Effects of Additions of Noble Metals on the Properties of Antiferromagnetic Invar-Type Mn-Ge Alloys*

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The thermal expansion, magnetic properties, hardness and workability were investigated in Mn-22%Ge based ternary ϵ phase alloys containing noble metals in groups VIIA, VIII and IB of the periodic table. In the thermal expansion curves of the ternary alloys there appears a minimum corresponding to the Néel point of the ϵ phase, showing the Invar characteristics below this temperature. The thermal expansion coefficient of the ternary alloys in the vicinity of room temperature shows the zero or a negative value. The spontaneous volume magnetostriction of Mn-22%Ge-0.9%Ir, -1.7%Ag and -0.9%Au alloys at 77 K is about 1.3×10^{-2} . The value is hardly affected by the additions and is nearly equal to those of a Mn-22%Ge binary alloy and Invar-type Fe-Ni or Fe-Pt alloys. The magnetization of the ternary alloys shows almost the same temperature dependence as that of the Mn-22%Ge binary alloy which shows a parasitic ferromagnetism. The magnetization at $T/T_N=0.65$ decreases with increase of the additions except Ag. The Néel point of the ϵ phase is scarcely affected by the additions except Ir, Pt and Re.

The Vickers hardness of almost all ternary alloys containing the noble metals less than 2% shows a value lower than that of Mn-Ge alloys, and they are superior in workabilities such as cutting and forging to the binary alloys.

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I. Introduction

The appearance of the pronounced Invar characteristics of Mn-Ge alloys in the antiferromagnetic ϵ phase region has been discovered and reported in detail by the present authors⁽¹⁾⁽²⁾. Despite their excellent Invar characteristics, these alloys are in need of improvements in workability, particularly cold working, because the composition range of the binary alloys is close to the Mn_{3.25}Ge compound⁽³⁾. To improve these disadvantages, the effects of additions of third elements and various heat treatments were investigated. The results showed that the Mn-Ge-Fe ternary alloys⁽⁴⁾ and several ternary alloys containing a

bcc metal such as Zr, V or Cr⁽⁵⁾ had better workability than that of the binary alloys.

Generally, noble metals in groups VIII and IB of the periodic table have a fcc structure and excellent malleability and ductility. Furthermore, Mn and the noble metals are known to form compounds or alloys with various interesting characteristics⁽⁶⁾. For example, Mn₂Pd₃ is an antiferromagnetic compound showing the Invar characteristics⁽⁷⁾. In the present paper, investigations have been made on the effects of additions of noble metals and Re in group of VII A on the thermal expansion, magnetization, hardness and workability of the Invar-type Mn-Ge alloys.

II. Experimental

Starting materials used were 99.8%[†] purity electrolytic Mn, 99.999% purity metallic Ge⁽²⁾⁽⁴⁾⁽⁵⁾ and nine 99.8–99.9% purity noble

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[†] The alloy compositions except the purities of the elements are shown in units of atomic per cent.

metals. These elements were weighed out and melted in alumina crucibles using a Tammann or an induction furnace while blowing Ar gas onto the melt surfaces. The molten alloys were sucked up into silica tubes about 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 alloys were cast into iron molds 5 mm in inner diameter and 150 mm in length. All specimens were heated at about 1100 K (830°C) for 10.8 ks (3 h) in silica tubes filled with Ar gas for homogenization and then allowed to cool in air to room temperature or quenched into water.

The linear thermal expansion was measured by a horizontal and a vertical type dilatometer at a rate of 27.8×10^{-3} K/s (100°C/h) or less in the temperature range between 120 and 500 K in an Ar atmosphere. The magnetization measurement was carried out in an external magnetic field of about 800 kA/m (10 kOe) under the same condition as for the measurement of thermal expansion. The hardness was obtained at room temperature using a micro-Vickers hardness tester under a load of 4.9 N (500 gf). The cutting and forging abilities were also tested by a bench lathe and a swaging hammer under the same conditions reported already⁽⁴⁾⁽⁵⁾.

III. Results and Discussion

1. Thermal expansion

Figures 1(a)–(c) show the thermal expansion curves of Mn–22%Ge base ternary alloys containing noble metals, which have the remarkable Invar characteristics measured over the temperature range from 120 to 500 K after heating at 1100 K for 10.8 ks in Ar atmosphere, followed by air cooling. All the curves changed reversibly by heating and cooling at a rate less than 27.8×10^{-3} K/s. In the figure, the arrow indicated to the minimum shows the Néel point T_N of the antiferromagnetic ε phase. Almost all alloys have a small thermal expansion coefficient over a wide temperature range below T_N and show good Invar characteristics. When Ru, Rh or Pd is

added to the binary alloy, the Invar characteristics appears distinctly around 3.5% or less (Fig. 1(a)). By addition of Ir or Pt, the anomaly in the thermal expansion curve disappears above 2% (Fig. 1(b)). The alloy added by 3.4%Ag retains the Invar characteristics similar to that for the addition of Ru, Rh or Pd, while the Invar characteristics is weakened by the addition of about 2% of Au or Re (Fig. 1(c)).

The spontaneous volume magnetostriction of Mn–22%Ge–0.9%Ir, –1.7%Ag and –0.9%Au ternary alloys was about $1.2\text{--}1.3 \times 10^{-2}$, which was calculated from the difference in the thermal expansion between the alloys mentioned above and other Mn–Ge alloys showing no anomaly in the thermal expansion. The value is of the same order of magnitude as that of the binary alloy and ferromagnetic Fe–Ni⁽⁸⁾ and Fe–Pt⁽⁹⁾ Invar alloys.

The Invar characteristics of the Mn–Ge alloys are retained fairly well up to 2% of the noble metals as mentioned above. To make clear the effects of the noble metals, the thermal expansion coefficient α_{RT} at temperatures between 270 and 310 K was measured for each alloy. Figure 2 shows the variation of α_{RT} with the concentration of the third elements. In the figure, the curves are classified into 3 groups; Ru, Rh and Pd of the fifth period, In, Pt and Os of the sixth period in group VIII of the periodic table, and Ag, Au and Re group. Although the expansivity of the alloys containing Ru, Rh or Pd shows a quite small value in the concentration range less than 3%, the alloys with Ir, Pt and Os additions shows a minimum at 1% or less and then increases with increasing concentration of additional element. The addition of Au or Re brings about a large effect as in the case of the alloy with the sixth period element Ir, Pt or Os in group VIII, while the alloys with the addition of Ag shows a small value of α_{RT} even at 3.4%. From the results mentioned above, it becomes clear that the narrow composition range in the binary alloy in which the Invar characteristics appear is expanded by the addition of noble metals in a way similar to the Mn–Ge alloys containing Fe⁽⁴⁾ or Cr⁽⁵⁾.

Fig. 1 (a) Thermal expansion curves of Mn-22%Ge alloys containing Ru, Rh or Pd. (b) Thermal expansion curves of Mn-22%Ge alloys containing Os, Ir or Pt. (c) Thermal expansion curves of Mn-22%Ge alloys containing Ag, Au or Re.

Fig. 2 Effects of noble metals on the thermal expansion coefficient in the vicinity of room temperature in Mn-22%Ge alloy.

2. Magnetization

Figures 3(a) and (b) show the relation between temperature and magnetization σ of the typical ternary alloys air-quenched after heating at 1100 K for 10.8 ks. The measurements were carried out by heating and cooling at a rate of about 27.8×10^{-3} K/s. The σ - T curves in (a) are similar in shape, although T_N slightly shifts upwards or downwards by addition of the third element. The variation in the temperature dependence of magnetization with Ag concentration is shown in (b), in which T_N hardly changes with increasing Ag concentration, the magnetization at low temperature increases slightly and steep change in σ is observed just below T_N . In particular, these alloys have a relatively large magnetization and exhibit a ferromagnetic temperature variation due to the existence of weak ferromagnetism⁽¹⁰⁾ in the antiferromagnetic ϵ phase. It has been reported that the spin structure of $\text{Mn}_{3.25}\text{Ge}$ intermetallic compound is a D0_{19} type⁽¹¹⁾⁽¹²⁾.

In order to confirm the phase structures of the ternary alloys, diffraction patterns of powdered samples were measured by FeK_α X-rays. The result showed that in the alloys with about 3.5% of Ru, Rh, Pd or Ag there was

Fig. 3 (a) Temperature dependence of magnetization of Mn-22%Ge-X alloys. (b) Temperature dependence of magnetization of Mn-22%Ge-Ag alloys.

a small amount of the antiferromagnetic ζ phase mixed with the ϵ phase and the amount of the ζ phase increased in the order of Ag, Ru, Rh and Pd. In the alloys containing Ir or Pt, the ζ phase pattern began to appear above 1.9%.

In order to examine the relation between the magnetization and the concentration of the third elements, the magnetization σ_T at

Fig. 4 Effects of noble metals on the magnetization of Mn-22%Ge alloy at the temperature $T/T_N = 0.65$.

temperature T where $T/T_N = 0.65$ is shown in Fig. 4 as an example. In general, the σ_T decreases linearly with increasing concentration of the third element. However, the value in the case of the Ag addition tends to increase up to about 3%.

Figure 5 shows the effects of the addition of the third elements on T_N of the Mn-22%Ge binary alloy. The effects of Ru, Rh, Pd or Ag of the fifth period in groups VIII and IB of the periodic table are small, while those of Os, Ir or Pt of the sixth period in group VIII are large. The addition of Pd, Ir or Au increases T_N , and thereby the Invar characteristics appear over a wider temperature range. Furthermore, the alloys with 1–2% Pd or Au show an excellent cutting ability by a bench lathe. Therefore, it seems that the Invar type Mn-Ge alloys containing a small amount of the noble metals are very promising materials for practical use in a similar way to the alloys containing Fe⁽⁴⁾ or Cr⁽⁵⁾.

There have been a number of investigations on various physical properties of the Mn-noble metals alloys. Yamaoka⁽¹³⁾ reported a drastic increase of T_N as large as 9 K/at%Ir in the γ -phase Mn-Ir alloys containing Ir less than 15%. In the present work, it is apparent from Fig. 5 that only 1% Ir gives rise to a marked increase in T_N of about 15 K, and the phenomenon is considered in a way similar to the Mn-Ir alloys.

Fig. 5 Effects of noble metals on the Néel point of Mn-22%Ge alloy.

Vickers hardness H_V was measured in the Mn-22%Ge base alloys containing a few per cent of the noble metals under a load of 4.9 N (500 gf) at room temperature, as shown in Fig. 6. The alloy with 2% Ir tends to develop a higher H_V by about 50 as compared with the binary alloy. The addition of other elements except Ir lowers the H_V ; particularly the addition

Fig. 6 Effects of noble metals on the room-temperature Vickers hardness of Mn-22%Ge alloy.

of Pd, Pt and Au lowers the value by only 1% addition to the same order of magnitude as that by the addition of Fe⁽⁴⁾, and the addition of Ru and Ag decreases it to a value of 400 or less.

The forgeability test for the ϕ 5 mm rod alloys with 1–2% noble metals was carried out by a swaging hammer at room temperature. Except in the alloys with Os, Ir or Re, the workability of about 5% in the reduction area was possible in the other alloys. From the turning tests made by a bench lathe in the same condition as used in previous works⁽⁴⁾⁽⁵⁾, it has been found that the alloys with Pd or Au have a good workability, while those with Os, Ir or Re are difficult of cutting. The former two alloys show better workability than the binary alloy, and this is a tendency similar to the alloys containing Fe⁽⁴⁾ or Cr⁽⁵⁾.

From the results mentioned above, it is apparent that the antiferromagnetic ε -phase Mn–Ge alloys containing 3% or less noble metals show the excellent Invar characteristics and good workability. So, these alloys are suitable for precision measuring instruments such as the optical system in which the microscopic dimensional change by heating and/or application of magnetic fields should be avoided.

IV. Summary

The Mn–22%Ge Invar alloy has been used as the base alloy for the investigation of the effect of small additions of the noble metals of the fifth and sixth periods in groups VIII and IB of the periodic table. Measurements of the magnetization, the thermal expansion, the hardness and the workability (mainly cutting ability) were performed on the ternary alloys air-quenched or water-quenched after heating at 1100 K for 10.8 ks. The results are summarized as follows:

(1) In the thermal expansion vs temperature curves of the Mn–22%Ge based ternary alloys, there exists a bend or a minimum at the Néel point of the antiferromagnetic ε phase. Most alloys have a small thermal expansion coefficient and show the Invar characteristics below the Néel point.

(2) The thermal expansion coefficient in

the vicinity of room temperature takes the zero or a small negative value by the addition of some of the noble metals, and the Invar characteristics are obtained over a wide composition range.

(3) The spontaneous volume magnetostriction of the Mn–22%Ge–0.9%Ir, –1.7%Ag and –0.9%Au alloys at 77 K is $1.2\text{--}1.3 \times 10^{-2}$, and this is nearly the same value as those of the binary alloy and ferromagnetic Fe–Ni and Fe–Pt Invar alloys.

(4) In the antiferromagnetic Mn–22%Ge base ternary alloys, the variation in the temperature dependence of magnetization is similar to that of the ferromagnetic alloys because of the existence of weak ferromagnetism.

(5) The magnetization of the Mn–22%Ge base ternary alloys at the temperature of $T/T_N=0.65$ decreases with addition of third element, but the value increases in the case of addition of about 3% Ag.

(6) The Néel point in the alloys with Pd, Ir or Au shows values higher than in the binary alloy, but that in the alloys with Ru, Rh or Ag shows values little affected by the addition.

(7) In comparison with the binary alloy, the Vickers hardness of the ternary alloys containing 2% or less noble metals shows a lower value, except for the addition of Ir. The ternary alloys containing the noble metals except Os, Ir and Re have forgeability of about 5% reduction rate in the sectional area and show improvements in the cutting ability by a bench lathe.

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