Effect of Vanadium Addition on the Properties of a New Magnet Alloy "Malcolloy" in the Co-Al System*

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The present authors previously discovered a high coercivity magnet alloy "Malcolloy" in the cobalt and aluminum system. They have ever since carried out investigations on the effect of the additions of nickel, molybdenum and titanium on its magnetic properties; the highest coercive force obtained is 1600 Oe. Further, they have investigated the effect of the addition of vanadium on the magnetic properties of Co-Al alloys and found that the addition of vanadium also increases the coercive force of the binary alloys. Thus, an alloy having the composition of 81.93% Co, 13.42% Al and 4.65 %V shows a coercive force of 1450 Oe, a residual magnetic flux density of 3200 G and a maximum energy product of 1.40 MG·Oe, when tempered at 550°C for 15 hr after water-quenching from 1370°C. These alloys consist of many ferromagnetic elongated particles about 300~400Å in diameter which are dispersed in the matrix of nearly nonmagnetic β' phase. Consequently, it may be concluded that the high coercivity of these alloys is mainly caused by the existence of the small particles of the single magnetic domain.

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I. Introduction

The present authors⁽¹⁾ discovered that when cobalt-

rich alloys of the Co-Al system were tempered after quenching from the high temperature range in which the nonmagnetic β' phase of body-centered cubic lattice exists, the alloys exhibited high coercive forces presumably due to the fact that the a_c phase particles of face-centered cubic lattice and the ϵ_c phase particles of hexagonal close-packed lattice precipitated in matrix are of the single magnetic domain. The authors have made a series of research on the effect of the additions of nickel⁽²⁾, molybdenum⁽³⁾ and titanium⁽⁴⁾ by which

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(1) H. Masumoto, T. Kobayashi and K. Watanabe: J. Japan Inst. Metals, **27** (1963), 561; Trans. JIM, **6** (1965), 187.

(2) H. Masumoto, T. Kobayashi and K. Watanabe: J. Japan Inst. Metals, **28** (1964), 390; Trans. JIM, **7** (1966), 286.

Table 1 Effect of the cooling rate from 1370°C (β' phase) on the magnetic properties of Co-13.42% Al-4.65% V alloy. The coercive force after tempering is the highest value among those obtained by varying the tempering temperature and time.

Heat treatment		Residual flux density B_r (G)	Coercive force H_c (Oe)	Maximum energy product $(BH)_{max}$ (MG·Oe)
1	(a) As iron-mould cast	1600	19	—
	(b) Tempered at 550°C for 15 hr	3000	1160	1.04
2	(a) Water-quenched from 1370°C (β' phase)	400	2	—
	(b) Tempered at 500°C for 55 hr	3200	1450	1.42
3	(a) Air-quenched from 1370°C	2400	7	—
	(b) Tempered at 550°C for 12 hr	3150	1360	1.42
4	(a) Cooled at the rate of 3000°C/hr from 1370°C	4500	160	0.19
	(b) Tempered at 550°C for 15 hr	2950	480	0.36
5	(a) Cooled at the rate of 1000°C/hr from 1370°C	1800	20	—
	(b) Tempered at 550°C for 10 hr	3000	420	0.32
6	(a) cooled at the rate of 250°C/hr from 1370°C	600	15	—

the highest coercive forces of 1500, 1600 and 1550 Oe were obtained, respectively. In this report the effect of vanadium addition on the magnetic properties of Co-Al alloys has been investigated.

II. Specimens and Experimental Method

Cobalt and aluminium used as raw materials were those indicated in the early report⁽¹⁾, and vanadium used was of 99.8% purity. The prepared specimens were 35 alloys containing 4.55~20.63% aluminium and 0.52~19.66% vanadium. The method for the preparation of specimens was entirely the same as stated in the early report⁽¹⁾. They were first cooled either in water or in air at varying rates after solution treatment at 1300~1400°C and then tempered at temperatures between 450° and 800°C for varying times. The method of measurements of the magnetic properties was also entirely the same as previously described⁽¹⁾.

III. Experimental Results and Consideration

In order to examine the effect of the heating temperature and time in the solution treatment and the cooling rate on the magnetic properties after tempering, experiments were at first conducted on four specimens of different composition. As the experimental results were almost similar to one another, only the result of No. 12 alloy containing 13.42% aluminium and 4.65% vanadium is shown in Table 1. In the column (a) are illustrated the magnetic properties of the specimens as cast into the iron mould and the same cast specimens which were cooled at varying rates after heating at 1370°C. The column

(b) shows the magnetic properties which correspond to the highest value of coercive force obtained at varying tempering temperatures and times in the specimen shown in the column (a). As can be seen in the table, in the as-cooled state from the solution treatment temperature as indicated in (a) the coercive force is generally small, but the coercive force after tempering as shown in (b) becomes larger and indicates the highest value after water-quenching. As for the specimen tempered after cooling at a rate of 1000°C/hr, the demagnetization curve exhibits a snake form and its coercive force is 420 Oe. This is considered due to the coexistence of comparatively large size precipitates grown during the slow cooling after solid solution treatment and smaller particles precipitated during the subsequent tempering. Consequently, in the present research all the specimens were subjected to water-quenching after heating at 1300~1400°C for 5~10 min and then tempered at varying temperatures and times so as to obtain normal hysteresis curves and high coercive forces.

As an example, the result of No. 12 alloy is shown in Fig. 1. With increasing tempering time, the coercive force increases gradually, attains the highest value and then decreases gradually. That is, the coercive force vs. tempering time curve has a maximum, and the maximum shifts to a point where the time is shorter with rising tempering temperature. The maximum value of coercive force is the highest (1450 Oe) at tempering temperatures of 500~550°C, beyond which it decreases. The residual magnetic flux density is found generally to decrease gradually with increasing tempering time. Further, the maximum energy product $(BH)_{max}$ shows a change similar to that of coercive force against tempering time; the time required to attain the maximum is somewhat shorter than that for the coercive force. The maximum value is the highest at the tempering temperature of 500°C and decreases gradually with tempering temperature. The relationship between magnetic properties in the

(3) H. Masumoto, T. Kobayashi and K. Watanabe: J. Japan Inst. Metals, **29** (1965), 217; Trans. JIM., **8** (1967), 8.

(4) H. Masumoto, T. Kobayashi and K. Watanabe: J. Japan Inst. Metals, **29** (1965), 222; Trans. JIM., in the press.

Fig. 1(A).

Fig. 1(B).

Fig. 1 Effect of the tempering temperature and time after water-quenching from 1370°C on the magnetic properties of a Co-Al-V alloy containing 13.42% Al and 4.65% V.

Fig. 2 Highest coercive force in each of Co-Al-V alloys tempered after water-quenching from 1300°~1400°C.

Fig. 4 Maximum energy product corresponding to the highest coercive force in each of Co-Al-V alloys tempered after water-quenching from 1300°~1400°C.

Fig. 3 Residual magnetic flux density corresponding to the highest coercive force in each of Co-Al-V alloys tempered after water-quenching from 1300°~1400°C.

Fig. 5 Intrinsic saturation flux density corresponding to the highest coercive force in each of Co-Al-V alloys tempered after water-quenching from 1300°~1400°C.

Table 2 Magnetic properties of Co-Al-V alloys tempered after water-quenching from 1300°~1400°C.

Alloy number	Al (%)	V (%)	Tempering		Br (G)	Hc (Oe)	(BH) _{max} (MG·Oe)	4πIs (G)	Density (g/cc)	Remarks
			tempera- ture (°C)	time (hr)						
Co-Al										
13	12.84	—	550	8	5450	860	2.00	7550	7.42	Forgeable
14	13.53	—	500	20	5200	1000	2.11	7250	—	"
17	15.02	—	"	30	4200	1200	1.71	6250	7.24	Somewhat forgeable
1	13.21	0.52	550	8	4950	1040	2.00	7000	7.39	Forgeable
4	10.85	2.01	"	"	4700	630	1.05	6950	7.61	"
5	12.72	2.36	"	"	4250	1180	1.70	6040	—	"
6	16.67	2.44	"	12	2350	1200	0.96	4200	7.22	Unforgeable
7	20.63	2.46	"	20	1000	460	0.14	1920	—	"
8	14.23	3.72	"	15	3100	1400	1.37	4750	7.18	"
10	11.04	4.87	"	10	3700	1120	1.20	5350	7.30	Forgeable
12	13.42	4.65	"	15	3200	1450	1.40	4660	7.19	Unforgeable
14	17.47	4.91	"	"	1450	620	0.28	2400	—	"
19	9.65	7.25	"	8	3000	970	0.75	4450	—	Forgeable
20	11.01	7.46	"	"	2950	1300	1.08	4120	—	Somewhat forgeable
21	12.40	7.10	"	12	2600	1450	1.10	3940	—	Unforgeable
22	14.70	7.44	"	15	1800	1150	0.69	2750	—	"
25	8.62	9.43	"	6	2300	800	0.52	3340	—	Forgeable
26	14.34	9.74	"	15	1250	840	0.30	1950	—	Unforgeable
27	10.42	11.33	"	8	2100	1220	0.75	3020	—	"
28	8.40	12.85	"	"	1650	880	0.40	2250	—	Somewhat forgeable
29	11.36	12.65	"	10	1400	940	0.44	2050	—	Unforgeable
33	6.12	15.98	"	6	700	340	—	1240	—	Somewhat forgeable
34	8.04	16.75	"	8	800	450	—	1300	—	Unforgeable

state having the highest coercive force in each alloy and compositions is shown in Figs. 2~5. The closed circles denoted in the figures represent the specimen compositions. As shown in Fig. 2, with the amount of vanadium, the coercive force increases gradually until it attains a maximum value of 1450 Oe and then decreases gradually. That is, in a way similar to the alloys of the Co-Al system, the alloys of the Co-Al-V system exhibit high coercive forces by the precipitation of single magnetic domain particles of the ferromagnetic $\alpha_{Co} + \epsilon_{Co}$ phase in the nonmagnetic β' phase. Fig. 3 shows the relationship between residual magnetic flux density in the state having the highest coercive force in each alloy and composition; the value of residual magnetic flux density is known to decrease with increasing vanadium addition. As shown in Fig. 4, the maximum energy product also decreases gradually with increase in vanadium content.

The intensity of saturation magnetization was obtained at effective fields of 14000~15000 Oe, and Fig. 5 shows the relationship between intrinsic saturation flux density and composition. As shown in the figure, the shape of the curve is almost similar to that on the relationship between residual magnetic flux density and composition, and the intrinsic saturation flux density decreases gradually with increase in vanadium content.

The typical examples of the measured alloys under various heat treatment are shown in Table 2, with their magnetic properties, density and forgeability. As given in the table, in the Co-Al system the alloy containing 15.02% aluminium shows the highest coercive force of 1200 Oe, a residual magnetic flux density of 4200G and a maximum energy product of 1.71 MG·Oe, whereas the highest value of coercive force in the Co-Al-V system is 1450 Oe for the alloy containing 12.40%

aluminium and 7.10% vanadium which shows a residual magnetic flux density of 3200 G and a maximum energy product of 1.40 MG·Oe. That is, the addition of vanadium to the Co-Al alloys results in an increase in coercive force, though both the residual magnetic flux density and the maximum energy product decrease. The density decreases gradually with increases in aluminium and vanadium contents, being 7.2 g/cc at the composition which shows the maximum coercive force. The forgeability of the Co-Al-V alloys is also shown in Fig. 2 and Table 2. In the range of aluminium content less than the ab line in Fig. 2, forging is possible at temperatures above about 1100°C, but the alloys containing aluminium in excess of this range are unforgeable. In Fig. 6 are shown demagnetization curves of No. 1 alloy having the highest maximum energy product, No. 12 alloy with the highest coercive force in the Co-Al-V system and No. 17 alloy with the highest coercive force in the Co-Al system. As can be seen from the figure, the magnetic properties of the Co-Al-V alloys are also fairly good.

Finally the micrographs of No. 1 and No. 12 alloys are presented in Photos. 1 and 2, when they were slowly cooled at a rate of 250°C/hr from 1380° and 1370°C (β' phase), respectively. In the micrographs the precipitation of fairly large crystal grains of $\alpha_{Co} + \epsilon_{Co}$ phase can be observed. Photos. 3 and 4 show electron micrographs of the same specimen taken by the carbon-replica method. Photo. 3 represents a solid solution of β' phase when quenched in water from 1370°C, and Photo. 4 a dispersed structure of the fine elongated particles in the matrix when tempered after water quenching. The size of the particles is about 150~1000Å in length and 350Å in mean diameter with an estimated mean dimension ratio of about 6, which is within the range of the critical size of single

Fig. 6 Demagnetization curves of No. 1 and No. 12 Co-Al-V alloys and No. 17 Co-Al alloy.

Photo. 1 No. 1 alloy (13.21% Al, 0.52% V) cooled from 1380°C at the rate of 250°C/hr (β' and $\alpha_{Co} + \epsilon_{Co}$ phases). ($\times 150$)

Photo. 3 Electron micrograph of the specimen in Photo. 2, water-quenched from 1370°C (β' phase). ($\times 40000$)

Photo. 2 No. 12 alloy (13.42% Al, 4.65% V) cooled from 1370°C at the rate of 250°C/hr (β' and $\alpha_{Co} + \epsilon_{Co}$ phases). ($\times 150$)

Photo. 4 Electron micrograph of the specimen in Photo. 2, water-quenched from 1370°C and tempered at 550°C for 15 hr (β' and $\alpha_{Co} + \epsilon_{Co}$ phases). ($\times 40000$)

magnetic domain. The difference in demagnetization factor of the particles, $N_b - N_a^{(5)}$, may be estimated to be about 5.5 from the dimension ratio. The precipitated particles was determined to be a mixture of α_{Co} and ϵ_{Co} at the ratio of 2:1 by means of X-ray analysis. As aluminium and vanadium are dissolved in the ϵ_{Co} phase to some extent, the intensity of saturation magnetization is estimated to be 1100 G. Consequently the coercive force, H_c , of No. 12 alloy will be about 2900 Oe according to the equation $H_c = 0.479 (N_b - N_a) I_s$ of Stoner and Wohlfarth⁽⁵⁾. Since this

value approximately agree with the measured value, it seems reasonable to ascribe the high coercive force in the Co-Al-V system to the shape magnetic anisotropy energy.

IV. Summary

The magnetic and other properties after quenching and tempering were measured on 35 alloys of the Co-Al-V system containing 4.55~20.63% aluminium and 0.50~19.66% vanadium.

The results obtained are as follows:

- (1) The maximum value of coercive force in each

(5) E. C. Stoner & E. P. Wohlfarth : Phil. Trans. Roy. Soc., A240(1948), 599.

alloy which was tempered at varying temperatures and times after solution treatment, heated at $1300^{\circ} \sim 1400^{\circ}\text{C}$ for 5~10 min and then water-quenched increases initially until it attains a maximum and then decreases with increasing vanadium content; the highest maximum value obtained in the Co-Al-V alloys is 1450 Oe.

(2) The residual magnetic flux density and the maximum energy product in the state having the maximum coercive force in each alloy decrease gradually with increase in vanadium content.

(3) The Co-Al-V alloy containing 13.42% aluminium and 4.65% vanadium, when tempered at 550°C for 15 hr after water-quenching from 1370°C , exhibits the highest coercive force of 1450 Oe, a residual magnetic flux density of 3200 G, a maximum energy product of 1.40 MG·Oe, and a density of 7.19 g/cc.

(4) According to the electron microscope observation of the alloy containing 13.42% aluminium and

4.65% vanadium having the highest value of coercive force, fine elongated particles of the ferromagnetic $\alpha_{\text{Co}} + \varepsilon_{\text{Co}}$ phase are dispersed in the β' phase matrix, and the size of the fine particles is within the range of the critical diameter of single magnetic domain. Therefore, the high coercive force of the ternary alloy is considered mainly due to the shape magnetic anisotropy energy.

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