Elinvar Characteristics of Nonferromagnetic Mn–Cu–Ti and Mn–Cu–Zr Alloys*

By Hakaru Masumoto**, Showhachi Sawaya** and Michio Kikuchi**

Measurements of Young's modulus at 150–700 K, thermal expansion, hardness and tensile strength at room temperature were carried out for Mn–Cu–Ti and Mn–Cu–Zr alloys subjected to various heat treatments and cold-working. Young's modulus vs temperature curves of the annealed alloys have a distinct minimum and a maximum, in association with the antiferromagnetic→paramagnetic transition. The Elinvar properties appear in the temperature range in the neighborhood of this anomaly.

The temperature coefficient of Young's modulus at room temperature is affected by annealing, cold-working, reheating after cold-working and the alloy composition. Young's modulus and hardness increase with addition of titanium or zirconium. The tensile strength shows a maximum at 3–4% titanium or zirconium. No aging effect on mechanical strength and hardness is observed in the ternary alloys.

Therefore, these alloys are very suitable for use as materials of precision instruments. We call these alloys “MANGALOY”.

(Received February 12, 1983)

Keywords: Elinvar alloy, Young's modulus, thermal expansion, antiferromagnetic alloy, manganese-copper based alloy

I. Introduction

Elinvar-type alloys have been developed for ferromagnetic fcc alloys such as the Fe–Ni(1) and Co–Fe–Cr systems(2), and these alloys find wide applications in the materials of precision instruments because of the small temperature coefficient of the elastic modulus. In spite of the excellent elastic property, the ferromagnetism of these Elinvar alloys limits the range of application(2)(3). While, the antiferromagnetic Elinvar alloys have no such inconvenience. Directing our attention to the fact that the antiferromagnetic properties of γ-manganese undergo a considerable alteration with additions of other elements(4)–(8), we have studied the elastic modulus of various γ-manganese based alloys.

A number of manganese based Elinvar-type alloys such as those in the Mn–Cu(9), Mn–Ni(10) and Mn–Ge, -Pt(11) systems have been developed by the authors. More recently investigations on the effect of additions of the third elements on these binary alloys have confirmed that the Elinvar characteristics appear over a wide range of composition(12). These binary and ternary Elinvar alloys have relatively low values of the mechanical properties; that is, 90–150 GPa in Young's modulus, 150–300 in Vickers hardness and 200–400 MPa in tensile strength, coupled with the embrittlement due to age-hardening. It has been found that the most effective additional elements to improve the mechanical properties of these alloys are molybdenum and wolfram(12) in group VIB of the periodic table and vanadium, niobium and tantalum(13) in group VB having relatively large atomic radii. However, the age-hardening is an obstacle to applications of the alloys.

Therefore, an attempt to improve the mechanical and Elinvar properties with the addition of titanium or zirconium in group IVB whose atomic radius is nearly the same as those of the above-mentioned elements has been made in the present study.

II. Experimental

Raw materials of the alloys used were 99.8%
electrolytic manganese, 99.9% electrolytic copper\(^9\) and 99.6% sponge-like titanium and zirconium. Rod-shaped pieces of 10 mm diameter which were obtained by casting of the melt were reduced to 5 mm diameter by forging at high temperatures and then further reduced to 2 mm diameter by swaging and drawing at room temperature. This final diameter corresponds to 80% reduction in area. Finally, rods 110 mm in length were cut from them as specimens for the measurements. Other pieces of ribbon-like specimens 0.16 mm thick were obtained by cold-rolling with 98% reduction in area. The ternary phase diagrams for the Mn–Cu–Ti and Mn–Cu–Zr systems have not been established clearly in the literature. For this reason the melting points of the present alloys were determined.

The specimens in the annealed state were prepared by heating for 7.2 ks (2 h) at temperatures 100 K lower than the melting point and by cooling at the rate of 0.03 K/s (100°C/h). The specimens in the quenched state were obtained by water-quenching from the annealing temperature. The specimens thus cold-worked or water-quenched were reheated for 7.2 ks at an appropriate temperature between 450 and 1070 K and cooled at the rate of 0.03 K/s.

The composition ranges of the specimens studied were 35–80% manganese\(^\dagger\), 15–65% copper and 0–25% titanium for the Mn–Cu–Ti system and 30–70% manganese, 20–65% copper and 0–30% zirconium for the Mn–Cu–Zr system.

X-ray analysis has been carried out for determination of crystallographic phases in the alloys. Values of Young's modulus were obtained by a modified static oscillator method\(^{14}\). Young's modulus \(E\) is given by

\[
f_i = \frac{m_i^2 d}{8\pi l^2} (E/D)^{1/2},
\]

where the mode constant \(m_i\) is 4.73 for the fundamental mode \(i = 1\)\(^{(14)}\), \(d\) the diameter, \(l\) the length, \(f_i\) the resonance frequency and \(D\) the density. The linear thermal expansion was measured at room temperature by means of a horizontal and vertical type dilatometers\(^{(15)}\).

\(^\dagger\) All the compositions are shown in units of mass %.

The temperature coefficient of Young's modulus was calculated from the values of Young's modulus and thermal expansion coefficient. The thermomagnetizations were obtained in magnetic fields up to 800 kA/m using a magnetic balance, and the electrical resistivity measurements were carried out by the four-terminal method. A micro-Vickers hardness tester and an Instron-type testing machine were used to obtain values of hardness and tensile strength at room temperature, respectively.

### III. Results and Discussion

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

Figure 1 shows the temperature dependence of Young's modulus \(E\) for several Mn–Cu–Ti and Mn–Cu–Zr alloys in the annealed state. The changes in \(E\) with temperature are reversible and take an apparent minimum and maximum in almost all curves. The minimum is very close to the antiferromagnetic...
paramagnetic transition point indicated by the arrow. The similar behavior has also been observed by Smith et al.\(^{16}\) 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 characteristics. As the content of the element titanium or zirconium increases, these characteristics disappear gradually and show monotonic \(E-T\) curves with the negative gradient. It is considered that the disappearance of the minimum and maximum occurs by the change in the magnetic state (from the antiferromagnetic to paramagnetic state due to a large content of titanium or zirconium).

Figure 2 shows the temperature variation of \(E\) for the Mn–30%Cu–2%Ti and the Mn–30%Cu–5%Zr alloys. The former alloy was reheated at 473 and 673 K for 7.2 ks, after homogenizing at 1053 K for 7.2 ks and subsequent 80% cold-working. The latter was reheated at the same temperatures, after homogenizing at 1053 K and subsequent water-quenching. The observed Neel point, \(T_N\), depends on the kind of the third element and reheating temperatures. In the case of reheating after cold-working, \(T_N\) increases gradually with the reheating temperature. On the contrary, in the case of reheating after water-quenching, the shift of \(T_N\) from 473 to 673 K becomes very steep. It is seen that the temperature coefficient of Young’s modulus at room temperature varies with the movement of \(T_N\) from positive to negative sign\(^9\)–\(^{11}\)\(^{16}\). In Fe–Mn alloys, Bogachev et al. have found the same behavior for a cold-worked specimen\(^{17}\)\(^{18}\).

Figure 3 shows the alterations in the mean temperature coefficient of Young’s modulus \(e = (1/E)(\Delta E/\Delta T)\) at room temperature (273–313 K) and in \(T_N\) as a function of reheating temperature. Independent of the composition and the treatment of cold-working or water-quenching, the \(e\) and \(T_N\) behave similarly against reheating temperature, showing a drastic change around 600 K.

Figure 4 shows the typical temperature dependence of magnetic susceptibility \(\chi_B\) and specific electrical resistivity \(\rho\) of the annealed Mn–Cu based alloys. The curves are reversible in the same manner during heating and cooling with the presence of a distinct anomaly point corresponding to the Neel temperature\(^{19}\).

2. Temperature coefficient of Young’s modulus at room temperature

Figure 5 shows the relation between \(e\) at 273–313 K and the additional element titanium.
Figures 6 and 7 show the effect of the addition of the third element on $e$ for the Mn–30%Cu alloys subjected to 80% cold-working or water-quenching from 1053 K and subsequent slow-

or zirconium for Mn–30%Cu and Mn–57%Cu alloys in the annealed state. The composition range of positive $e$ values is found only in the Mn–30%Cu alloys to which about 15% titanium and 20% zirconium was added, and the area where $e$ is equal to zero is very narrow. In other ranges of composition, the value $e$ takes a large negative sign with shift of the magnetic transformation point. Alloys based on the Mn–57%Cu alloy shows negative $e$ values by the addition of only 1% of the third element.

Fig. 5 Effect of alloying elements on the mean temperature coefficient of Young's modulus at room temperature for Mn–30% and –57%Cu alloys furnace-cooled after heating at 1053 K for 7.2 ks.
cooling after reheating at 673 K. By increasing titanium, the value of \( e \) becomes positive or negative depending on the kind of the heat-treatments as shown in Fig. 6. Above all, the alloys containing titanium less than 10% show only positive \( e \) values in the state of cold-working and reheating after water-quenching, thus it is expected that the Elinvar characteristics appear in a broader region. In the case of zirconium addition, as shown in Fig. 7, the value of \( e \) takes positive or zero in the states of cold-working and water-quenching, while it becomes negative when reheated at 673 K. Especially, the values of \( e \) obtained by the reheating treatment after water-quenching remarkably increase in the negative sign. The amount of the additions to attain a zero value of \( e \) is 2–18% for titanium and 4–10% for zirconium. The region of positive \( e \) in both cases (Figs. 6 and 7) is wider than that in the annealed state (Fig. 5).

It should be noted, however, that the workability is greatly altered by the additions of titanium and zirconium; it is limited to 9% 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 these manganese based ternary alloys some kinds of intermetallic compounds are formed and besides the phase region of \( \alpha \)-Mn or rich in \( \alpha \)-Mn becomes broader. This results in a considerable increase in brittleness.

The above experiments, reveal that the alloys with an almost zero value of the temperature coefficient of Young's modulus at room temperature can be obtained in the Mn–Cu based ternary alloy systems. Figure 8 shows a typical Elinvar-type temperature dependence of \( E \) at 220–360 K for several ternary alloys subjected to slow-cooling at a rate of 0.03 K/s after heating at 100 K below the melting point for 7.2 ks or reheating at 473 and 673 K for 7.2 ks after 80% cold-working or water-quenching from the annealing temperature. As seen from the figure, all the curves are reversible throughout the heating and cooling processes, and the temperature dependence of \( E \) is very small, showing a nearly zero value of \( e \).

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

The present work has further revealed that by the addition of the third elements, the value of \( E \) of Mn–Cu alloys become smaller both in the cold-worked and in the water-quenched states, but the values are increased on reheating. Equi-value curves of \( E \) vs composition at room temperature for the annealed Mn–Cu–Ti and Mn–Cu–Zr alloys are shown in Fig. 9. \( E \) is depending on the manganese concentration rather than on the content of the third elements, becoming higher with increasing manganese content. It is noted that the \( E \) takes high values nearly equal to 130–160 GPa of the practical materials in the composition range where the Elinvar characteristics appear as \( e < \pm 20 \times 10^{-5} \text{K}^{-1} \).

Figure 10 shows the effect of the alloying elements on \( E \), Vickers hardness \( H_v \) and tensile strength \( \sigma_t \) at room temperature for the Mn–30%Cu alloy which was water-quenched and reheated at 673 K for 7.2 ks. \( E \) increases with an increase in both the additions, with no marked discrepancy between different heat treatments. The values of \( E \) of the Mn–Cu–Ti alloys are higher in the whole composition range than those of the Mn–Cu–Zr alloys. On the other hand, the values of \( \sigma_t \) of the ternary Mn–Cu–Ti

\[ ^{\ddagger} \text{X-ray diffraction analysis confirmed the intermetallic compounds to be Mn}_2\text{Ti and MnTi for the Mn–Cu–Ti system and Mn}_2\text{Zr for the Mn–Cu–Zr system, in addition to other compounds of a few per cent.} \]
and Mn–Cu–Zr alloys which were reheated after water-quenching gradually increase at first with increase of the third elements, pass through a maximum, and decrease thereafter. The maximum values of $\sigma_t$ attain 520 and 400 MPa by the addition of about 3% of titanium and 4% of zirconium, respectively, showing much higher values than in common Elinvar materials. However, there has been found to be no large increment in $\sigma_t$ due to the additions in the cases of water-quenching or cold-working and subsequent heat treatment.

The values of $E$ obtained in this work are higher than those of the ternary alloys with Cr, Mo\(^{(20)}\) and W\(^{(12)}\) as additions and are almost equal to those of the ternary alloys with V\(^{(21)}\). It seems very likely that the increment in Young's modulus is caused by solid-solution hardening due to the relatively large atomic radius of the alloying elements. A large amount of the additions brings an increase in hardness or Young's modulus as a result of the disappearance of the $\gamma$-phase and the appearance of the intermetallic compounds in the $\alpha$-Mn phase. On the other hand, the workability and the Elinvar characteristics of these alloys are deteriorated.

To examine the aging phenomena, particularly, the age-hardening of the ternary alloys, hairsprings of a Mn–30%Cu–2%Ti alloy in the form of a thin ribbon 0.37 mm in width and 0.16 mm in thickness were made by winding spirally. The hairspring subjected to cold-working or reheating at 783 K for 7.2 ks after cold-working was aged at room temperature for 15 Ms (about 6 months). In this case, changes in mechanical strength and hardening were hardly observable. Therefore, it seems reasonable to conclude that the brittlement due to aging, which has often been observed in many manganese based alloys, can also be improved by the addition of appropriate third elements such as zirconium and titanium.

In Table 1 are listed results of measurements on Young's modulus and its temperature coefficient, thermal expansion coefficient $\alpha_t$ and hardness at room temperature for the typical Elinvar-type alloys in the ternary Mn–Cu–Ti and Mn–Cu–Zr systems.

The addition of titanium or zirconium to the Mn–Cu alloys exhibit the Elinvar characteristics over a wide range of composition. The ternary alloys are nonmagnetic and have high values of Young's modulus with almost no age-hardening effect. These results suggest the suitability of the alloys for use as structural materials of precision instruments such as tuning forks, hairsprings of watches, vibrating reeds and delay lines. The Mn–Cu alloys have
be named “MANGALOY” as the abbreviation of manganese and copper alloys.

### IV. Conclusion

Young’s modulus at 150–700 K and thermal expansion, hardness and tensile strength at room temperature have been measured for Mn–Cu based ternary alloys, with titanium or zirconium as third elements, subjected to various heat treatments and cold-working. The results are as follows:

1. In the temperature dependence of Young’s modulus at 150–700 K for the ternary alloys cooled at 0.03 K/s after heating for 7.2 ks at 100 K below the melting point, a minimum and a maximum appear. This minimum appears due to the antiferromagnetic-paramagnetic transformation. The Elinvar characteristics appear near the minimum or the maximum in the Young’s modulus vs temperature curves.

2. The temperature coefficient of Young’s modulus at room temperature for the ternary alloys changes drastically by addition of the third elements. In the case of titanium addition, the composition range where the coefficient of Young’s modulus has the positive sign becomes wider after various heat treatments. On the other hand, in the case of zirconium addition, the positive coefficient does not appear at all by reheating after cold-working or water-quenching.

3. Young’s modulus at room temperature for the ternary alloys shows a low value in the state of annealing or cold-working, but it takes a high value by water-quenching and reheating after water-quenching; especially in the case of titanium addition such values as 110–160 GPa are obtained.

4. By the addition of titanium or zirconium, the Vickers hardness of the Mn–Cu systems takes a high value and alters complicatedly from 200 to 400 depending on the heat treatments.

5. With any additional elements, the tensile strength of the Mn–Cu system gradually increases at first with increase of the third elements, passes through a maximum and decreases thereafter. The maximum values are 520 and 400 MPa at 3% titanium and 4% zirconium, respectively.

6. The ternary Mn–Cu–Ti and Mn–Cu–Zr alloys excel as the Elinvar materials, because of the nonferromagnetic nature, relatively high values of Young’s modulus and negligible aging effect on mechanical properties. These alloys are suitable for use as precise structural materials such as tuning forks, vibrating reeds, hairsprings of watches and delay lines.

This study was supported by the 1980 Grant-in Aid for developmental Scientific Research.
REFERENCES
(13) H. Masumoto, S. Sawaya and M. Kikuchi: Trans. JIM, 18 (1977), 204.