Nonmagnetic Elinvar-Type Alloys in the Mn-Cu-Co System*

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Measurements of Young's modulus at $-150 \sim 400^\circ\text{C}$ and of rigidity modulus and hardness at room temperature have been carried out for Mn-Cu-Co alloys subjected to a variety of heat treatment and cold working conditions. It is shown that the ternary alloys slow-cooled after heating at 900°C for 1 hr reveal anomalous changes associated with antiferromagnetic $\rightleftharpoons$ paramagnetic transformation on the Young's modulus at room temperature curves. The Young's modulus at room temperature does not show any appreciable difference by the state of annealing, cold working or water quenching while the Mn and Co concentrations are relatively small. The difference becomes conspicuous as the Mn or Co concentration is increased. The temperature coefficient of Young's modulus undergoes a marked variation by annealing, cold working, water quenching, and reheating after cold working or water quenching as well as with alloy composition. It is also to be noted that the temperature coefficient of Young's modulus vs composition curves show large maxima in positive and negative signs, thus indicating the Elinvar characteristics. The rigidity modulus and its temperature coefficient at room temperature represent a very analogous variation to that of Young's modulus and its temperature coefficient with composition, heat treatment and cold working. The values of hardness are higher in the state of reheating after cold working or water quenching than those in the state of annealing, cold working or water quenching, and the corrosion resistance is fairly satisfactory.

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I. Introduction

In a previous paper the present authors reported that in the composition range in which the γ phase with the *fcc* structure is retained Mn-Cu alloys exhibit the Elinvar characteristics with an anomaly resulting from the antiferromagnetic to paramagnetic transformation, and their properties undergo a wide variation by cold working and various heat treatments⁽¹⁾. In the subsequent studies on the effects of additions of Cr⁽²⁾, Ni⁽³⁾ and Fe⁽⁴⁾ on the properties of this binary alloy system, they made that the Elinvar characteristics are revealed over an extensive composition range with improvements in corrosion resistivity. More recently the variations in the Elinvar characteristics with the addition of various third elements to the Mn-Cu alloy system have been investigated. The present paper is intended to report the experimental data on the addition of Co.

II. Experimental Procedure

The alloying materials used were electrolytic Mn, electrolytic Cu and electrolytic Co; the former two had the same purities as those of the binary alloys⁽¹⁾ and the purity of the latter is shown in Table 1. Since the methods for specimen preparation, heat treatments and measurements were entirely the same as those for

the binary alloys except for the annealing temperature, no description will be made of the methods here. The annealing temperature of 900°C was uniformly employed because the temperature cannot be determined from the solidus line as its standard for lack of the ternary phase diagram of the Mn-Cu-Co system. The number of specimens used was 28 kinds with compositions of 30.0 ~ 88.0%Mn, 0.1 ~ 67.0%Cu and 0 ~ 40.0%Co. The resonance frequency used for Young's modulus measurements was 470 ~ 880 Hz.

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-Co alloys in the annealed state. As can be seen from the figure, the variation of E with temperature is reversible in all the alloys investigated, and distinct minima and maxima appear on the E vs temperature curves for the ternary alloys. The variation of E with temperature is very small in the neighborhood of these minima and maxima. The temperature which corresponds to the minima seems to indicate the Néel point. Figure 2 shows the equi-value curves drawn for the composition dependence of the temperature coefficients of Young's modulus, e , at $0 \sim 40^\circ\text{C}$ for the ternary alloys in the annealed state. In general e takes a negative value, but its positive values exist in

Table 1 Analytical results of electrolytic cobalt used.

Elements	Ni	Fe	Cu	Al	Mn	Si	C	S	P
(%)	0.18	0.004	0.004	trace	0.005	0.005	0.005	0.005	0.004

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(1) H. Masumoto, S. Sawaya and M. Kikuchi: J. Japan Inst. Metals, **35** (1971), 723; Trans. JIM, **13** (1972), 21.

(2) H. Masumoto, S. Sawaya and M. Kikuchi: J. Japan Inst. Metals, **35** (1971), 1150.

(3) H. Masumoto, S. Sawaya and M. Kikuchi: J. Japan Inst. Metals, **35** (1971), 1155.

(4) H. Masumoto, S. Sawaya and M. Kikuchi: J. Japan Inst. Metals, **36** (1972), 57.

the vicinity of a line which connect the composition of Mn-15% Cu-12% Co to that of Mn-53% Cu-0% Co. The alloys near in composition to the boundary between the positive and negative values exhibit the Elinvar characteristics.

Figure 3 shows the equi-value curves for the composition dependence of e for the ternary alloys subjected to 96% cold working. As shown in the figure,

Fig. 1 Temperature dependence of Young's modulus in several Mn-Cu-Co alloys.

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

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

the maximum value of e which appears in the annealed state is decreased by cold working, but the region where the Elinvar characteristics are revealed becomes much larger. Figure 4 shows the values of e in the slow-cooled state after 96% cold working and heating at 200°C for 1 hr. In this case, the values of e undergo nearly the same variation as that in the state of cold working. When the ternary alloys are further heated at 400°C for 1 hr after 96% cold working and then slowly cooled, the positive values of e become larger as shown in Fig. 5. Figure 6 shows the variation of e in the state of slow-cooling after 96% cold working and heating at 600°C for 1 hr, and it is clear that the region of the positive e values is generally reduced. However, the composition dependence of e in the state of slow-cooling after cold working and heating at 800°C for 1 hr resembles that in the annealed state as shown in Fig. 7.

Fig. 4 Temperature coefficients of Young's modulus at 0 ~ 40°C for Mn-Cu-Co 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-Co 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-Co 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-Co alloys in the state of reheating at 800°C after cold working.

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

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

Fig. 11 Temperature coefficients of Young's modulus at 0 ~ 40°C for Mn-Cu-Co 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-Co 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-Co alloys.

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

Figure 8 shows the case subjected to water quenching after heating at 900°C for 1 hr. The composition range where the positive values of e are embraced becomes narrower than that in the state of cold working. In this case it is to be noted that another small region of the positive values appears near the

composition of Mn-58%Cu-2%Co. Figures 9, 10, 11 and 12 show the equi-value curves for the composition dependence of e for the ternary alloys which were water quenched, heated at 200, 400, 600 and 800°C for 1 hr and then slowly cooled. It is shown that the variation of e with composition and reheating

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-Co alloys.

Composition (%)			$e (\times 10^{-5}, 0 \sim 40^\circ\text{C})$				
Mn	Cu	Co	170°C/sec (Water quenching)	9°C/sec (Air quenching)	500°C/hr (Annealing)	100°C/hr (Annealing)	10°C/hr (Annealing)
42.57	55.35	2.08	-7.96	-5.11	-2.55	-1.11	-0.05
49.60	45.22	5.18	-13.45	-7.10	+0.91	+4.05	+6.50
59.28	30.39	10.33	-21.05	-8.78	+6.50	+13.01	+17.21
74.46	10.36	15.18	-12.55	-10.06	-8.02	-7.00	-6.06

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

temperature has a similar tendency that in the state of the same heat treatments after 96% cold working.

For the purpose of clarifying the effects of cold working, quenching temperature and cooling rate after heating on e , experiments were performed on the ternary alloys of Mn-30.39%Cu - 10.33%Co, Mn-10.36%Cu - 15.18%Co, Mn-45.22%Cu - 5.18%Co and Mn-55.35%Cu - 2.08%Co. The experimental results are given in Figs. 13 and 14 and Table 2. As shown in Fig. 13, in the state of cold working there is a pronounced variation of e with increase of sectional reduction rate; the e changes drastically from a positive to a negative value or from a negative to a positive value. In the state of water quenching a remarkable variation of e with quenching temperature is also observed as shown in Fig. 14. Table 2 illustrates the values of e for the same alloys which were cooled down to room temperature at various rates after heating 900°C. As is evident from the table, the values of e in all the alloys indicate a marked variation with cooling rate as in the above cases of cold working

and water quenching. It is self-evident from these results that the alloys whose Young's modulus is nearly zero at room temperature can be obtained by an appropriate selection of the cold reduction rate, water quenching temperature and cooling rate.

Figure 15 shows the temperature dependence of E in the range of $-50 \sim 80^\circ\text{C}$ for the several 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 after cold working, respectively. Each of the E vs temperature curve exhibits a broad maximum or minimum, and this trend is similarly observed in the states of heating and cooling. Figure 16 shows the temperature dependence of E for the several alloys in the state of water quenching after heating at 900°C for 1 hr and of reheating at 200, 400, 600 and 800°C for 1 hr. In this case it is also shown that the E vs temperature curves have a broad maximum or minimum as is observed in the state of cold working or of reheating after cold working.

For investigating the corrosion resistivity of Mn-

Table 3 Young's modulus E and its temperature coefficient e , rigidity modulus G and its temperature coefficient g , and Vickers hardness Hv for Mn-Cu-Co alloys in the annealed state at 900°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)	Hv (20°C)
Mn	Cu	Co					
42.57	55.35	2.08	8.66	-1.11	4.10	-2.57	135
49.60	45.22	5.18	8.80	+4.05	4.10	+2.66	163
59.28	30.39	10.33	9.02	+13.01	4.18	+12.47	205
67.73	25.23	7.04	8.85	-1.25	4.13	-2.65	167
74.46	10.36	15.18	15.66	-7.00	6.25	-9.13	402

Table 4 Ditto 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)	Hv (20°C)
Mn	Cu	Co					
96% cold worked after annealing							
59.56	35.34	5.10	9.31	−11.75	4.26	−13.18	217
64.19	15.36	20.45	12.00	+ 2.57	5.10	+ 2.00	263
74.61	20.23	5.16	9.10	− 3.89	4.20	− 5.65	191
74.76	5.11	20.13	10.35	−16.25	4.58	−17.11	260
79.56	10.16	10.28	9.30	+11.97	4.26	+10.10	206
Reheated at 200°C for 1 hr after cold working							
59.28	30.39	10.33	11.87	−11.71	4.82	−14.12	245
59.56	35.34	5.10	11.63	− 1.15	5.11	− 2.85	235
74.61	20.23	5.16	9.12	− 3.22	4.22	− 5.34	190
74.76	5.11	20.13	12.13	−11.40	5.13	−13.74	262
79.56	10.16	10.28	13.56	+10.25	5.58	+ 8.77	339
Reheated at 400°C for 1 hr after cold working							
49.60	45.22	5.18	11.54	− 4.34	4.95	− 5.54	226
59.28	30.39	10.33	11.81	+ 1.40	5.15	+ 0.97	241
69.86	28.13	2.01	9.33	− 2.54	4.27	− 4.13	209
74.76	5.11	20.13	12.16	−14.25	5.14	−16.36	265
79.56	10.16	10.28	13.72	+ 0.55	5.63	+ 0.11	345
Reheated at 600°C for 1 hr after cold working							
49.60	45.22	5.18	10.03	−15.55	4.48	−17.15	217
59.28	30.39	10.33	12.13	+ 6.52	5.14	+ 4.77	261
59.56	35.34	5.10	11.96	+ 7.71	5.18	+ 5.26	251
59.79	20.13	20.08	13.44	−16.17	5.55	−18.22	324
69.62	20.27	10.11	12.18	+ 9.77	5.13	+ 6.97	266
Reheated at 800°C for 1 hr after cold working							
44.39	50.25	5.36	8.82	−11.07	4.11	−13.10	163
54.59	35.19	10.22	9.34	+ 1.42	4.27	+ 0.95	210
59.62	25.16	15.22	12.56	− 6.25	5.27	− 8.22	282
69.56	15.18	15.26	13.75	+ 5.50	5.66	+ 4.35	335

Table 5 Ditto in the 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)	Hv (20°C)
Mn	Cu	Co					
Water quenched from 900°C after annealing							
37.11	60.88	2.01	8.16	+ 1.55	3.90	+ 1.16	116
55.05	40.92	4.03	8.21	-18.22	3.92	-19.66	140
59.79	20.13	20.08	9.04	-12.27	4.17	-13.65	208
64.73	30.22	5.05	8.33	+ 8.68	3.95	+ 6.21	152
79.77	15.11	5.12	8.85	- 1.15	4.11	- 2.33	141
Reheated at 200°C for 1 hr after water quenching							
42.19	52.46	5.35	8.18	- 2.20	3.92	- 6.34	130
59.79	20.13	20.08	9.00	-12.06	4.18	-13.72	182
64.73	30.22	5.05	8.36	+ 9.74	3.97	- 8.22	154
73.85	21.12	5.03	8.22	+15.50	3.92	+13.25	140
Reheated at 400°C for 1 hr after water quenching							
44.39	50.25	5.36	8.13	- 0.90	3.90	+ 0.25	127
56.38	40.54	3.08	8.15	+ 5.51	3.90	+ 4.46	130
59.28	30.39	10.33	8.33	+ 5.39	3.96	+ 4.21	151
69.56	15.18	15.26	8.86	+15.11	4.11	+13.64	170
Reheated at 600°C for 1 hr after water quenching							
44.10	45.36	10.54	9.32	+ 9.08	4.26	+ 7.02	218
54.59	35.19	10.22	9.00	-11.84	4.16	-13.15	202
69.66	20.25	10.09	8.99	+ 9.96	4.15	+ 7.76	180
85.92	10.03	4.05	11.61	+10.00	4.98	+ 8.92	230
Reheated at 800°C for 1 hr after water quenching							
44.39	50.25	5.36	8.17	+14.67	3.90	+12.19	135
54.59	35.19	10.22	9.33	- 9.74	4.26	-13.64	212
61.55	25.16	13.29	9.33	- 2.50	4.26	- 4.11	210
78.40	16.27	5.33	8.79	+10.03	4.10	+ 8.29	195

Cu-Co alloys, the specimens were immersed in brine water with the same concentration as sea-water for 567 days and the corrosion condition of the specimens was examined qualitatively. The results show that the corrosion resistance increases with increasing Cu content in the composition range of more than about 20% Cu, and it does not depend on the Co content. And at compositions below this range the corrosion resistance is reduced rapidly with increase in Mn content.

The Elinvar characteristics of the Mn-Cu-Co alloys at room temperature are summarized in Table 3 ~ 5. These tables lead to the explicit understanding that the Elinvar characteristics appear over a wide composition range in each state of annealing, cold working, water quenching or reheating. The effects of water quenching and cold working on G and g in the state of annealing are found to bear a close resemblance to those on E and e . The hardness is relatively low in the state of annealing, cold working or water quenching, but in the state of reheating after cold working or water quenching its value becomes somewhat higher with increase in Mn or Co content.

In short, the ternary alloys of less than 67.0% Cu and 24% Co and 32.8 ~ 87.5% Mn not only exhibit the Elinvar characteristics that arise from the anti-ferromagnetism possessed by the γ phase but also are nonferromagnetic. For the reasons stated above, the ternary alloys are very favorable for use as materials of tuning forks, hair springs of watches, etc.⁽⁵⁾

IV. Conclusions

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

(5) H. Masumoto, S. Sawaya and M. Kikuchi: Patent pending (No. 020805, March 13, 1970).

(1) The Young's modulus vs temperature curves at $-150 \sim 400^\circ\text{C}$ show a maximum and a minimum, respectively, in the ternary alloys which were cooled at a rate of 100°C/hr after heating at 900°C for 1 hr. The temperature which corresponds to the minimum is considered to indicate the Néel point. At compositions of low Mn and Co contents there is little difference in Young's modulus at room temperature by the states of annealing, cold working and water quenching, but the difference becomes prominent with increase in Mn or Co content.

(2) The temperature coefficient of Young's modulus differs greatly by annealing, cold working, and reheating after cold working or water quenching. The temperature coefficient also varies greatly with composition. Large maximum values in positive and negative signs are found on the temperature coefficient of Young's modulus vs composition curves, thus revealing the Elinvar characteristics.

(3) The variation in rigidity modulus and its temperature coefficient at room temperature with heat treatment, cold-working and composition shows a strong resemblance to that in Young's modulus and its temperature coefficient.

(4) The hardness in nearly all the cases is higher with increase in Mn or Co content. Also, there is the tendency that the hardness in the state of reheating after cold working or water quenching is higher than that in the state of annealing, cold working or water quenching.

(5) Nonmagnetic ternary alloys of less than 67% Cu and 24% Co and 32.8 ~ 87.5% Mn reveal pronounced Elinvar characteristics, with fairly good corrosion resistivity. For the reasons stated above, these ternary alloys are suitable for practical applications as materials of high precision measurement instruments.

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