New Type Fe-Mn Based Alloys with Super Elinvar and Invar Characteristics

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In the present study, both excellent Elinvar and Invar characteristics have been found in the antiferromagnetic Fe-Mn based alloys consisting of about 25 mass%Mn and a small amount of Mo, W, Nb, Ta, Ti, Zr and Hf which are belonging to the 4–6 families in the periodic table. The best characteristics obtained in the present study were constant Young’s modulus (Elinvar characteristics) of $1 \times 10^{-5}$ K$^{-1}$ and a small thermal expansion coefficient (Invar characteristics) of $8 \times 10^{-6}$ K$^{-1}$ in the temperature range of 293–353 K under appropriate treatment of cold working and annealing. Such alloys will be expected as applications in a wide field such as precision instruments, electromagnetic devices and controlling devices. [doi:10.2320/matertrans.M2017027]

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1. Introduction

Conventionally known Iron based Elinvar alloys are mainly Fe-Ni-Cr, Fe-Co-Ni-Cr and Fe-Co-Ni-Cr-Mo systems which exhibit ferromagnetic properties. Therefore, these alloys have high magnetic flux density of about 80 kA/m or more at room temperature, and their properties are significantly affected by the external magnetic field. Recently, various kinds of machines that generate strong magnetic field have developed, so that the Elinvar and Invar alloys insensitive to magnetic field are required.

In the present study, we have focused on the antiferromagnetic Fe-Mn based alloys which are reported to exhibit Elinvar1–6 or Invar7–12 characteristics. According to previous studies, it has been reported that the properties of the Fe-Mn based alloys are sensitively affected by alloy compositions and processing conditions, and most of these alloys are paramagnetic containing large amounts of various elements such as Co, Cr, Ni, W, V, C, Si, etc. However, the Fe-Mn based alloys showing Elinvar or Invar have not been practically used to date because of poor characteristics and its narrow temperature range.

Recently, we have found out that excellent characteristics of Elinvar and Invar are simultaneously obtained by adding the 4–6 family elements such as Mo, W, Nb, Ta, Ti, Zr and Hf to Fe-25 mass%Mn alloy. The main results are reported here as a rapid publication.

2. Experimental Procedure

A raw material of 500 g was inserted into alumina crucible, melted by a high-frequency induction furnace in argon atmosphere, and injected into the mold of 20 mm diameter. Then, the cast material was deformed until 10 mm square bar by forging and swaging at 1273 K. The bar was annealed by the final heat treatment of 1173 K and 3600 s in argon gas atmosphere. Instruments used were the free resonant modulus apparatus for measurement of Young’s modulus, the constant vibration magnetometer for measurement of magnetic susceptibility and the inflatable dilatometer for measurement of thermal expansion coefficient.

3. Experimental Results

A number of studies have been performed already about a constitutional diagram and magnetism of Fe-Mn binary alloy. Figure 1 shows changes in magnetic susceptibility ($\chi$) at room temperature13 and Neel temperature ($T_N$)14 in the range of 15–50 mass%Mn. As seen in the figure, the magnetic susceptibility largely decreases as Mn content increases, and it approaches to the level of $1 \times 10^{-5}$ emu g$^{-1}$ at 30 mass%Mn or more. In the range of 26 mass%Mn or less, the alloys consist of two phases of $\alpha$ and $\gamma$ due to martensitic transformation13, and the alloys with more than 26 mass%Mn become a single phase of $\gamma$ which exhibits Neel temperature of above 400 K14. From this result, the Mn content in the present study was limited within the range of 21–31 mass%Mn.

In the figure, the values of Neel temperature measured in this study are plotted, and these measured values are in agreement with the previous curves.

Figure 2 shows the temperature coefficients of both Young’s modulus and thermal expansion coefficient of the Fe-Mn binary alloys in the range of 21 to 31 mass%Mn. The Young’s modulus temperature coefficient ($\alpha$) of alloys consisting of less than about 26 mass%Mn changes largely from positive to negative as the Mn content increases, and it becomes nearly constant at more than 26 mass%Mn. On the other hand, the thermal expansion temperature coefficient ($\alpha$) is almost con-
stant below 26 mass%Mn, but it decreases largely as the amount of Mn increases. In this figure, it is found that the alloy having Young’s modulus temperature coefficient of zero is about 23 mass%Mn, and the alloy having thermal expansion temperature coefficient of $1 \times 10^{-5}$ K$^{-1}$ is about 30 mass%Mn. This result shows that it is impossible to obtain an alloy having both characteristics of Elinvar and Invar for the antiferromagnetic Fe-Mn binary alloy.

In Fig. 3, the temperature changes of Young’s modulus, thermal expansion coefficient and magnetic susceptibility in the range of room temperature to 373 K for the Fe-25 mass%Mn binary alloy. As seen in the figure, both the magnetic transition temperature ($T_N$) and the phase transition temperature ($M_s$) are observed in the temperature curves of three properties. That is, the Fe-25 mass%Mn binary alloy is composed of two phases of $\varepsilon$ and $\gamma$, indicating that it is an antiferromagnetic material. However, unfortunately it does not show clear Elinvar and Invar properties.

From the above results, we have tried to improve the Elinvar and Invar characteristics of Fe-Mn binary alloy by adding other elements. Here, from the result in Fig. 1, the amount of Mn was determined to be 25 mass% at which Neel temperature was 373 K. Also, as an additive element, Mo which was hardly investigated so far was first selected.

As a result, we have found that the addition of Mo is extremely effective in improving Elinvar and Invar properties. Figure 4 shows the change in Young’s modulus temperature coefficient at as-prepared and annealed states of the Fe-25 mass%Mn-3 mass%Mo alloy. As seen in the figure, Young’s modulus of as-prepared alloy shows a negative temperature coefficient, but it changes to a positive value by annealing at 873 K. And then, it becomes almost zero at annealing temperature of 1073 K. Based on this result, the standard annealing condition was determined to be 3600 s at 1173 K.

Figure 5 shows the effects of Mn and Mo content on the temperature coefficients of Young’s modulus and thermal expansion coefficient and the Neel temperature for Fe-Mn-Mo alloy. From this figure, for alloys with a constant Mo content
of 3 mass% (Fig. 5(a)), the optimum Mn content is exactly 25 mass%, while for alloys with a constant Mn content of 25 mass%Mn (Fig. 5(b)), the optimum Mo content is 2–3 mass%. Also, the Neel temperature increases with the Mn content in the case of 3 mass%Mo alloys, whereas in the case of the 25 mass%Mn alloys, it decreases with the Mo content. And it is found that it is retained in about 373 K for Fe-25 mass%Mn-3 mass%Mo.

From all of the above results, it is concluded that the Fe-25 mass%Mn-3 mass%Mo alloy annealed at 363 K for 3600 s exhibits the best characteristics of Elinvar and Invar. Figure 6 shows the temperature dependences of Young’s modulus and thermal expansion coefficient between 293 K and 473 K for Fe-25 mass%Mn-3 mass%Mo alloy annealed at 1173 K for 3600 s. In Fig. 6 (a), Elinvar behavior is observed over a wide temperature range lower than 350 K, in which a large jump of Young’s modulus is induced by the so-called ΔE effect. Also, in Fig. 6 (b), the thermal expansion temperature coefficient obtained in the range from 293 K to 367 K is 1.0 × 10⁻⁵ K⁻¹, which is close to the characteristics of commonly known Invar alloys.

Subsequently, we have tried to examine the effect of other elements that have better effect than Mo element. As a result, we have found that some elements of the 4 to 6 families in the periodic table have the similar effect as Mo element. Figures 7 and 8 show the effects of Cr, V, Mo, W, Nb, Ta, Ti, Zr and Hf on the temperature coefficient of Young’s modulus and the thermal expansion coefficient of the Fe-25 mass%Mn binary alloy, respectively. In Fig. 7, it is seen that the Young’s modulus temperature coefficient greatly decreases to the range of ±5 × 10⁻⁵ K⁻¹ from a large negative value of −14.5 × 10⁻⁵ K⁻¹ of the Fe-25 mass%Mn binary alloy by addition of a small amount of Mo, Nb, Ta, Ti, Zr or Hf. On the contrary, the effects of Cr and V are hardly observed. In Fig. 8, it is seen that the thermal expansion temperature coefficient decrease to 1 × 10⁻⁵ K⁻¹ from 1.45 × 10⁻⁵ K⁻¹ of Fe-25 mass%Mn binary alloy by the addition of 1 mass% of Nb, Ta, Ti, Zr or Hf. Among these elements, Nb is most effective, and a minimum value of 0.8 × 10⁻⁵ K⁻¹ is obtained. On the other hand, the addition of Cr has little effect.

4. Discussion

All Elinvar or Invar alloys widely used as practical materials are ferromagnetic materials, and, therefore, they have the disadvantage which is strongly influenced by an external magnetic field. In the present study, we selected antiferromagnetic Fe-Mn alloy as the alloy having Invar and Elinvar characteristics without being affected by external magnetic field. From the results of Fe-Mn binary alloy shown in Fig. 1, we have leaned that there was no composition to obtain both Elinvar and Invar characteristics. That is, Elinvar property is obtained in a two-phase region of ε and γ, whereas Invar property is obtained in a single phase region of γ. From this fact, we have attempted to add various elements to the Fe-25 mass%Mn binary alloy at the ε-γ phase transformation boundary. As a result, we have found that both excellent Elinvar and Invar properties are realized by adding elements of the 4, 5 and 6 families of the periodic table. Such a result seems to be caused by complicated phenomenon in which both of antiferromagnetism and ε-γ phase transformation are intertwined. For the elucidation of this reason, detailed experiments and considerations in the future are necessary.

According to previous other studies on the antiferromagnetic Fe-Mn alloy, it has been explained that a large decrease
in Young’s modulus appearing below Neel temperature is induced due to $\Delta E$ effect\(^{4,5}\) and a decrease in thermal expansion coefficient below Neel temperature is induced due to spontaneous volume magnetostriction\(^{7,8,10}\). However, it is difficult to explain clearly that the excellent Elinvar and Invar characteristics appear by adding the 4~6 family elements in the periodic table to the Fe-25 mass\%Mn alloy. In particular, the reason why the sign of Young’s modulus temperature coefficient largely changes due to a small amount of additive element is not known at the moment. More detailed research on the behaviors of phase transformation and magnetism of these alloys is necessary in the future.

5. Conclusion

We have tried the development of the antiferromagnetic Fe-Mn based alloys with both Elinvar and Invar characteristics which can be used under a high magnetic field. As a result, we have found that the Fe-Mn based alloys which simultaneously exhibit excellent Elinvar and Invar properties can be obtained by adding a small amount of Mo, W, Nb, Ta, Ti or Hf of the 4~6 families in the periodic table to the Fe-25 mass\%Mn alloy. In particular, the addition of Nb, Ta, Ti or Zr is more effective to improve both characteristics.

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REFERENCES