Influence of Addition of Fe, Co or Ni on the Properties of Antiferromagnetic Invar Mn-Ge Alloys*

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Investigations have been made on the effect of Fe, Co or Ni addition on the thermal expansion, magnetization, lattice constants, hardness and workability of Invar-type Mn-20 and 22%Ge alloys cooled to room temperature at various rates after homogenizing at 1100 K (830°C) for 10.8 ks (3 h). In the thermal expansion vs temperature curves of the ternary alloys containing 10%Fe and Co or Ni less than 5%, a bending point corresponding to the Néel temperature of the ϵ phase was distinctly observed. Below the Néel temperature, these alloys show very small values of thermal expansion coefficient and the Invar characteristics. The region in which the thermal expansion coefficient at room temperature becomes zero is expanded by the Fe addition, while it is rather reduced by the Ni or Co addition. Temperature dependence of the magnetization of these alloys is very analogous to that of the binary alloys. The ϵ phase which shows antiferromagnetism at room temperature is stabilized by the addition of Fe, Co or Ni.

The Vickers hardness of the Mn-20%Ge alloy is decreased at first from 500 to about 400 by the addition of a few per cent of Fe, and then a value of about 400 persists up to 10%Fe. The performance of cutting and forging of the binary alloys has much more been facilitated by the addition of Fe, Co or Ni.

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I. Introduction

Mn-Ge alloys containing 20–25%Ge have the antiferromagnetic ϵ phase (*hcp* structure) at higher temperatures⁽¹⁾ and the ferrimagnetic ϵ_1 phase (*fct* structure) at lower temperatures⁽²⁾ with a temperature boundary at about 860 K (590°C)⁽³⁾⁽⁴⁾. In 1980, we examined the relationship between the thermal expansivity and heat treatments for the alloys having ϵ and ϵ -rich phase structures. It was found that the alloys became non-ferromagnetic Invar alloys when cooled to room temperature from a temperature higher than the magnetic transformation point at the rates faster than 0.19×10^{-3} K/s (0.7°C/h) and that they consisted of the antiferromagnetic ϵ phase and showed a

large positive spontaneous volume magnetostriction in the temperature range below the magnetic transformation point. We named the alloy “Volcoloy”⁽⁵⁾⁽⁶⁾.

The alloy has the remarkable Invar characteristics, but some problems are left to be solved for applications; that is, (1) narrowness of the composition and temperature ranges to reveal the Invar characteristics, (2) insufficient mechanical workability, and (3) low mechanical strength. As the alloy has the compound $\text{Mn}_{3.25}\text{Ge}$ in the ϵ phase region, it is difficult to settle these problems. To improve these defects, the influence of addition of various third elements on the thermal, magnetic and structural properties of the Mn-Ge Invar alloys were investigated. In this paper, experimental results concerning Fe, Co or Ni addition are reported in detail.

II. Experimental

Starting materials used were electrolytic Mn, metallic Ge, and electrolytic Fe, Co and Ni containing impurities tabulated in the Table 1, and the former two had the same purities as

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Table 1 Results of chemical analysis of metals used (mass %).

Metal	Fe	Co	Ni	Cu	Mn	Si	C	S	P
Fe	—	—	—	0.004	0.005	0.005	0.005	0.005	0.004
Co	0.003	—	0.046	—	—	0.001	0.003	0.001	—
Ni	0.001	0.01	—	—	—	—	trace	0.002	—

described in a previous paper⁽⁶⁾. These elements were melted in an alumina crucible placed in a Tammann furnace while blowing Ar gas onto the melt surface, and sucked up into a silica tube 2.5–3.0 mm in inner diameter. The specimens were cut to a length of about 100 mm for the thermal expansion measurement. For the workability test, the melt was cast into an iron mold 5 mm in inner diameter and cut to a length of 150 mm. All specimens were heated at about 1100 K (830°C) for 10.8 ks (3 h) in a silica tube filled with Ar gas for stabilization and homogenization of the ϵ phase and then cooled down to room temperature in furnace or in air. For the X-ray analysis, the ternary alloys which were reduced to 325-mesh powder were heated at about 1000 K (730°C) for 1.8 ks (30 min) in a fused silica tube filled with Ar gas and then quenched into water.

The linear thermal expansion was measured using horizontal- and vertical-type dilatometers⁽⁷⁾ at the cooling and heating rates of about 27.8×10^{-3} K/s (100°C/h) in the temperature range between 120 and 1100 K under Ar atmosphere. The magnetization measurement was carried out in vacuum using a magnetic balance under an external magnetic field of about 800 kA/m under the same condition as used for the thermal expansion measurement. The crystal structures and lattice constants were determined from X-ray diffraction patterns obtained at room temperature. The values of hardness were obtained at room temperature using a micro-Vickers hardness tester under a load of 4.9 N (500 g). The machinability of the alloys in the as-cast state was also tested by a usual lathe (gyration of spindle: 1000–1500 rpm; 17–25 rps), and the forgeability was tested by a swaging hammer (gyration of spindle: 1000–1600 rpm; 17–27 rps).

III. Results and Discussion

1. Thermal expansion at high temperature

In this work two kinds of Mn-base binary alloys containing 20 and 22%Ge[†] were used as the base alloys having the pronounced Invar characteristics.

Figures 1–3 show linear thermal expansion curves of the binary alloys, to which Co, Ni and Fe were added, respectively, heated at 1100 K for 10.8 ks in fused silica tubes filled with Ar gas and quenched in air. The measurement was performed at the heating and cooling rate of about 27.8×10^{-3} K/s in the temperature range between 150 and 500 K. The ternary alloys are all reversibly temperature-dependent. In the figures the open circles denote the Mn–20%Ge base alloys, and the solid circles the Mn–22%Ge base alloys.

As indicated in Fig. 1, there is a large contraction or a bending near the Néel point in each of the ternary alloys having only 1%Co, showing the Invar characteristics similar to the binary alloys shown by the dotted lines. However, with increasing Co addition, the Néel points in the curves are obscured, and slight changes appear for the additions of 5%Co to the Mn–20%Ge alloy and of 4%Co to the Mn–22%Ge alloy. The thermal expansion coefficients of these alloys increase to such large values as 18×10^{-6} K⁻¹ and 13×10^{-6} K⁻¹, respectively. The Néel temperatures of the alloys decrease by the addition of 1%Co but undergo little changes by the addition of 2%Co or more. It is postulated that the thermal expansion curves of the ternary alloys containing Co alter to some extent depending on the Ge

[†] All alloy compositions were shown in units of atomic per cent.

Fig. 1 Influence of Co addition on the linear thermal expansion curves of Mn-20 and 22%Ge alloys.

concentration, but the Invar characteristics are attenuated rapidly with the increase in Co addition.

As seen in Fig. 2, the Invar characteristics of the ternary alloys containing 1%Ni appear distinctly as in the binary alloys. With increase in Ni addition, the Invar characteristics are attenuated continuously. However, there are still distinct bending points in the curves of the alloys containing 4 and 5%Ni, being different from the alloys containing the same amounts of Co. The thermal expansion coefficients of the alloys below the Néel points are 12.5×10^{-6} and $6.5 \times 10^{-6} \text{ K}^{-1}$ for the Mn-20%Ge-5%Ni and Mn-22%Ge-4%Ni alloys, respectively. While the Néel point of the Mn-20%Ge-Fe alloy decreases at first and then increases with increase in Ni addition, it monotonically decreases in the case of the Mn-22%Ge-Fe alloy.

Fig. 2 Influence of Ni addition on the linear thermal expansion curves of Mn-20 and 22%Ge alloys.

In the case of the Mn-20%Ge-Fe ternary alloy, as seen in Fig. 3, the Néel point of the binary alloy, 370 K, decreases gradually with increase in Fe addition, but the Invar characteristics remain almost unchanged for the addition up to 8.4%Fe. This result is different from the case of the Ni or Co addition.

2. Thermal expansion at room temperature

From the above measurements of thermal expansion at high temperatures, it has become obvious that the composition range of binary alloys showing the Invar characteristics is remarkably expanded by the Fe addition. The thermal expansion coefficients $\alpha_{R.T.}$ at room temperature for the Mn-Ge base ternary alloys containing various amounts of Fe were measured and are shown in Fig. 4. The $\alpha_{R.T.}$ value is zero or slightly negative in the wide composition range between about 71 and 76%Mn,

Fig. 3 Linear thermal expansion vs temperature curves of Mn-20%Ge-Fe ternary alloys.

Fig. 4 Thermal expansion coefficient at room temperature of Mn-Ge-Fe ternary alloys.

20 and 25%Ge or 0 and 7%Fe, and the positive large $\alpha_{R.T.}$ values are shown in the other composition range. This predicts that the composition range of the Mn-Ge binary alloys for the zero value of $\alpha_{R.T.}$ is greatly expanded by the Fe addition.

Figure 5 shows the dependence of Fe concentration on $\alpha_{R.T.}$ for the Mn-20 and 22%Ge alloys obtained from Fig. 4, together with the data in the case of Ni or Co addition for reference. The values of $\alpha_{R.T.}$ of both alloys decrease at first with increase in Fe addition and become zero at the Mn-20%Ge-3-5%Fe and Mn-22%Ge-2-4%Fe compositions. With further increase in Fe addition, $\alpha_{R.T.}$ becomes negative, shows a minimum of $-3 \times 10^{-6} \text{ K}^{-1}$ at 6%Fe in both alloys regardless of the Ge content, and then increases to a positive value through the zero value. Moreover, $\alpha_{R.T.}$ of both alloys shows a minimum positive value at the composition of about 1%Co or 1%Ni and also shows a remarkable variation for the increased addition of Co or Ni.

The spontaneous volume magnetostriction of the Mn-20%Ge-base ternary alloy with 2.1 or 4.2%Fe, having the most remarkable Invar characteristics, was measured at 77 K to be 1.3×10^{-2} in both cases. This value is nearly equal to that of the Mn-20%Ge binary alloy and is comparable to those of ferromagnetic Fe-Ni⁽⁸⁾ and Fe-Pt⁽⁹⁾ Invar alloys.

It is apparent that the Invar characteristics does not disappear even if the third element is

Fig. 5 Influence of Fe, Co, or Ni addition on the thermal expansion coefficients $\alpha_{R.T.}$ of Mn-20%Ge and Mn-22%Ge alloys.

Fig. 6 Lattice constants of Mn-20%Ge-Fe ternary alloys.

added to Mn-Ge binary alloys. So, dependence of the lattice constants of the Mn-20%Ge-base alloys on the content of the third element was determined at room temperature, and the result is shown in Fig. 6. The constants, a and c , are decreasing monotonically with increasing Fe addition, and its ratio c/a changes very little. On the other hand, the X-ray analysis reveals that the ternary alloy containing about 6%Fe, 1%Co or 1%Ni showing a minimum value of $\alpha_{R.T.}$ is in the ϵ -single phase range. When the addition of the third element increased, the ζ phase (*hcp* structure) which is adjacent to the ϵ phase is mingled gradually. From the results mentioned above, the addition of Fe makes the ϵ -phase region of the Mn-Ge alloys broader, but the addition of Co or Ni tends to reduce the region, and the ζ phase contained in small quantities in the ϵ phase alloy has no effect on the Invar characteristics.

3. Magnetization

Figure 7 shows the relation between temperature and magnetization σ of the Mn-Ge-Fe alloys in the state of air-quenching after heating at 1100 K for 10.8 ks. The measurements were carried out at the cooling and heating rates of about 27.8×10^{-3} K/s. All the curves show such a similar behaviour that the relatively high value of σ around room temperature decreases gradually with increasing temperature, then rapidly decreases and forms a bending point at a temperature just below the Néel point of the ϵ phase. With further increase in temperature up to 800 K, σ decreases very slowly. The Néel point $T_N(\epsilon)$ shifts to the low temperature side

Fig. 7 Temperature variation of magnetization in Mn-20%Ge-Fe alloys.

with increase in Fe addition, in good agreement with the result of Fig. 3. This value of $T_N(\epsilon)$ does not change even when cooled from a high temperature of about 800 K. There is a small maximum marked with $T_N(\gamma)$ appearing in the higher temperature range from 500 to 550 K, which is thought to be the Néel point of the γ phase of the Mn-Ge alloys⁽¹⁰⁾. When the Mn-20%Ge-4.2%Fe alloy was held at 770 K, just below the $\epsilon \rightleftharpoons \epsilon_1$ phase transformation temperature, for 54 ks (15 h), the magnetization σ increases slightly from 0.14×10^{-6} to 0.4×10^{-6} Wb·m/kg. This is most likely to indicate the initiation of the ϵ to ϵ_1 transformation. When cooled from the above-mentioned state, the value of σ shown by the solid circles decreases linearly and returns to the value measured upon heating near the Néel point, and then takes a value close to that in the air-quenched state. This result provides good evidence that the $\epsilon \rightleftharpoons \epsilon_1$ phase transformation takes place very slowly by the Fe addition and the ϵ phase is stabilized.

The temperature dependence of magnetization in Mn-20%Ge-Fe alloys can be seen as with ferromagnetic materials. In 1982, the experiment of polarized-neutron diffraction from Mn_3Ge has been reported by Nagamiya *et al.*⁽¹¹⁾ According to them, the compound Mn_3Ge has a weak ferromagnetic moment in the *c*-plane depending on the triangular spin orientation itself. The magnetization of the alloys containing a ferromagnetic element such

as Fe is $0.7\text{--}0.8 \times 10^{-6} \text{ Wb} \cdot \text{m/kg}$ at most in the temperature range as shown in Fig. 7. Therefore, it does not matter to use the present alloys in a magnetic field.

4. Hardness and workability

In a previous paper⁽⁶⁾, we pointed that the Mn-Ge alloys have a high value of Vickers hardness such as 500 and poor machinability and that they have remarkable Invar characteristics in the state of the antiferromagnetic ϵ phase. So, mention will be made of the effect of Fe addition on the workability. Figure 8 shows the Fe concentration dependence of

Fig. 8 Micro-Vickers hardness of Mn-20%Ge-Fe ternary alloys.

Vickers hardness (measured under a load of 4.9 N: 500 g) of the Mn-20%Ge-Fe alloys air-quenched after heating at 1100 K for 10.8 ks. The Vickers hardness of the ternary alloy decreases at first by about 100 by addition of Fe compared with the binary alloy, and then maintains about 400 up to the addition of 10%Fe. The reason why these alloys show high hardness values when Fe is added is that the alloys contain the compound $\text{Mn}_{3.25}\text{Ge}$, and the mechanical strength of these alloys is, therefore, not improved.

The forgeability of 5 mm ϕ rods of the ternary alloys containing 2–4%Fe was examined using a swaging hammer at room temperature. It was possible to reduce the sectional area by 5–6%. In the next step, a cutting test without cutting oil for the ternary alloys was carried out by a normal desk-top lathe with a high speed steel blade (cutting condition: 1.7 m/s speed, 1 mm/rev. feed and 0.05–1 mm depth). A drilling test was also performed by the same lathe with drills having a 120° blade angle (1 mm/rev. feed) for the same alloys. The results for the two alloys are shown in Fig. 9. Cutting and drilling workabilities of the ternary alloys containing Fe were well improved as com-

Fig. 9 Lathing and drilling tests of Mn-Ge-Fe alloys, (a) Mn-20%Ge-4%Fe and (b) Mn-22%Ge-4%Fe.

pared to the binary alloys. Namely, cutting under the above-mentioned condition was easier, and the scraped chips were less sticking to the tool blade, and the worked surface was very smooth and bright, as seen in Fig. 9(a) and (b). Despite the high hardness of the alloys, the shape of the scraped chips were continuous. The drilling test was carried out with ease, but there were small chips-off from the drilling edge, as shown in Fig. 9(a).

From the results mentioned above, it is clear that the addition of 0–10%Fe expands the Invar region of the antiferromagnetic Mn-Ge binary alloys and improves the cutting ability of them. However, the workability and mechanical strength are not sufficient for applications. Further experiments on heat treatments and multiple-additions of other elements to the Mn-Ge and Mn-Ge-Fe alloys are now in progress, in order to solve the above problem.

IV. Summary

Mn-20 and 22%Ge Invar alloys have been used as the base alloys for the investigation of the effect of Fe, Co, or Ni addition. The thermal expansion, magnetization, lattice constants, hardness and machinability were examined on the ternary alloys furnace-cooled, air-quenched or water-quenched from 1100 or 1000 K after heating at 1100 K for 10.8 ks. The results are as follows:

(1) In the thermal expansion vs temperature curves of the Mn-20 and 22%Ge-base alloys containing the third elements, the Néel point of the ε phase can clearly be observed in the alloys containing Co or Ni up to 5%, or Fe up to 10%. These alloys have the small thermal expansion coefficient and show the Invar characteristics below the Néel temperature.

(2) The thermal expansion coefficient $\alpha_{R.T.}$ near room temperature takes a zero or nearly zero value in a wide region surrounded by 71–76%Mn, 20–25%Ge and 0–7%Fe, but in the case of Ni or Co addition, the zero region becomes narrower. $\alpha_{R.T.}$ of both the Mn-20 and 22%Ge-base alloys shows a minimum at 1%Co, 1%Ni or 6%Fe. In the region where the expansion coefficient takes a positive value, the increment of $\alpha_{R.T.}$ for the increased addition

of the third element was very small in the case of Fe addition. That is, the addition of Fe expands the Invar region of the Mn-Ge alloys, but Ni or Co rather reduces the region.

(3) The composition range showing the minimum value of $\alpha_{R.T.}$ means the critical point of the ε -single phase, and the Invar characteristics are weakened gradually by an excess addition of the third elements because of mixing of the ζ phase with the adjacent ε phase.

(4) The spontaneous volume magnetostriction of the ternary alloy of Mn-20%Ge-2.1 or 4.2%Fe at 77 K shows the same value of 1.3×10^{-2} .

(5) The temperature dependence of magnetization of the ternary alloys varies in a similar way to that of the binary alloys, and the value of magnetization decreases sharply at the Néel point. The feature that the ε to ε_1 transformation hardly occurs in the binary alloys is not lost by the addition of Fe, Co, or Ni, indicating the high degree of stability of the ε phase.

(6) The Vickers hardness of the Mn-20%Ge-Fe alloys decreases by about 100 from 500 of the binary alloys by a small Fe addition, and the value of about 400 is maintained up to 10%Fe.

(7) By the addition of Fe to the binary alloys, the cutting property is greatly improved and the reduction rate in sectional area by a swaging hammer is 5–6%. However, much work is necessary for the improvement of defects in workability such as chips from the drilled edge.

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