New Gold Permanent Magnet Alloys

New Gold Permanent Magnet Alloys

MOTOFUMI HOMMA, MEMBER, IEEE, SEI-ICHI TSUTSUMI, MASUO OKADA, AND TAKEHISA MINOWA

Abstract—A gold permanent magnet for an ornamental material is developed in a Au-Fe-Co system. The magnetic properties of the various Au-based alloys are studied. It is found that the magnetic properties of the Au-7.2wt %Fe-4.8wt %Co alloy aged at 600°C for 10 min and subsequently controlled-cooled to 400°C at a cooling rate of 50°C/h, are Br = 0.27 T (2700 G), iHc = 41.2 kA/m (515 Oe), and (*B-H*) max = 3.4 kJ/m^3 (0.43 MGOe). The cold-swaging improved the magnetic properties of the alloy as Br = 0.34 T (3400 G), iHc = 81.2 kA/m (1015 Oe), and (*B-H*) max = 8.2 kJ/m^3 (1.03 MGOe). Microstructural observations indicate that the magnetic hardening is due to the fine iron-cobalt particles precipitated in the Au matrix.

INTRODUCTION

THE APPLICATIONS of magnetically hard materials can be classified in various ways. A recent unique application is that the permanent magnets are used for ornaments such as necklaces and rings. Among the many permanent magnet materials, Au-based alloys are most suitable for such ornamental applications because of their excellent ornamental characteristics, but they are not developed yet. The purpose of this work is to develop the Au-based permanent magnet alloys appropriate for such ornamental applications.

The magnetic properties of the various Au-based alloys such as Au-6-9%Ni (weight percent unless specified otherwise) and Au-1.5%Co alloys have been measured by Lothian *et al.* [1] and Gaunt [2], respectively. Their results show that these alloys exhibited high coercive forces such as 50-280 kA/m (630-3500 Oe), but have low magnetization intensity Is = 0.007-0.019 T (4πIs = 70-190 G). Livingston [3] studied the magnetic properties of the Au-10%Co aligned eutectic alloy and obtained Br = 0.28 T (2800 G), iHc = 74 kA/m (925 Oe) by wire drawing to 99.7 percent reduction in area, but this process of the alloy involves the eutectic alloy preparation and requires the severe rate of the wire drawing and is therefore not practically attractive.

One of the promising ways of designing a permanent magnet is to use an alloy consisting of a microstructure such as a ferromagnetic phase finely dispersed by precipitation or spinoidal reactions in a nonferromagnetic matrix (e.g., Alnico, Cu-Ni-Fe, Cu-Ni-Co, and Fe-Cr-Co permanent magnets) [4]. Based on the criterion for obtaining such a microstructure, this study began with gold binary alloys and proceeded to ternary alloys.

Manuscript received May 4, 1981; revised August 6, 1981.
The authors are with the Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai, Japan 980.

EXPERIMENTAL PROCEDURE

The alloys were prepared from commercial pure gold (99.99 percent), electrolytic iron (99.9 percent), electrolytic cobalt (99.9 percent), and Mond nickel (99.97 percent). They were melted in an argon atmosphere with a high-frequency induction furnace and then cast into a steel mold of 6.5-mm inside diameter. A small amount of Ti (0.2 percent) was added into the melt as a grain refining element.

The specimens were solution-treated at 850-1000°C for 1 h and quenched in ice water. Then they were aged at 350-600°C. Some of the specimens underwent controlled cooling. All heat treatments were carried out in an argon atmosphere or in a vacuum. In order to further improve the magnetic properties, some of the specimens were cold-swaged after aging.

Magnetic properties were measured with an automatic recording fluxmeter. The maximum applied field was 300 kA/m (3.8 kOe). In this paper the symbol Is represents the magnetization intensity at 300 kA/m (3.8 kOe) at room temperature.

Vickers hardness was the standard used to determine whether the alloy could be swaged. The microstructures of some alloys were observed by transmission electron microscopy. Thin disk samples were prepared by electropolishing in a solution of 67 vol/percent hydrochloric acid and 33 vol/percent acetic acid.

RESULTS AND DISCUSSION

Magnetic Properties of Au Binary Alloys

The ferromagnetic elements such as Fe, Co, and Ni show limited solid solubility in Au. The compositions of the studied alloys in the binary systems were selected by the criterion that the alloys have a solid-solution region at high temperatures and a ferromagnetic phase precipitated out of a gold-rich phase at low temperatures. The compositions of the alloys tested were Au-25%Fe, Au-6%Co, and Au-25, 33, 42%Ni.

The best magnetic properties of these alloys obtained by isothermal aging are summarized in Table I. The Au-25%Fe alloy has sufficient magnetization intensity but low coercive force. The Au-6%Co alloy has high coercive force but low magnetization intensity. The Au-Ni alloys show the small value of both iHc and Is. Consequently, it seems to be difficult for these binary alloys to simultaneously have both high coercive force and sufficient magnetization intensity. It should be added that the alloys of the Au-25%Fe and Au-Ni systems could not be cold-swaged after aging. The Au-6%Co

0018-9464/82/0100-0242$00.75

TABLE I
MAGNETIC PROPERTIES OF ISOTHERMALLY AGED Au-25% Fe, Au-6% Co, AND Au-Ni ALLOYS

	Heat treatment	Is/T (G)	iHc/kAm^{-1} (Oe)	(BH)max/kJm^{-3} (MGOe)
Au-25%Fe	950°C 1 h W.Q. 500°C 3 h	0.67 (6700)	16 (200)	2.0 (0.25)
Au- 6%Co	950°C 1 h W.Q. 350°C 35 h	0.18 (1800)	54 (680)	0.6 (0.08)
Au-25%Ni	850°C 1 h W.Q. 350°C 12 h	0.18 (1800)	17 (210)	0.7 (0.09)
Au-33%Ni	850°C 1 h W.Q. 400°C 8 h	0.25 (2500)	14 (180)	0.8 (0.10)
Au-42%Ni	850°C 1 h W.Q. 400°C 6 h	0.32 (3200)	13 (160)	0.9 (0.11)

W.Q. : quenching in ice water.

alloy could be deformed because of its low cobalt content but gave a low energy product after its deformation.

Au-Fe-Co Ternary Alloys

In order to increase the magnetization intensity of the Au-Co alloys, the present study was extended to Au-Fe-Co ternary alloys. The studied Au-Fe-Co alloys contain 10~15 percent ferromagnetic elements (iron and cobalt), and the ratio of iron to cobalt content varies from 1:1 to 7:3. The Au-7.2%Fe-4.8%Co alloy was found to be the best composition among these alloys.

The Au-7.2%Fe-4.8%Co alloy can be solution-treated easily at 1000°C and shows 0.48 T (4800 G) magnetization intensity after aging. The variation of intrinsic coercive force iHc and Vickers hardness Hv of the alloy aged at 500°C is shown in Fig. 1 with varying aging time. The Vickers hardness of the alloy increases from 210 to 250 after a short time of aging and then monotonically decreases. It is found that the alloy can be cold-swaged when its Vickers hardness value is below 200. The coercive force has a maximum value at 12 h aging and then decreases.

Increasing the total content of the Fe and Co in the Au-Fe-Co alloys from 12 to 15 percent makes the solution treatment difficult (e.g., Au-9%Fe-6%Co alloy). However, the increment of ratio of the Fe to Co content in Au-15% (Fe, Co) alloys makes the solution treatment possible (e.g., the Au-10.5%Fe-4.5%Co alloy can be solution-treated at 1000°C). It should be noted that the magnetic properties of the Au-10.5%Fe-4.5%Co alloy are inferior to those of the Au-7.2%Fe-4.8%Co alloy. Thus the Au-7.2%Fe-4.8%Co alloy is studied in detail, with various aging temperatures and time.

Au-7.2%Fe-4.8%Co Alloy

Isothermal Aging: The variation of intrinsic coercive force iHc and magnetization intensity Is of the Au-7.2%Fe-4.8%Co alloy aged at 600°C, 500°C, and 400°C with varying aging time is shown in Fig. 2. Aging at 600°C, 500°C, and 400°C produces the intrinsic coercive force up to 40 kA/m (500 Oe).

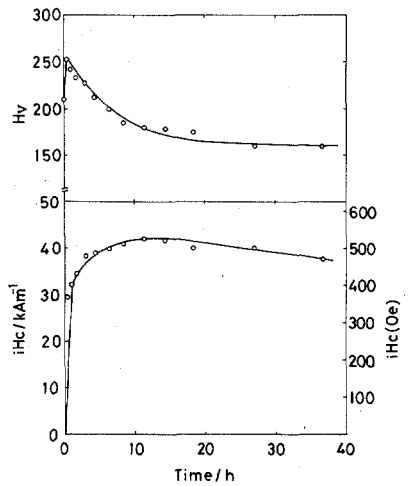

Fig. 1. Variation of intrinsic coercive force iHc and Vickers hardness of Au-7.2%Fe-4.8%Co alloy aged at 500°C with aging time.

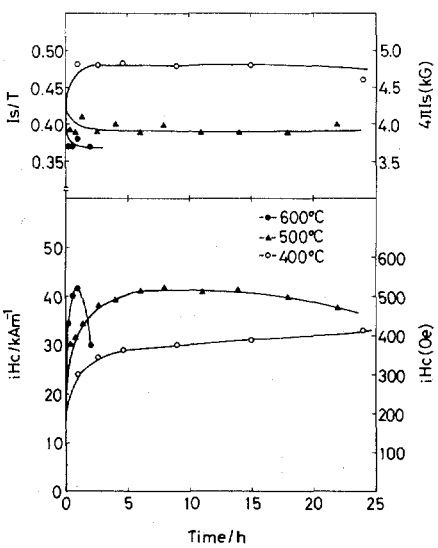

Fig. 2. Variation of intrinsic coercive force iHc and Is of Au-7.2%Fe-4.8%Co alloy aged at 600°C, 500°C, and 400°C with aging time. Is represents magnetization intensity at 300 kA/m (3.8 kOe) at room temperature.

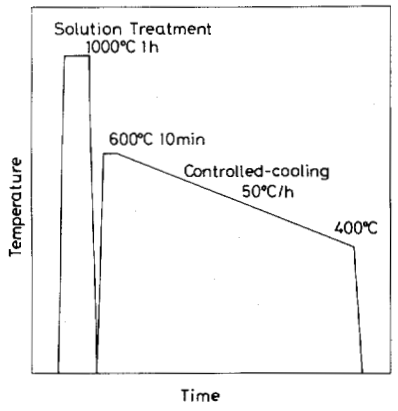

Fig. 3. Schematic diagram of heat treatment for Au-7.2%Fe-4.8%Co alloy.

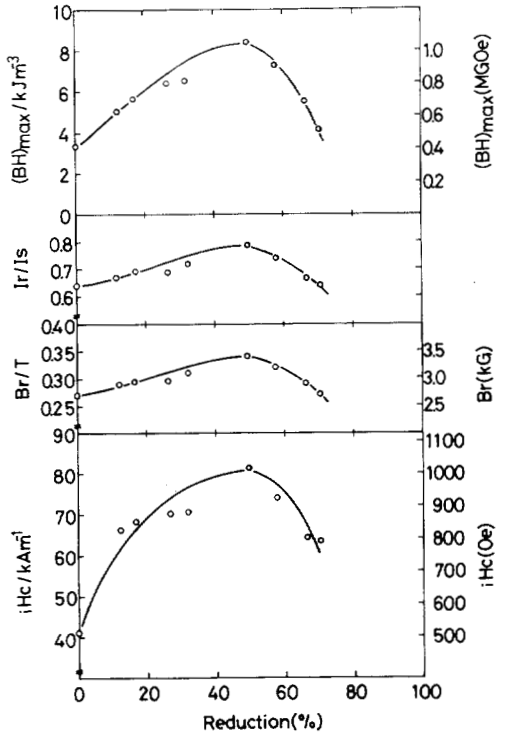

Fig. 4. Effect of cold-swaging on magnetic properties of Au-7.2%Fe-4.8%Co alloy.

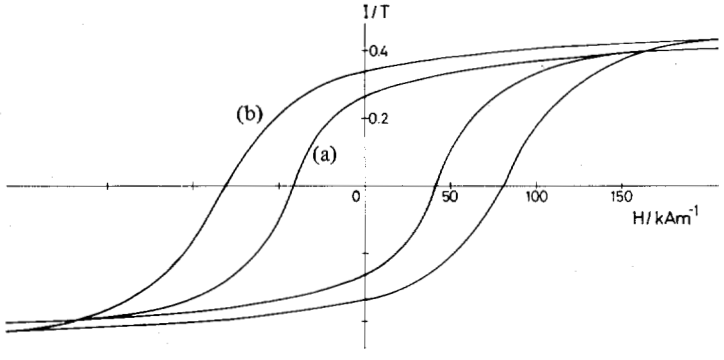

Fig. 5. Magnetization curves of Au-7.2%Fe-4.8%Co alloy. (a) Before swaged. (b) After swaged, 50 percent reduction in area.

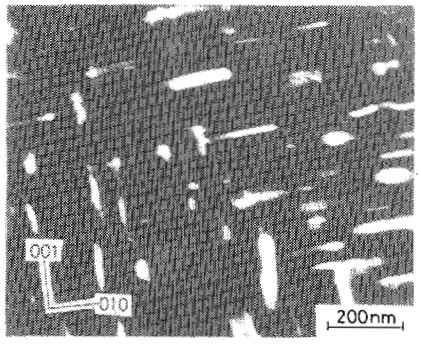

Fig. 6. Microstructure of Au-7.2%Fe-4.8%Co alloy heat-treated as shown in Fig. 3.

The maximum coercive force occurs at shorter aging time with increasing aging temperature. For example, it takes 300 h for aging at 400°C to show its maximum. On the other hand, the Is increases at lower aging temperatures. This could be due to the increment of volume fraction of the precipitated ferromagnetic phase at the lower aging temperature. This makes low temperature aging attractive; however, the kinetics of the formation of the precipitates is extremely slow at these low aging temperatures.

Controlled Cooling: In order to take advantage of the high-temperature kinetics and also to achieve a high Is, the heat-treatment procedure shown in Fig. 3 is adopted. After the solution treatment, the alloy is aged at 600°C for 10 min and then controlled-cooled from 600°C to 400°C at a cooling rate of 50°C/h. This heat treatment gave the magnetic properties as Br = 0.27 T (2700 G), iHc = 41.2 kA/m (515 Oe) and (*B-H*) max = 3.4 kJ/m^3 (0.43 MGOe).

Swaging: In order to further improve the magnetic properties of the alloy, a cold-swaging was introduced in the following heat-treatment processes: 1) before aging, 2) middle of aging, and 3) after aging. The alloy could be cold-swaged in these processes because of the Vickers hardness of about 200. It is found that the introduction of the cold-swaging before aging and in the middle of aging had no effect on or decreased the magnetic properties, but the cold-swaging after aging improved the magnetic properties. The effect of the introduction of the swaging on the magnetic properties is summarized in Fig. 4. The magnetic properties of the alloy are increased by the cold-swaging, and are at their maximum by 50 percent reduction in area as Br = 0.34 T (3400 G), iHc = 81.2 kA/m (1015 Oe), Ir/Is = 0.79 and (*B-H*) max = 8.2 kJ/m^3 (1.03 MGOe). The magnetization curve of the alloy swaged by a 50 percent reduction in area is shown in Fig. 5 in comparison with that of the unswaged alloy.

Microstructure: Fig. 6 shows the microstructure of the Au-7.2%Fe-4.8%Co alloy heat-treated as shown in Fig. 3. The light contrast shows holes 20-30 nm thick and 200-nm long, corresponding to etched-out iron-cobalt precipitates, and the phase with dark contrast is identified as the Au-rich phase. Since the precipitates are etched out, their structure could not be determined in this investigation. According to the Fe-Co binary phase diagram [5], $\gamma \rightarrow \alpha$ transformation

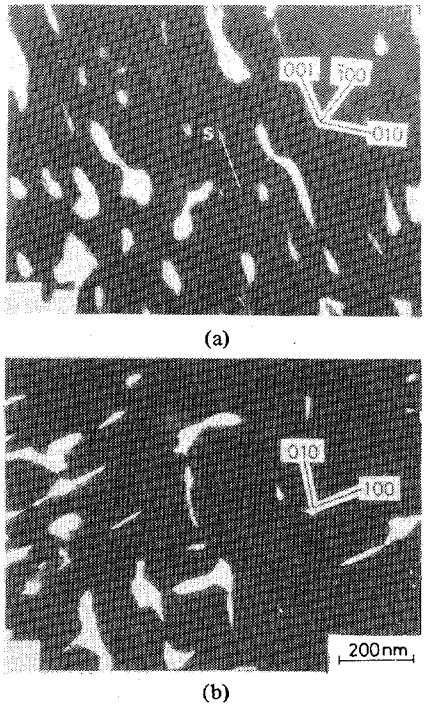

Fig. 7. Microstructures of Au-7.2%Fe-4.8%Co alloy swaged to 50-percent reduction in area. (a) Parallel to direction of swaging. (b) Perpendicular to direction of swaging.

takes place around 970°C if the ratio of Fe to Co content in precipitates is 3:2. If, therefore, aging is carried out at 600°C-400°C, the equilibrium precipitate will have a body centered cubic structure. The precipitate particles are aligned along ⟨100⟩ directions, and this is consistent with the results obtained in the Au-1.5%Co alloy [6]. Fig. 7 shows the microstructures of the alloy swaged to 50 percent reduction (a) parallel and (b) perpendicular to the direction of swaging. The micrographs indicate that the improvement of the magnetic properties of the swaged alloy would be due to the elongation of the iron-cobalt particles parallel to the swaged direction marked *S*, and suggest that the contributions to the coercive force may arise from the shape anisotropy of FeCo precipitates in this alloy.

The maximum value of $(B\text{-}H)$ max obtained in the present investigation is 8.2 kJ/m^3 (1.03 MGOe) and corresponds to that of the commercially used isotropic barium ferrite magnets.

Color: It should be noted that the Au-7.2%Fe-4.8%Co alloy changes its color during the heat treatment. The alloy is silver-white in the solid solution state and approaches the gold color with the advance of aging.

Acknowledgment

The authors wish to thank Ishifuku Metal Industry Co., Inc., for providing raw materials. One of the authors (M. Okada) expresses his sincere appreciation to The Sakkokai Foundation for the fellowship during this work.

References

[1] B. W. Lothian, A. C. Robinson, and W. Sucksmith, "Some magnetic properties of dilute ferromagnetic alloy II," *Phil. Mag.*, vol. 3, p. 999, 1958.
[2] P. Gaunt, "A magnetic study of precipitation in a gold-cobalt alloy," *Phil. Mag.*, vol. 5, p. 1127, 1960.
[3] J. D. Livingston, "Structure and magnetic properties of Au-Co aligned eutectic," *J. Appl. Phys.*, vol. 41, p. 197, 1970.
[4] M. McCaig, *Permanent Magnets in Theory and Practice*. Pentech Press, 1977, ch. 4, pp. 87-150.
[5] M. Hansen, *Constitution of Binary Alloys*. New York: McGraw-Hill, 1958, p. 471.
[6] P. Gaunt and J. Silcox, "An electron microscope examination of small cobalt particles precipitated in a gold matrix," *Phil. Mag.*, vol. 6, p. 1343, 1961.