Effect of Additive Elements on the Elinvar and Invar Characteristics of Fe–Mn Base Alloys

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This study investigated the temperature dependence of Young’s modulus and the thermal expansion of Fe–26 at%Mn base alloys. The addition of a few % of Ti, Mo, Nb, Zr, Ta, or Hf to the alloys limited the temperature coefficient of Young’s modulus to within ±5 × 10⁻⁵/K. In alloys with added Nb, Zr, and Hf, the temperature coefficient of thermal expansion was 1 × 10⁻⁵/K or less, whereas the Néel temperature was 380 K or greater. Fe–Mn–based alloys containing a few at% of elements from families 4 and 5 of the periodic table exhibited both Elinvar and Invar characteristics at temperatures up to approximately 380 K. The effect on the properties was shown to be correlated with the number of electrons in the outer shell of the added element and its atomic radius.

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1. Introduction

In recent years, a range of devices have been developed that require the use of powerful or superconducting magnets. These produce magnetic fields that interfere with precision instruments in their vicinity. This is increasing the demand for the Elinvar and Invar alloys, which can be made insensitive to magnetic fields. Other areas of application include nuclear fusion reactors, power storage devices, and space satellite equipment that is exposed to solar magnetic flares.

However, nearly all commercial Elinvar and Invar alloys include ferromagnetic materials. As insensitivity to residual magnetic fields becomes more desirable, antiferromagnetic Elinvar alloys are attracting increasing attention.

Existing studies of antiferromagnetic Elinvar have focused on the use of Mn-based, Cr-based, and Fe–Mn-based alloys. Between 1970 and 1990, extensive study was made of Fe–Mn alloys, and of their Elinvar or Invar characteristics. Previous studies have reported that the sensitivity of Fe–Mn alloys depends largely on the composition of the alloy and the processing conditions. Most such alloys contain significant loadings of elements such as Co, Cr, Ni, Si, and Al. The Fe–Mn-based Elinvar or Invar alloys developed to date have been impractical because their characteristics are poor, and they can only operate within a narrow temperature range.

In a previous paper, we proposed antiferromagnetic Fe–26 at%Mn base alloys with the inclusion of small amounts of Mo, W, Nb, Ta, Ti, Zr, or Hf. These were demonstrated to have both excellent Elinvar and Invar characteristics. In this study, we have systematically investigated the Young’s modulus temperature coefficient (\(\varepsilon\)), thermal expansion temperature coefficient (\(\alpha\)), and Néel temperature (\(T_N\)) of Fe–26 at%Mn–based quasi-ternary alloys containing transition metals (X-type), magnetic metals (W-type), or nonmagnetic metals (Z-type), in order to identify a material with both Elinvar and Invar characteristics that can be used in practical applications. These Elinvar and Invar characteristics are also discussed qualitatively, based on the number of outer shell electrons and the atomic radii of the added elements. In this study, we set the criteria that the Elinvar characteristics should be preserved in the range ±5 × 10⁻⁵/K, and the Invar characteristic at 1 × 10⁻⁵/K or below. These limits are denoted by a dashed line in the figures.

2. Experimental Procedure

Samples were prepared of Fe–26 at%Mn base alloys containing a few at% of the transition metals Cr, V, Mo, W, Nb, Ta, Ti, Zr, or Hf (X-type), the magnetic metals Co or Ni (W-type), and the nonmagnetic metal Si, Al, or Cu (Z-type).

The electrolytic iron and electrolytic Mn were of 99.99 mass% purity and the X, W, and Z elements were of 99.9 mass% purity. 500 g of the material was inserted into an alumina crucible, melted in a high-frequency induction furnace under an argon atmosphere, and injected into a 20 mm diameter mold. To allow measurements to be made of each characteristic, the cast materials were formed in size by forging and swaging at 1273 K. As a final heat treatment, the samples were annealed in argon gas for 60 min at 1173 K.

The Young’s modulus was measured using a free resonant modulus apparatus, thermal expansion using an inflatable dilatometer, and the magnetic properties using a vibration magnetometer. The structure was analyzed using a multipurpose X-ray diffractometer with an Ag target.

3. Results

3.1 Elinvar and Invar characteristics of Fe–Mn–Mo ternary alloys

We first investigated the optimal composition at which the Elinvar and Invar characters appeared simultaneously. This was first done using Fe–Mn base alloys containing a few percent of Mo. Figure 1 shows the relationship between the Mn and Mo content and the values of \(\varepsilon\) and \(\alpha\), for Fe–Mn–Mo alloys annealed at 1173 K for 60 min. In the case of the Fe–Mn binary alloy, the \(\varepsilon\) value changed from positive to negative as the loading of Mn was increased to 26 at%Mn, reached zero at approximately 24 at%Mn, and became constant at approximately −15 × 10⁻⁵/K at 26 at%Mn. The \(\alpha\) value remained constant at approximately 1.4 × 10⁻⁵/K up to
26 at\% Mn, then decreased to $1.0 \times 10^{-5}$/K at approximately 30 at\% Mn. When Mo was added at 1.8 at\% and 3 at\%, the $e$ value changed in a similar way, becoming zero at 26 at\% Mn, while the $\alpha$ value was almost constant at $1.0 \times 10^{-5}$/K at 26 at\% Mn or more (Fig. 1(a)). As the Mo content was increased, the $e$ value of the alloys increased to a broad maximum at approximately 1~4 at\% Mo, while the $\alpha$ value decreased to a broad minimum at approximately 2~4 at\% Mo (Fig. 1(b)). The addition of Mo to the Fe–26 at\% Mn to 1.8 at\% Mo alloy was shown to greatly improve both the $e$ and $\alpha$ values at $1.1 \times 10^{-5}$/K and 1.0 $\times 10^{-5}$/K. This reflected a structural change, specifically an $\epsilon$–$\gamma$ phase transition through the temperature cycle. Major hysteresis was observed in the heating and cooling curves of both $e$ and $\alpha$ of the Fe–26 at\% Mn binary alloy. This was suppressed by induction of the $\epsilon$ single phase when Mo was added.

The key point is that, within the $\gamma$+$\epsilon$ phase region at 26 at\% Mn or less, a contradictory effect was observed on the composition, in which the $e$ value remained constant whereas the $\alpha$ value decreased. This phenomenon in the $\epsilon$–$\gamma$ phase transition of the Fe–Mn alloys was suppressed by the addition of Mo, improving both the $e$ and $\alpha$ values.

Figure 2 shows the temperature dependence of the Young’s modulus for alloys of Fe–26 at\% Mn to 1.8 at\% Mo over a wider temperature range than those previously reported.\(^{14}\) As can be seen, the Elinvar characteristic was observed across a wide temperature range of 173 K to 373 K. This would be useful in practical applications. A small change in the temperature coefficient was also observed at approximately 253 K. The cause of the change is unknown, but may be related to the existence of the $\epsilon$ phase, in which Mossbauer demonstrated $T_N$ to be below room temperature.\(^{15}\)

### 3.2 Elinvar and Invar in Fe–Mn-based alloys containing other elements

A previous study\(^{14}\) reported that the addition of elements from families 4 to 6 of the periodic table (X) to Fe–26 at\% Mn binary alloy, or to Fe–Mn–based ternary alloys with X elements excluding Cr and V, exhibited both Elinvar and Invar characteristics. The best values were found in Nb-added alloys, which achieved an Elinvar value of $0 \times 10^{-5}$/K, and an Invar value of $0.8 \times 10^{-5}$/K with a $T_N$ of approximately 393 K.

However, the W or Z elements, which are from a family higher than Fe or Mn, have a different effect from the X elements. The effect of adding Si or Al was particularly notable (Fig. 3). The alloys containing W and Z elements exhibited neither Elinvar nor Invar characteristics.

The Elinvar characteristic is known to originate from the compensating effect of the anomaly in the Young’s modulus
created by magnetic ordering. To investigate the effect of adding different elements to the Fe–Mn binary alloys, we measured the temperature dependence (T) of magnetization (M) of all ternary alloys. Two types of M-T curve emerged (Fig. 4). The first reflected the typical temperature dependence of an antiferromagnet, and was observed in the alloys with added Mo and Nb (Fig. 4(a)). The second reflected weak ferromagnetic behavior and was observed in Fe–Mn–(Zr, Hf) alloys with a low Tc. The ferromagnetic component of the alloys may correspond to a small Laves phase (Fig. 4(b)). The measured Néel points ($T_N$) were arranged by elemental family (Fig. 5). The $T_N$ of the Fe–Mn–(Zr, Hf) alloys could not be measured, however, as the paramagnetic components covered the $T_N$ of their γ phase. The $T_N$ of Fe–26 at%Mn binary alloy is approximately 373 K. As can be seen from (Fig. 5(a)), the addition of X elements had little effect on the $T_N$, which is the upper limiting temperature for both Elinvar and Invar characteristics. In contrast, the addition of W and Z elements induced an ε–γ phase transition, which significantly reduced the $T_N$ value (Fig. 5(b)). The addition of extra elements weakened the itinerant electron characteristics of the Fe–Mn–X, W, Z alloys. The degree of localized moment plays an important role in the anomalies of the $\Delta E$–T and $\Delta L$–T properties.

4. Discussion

Previous studies of antiferromagnetic Fe–Mn alloy have demonstrated that a large increase in the Young’s modulus at around $T_N$ is due to the $\Delta E$ effect of spin ordering, and that a decrease in the thermal expansion coefficient below $T_N$ is due to spontaneous volume magnetostriction. However, it is difficult to explain the creation of Elinvar and Invar characteristics by the addition of elements from the 4–6
families of the periodic table to Fe–26 at% Mn alloy. In particular, the sign change of $e$ when a small amount of the element is added remains obscure. Two approaches were used in an attempt to explain this, with a focus on the $\gamma$ phase of the alloys.

We first investigated the structure of Fe–Mn base ternary alloys with added X, W, and Z elements by X-ray diffraction method. Cu-K$\alpha$ diffraction showed all alloys to be mainly $\gamma$ phase, which greatly differ from the experimental mechanical results. We next used an Ag target in place of a Cu target, as it is known that the X-ray penetration reaches a depth 10 times or more greater than that of Cu-K$\alpha$. Figure 6 shows representative Ag-K$\alpha$ X-ray diffraction patterns for Fe–Mn-base ternary alloys. The patterns suggest that the alloys have two phases of $\varepsilon + \gamma$.

Taking into account the Cu-K$\alpha$ results, the alloys are assumed to consist of an internal $\gamma$ phase with a surface $\varepsilon$ phase. The $\gamma$ phase intensity of Fe–Mn–Co alloy, which did not exhibit both characteristics at the same composition, was weaker than that of other alloys containing elements from families 4 and 5. The co-existence of both characteristics in the Fe–Mn-based alloys was attributed to the volume ratio of the phase in the alloys. We are currently conducting more detailed analyses of the $\varepsilon$ phase of alloys, using neutron diffraction.

To better understand the effect of the additional elements, we next examined the influence of the atomic radius. Figure 7 maps the correlation between the two characteristics against the atomic radius of the added elements for all samples. Although the data are quite scattered, a relationship can be

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**Fig. 5** Effects of the addition of X, W, Z elements on Neel temperature of Fe–26 at% Mn binary alloy annealed at 1173 K for 60 min.

**Fig. 6** X-ray diffraction patterns of Fe–26 at% Mn–(Mo, Co, Zr, Nb) alloys.

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detected between the factors. As the atomic radius becomes larger, the $e$ value converges on $0 \times 10^{-5}/K$, while the $\alpha$ value decreases to $1.0 \times 10^{-5}/K$ or below. When the added element has an atomic radius larger than that of the Mn atom, both characteristics are improved. This is less clear when the added element has an atomic radius smaller than that of the Mn atom. The Néel temperature increases linearly with the atomic radius of the added element, reaching 410 K at 2.0 at% (1.0 at% Ta). Magnetization, which was measured at 1.5 T and room temperature, is constant until 2.0 Å, then increases drastically as the atomic radius increases (Fig. 8). This rapid increment of magnetization at 2.0 Å or more was attributed to the small amount of chemical compounds (the Laves phase).

As can be seen, the atomic radius of the added elements was related to the co-appearance of Elinvar and Invar characteristics in the Fe–Mn base alloys. However, no correlation was found between the atomic radius of the added element and the lattice parameter of the $\gamma$ phase of the Fe–Mn based alloys. Our results suggest that the co-existence of Elinvar and Invar characteristics in an Fe–Mn base alloy is not related to the atomic distance between the Fe–Mn atoms, but rather to the number of electrons in the outer shell of the added element. These overlap with the d band of the Fe–Mn alloy, inducing or enhancing localization at the Fe atom sites. The change in the magnetic structure of the $\gamma$ phase was therefore attributed to the substitution of atoms with atomic radii larger than that of Mn. We are exploring this further in the neutron diffraction experiments.

These peculiar phenomena, caused by antiferromagnetic ordering, will play a role in the development of physics and materials science.

5. Summary

In this study, we investigated Fe–Mn base alloys with both Elinvar and Invar characteristics. Our key findings are as follows.

(1) The addition to Fe–26 at%Mn base alloy of 1.8 at%Mn or greater resulted in both Elinvar and Invar characteristics.

(2) When elements from families 4 to 6 of the periodic table, excluding Cr and V, were added at a few at% to
Fe–26 at%Mn alloy, Elinvar and Invar characteristics were obtained simultaneously across a wide temperature range below $T_N$.

3) The optimum characteristics were obtained in Nb-added alloys, at an Elinvar value of $0 \times 10^{-5}$/K, Invar value of $0.8 \times 10^{-5}$/K, and $T_N$ of approximately 393 K.

4) Elinvar and Invar characteristics appeared in the $\gamma$ phase of the Fe–Mn base alloys, and were related both to the number of electrons in the outer shell of the added elements and to their atomic radius.

We are currently conducting neutron diffraction experiments to quantitatively clarify this.

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REFERENCES