JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-I, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. I

The Induced Anisotropy in Cobalt and Cobalt-Nickel Alloys

C. D. GRAHAM, JR.*
General Electric Research Laboratory, Schenectady New York, U.S.A.

The very large induced anisotropy in cobalt and in the hexagonal cobalt-nickel alloys is attributed to a crystallographic texture produced by cooling through the face-centered-cubic to hexagonal phase change in a strong magnetic field. Evidence for this view includes:

1. The temperature dependence of the anisotropy in pure cobalt, which is the same as the temperature dependence of the crystal anisotropy. Both the induced anisotropy and the crystal anisotropy change sign near 300°C.
2. The temperature at which the induced anisotropy appears on cooling, which decreases with increasing nickel content in the alloys in the same way that the fcc→hcp transformation temperature decreases.

Attempts to observe the postulated texture directly by X-ray diffraction experiments have been unsuccessful. Measurements of the magnetic anisotropy as a function of temperature give some information about the crystal anisotropy about the nature of the fcc→hcp phase change in these alloys.

Introduction

Some remarkable effects produced by the magnetic annealing of cobalt-nickel alloys above 75% Co have been reported by Takahashi and Kōno.[1] The results are remarkable for three reasons: first, the magnitude of the induced anisotropy is about fifty times larger than the usual magnetic annealing anisotropies; second, alloys above 95% Co show negative anisotropies, meaning that the easy direction (at room temperature) is perpendicular to the direction of the field applied during cooling; and third, there is a large induced uniaxial anisotropy in pure cobalt, although pure bulk metals are usually considered not to respond to magnetic annealing. In their original note, Takahashi and Kōno suggested that their results were connected with the face-centered-cubic to hexagonal phase transformation which occurs in cobalt-nickel alloys above about 75% Co.

In a previous note[2], I have proposed a more detailed mechanism for the magnetic annealing process and presented some evidence to support this mechanism. Very similar results and conclusions were published simultaneously by Sambongi and Mitui[3]. The present paper summarizes the proposed mechanism, reports the original experiment in greater detail, and gives some additional experimental results.

* Temporarily at The Institute for Solid State Physics, University of Tokyo.

Proposed mechanism

My suggestion is that when the fcc→hcp transformation in polycrystalline Co and Co-Ni alloys is carried out in the presence of a strong magnetic field, crystallographic texture can be produced in the hcp material. The texture will be uniaxial, from symmetry considerations, and will lead to a uniaxial magnetic anisotropy. If the texture is the only source of the induced anisotropy, the induced anisotropy should have exactly the same temperature dependence as the crystal anisotropy. The texture is produced because there is an energy difference given by (K_1+K_2) between hcp grains which form with their easy axes parallel and perpendicular to a large applied field (K_1 and K_2 are the magnetocrystalline anisotropy constants of the hcp phase at the temperature of the transformation). Presumably this effect is appreciable in Co and hcp Co-Ni alloys because the crystal anisotropy is relatively large and the energy difference between the two phases is small. Sucksmith and Thompson[4] give $K_1+K_2=-1.6\times10^6$ erg/cm^3 for Co at 400°C, and the handbook values[5] for the phase change in Co are $\Delta H=0.005$ kcal/mol$=31\times10^6$ erg/cm^3 and $\Delta S=0.007$ cal/mole-deg$=0.04\times10^6$ erg/cm^3-deg; the temperature hysteresis in the transformation is generally of the order of 50°.

The crystallography of the transformation from the point of view of the magnetic annealing effect has been discussed in the previous note[2]; here it is sufficient to point out that since (K_1+K_2) for pure Co is negative at the transformation temperature, the c axis of the hcp grains is the hard direction of magnetization, and those hcp grains will be favored whose c axes are perpendicular to the applied field. The predicted texture is therefore a special kind of fiber texture in which the c axes of the hcp grains tend to lie in the plane perpendicular to the direction of the field applied during cooling. Such a texture will give a positive magnetic uniaxial anisotropy (easy direction parallel to the annealing field) as long as (K_1+K_2) remains negative. In Co, (K_1+K_2) goes through zero and becomes positive at about 300°C; at this temperature the induced anisotropy should therefore also go through zero and change sign, becoming negative at lower temperatures (easy direction perpendicular to the annealing field). The temperature dependence of the induced anisotropy should be the same as that of the crystal anisotropy at all temperatures below the transformation temperature, assuming that no further crystallographic changes occur once the transformation is complete.

Experimental procedure and results

Disk samples 12.5 mm in diameter and 0.125 mm thick of pure Co (containing 0.4% Ni, 0.01% Fe, and less than 0.01% Mn as impurities) and of alloys containing 5.5, 10.3, 20.1, and 29.9% Ni in Co were cut from hot-worked bars, annealed four hours at 1000°C in hydrogen, and slowly cooled to room temperature. In the first experiments, the disks were reheated into the temperature range 500–900°C, in hydrogen, and cooled in a field of 300 Oe; the anisotropy was determined by measuring torque curves in a field of 10,000 Oe, which was found to saturate the torque. Later, the torque magnetometer was modified to permit torque measurements at temperatures up to about 800°C with the sample in hydrogen or argon; then the cooling was done with the sample in the magnetometer and with an applied field of 10,000 Oe.

The primary test of the proposed mechanism of magnetic annealing was a measurement of the temperature dependence of the induced anisotropy in pure Co. After cooling from about 800°C in a field of 3000 Oe, the sample was heated in a silicone oil bath so that the temperature could be accurately measured, and torque curves were taken at intervals from room temperature to 322°C and back. the torque curves for increasing temperatures are shown in Fig. 1, and the resulting values of the uniaxial anisotropy K_u are plotted against temperature in Fig. 2. Since the values of K_u are the same for increasing and decreasing temperatures, no irreversible changes occurred during the measurements. Fig. 2 also shows the crystal anisotropy (K_1+K_2), as determined by Sucksmith and Thompson[4]. Both curves show the same temperature dependence, and both go through zero just below 300°C. This is precisely the behavior expected if the induced anisotropy is due solely to crystallographic texture.

Measurement of torque curves as a function of temperature while cooling in steps through

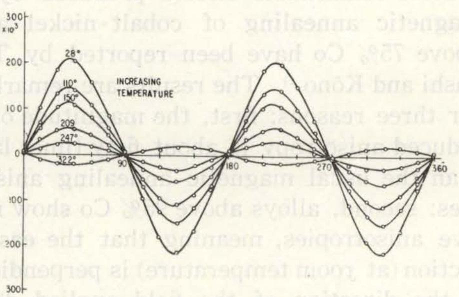

Fig. 1. Torque curves for Co at increasing temperatures. Field applied at 0° during original magnetic anneal.

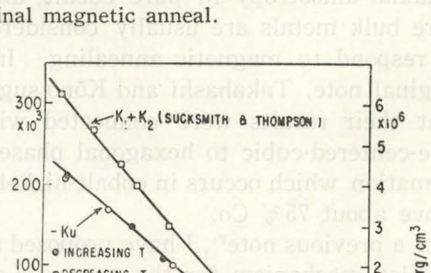

Fig. 2. Uniaxial anisotropy K_u and crystal anisotropy (K_1+K_2) for Co as a function of temperature. Note different scales for K_u and (K_1+K_2).

the transformation temperature range showed that the temperature at which the uniaxial anisotropy first appeared was lowered by the addition of Ni to Co, which agrees with the fact that the temperature of the fcc→hcp transformation drops with additions of Ni to Co[6]. The 70 Co-30 Ni alloy showed no induced anisotropy on cooling to room temperature, but a large anisotropy appeared on cooling the sample to −78°C in a strong field. This anisotropy was retained on heating to room temperature. This is entirely consistent with a low-temperature martensitic transformation and quite inconsistent with any magnetic annealing mechanism which requires diffusion.

The maximum induced anisotropy observed in these measurements is shown for each composition in Fig. 3, along with the earlier results of Takahashi and Kōno[1]. There is qualitative but not quantitative agreement.

For pure Co, it is possible to predict the magnitude and the form of the torque curve which would result if an initially untextured fcc sample transformed to hcp with the maximum possible magnetically-induced texture,

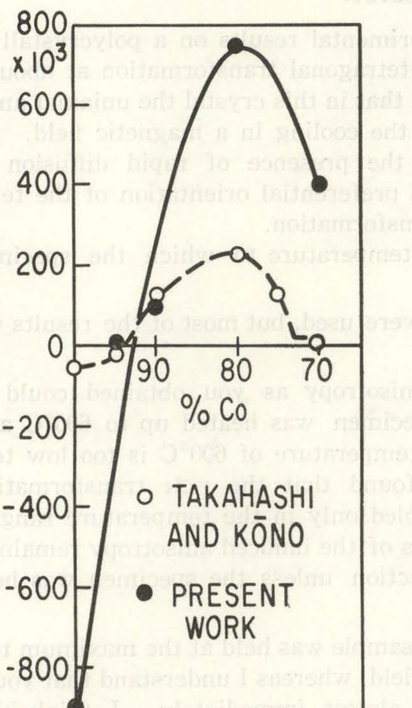

Fig. 3. Maximum induced anisotropy (at room temperature) as a function of composition.

subject to the crystallographic requirement that the transformation occur so that the *c* axis of each hcp grain is parallel to a ⟨111⟩ direction of its parent fcc grain[7]. The prediction involves constructing a pole figure of the expected texture, and then deducing the torque curve which would result from the texture. Both these operations were performed graphically with the aid of stereographic projections. The predicted torque curve is roughly sin 2θ in form with a peak torque of 3×10^6 dyne-cm/cm^3 at room temperature. The maximum torque observed in Co was 0.9×10^6 dyne-cm/cm^3, which would indicate nearly 30% texture. Attempts to observe this texture directly by x-ray diffraction were unsuccessful because of the coarse grain size of the samples.

If one accepts the conclusion that the induced anisotropy results only from crystallographic texture, then the torque measurements on the alloy samples can give some information about their crystal anisotropy. Since the alloys between 5 and 30% Ni have positive uniaxial anisotropy at room temperature, there is no reversal in the sign of the crystal anisotropy between the transformation temperature and room temperature. Measurements down to 77°K show that the induced anisotropy remains positive. Therefore the temperature at which (K_1+K_2) changes sign either remains constant or increases as Ni is added to Co, and at Ni $\geqq 5\%$, (K_1+K_2) is positive for all temperatures between the transformation temperature and 77°K. The very small induced anisotropy near 5% Ni could be the result of a very weak texture, or of a very small crystal anisotropy at room temperature for this composition. Measurements to 77°K showed that the induced anisotropy remained small, leading to the conclusion that the texture rather than the crystal anisotropy was small.

The magnetic measurements also give some information about the nature of the fcc→hcp transformation, which is of considerable metallurgical interest because it is the simplest crystallographic case of a martensitic transformation. Torque measurements at elevated temperatures can easily determine the transformation temperatures on both heating and cooling; measurements of this kind confirm the large temperature hysteresis in the transformation which has been found by other methods.

From experiments in which a sample is repeatedly heated and cooled with a magnetic field applied in various directions, it is found that the axis of the uniaxial anisotropy cannot be switched from one direction to another unless the sample is heated well above its transformation temperature. Furthermore, the magnitude of the induced anisotropy increases with increasing maximum temperature during the magnetic annealing cycle. This suggests that the hcp→fcc→hcp transformation is microscopically reversible if the sample is heated only a little way, say 25 to 50°C, into the fcc region. A dislocation mechanism of the kind proposed by Seeger[8] for the transformation would presumably be reversible in this way. If the maximum temperature in the fcc region is high enough for appreciable irreversible dislocation motion to occur, the transformation will not reverse exactly, and new hcp orientations may appear. If these orientations are selected by an applied field, the result will be a crystallographic texture and a corresponding induced anisotropy.

Acknowledgements

I have had helpful discussions with J. D. Livingston and J. M. Lommel. W. L. Roth has been generous with his time and advice in connection with the x-ray experiments.

References

1 M. Takahashi and T. Kōno: J. Phys. Soc. Japan **15** (1960) 936.
2 C. D. Graham, Jr.: J. Phys. Soc. Japan **16** (1961) 1481.
3 T. Sambongi and T. Mitui: J. Phys. Soc. Japan **16** (1961) 1478.
4 W. Sucksmith and J. E. Thompson: Proc. Roy. Soc. **A225** (1954) 362.
5 *American Institute of Physics Handbook*, McGraw-Hill, N. Y. (1957) Sect. **4** 139.
6 M. Hansen: *Constitution of Binary Alloys*, McGraw-Hill, N. Y. (1958) 485.
7 E. O. Hall: *Twinning and Diffusionless Transformations in Metals*, Butterworths, London (1954) 152.
8 A. Seeger, Z. Metallkunde **44** (1953) 247; **47** (1959) 653.

DISCUSSION

S. IIDA: I would like to present our experimental results on a polycrystalline pure copper ferrite. This ferrite has a cubic-tetragonal transformation at about 390°C, below its Néel temperature. Dr. Inoue found that in this crystal the uniaxial anisotropy of the order of 10^3 erg/gr was produced by the cooling in a magnetic field. Since in pure copper ferrites, it is hard to assume the presence of rapid diffusion at this temperature range, we think it is due to the preferential orientation of the tetragonal axis along the magnetization during the transformation.

M. TAKAHASHI: What was the maximum temperature to which the specimen was heated in your experiment?

C.D. GRAHAM, JR.: Various temperatures were used, but most of the results were obtained by heating to 600° or 700°C.

M. TAKAHASHI: Such a large induced anisotropy as you obtained could not be observed in my experiment when the specimen was heated up to 600°C and then cooled in a magnetic field. I think that the temperature of 600°C is too low to obtain a large induced uniaxial anisotropy. We found that the $\gamma \rightleftarrows \varepsilon$ transformation was reversible if the specimen was heated and cooled only in the temperature range below 600°C, that is, the direction of the easy axis of the induced anisotropy remained fixed in the direction of the original field direction unless the specimen was heated to about 800°C.

C.D. GRAHAM, JR.: In my experiments, the sample was held at the maximum temperature for at least an hour before cooling in the field, whereas I understand that you heated the samples to temperature and then cooled almost immediately. I think this can account for the difference. We also found the transformation to be reversible (in the sense you describe) if the sample was heated only slightly above the transformation temperature.