Magnetocrystalline Anisotropy in a Single-Variant Co-Ni-Al Ferromagnetic Shape Memory Alloy

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The single-variant state and the magnetocrystalline anisotropy in a single crystal Co₄₁Ni₃₂Al₂₅ ferromagnetic shape memory alloy (FSMA) have been investigated. After applying compressive stress, the single-variant state was confirmed by optical micrograph and linear thermal expansion measurements. In the heating process for the single-variant martensite phase, the shrinkage of about 7% takes place at the reverse transformation temperature. From the magnetization curves along the c-, a-axes and the [110]ₐ directions in the single-variant state, the c-axis is determined to be the hard axis and the magnetocrystalline anisotropy constant in the single crystal Co₄₁Ni₃₂Al₂₅ β' martensite phase is evaluated to be 3.2 × 10⁵ J/m² at 5 K.

(Received June 10, 2003; Accepted August 4, 2003)

Keywords: ferromagnetic shape memory alloy, martensitic transformation, cobalt-nickel-aluminum alloy, single-variant, magnetocrystalline anisotropy

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) show a thermoelastic martensitic transformation in the ferromagnetic state. In the martensite phase of FSMAs, the giant magnetic-field-induced strains (MFISs) have been observed. Therefore, FSMAs are expected to be useful for actuators and sensors in which magnetic controls would lead to more rapid response than the thermal controls. So far, many FSMAs have been reported, in particular, Ni₂MnGa alloys have been studied extensively.

The MFIS is related to the motion of the martensite twin boundaries. In martensite phase, various variants exist with keeping the energy of shear strains minimum. In zero magnetic field, magnetic domains exist in martensite variants so as to reduce the magnetic dipole energy. The magnetic domains of which the magnetization M direction is not parallel to the applied magnetic field H direction are diminished on applying H, and then M changes its direction to the H direction. Each variant has the magnetic easy axis with respect to the magnetocrystalline anisotropy. When the magnetocrystalline anisotropy energy is larger than the energy to move twin boundaries, the variants change to other variants so that the magnetic easy axis comes close to parallel to the H direction. Therefore, the magnetocrystalline anisotropy constant K is necessary to be sufficiently large to induce the motion of twin boundaries.

Recently, Co-Ni-Al alloys have been developed as new FSMAs. In the Co-Ni-Al alloys, a β phase (B2) exhibits a thermoelastic martensitic transformation to a β' phase (L₁₀ with c/α = 0.816), and a γ phase coexists as a second phase. The β + γ two phases excel in workability due to the presence of the γ phase. In addition, the Curie temperature Tᵉ and the martensitic transformation starting temperature Mᵉ in the Co-Ni-Al alloys can be individually controlled in a wide range of temperature by changing composition. The single crystal Co₃₇Ni₃₂Al₂₉ β’ martensite phase in a multi-variant state has a large magnetocrystalline anisotropy and the control of variants orientation through the martensitic transformation is possible by the magnetic field cooling. However, the evaluation of the magnetocrystalline anisotropy in the single-variant state is not yet established. Furthermore, for practical applications, the martensitic transformation finishing temperature Mᵉ should be above room temperature. The purpose of the present paper is to obtain the single-variant state in the single crystal Co-Ni-Al alloy with Mᵉ higher than room temperature, and to evaluate the magnetocrystalline anisotropy in the Co-Ni-Al β' martensite phase.

2. Experiment

The composition of Co-Ni-Al ingot was adjusted to be Co rich to obtain Mᵉ and the Curie temperature Tₑ above room temperature. A single crystal Co-Ni-Al alloy was grown by an optical floating-zone method under a helium atmosphere. The composition of the Co-Ni-Al β phase was determined to be Co₄₁Ni₃₂Al₂₇ by energy dispersion X-ray spectroscopy. In order to homogenize and obtain a single β phase, the single crystal was annealed at 1623 K for 120 h followed by quenching in ice water. The crystal structure of the Co₄₁Ni₃₂Al₂₇ was determined by X-ray diffraction using CuKα. The crystallographic orientations of the specimen were determined by both X-ray Laue backreflections and electron backscattering diffraction patterns. The specimen for the measurements was cut from the single crystal into a disk 2.10 mm in diameter with 0.58 mm thick. The martensitic and reverse transformation temperatures were determined by differential scanning calorimeter (DSC). When the martensitic transformation occurs, some variants are induced in a self-accommodating manner. Multi-variant state prevents us from investigating the magnetocrystalline anisotropy because

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the magnetocrystalline anisotropy is dispersed in the multi-variant state. In order to obtain the single-variant state, the compressive stresses were applied to the martensite phase sample. The surface relief structure was observed by optical microscopy in order to confirm the single-variant state. For investigation of the effect of the compressive stress on the formation of variants, the spontaneous \((H = 0)\) linear thermal expansion (LTE) of Co\(_{41}\)Ni\(_{32}\)Al\(_{27}\) in the direction perpendicular to the disk plane \((001)_P\) of the single crystal after applying compressive stress was measured in the temperature range from 300 to 380 K. The magnetization was measured with a superconducting quantum interference device (SQUID) magnetometer in fields up to 4.0 MAm\(^{-1}\) to evaluate the magnetocrystalline anisotropy constant.

3. Results and Discussion

The thermomagnetization curves in a magnetic field of \(H = 8.0\) kAm\(^{-1}\) in the cooling and heating processes for the Co\(_{41}\)Ni\(_{32}\)Al\(_{27}\) single crystal before applying the compressive stress are shown in Fig. 1. Since the martensitic transformation is the first-order transition, the transformation is accompanied by peaks in the heat flow due to the latent heat of transition. As shown in the inset in Fig. 1, both the martensitic and reverse transformations are accompanied by the exothermic and endothermic peaks in the cooling and heating processes, respectively. In the cooling process, the starting and finishing temperatures which change the caloric value are defined as the martensitic transformation starting temperature \(M_s^0\) and its finishing temperature \(M_f^0\), respectively. In the heating process, the reverse transformation starting temperature \(A_s^0\) and the finishing temperature \(A_f^0\) are also defined, respectively. In the cooling process, the increase in the magnetization \(M\) due to the transition from the paramagnetic to the ferromagnetic state is observed at high temperatures. This transition is of the second-order, and hence the Curie temperature \(T_C\) is defined as the minimum point of the derivative of magnetization \(dM/dT\). The decrease of \(M\) due to the change in the magnetocrystalline anisotropy caused by the martensitic transformation is observed below \(M_s^0\). From the thermomagnetization curves and the DSC curves in Fig. 1, \(T_C = 340\) K, \(M_s^0 = 302\) K, \(M_f^0 = 283\) K, \(A_s^0 = 316\) K, and \(A_f^0 = 335\) K are determined. In the single crystal Co\(_{41}\)Ni\(_{32}\)Al\(_{27}\) alloy, \(M_s^0\) and \(A_s^0\) are 283 and 316 K, respectively. Therefore, both the martensite phase and the parent phase coexist at room temperature.

Figure 2 shows the relation between the sample orientations and the applied compressive stress directions. The solid and dotted arrows indicate the crystal axes of the parent and martensite phases, respectively. The block-type arrows indicate the applied compressive stress directions.

Fig. 1 The thermomagnetization curves in a magnetic field of 8 kAm\(^{-1}\) in the cooling and heating processes for the single crystal Co\(_{41}\)Ni\(_{32}\)Al\(_{27}\) alloy before applying compressive stress. The dotted arrows stand for the martensitic and reverse transformation temperatures; \(M_s^0\) and \(M_f^0\) are the martensitic transformation starting and finishing temperatures, respectively, and \(A_s^0\) and \(A_f^0\) are the reverse transformation starting and finishing temperatures. The inset shows the DSC curves through its martensitic and reverse transformation temperatures. The solid arrows indicate the heating and cooling processes.

Fig. 2 The relationship between the sample orientations and the applied compressive stress directions. The solid and dotted arrows indicate the crystal axes of the parent and martensite phases, respectively. The block-type arrows indicate the applied compressive stress directions.
expansion (LTE) of the single crystal Co$_{41}$Ni$_{32}$Al$_{27}$ in the direction perpendicular to the disk plane of the specimen after applying compressive stress. A drastic shrinkage of about 7% is caused through the reverse transformation. By considering the change in the lattice constants, the $c$-axis corresponding to the [001)$_{P}$ direction shrinks, whereas the $a$-axis corresponding to the [110]$_{P}$ direction expands through the reverse transformation in the heating process. After applying stress, as shown in Fig. 4, the shrinkage to the measuring direction takes place through the reverse transformation. Therefore, the $c$-axis is preferentially developed in the direction perpendicular to the disk plane. The present shrinkage in the LTE curve is almost comparable to the value calculated from the difference between the lattice constants in the parent and the martensite phases. It should be noticed that the reverse transformation starting temperature $A_{s}^{f}$ and its finishing temperature $A_{f}^{s}$ are 316 and 335 K, respectively, before applying compressive stress, while both $A_{s}$ and $A_{f}$ are increased 338 and 342 K, respectively, after applying stress. When the martensitic transformation takes place in the Co-Ni-Al alloys, the multi-variant structure with micro-twin boundaries is formed in a self-accommodating manner without any change in the macroscopic shape of the specimen. By applying an external stress, however, the variants rearrange so as to accommodate the applied stress, bringing about a single-variant state without any micro-twin boundaries in the martensite phase. The reverse transformation is liable to progress with the formation of the lattice invariant shears named the micro-twins which are induced in the martensite phase close to the habit planes. The single-variant state is not likely to give rise to the reverse transformation in comparison with the above because the formation energy for the micro-twin boundaries are necessary. As a result, both $A_{s}$ and $A_{f}$ increase as seen from the figure.

The magnetization ($M$-$H$) curves at 5 K for the single crystal Co$_{41}$Ni$_{32}$Al$_{27}$ alloy in the single-variant state is shown in Fig. 5. The measured $M$-$H$ curves for the $a$-axis and [110]$_{P}$ directions are easy to be saturated, while the curve for the $c$-axis is hardly saturated below 2.8 MAm$^{-1}$. Therefore, the $c$-axis is regarded as the hard axis, and hence the $c$-plane becomes the easy plane. After correcting the demagnetizing field, the magnetocrystalline anisotropy constant $K$ is evaluated from the following expression.

$$K = \int_{0}^{M_{sat}} [H_{\text{hard}}(M) - H_{\text{easy}}(M)]dM,$$

where $M_{sat}$ is the saturation magnetization, $H_{\text{easy}}$ and $H_{\text{hard}}$ are the applied magnetic fields along the easy-axis and hard-axis, respectively. The value of $K$ at $T = 5$ K is evaluated to be $3.2 \times 10^{5}$ (J/m$^{3}$) from the present data. It has been reported that the value of $K$ in the martensite phase of a Co$_{37}$Ni$_{32}$Al$_{29}$ alloy is evaluated to be $K = 1.3 \times 10^{5}$ (J/m$^{3}$) by the same method. In comparison with the latter value noted above, the present Co$_{41}$Ni$_{32}$Al$_{27}$ martensite phase exhibits a relatively large value of $K$ which is reduced with increasing temperature close to $T_{C}$, and hence $K = 2.0 \times 10^{5}$ (J/m$^{3}$) at 300 K, comparable with that of Ni$_{2}$MnGa.15)

Fig. 3 Optical micrographs of a single crystal Co$_{41}$Ni$_{32}$Al$_{27}$ alloy (a) before and (b) after applying compressive stress.
4. Conclusion

The single-variant state in the single crystal Co$_{41}$Ni$_{32}$Al$_{27}$ was established after applying compressive stress. In the heating process from the single-variant martensite phase, a significant shrinkage of about 7% takes place at the reverse transformation temperature. From the magnetization curves along the $c$-, $a$-axes and [110]_M directions in the single-variant state, the $c$-axis is determined to be the hard axis and the magnetocrystalline anisotropy constant $K$ in the single crystal Co$_{41}$Ni$_{32}$Al$_{27}$ $\beta'$ martensite phase is evaluated to be $3.2 \times 10^5$ (J/m$^3$) at 5 K and $2.0 \times 10^5$ (J/m$^3$) at 300 K.

Acknowledgement

A part of the present study was supported by the Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

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