Elastic Properties and Thermal Expansion of Antiferromagnetic Mn–Ge–M (M=Zr or Nb) Alloys*

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Young’s modulus, thermal expansion and magnetization in the temperature range of 120–670 K and crystal structures at room temperature were investigated for Mn–Ge base ternary alloys containing Zr or Nb less than 16% with β, γ, ε and their mixture phases. These properties showed peculiar changes corresponding to the β→ε phase transformation point $T_t$, the Néel point of the antiferromagnetic ε-phase $T_N(ε)$ and that of γ-phase $T_N(γ)$. Elinvar characteristics were obtained in the temperature range between $T_t$ and $T_N(ε)$ and/or below the $T_N(γ)$. Invar characteristics were obtained below $T_N(ε)$ for the alloys having an ε-rich phase. These ternary alloys were possible to cut by a normal lathe in all of the phases, and the forgings was also possible in the γ-phase.

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I. Introduction

In the recent years, the use of nonferromagnetic Invar and Elinvar alloys has been developed as precision materials, particularly to meet the increasing demand for sample stage of electron-microscope, device holder to be set in wafer cutter and structural materials of magnetical and optical head. Along with this line, various attempts have been made for improvements of physical and mechanical properties of the alloys(1). In the Mn–Ge alloy system the elastic characteristics of the antiferromagnetic fcc-γ and hcp-ε phases and the ferrimagnetic fct-ε1 phase have been investigated by Masumoto et al.(2)–(4). They have found that the Elinvar characteristics appear below the Néel point of the ε phase, but they are attenuated with an increase of the ε1 phase. The ε1 phase changes to an antiferromagnetic ε phase above 860 K and it is stable up to 1170 K. In the ε phase, the Invar characteristics appear over a wide temperature range below the Néel point(3), and an anomaly in the temperature dependence of elastic modulus can be observed at the same temperatures(4). However, from a standpoint of practical applications as an elastic material, there are disadvantages in that the temperature range for the Elinvar characteristics is relatively narrow and the temperature coefficient of Young’s modulus on the ε-rich side takes a large negative value in the vicinity of room temperature. The effects of the third elements and heat treatments have been investigated for improving these disadvantages, and it has been found that the additions of Fe(4), Ti or V(5) can solve the above problem effectively. In the present study, the effects of additions of Zr and Nb identical in crystal structure to those of Fe, Ti and V have been investigated.

II. Experimental

Starting materials used were electrolytic Mn of 99.8% purity†, metallic Ge of 99.999% purity and Zr and Nb of 99.9% purity. Melting was carried out using a Tammann or an induction furnace while blowing Ar gas onto the molten surfaces. The alloys with the γ or the

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† The constitutional compositions described in the present paper are expressed by atomic per cent except for the purity of elements.
γ-rich phase were cast into molds 5 mm in diameter for cold working. The ingots were annealed at 1100 K for 10.8 ks and reduced to rods 2 mm in diameter by cold swaging. The rods were cut to a 110 mm length for the various measurements. On the other hand, the hardly forgenable molten ε and γ-rich phase alloys were sucked into quartz tubes 2.5–3.0 mm in inner diameter. These rods were cut to pieces of 90–110 mm length as cylindrical specimens.

For homogenizing, all the specimens were heated at 1100 K for 10.8 ks in quartz tubes filled with high purity dried Ar gas and were allowed to cool in air. Prior to the X-ray analysis, the ternary alloys reduced to 325 mesh grade powders were sealed into quartz tubes with the same Ar gas, heated at 1100 K for 1.8 ks and cooled in air. The specimens thus prepared were used for X-ray diffraction analysis.

The Young’s moduli were determined from the resonant frequency $f_i$ which had been measured by a modified electrostatic transversal vibrating method in the frequency range from 350 to 1600 Hz at temperatures of 120–670 K. Specifically, the Young’s modulus $E$ is given by the equation

$$E = \frac{64\pi^2 l^4 D}{m_t^4 \cdot f_i^2},$$

where $m_t$ is the constant defined by vibrating modes, $l$ the length, $d$ the diameter, and $D$ the density of specimens.

The linear thermal expansion was measured by horizontal and vertical type dilatometers. The magnetization was measured using a magnetic balance in external magnetic fields up to 800 kA/m. Both of the measurements were carried out at the heating and cooling temperatures in the range of 120–670 K at a rate of (14–28) × 10⁻³ K/s. The crystal structures were determined from the X-ray diffraction patterns obtained by using Fe-Kα X-ray at room temperature.

### III. Results and Discussion

1. Temperature dependence of magnetization, Young’s modulus and thermal expansion

Figure 1 shows the temperature dependences of magnetization $\sigma$ measured at 140–600 K for the Mn–Ge base ternary alloys with Zr and Nb additions and for the Mn–Ge binary alloys containing 16 and 18% Ge. All the curves show a reversible change. In the curves, there appears the temperature variation of magnetization, which occurs correspondingly to the magnetic transformation points $T_N(\epsilon)$ and $T_N(\gamma)$ of the ε and γ phases, respectively. The variation is remarkable at around $T_N(\epsilon)$, but only a small maximum appears at $T_N(\gamma)$ as is the case with Fe addition. This weak temperature dependence of magnetization is likely to be characteristic of the antiferromagnetic Mn base alloys with the γ phase. In the lower temperature range, the magnetization decreases progressively with lower temperature, and at the magnetic transformation points, there is a small hysteresis.

![Fig. 1](image-url)
temperature range below $T_N(\varepsilon)$, the temperature dependence of $\sigma$ behaves ferromagnetically. This may reflect the magnetic properties of the D0$_{19}$ type intermetallic compound Mn$_{3.25}$Ge in the $\varepsilon$ phase. In 1971 Kádár and Krén$^{(10)}$ reported that although the magnetic properties of the D0$_{19}$ type compound Mn$_{3.25}$Ge is essentially antiferromagnetic, a weak ferromagnetism exists parasitically below the Néel point. Thereafter, attempts have been made to explain the origin of weak ferromagnetism in terms of the triangular arrangement of spins as in the case of Mn$_3$Sn$^{(11)}$.$^{(12)}$

The figure also shows that the $T_N(\varepsilon)$ and $T_N(\gamma)$ points of the ternary alloys appear in nearly the same temperature range for the binary alloys even by a few per cent additions of Zr or Nb.

While the values of $\sigma$ of the Mn–16%Ge, Mn–18%Ge alloys and the Mn–18%Ge–4%Nb alloy are relatively small as $(0.2-0.4) \times 10^{-6}$ Wb m/kg at 200 K, those of the other alloys shown in Fig. 1 are large. Especially, the magnetization of Mn–20%Ge–4%Nb alloy attains a value of $1.4 \times 10^{-6}$ Wb m/kg, which is about three times larger than that of the binary alloys. This suggests that the contribution of weak ferromagnetism due to the triangular spin structure becomes much larger. For practical purposes, however, these values of $\sigma$ are small enough so that these alloys are also useful as nonferromagnetic materials.

Figures 2 and 3(a), (b) show the Young’s modulus vs temperature curves measured in the temperature range of 120–620 K. Figure 2 shows the results of the Mn–14%Ge alloy with the single $\gamma$ phase, the Mn–16–20%Ge alloy with $(\gamma + \varepsilon)$ mixture phase and the Mn–22%Ge alloy with the single $\varepsilon$ phase. Figure 3(a) and (b) show the results of the ternary alloys with Zr of less than 8% or Nb of less than 10%, which have three different phases mentioned above. The curves are all reversible upon heating and cooling at a rate of $(14-28) \times 10^{-3}$ K/s.

In the $E–T$ curves of the binary alloys, the $\beta \rightarrow \gamma$ or the $\beta \rightarrow \varepsilon$ phase transformation point, $T_i$, and the Néel points of the $\varepsilon$ and $\gamma$ phases, $T_N(\varepsilon)$ and $T_N(\gamma)$, appear evidently. In the case of the $\gamma$ phase Mn–14%Ge alloy, $E$ shows a steep minimum at $T_i$ and then increases abruptly above $T_N(\gamma)$. On the other hand, when the $\varepsilon$ phase appears as increased Ge content, the $T_i$ point shifts toward the low temperature side. As a result, the Young’s modulus tends to be insensitive to temperature between $T_i$ and $T_N(\varepsilon)$ and also between $T_N(\varepsilon)$ and $T_N(\gamma)$, thus showing the Elinvar characteristics. When the alloys become the $\varepsilon$ single-phase structure with a further increase of Ge content, the Young’s modulus shows only a steep minimum at $T_N(\varepsilon)$, as seen in the Mn–22%Ge alloy.

It should be noted that the temperature variation of the present alloys cooled in air differs from the previous result$^{(2)}$ obtained by the slow cooling, except for the alloys with $\gamma$ single-phase. This seems that the ratio of the precipitation of the $\beta$ and $\varepsilon$ phases in the Mn–Ge alloys differs by the cooling rate; the precipitation ratio in the air-cooled state are less than that in the slow-cooled state, and then the anomalous temperature dependence of elastic modulus appears clearly. Rapid cooling such as water quenching results in the ap-
appearance of a high temperature phase and accordingly the curves show an entirely different behavior from those in the slow-cooled state\(^2\). Thus it is known that the elastic property of the Mn–Ge system is extremely sensitive to the heat treatments.

In the case of the \(\gamma\)-rich ternary alloys with Zr, as shown in Fig. 3(a), the Elinvar characteristics are observed over a wide temperature range centering around room temperature below \(T_N(\gamma)\). The widening of the temperature range may be attributed to the retardation of the interdiffusion in solids during the \(\beta\rightarrow\gamma\) transformation by the addition of Zr. Further, in the alloy of the \((\gamma+\epsilon)\) mixture phase, there exists a region which shows a smaller temperature gradient in the temperature range of about 400–500 K between \(T_N(\epsilon)\) and \(T_N(\gamma)\). The region remains almost constant because each transformation point is almost unchangeable with increasing Zr content. In this case, the temperature gradient of Young's modulus at room temperature shows a negative value. Thus, Zr gives a little effect on the structure of the binary alloys and the characteristic of the \(\epsilon\) or the \(\gamma\) phase is retained even in the ternary alloys. Among the ternary alloys investigated, a Mn–14%Ge–4%Zr alloy shows a nearly zero value of the temperature coefficient of Young's modulus.

As shown in Fig. 3(b), the \(E-T\) curve of the ternary Mn–Ge–Nb system shows nearly the same temperature variation as in the case of Zr additions. In the curves of the \(\gamma\)-rich phase alloys, a broad minimum appears in place of the \(T_{\gamma}\) point, and the temperature-variation of Young's modulus becomes smaller between the minimum and the \(T_N(\gamma)\) point. However, in the alloy which shows a pronounced \(T_N(\epsilon)\) point, the temperature coefficient of Young's modulus \((1/E)(dE/dT)\) takes a large negative value below \(T_N\). Also in the Mn–Ge–Nb system, the alloys show a remarkable Elinvar characteristics when they are in the \((\gamma+\epsilon)\) mixture phase. The \(T_{\gamma}\) points definitely observed in the alloys with Ti, V or Cr\(^9\) can hardly be detected in the present alloys with Zr or Nb. Therefore, it is understood that Zr and Nb give rise to a characteristic effect on the Young's modulus. Among the ternary alloys with Nb,
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The Mn–18%Ge–8%Nb alloy shows the smallest temperature coefficient of Young’s modulus.

The Young’s modulus of antiferromagnetic alloys, in general, shows a peculiar change around the Neel point. The appearance of the change has been explained by the ΔE effect\(^{(13)(14)}\) when there is no contribution of phase transformation. The value of ΔE is obtained from the difference between the \(E–T\) curves which are observed in a paramagnetic state and in an antiferromagnetic state. The broken line, for example, illustrated in the Mn–18%Ge alloy in Fig. 2 regards to a paramagnetic state; this was drawn by the simple extrapolation from higher region of temperature than the \(T_N(\gamma)\). The \(\Delta E\) value thus estimated is about 25–30 GPa which is nearly equal to these of antiferromagnetic Elinvar type Mn–Cu\(^{(15)}\) and Mn–Ni\(^{(16)}\) alloys. It is well known that the magnitude of \(\Delta E\) effect of ferromagnetic Fe–Ni alloy is shown as

\[
\Delta E = \Delta E_a + \Delta E_m + \Delta E_i, \tag{2}
\]

where \(\Delta E_a\) is the anisotropic term of the \(\Delta E\), \(\Delta E_m\) the term corresponding to magnetostriction and \(\Delta E_i\) the spontaneous volume magnetostriction. The contribution of \(\Delta E_m\) and \(\Delta E_i\) is quite large for Elinvar characteristics. Although the magnetostriction \(\lambda\) on the Mn–Ge alloys has not been measured yet, the spontaneous volume magnetostriction \(\omega_i\) in an \(\epsilon\) phase alloy is known to be a large value of \(1.3 \times 10^{-2}\) as that of Fe–Ni alloy. From the facts mentioned above, it seems that the Mn–Ge alloys has a large magnetostriction.

The above observation and consideration lead to the conclusion that the Elinvar characteristics of the Mn–Ge base ternary alloys arise from a mutual effect of the \(\beta \leftrightarrow \gamma\) or the \(\beta \leftrightarrow \epsilon\) reversible phase transformation and the magnetic transformation of the antiferromagnetic \(\gamma\) or \(\epsilon\) phase, and then both of the transformations are the condition indispensable for obtaining the Elinvar characteristics. Although Cr\(^{(17)}\) and CoO\(^{(18)}\) show an Elinvar-type elastic change in the neighborhood of room temperature and are antiferromagnetic, Bolef and Klerk\(^{(19)}\) have studied the physical properties around \(T_N\) of Cr and detected a remarkable anisotropy in the elastic constants of each direction and their temperature-variation. Though, the cause of the Elinvar characteristics of Mn–Ge alloys is the reversible phase transformation or the magnetic transformation, it is also presumed that the elastic anisotropy is significant factor. Therefore, a study on single crystals is being carried out to make clear this phenomenon.

Next, we have examined the change in the temperature coefficient of Young’s modulus, \(\epsilon\), with temperature. The alloys examined were (a) Mn–18%Ge–4%Nb alloy which consists of the \((\gamma + \epsilon)\) mixture phase and is remarkable in the Elinvar characteristics and (b) Mn–22%Ge–4%Nb alloy which consists of the \(\epsilon\)-rich phase and does not possess the Elinvar characteristics. The values of temperature coefficient of Young’s modulus calculated at intervals of 10 K are shown in Fig. 4 as a function of temperature. The temperature coefficients of both alloys show maximum at slightly higher temperatures than \(T_N(\epsilon)\) and \(T_N(\gamma)\) respectively and the values are almost proportional to the phase states of the alloys. Alloy (a) shows that the temperature coefficient of Young’s modulus becomes zero over a fairly wide temperature region around 300 K and 450 K. On the other hand, alloy (b) shows mostly positive or negative values of the coefficient, except when the curve cut into the zero line. It is evident that the \(\epsilon\) phase alloys do not show any Elinvar characteristics near room temperature. As shown in the figure, the \(T_N(\gamma)\)

![Fig. 4 Temperature coefficient of Young's modulus as a function of temperature for Mn-18%Ge-4%Nb and Mn-22%Ge-4%Nb alloys air-quenched after annealing at 1100 K for 10.8 ks in Ar gas.](image-url)
point appears at a higher temperature by several tens of K than the minimum point as compared with the relation in $T_N(\epsilon)$. This means that the change in Young's modulus due to the atomic diffusion during the phase transformation proceeds very slowly in the $\epsilon \rightarrow \gamma$ transformation than that in the $\beta \rightarrow \epsilon$ transformation.

Figure 5 shows the thermal expansion $\Delta l/l$ vs $T$ curves of the Mn–18% Ge and Mn–20% Ge binary alloys and of the ternary alloys containing 4% Zr or 4% Nb, respectively. Each curve is reversible and shows a minimum or a bending corresponding to $T_I$, $T_N(\epsilon)$ and $T_N(\gamma)$. Below the $T_N(\epsilon)$ point, the $\Delta l/l$ curves for all the alloys have a small gradient or a negative one. In particular, the Mn–20% Ge base alloys show a more pronounced tendency and take a large value of the spontaneous volume magnetostriction, $(1.2-1.3) \times 10^{-2}$. As reported previously, the Invar-type behavior becomes more remarkable with the increase of Ge content which widens the $\epsilon$ phase range. On the contrary, the bending at $T_N(\gamma)$ which appears at a constant temperature regardless of the kinds of the third elements diminishes with increasing Ge content.

2. The temperature coefficient of Young's modulus and the thermal expansion coefficient at room temperature

Figure 6 shows the contour curves of the temperature coefficient of Young's modulus $e$ (solid lines) and the linear thermal expansion coefficient $\alpha$ (dashed lines) in the vicinity of room temperature (273–313 K) for the ternary alloys.
alloys. These have been obtained from the curves of Fig. 2, Fig. 3(a), (b) and Fig. 5. In the figure, the marks •, ○, △ denote the phase states of γ, (γ+ε), ε and (ε+ζ) determined by X-ray analysis, respectively. The composition range in which the temperature coefficient of Young’s modulus should be within a value of \(\pm 20 \times 10^{-5} \text{ K}^{-1}\) for practical Elinvar materials is wider in the case of Nb additions, while it is much narrower in the case of Zr additions. In this case, however, there is no improvement for the Invar characteristics.

According to Street and Smith\(^{(20)}\), the anomalous temperature-variation of elastic modulus including the Elinvar characteristics in the Mn base alloys can be explained in terms of the antiferromagnetic magnetostriction below the magnetic transformation point, and the effect is remarkable in the γ single phase. In the Mn–Ge base ternary alloys, as shown by the dashed lines in the figure, the γ-rich mixture phase region and the γ phase region in the Nb-added alloys exists along the 20%Ge–15% Nb line. However, in the alloy containing Zr, the γ phase region is narrow, but the composition range with the ε or ε-rich phase becomes much larger. This is the reason that the Elinvar region is different depending on the amount of the additional elements of Nb and Zr. There are two regions of the coefficient \(e \geq 0\) in the ternary alloys containing Zr. This seems to be due to the expansion of the composition range of the (γ+ε) mixture phase towards the low Ge concentration side. On the other hand, the composition range where the Invar characteristics appear is widened by Zr additions.

The elastic property mentioned above makes the alloys very useful as practical materials as in the case of the ternary alloys with Ti or V additions\(^{(5)}\).

### 3. Hardness and workability

Figure 7 shows the effect of Zr or Nb addition on the Vickers hardness \(H_v\) (load 4.9 N) in Mn–14–22%Ge alloy at room temperature. In both cases, \(H_v\) takes a low value such as about 200 in the γ phase state containing less Ge content, while it increases with Ge content and shows a high value such as about 500 in the ε phase state. However, the effects of Zr and Nb on \(H_v\) differ to some extent by amount of the addition; in the case of Zr addition, the \(H_v\) in the γ phase increases by several per cent with increasing Zr, whereas a small maximum at 6% Zr occurs in the ε phase. In the case of Nb addition, the \(H_v\) in any phases increase with Nb and the increment of \(H_v\) is conspicuous in the ε phase.

The experimental result suggests that the slight increase of \(H_v\) in the case of the small additions is caused by solid solution hardening, and that the lowering of \(H_v\) in the case of Zr additions to the ε phase alloy seems to be attributed to the formation of a mixture phase at the initial stage of precipitations of the adjacent ζ or κ phase. Both the ζ and κ phases have a ferrimagnetic fct structure. The explanation in terms of the precipitations of ζ and κ into the Mn–Ge matrix may be supported by the fact of the disappearance of the Invar and Elinvar characteristics with increasing Zr or Nb content\(^{(21)}\).

For the several kinds of the ternary alloys containing 1–5% of Zr or Nb, the forgiability of 6.5 mm rod specimens was determined by using a swaging hammer at room temperature. Cold forgings by about 80% in the reduction of sectional area were possible for the Mn–14
%Ge base ternary alloys of the γ single-phase. But the reduction rate was lowered to about 5–6% when the Ge content increases to more than 20%. This trend corresponds to the increase of $H_v$, and the cold forging of the ε phase alloy becomes difficult. However, the workability becomes improved compared with that of the binary alloys, being comparable with the ternary alloys containing Fe. For these ternary alloys, a dry turning test was also carried out by using an ordinary bench lathe with tool blades made of high speed steel. The turning test of the γ-phase alloys was readily performed. Even for the ε-rich phase alloys, the drilling of φ3.5 mm holes in the φ5 mm rods was possible. The scraped chips scarcely adhered to the tool blades and the worked surface was very smooth and bright. Thus, the cold workability of the Mn–Ge–Zr and Mn–Ge–Nb alloys was superior in cutting ability to the binary alloys, but much remains to be studied for improvements of forgiability of the ε phase alloys.

In Table 1 are listed various properties for the typical ternary alloys. As described above, the values of temperature coefficient of Young’s modulus, $e$, and the thermal expansion coefficient, $\alpha$, show the characteristic properties, respectively, which are advantageous as practical materials. As an example, the temperature coefficient of ultrasonic wave delay time, $t$, derived from the relation

$$t = -\frac{1}{2}(e + \alpha)$$

are listed. The $t$ value becomes smaller as $e$ approaches the zero value. In practical applications to the ultrasonic delay lines, there are many restrictions on the mechanical $Q$-value, insertion losses, vibration resistance and impact resistance. Unless these requirements are satisfied, the materials cannot be put in immediate use.

It could be problem for practical uses that the alloys having a desirable small values of $e$ and $\alpha$ show the low values of Young’s modulus about 90–100 GPa which are 40–50% lower than 180–200 GPa in the typical Elinvar alloys of Fe–Ni–Cr, Fe–Co–Cr, or Fe–Mn. The reason for the considerably lower values of Young’s modulus may be that the Young’s modulus of the γ-Mn alloys is essentially low and is affected by the $\Delta E$-effect. The increase in the modulus is made possible by the addition of other elements which have different atomic values. For example, the γ phase Mn–Cu alloys to which 10% of Mo is added show about a 20% increase of Young’s modulus. However, a further addition of the ε phase Mn$_{3.25}$Ge which is deemed to be most effective in the improvement of workability in the ternary alloys results in an increase of Young’s modulus but does not give a favorable effect on the temperature coefficient of Young’s modulus. Therefore, this problem should be further studied in connection with workability.

### IV. Summary

The ternary alloys used in this investigation were the γ, (γ + ε) and ε phase Mn–Ge alloys.

| Ge-X (at%) | $E$/GPa | $e$/10$^{-5}$ K$^{-1}$ | $\alpha$/10$^{-6}$ K$^{-1}$ | $t$/10$^{-5}$ K$^{-1}$ | $T_N(\gamma)$/K | $T_N(\varepsilon)$/K | $H_v$/293 K |
|-----------|---------|------------------------|------------------------|------------------------|----------------|----------------|-------------|
| 17–1Zr   | 103     | 0.5                    | 9.0                    | -0.7                   | 360            | 515            | 250         |
| 17–8Zr   | 105     | 2.0                    | 10.0                   | 0.5                    | 360            | 510            | 280         |
| 14–4Zr   | 86      | 0.5                    | 12.5                   | -0.9                   | -              | 510            | 180         |
| 22–4Zr   | 124     | -48.0                  | 0.6                    | 24.0                   | 360            | -              | 520         |
| 18–3Nb   | 98      | -3.6                   | 14.8                   | 1.1                    | -              | 515            | 290         |
| 18–8Nb   | 111     | -4.0                   | 2.0                    | 19.9                   | 370            | -              | 540         |

Table 1 Young’s modulus $E$ and its temperature coefficient $e$, linear thermal expansion coefficient $\alpha$, temperature coefficient of delay time $t$, Néel temperature of ε or γ phase $T_N$, and micro-Vickers hardness $H_v$ for typical Mn–Ge base ternary alloys air-quenched after annealing at 1100 K for 10.8 ks in Ar gas.
with additions of less than 16% of Zr or Nb. The crystal structure, magnetization, Young's modulus and thermal expansion of the ternary alloys were measured after being heated at 1100 K for 10.8 ks and subsequently air cooled. The results are as follows:

1. In each additional element, the magnetization of the ternary alloys shows the similar temperature variation to that of the binary alloys in a temperature range above the Neél point of the \( \varepsilon \) phase, \( T_N(\varepsilon) \), but it shows a fairly different behavior below \( T_N(\varepsilon) \). Especially, in the case of Zr additions, the magnetization takes a large value as \( 1.4 \times 10^{-6} \) Wb·m/kg at 200 K, being 3.5 times larger than that of the binary alloys. In the magnetization vs temperature curves, the changes corresponding to the \( \beta\varepsilon \) phase transformation point, \( T_t \), the Neél point of the \( \varepsilon \) phase, \( T_N(\varepsilon) \), and that of the \( \gamma \) phase, \( T_N(\gamma) \), appears, respectively.

2. The Young's modulus vs temperature curves for the ternary alloys are reversible in the heating and cooling cycles. In the curves, \( T_N(\varepsilon) \) and \( T_N(\gamma) \) points appear clearly in the same way as observed in the binary alloys. On the other hand, for the \( \gamma \)-rich phase alloys, temperature \( T_t \) becomes indistinct and shows a broad minimum. Thus, the Elinvar characteristics appear over a wide temperature range from the minimum point to the \( T_N(\gamma) \) point.

3. The thermal expansion curves of the ternary alloys are all reversible, the change corresponding to \( T_t \), \( T_N(\varepsilon) \) and \( T_N(\gamma) \) appear in the curves, and the Invar characteristics appear at temperatures below \( T_N(\varepsilon) \). The Invar region remains almost unchanged by any of the additions. The spontaneous volume magnetostriction of Mn-20%Ge base alloys show nearly the same value of \( 1.2-1.3 \times 10^{-2} \).

4. The composition range where the temperature coefficient of Young's modulus at room temperature for the ternary alloys above \(-20 \times 10^{-3} \) K\(^{-1}\) becomes wider in the case of Nb additions. This is caused by the fact that the \( \gamma \) or \( \gamma \)-rich mixture phases are widened by the additions.

5. For any additional elements, the Vickers hardness of the ternary alloys show such low values as about 200 in the \( \gamma \) phase state with small Ge content. However, this value increases with Ge content and show such a high value as about 500 in the \( \epsilon \) phase state. The effect of additional elements on the hardness of binary alloys differs somewhat by amounts of additions.

6. The Mn-Ge ternary alloys with Zr or Nb have good workability, the cold-forging rate of about 80% in the \( \gamma \) phase state and about 5% in the \( \epsilon \) phase are possible. The cutting ability with a bench lathe is good for any of the phase state. These ternary alloys reveal the pronounced Elinvar characteristics and are nonferromagnetic. The alloys are accordingly suitable for special precision instruments such as tuning forks and vibrating reeds.

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REFERENCES

(1) H. Saito: Physics and Applications of Invar Alloys, Maruzen, Tokyo, (1978), p. 595.
(2) H. Masumoto, S. Sawaya and M. Kikuchi: Trans. JIM, 16 (1975), 163.
(3) H. Masumoto, M. Kikuchi and T. Nakayama: Trans. JIM, 24 (1983), 42.
(4) H. Masumoto, M. Kikuchi and T. Nakayama: Trans. JIM, 24 (1983), 689.
(5) M. Kikuchi, H. Masumoto and T. Nakayama: Trans. JIM, 27 (1986), 393.
(6) Y. Shirakawa and I. Oguma: Sci. Rep. RITU, A-18 Supple. (1966), 523.
(7) e.g., R. Hashiguchi, G. Kamoshita and N. Igata: Kinzoku Butsuri, 2 (1956), 163.
(8) H. Masumoto and T. Kobayashi: Sci. Rep. RITU, A-2 (1950), 856.
(9) e.g., T. Yamaoka: J. Phys. Soc. Japan, 36 (1974), 445.
(10) G. Kádár and E. Krén: Intern. J. Magnetism, 1 (1971), 143.
(11) G. J. Zimmer and E. Krén: Magnetism and Magnetic Materials, 1972 (AIP Conf. Proc. No. 10), American Institute of Physics, New York, (1973), p. 1379.
(12) T. Nagamiya, S. Tomiyoshi and Y. Yamaguchi: Solid State Commun., 42 (1982), 385.
(13) O. A. Khomenko, I. F. Khilkevich and G. Yu. Zrigintseva: Phys. Metal. and Metallog., 46-6 (1978), 1190.
(14) J. T. Lenkkeri and J. Levoska: Phil. Mag., A-48 (1983), 749.
(15) H. Masumoto, S. Sawaya and M. Kikuchi: Trans.
(16) N. Honda, Y. Tanji and Y. Nakagawa: J. Phys. Soc. Japan 41 (1976), 1931.
(17) M. E. Fine, F. S. Greiner and W. S. Ellis: Trans. AIME, 189 (1951), 56.
(18) M. E. Fine: Phys. Rev., 87 (1952), 1143.
(19) D. I. Bolef and J. de Klerk: Phys. Rev., 129 (1963), 1063.
(20) R. Street and J. H. Smith: J. Phys. Rad., 20 (1959), 82.
(21) H. Masumoto, T. Nakayama and M. Kikuchi: Trans. JIM, 25 (1984), 828.

(22) K. Narita, D. Hayakawa, M. Akimoto and R. Sato: National Tech. Rep., 26 (1980), 363.
(23) H. Saito: Oyo-Kinzokugaku-Taikei, Vol. 9, Seibundo-Shinkosha, Tokyo, (1965), p. 360.
(24) O. G. Sokolov and A. I. Mel'ker: Sov. Phys.-Doklady, 9 (1965), 1019.
(25) On Young's modulus of γ-Mn, J. H. Smith and E. R. Vance: J. Appl. Phys., 40 (1969), 4853. On Young's modulus of α-Mn, M. Rosen: Phys. Rev., 165 (1968), 357.
(26) H. Masumoto, S. Sawaya and M. Kikuchi: Trans. JIM, 14 (1973), 183.