reheating at 400°C after cold

Fig. 8 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of water quenching.

Fig. 9 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of reheating at 200°C after water quenching.

Fig. 10 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of reheating at 400°C after water quenching.

working. But, in the case of reheating at 600 and 800°C after water quenching, the composition range for the positive e values disappears or becomes very narrow as in the case of reheating at the same temperatures after cold working (Figs. 11 and 12).

In order to obtain a better understanding of the effects of the cold reduction rate, quenching temperature and heating temperature on e in the annealed state, experiments were performed on the ternary alloys of Mn-5.05% Cu-20.10% W, Mn-30.10% Cu-13.05% W, Mn-50.30% Cu-2.02% W and Mn-55.30% Cu-4.85% W. The experimental results are shown in Figs. 13 and 14 and Table 2. As shown in Fig. 13, the e in the state of cold working changes drastically from a positive to a negative value and from a negative to a positive value with increase in sectional reduction rate. A remarkable variation of

Fig. 11 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of reheating at 600°C after water quenching.

Fig. 12 Temperature coefficients of Young's modulus at 0~40°C for Mn-Cu-W alloys in the state of reheating at 800°C after water quenching.

Fig. 13 Effect of cold reduction rate on the temperature coefficient of Young's modulus of Mn-Cu-W alloys.

Fig. 14 Effect of quenching temperature of the temperature coefficient of Young's modulus of Mn-Cu-W alloys.

e with quenching temperature is similarly observed in the state of water quenching as shown in Fig. 14. In Table 2 are shown the values of e for the same specimens which were subjected to cooling to room temperature at various rates after heating at 900°C. As can be seen from the table, the e in all the alloys gives rise to a large variation with cooling rate in a similar way to the cases of cold working and water quenching.

From the above results it is evident that an appropriate selection of the cold reduction rate, quenching temperature and cooling rate makes it feasible to obtain the ternary alloys with nearly zero temperature coefficient of Young's modulus.

Figure 15 shows how E changes with temperature in the range of -50~80°C for several of the ternary alloys in the state of 96% cold working after heating at 900°C for 1 hr and in the state of reheating at 200, 400, 600 and 800°C for 1 hr after cold working. All the E vs temperature curves indicate very small maxima and minima, and the curves show good coincidence between the states of heating and cooling. Figure 16 shows the temperature dependence

Fig. 15 Temperature change of Young's modulus for Mn-Cu-W alloys in the state of cold working and reheating for 1 hr at 200, 400, 600 and 800°C after cold working.

Fig. 16 Temperature change of Young's modulus for Mn-Cu-W alloys in the state of water quenching and reheating for 1 hr at 200, 400, 600 and 800°C after water quenching.

Table 2 Effect of cooling rate after heating for 1 hr at 900°C on the temperature coefficients of Young's modulus of Mn-Cu-W alloys.

Composition(%)			$e (\times 10^{-5}, 0 \sim 40^\circ\text{C})$				
Mn	Cu	W	170°C/sec (Water quenching)	9°C/sec (Air quenching)	500°C/hr (Annealing)	100°C/hr (Annealing)	10°C/hr (Annealing)
39.85	55.30	4.85	-11.50	-5.10	+2.00	+4.50	+7.70
43.68	54.30	2.02	-4.70	+1.50	+8.30	+10.63	+13.00
74.85	5.05	20.10	+15.30	-0.50	-18.50	-24.80	-31.10

of E for several of the ternary alloys in the state of water quenching after heating at 900°C for 1 hr and in the state of reheating at 200, 400, 600 and 800°C for 1 hr. In all the cases, the value of E shows a very small change with temperature in the same way as in the case of cold working.

As mentioned above, Mn–Cu–W alloys in the composition range of 30~91% Mn, 0.1~67% Cu and 0~38% W exhibit excellent Elinvar characteristics by cold working or heat treatment. Although the phenomenon appears to be associated with antiferromagnetic transformation, the nature is characteristic of the ternary alloys in the ($\gamma + \alpha$) phase region as has been observed for Mn–Cu binary alloys. Since Mn and W are not solid soluble with each other, it is very likely that the antiferromagnetic nature of Mn is retained in the Mn-rich corner of the alloy system. However, in order to confirm this, much work will be required in other W composition ranges which have not been investigated in this paper.

In order to investigate the corrosion resistivity of Mn–Cu–W alloys, the specimens were immersed in brine water with the same concentration as sea-water for 60 weeks, and the degree of corrosion was qualitatively examined. The results show that these alloys have a fairly large resistivity in the composition range of about 20~50% of Cu regardless of the amount of W, but the resistivity is reduced rapidly at composi-

tions out of this range with increase in Mn or Cu content.

The measurement results of some representative Elinvar alloys in the Mn–Cu–W system are summarized in Tables 3~5. It is shown that the Elinvar characteristics are revealed over a wide composition range in either state of annealing, cold working and reheating.

The effects of water quenching and cold working on G and g are very similar to those on E and e , respectively. The hardness indicates a complicated variation over a range of 105~662 in Vickers hardness with composition, heat treatment and cold working.

In summary, the ternary alloys of less than 67% Cu and 38% W and 30~91% Mn exhibit the Elinvar characteristics and are nonmagnetic, so that these alloys are very reliable materials for high precision instrumentation uses such as tuning forks and hair springs.

IV. Conclusions

Measurements have been made of the Young's modulus at low and high temperatures and of the rigidity modulus, density and hardness at room temperature for Mn–Cu–W alloys subjected to cold working and various heat treatments. The results obtained are summarized as follows:

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–Cu–W alloys in annealed state at 900°C for 1 hr.

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	Cu	W						
40.85	56.30	2.85	12.40	-1.83	5.22	-1.95	23.50	190
44.18	53.80	2.02	12.53	+1.06	5.26	+1.55	23.51	160

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–Cu–W alloys in 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	Cu	W						
96% cold worked after annealing								
54.80	35.02	10.18	12.25	+3.20	5.17	+2.50	23.95	202
56.44	25.10	18.45	12.45	+0.25	5.23	+0.66	24.02	201
Reheated at 200°C for 1 hr after cold working								
53.83	36.10	10.07	12.44	+2.20	5.22	+1.50	23.93	120
64.00	24.70	11.30	13.50	-1.25	5.56	-2.30	24.01	151
Reheated at 400°C for 1 hr after cold working								
35.45	44.50	20.05	11.40	+0.55	4.90	+0.72	23.86	405
38.14	35.05	26.81	15.20	-0.15	4.84	-1.20	23.89	625
Reheated at 600°C for 1 hr after cold working								
41.40	55.10	3.50	12.60	-8.20	5.28	-9.00	23.56	140
43.45	55.30	1.25	12.40	-6.30	5.22	-6.85	23.51	133
Reheated at 800°C for 1 hr after cold working								
39.85	55.30	4.85	12.55	+1.50	5.27	+1.25	23.55	145
43.39	53.50	3.11	12.70	-0.55	5.31	-1.08	23.52	175

Table 5 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-Cu-W alloys in 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	Cu	W						
Water quenched from 900°C after annealing								
40.35	55.85	3.80	12.45	+0.60	5.23	+0.92	23.54	118
54.80	35.02	10.18	12.55	-2.50	5.27	-3.60	23.91	135
Reheated at 200°C for 1 hr after water quenching								
43.85	55.30	0.85	12.50	-1.80	5.24	-2.00	23.40	130
73.80	16.10	10.10	12.45	+1.22	5.23	+1.96	24.21	130
Reheated at 400°C for 1 hr after water quenching								
32.40	40.05	27.55	15.35	-1.35	5.20	-1.50	23.85	662
39.85	55.30	4.85	12.55	+1.50	5.26	+0.65	23.47	133
Reheated at 600°C for 1 hr after water quenching								
43.85	55.30	0.85	12.43	-3.00	5.17	-3.77	23.53	105
Reheated at 800°C for 1 hr after water quenching								
41.85	55.30	2.85	12.40	+0.20	5.16	+0.65	23.66	103
43.75	54.15	2.10	12.35	-0.10	5.15	-0.55	23.50	155

(1) A minimum and a maximum are observed on each of the Young's modulus vs temperature curves at $-150 \sim 400^\circ\text{C}$ for Mn-Cu-W alloys in the state of cooling at 100°C/hr after heating at 900°C for 1 hr. The temperature for the minimum appears to correspond to the Néel temperature. In the states of annealing, cold working and water quenching, there is little difference in Young's modulus at room temperature, but the difference becomes prominent with increase of the Mn and W content.

(2) The temperature coefficient of Young's modulus near room temperature show conspicuously large changes by annealing, cold working, water quenching and reheating after cold working or water quenching. In addition, these values undergo a remarkable variation with composition. In general the temperature coefficient of Young's modulus vs the composition

curve possesses a large maximum value of positive sign, thus indicating the appearance of the Elinvar characteristics.

(3) The rigidity modulus and its temperature coefficient at room temperature show a variation closely similar to that of Young's modulus and its temperature coefficient with composition.

(4) The hardness of the ternary alloys shows a complicated variation over a range of $100 \sim 660$ in Vickers hardness by the composition, cold working and heat treatment.

(5) Since the ternary alloys of less than 67% Cu and 38% W and 30~91% Mn exhibit clearly the Elinvar characteristics and fairly good corrosion resistivity, these alloys are highly suitable for particular applications as high precision materials.