

The Magnetic Properties and the Microstructure of High-C, High-Cr Magnet Steel

By

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Summary. High coercive force and high energy product ($B_r \sim 6900$ G, $H_c \sim 140$ Oe and $(BH)_{\max} \sim 4 \times 10^5$) are obtained in high-C, high-Cr steel containing 1.0% C and 18% Cr. The most suitable heat treatment for obtaining the best magnetic properties of this magnet steel is primary heating at $600^\circ\text{C} \sim 900^\circ\text{C}$ and subsequent heating for 15 mins. at 1060°C followed by air-cooling. During the air-cooling from 1060°C , a large number of fine spherical carbides precipitate, whereas water-quenching from 1060°C suppresses the precipitation of the fine carbides. By the primary heating followed by the air-cooling from 1060°C , the quantity of the retained austenite is decreased and the precipitation of the fine spherical carbides promoted. When water-quenched specimen is tempered at 300°C , the fine spherical carbides are found to precipitate. Both coercive force and residual induction of the specimen are increased, whereas hardness is decreased by the precipitation of the fine carbides. The coercive force of the magnet steel of the present study seems to be due to the magnetization fluctuation of the martensite which fluctuation is caused by the precipitation of a large number of fine spherical carbides and also to the internal stress in the martensite. The magnetic properties of this magnet steel is improved by addition of Co and W.

1. INTRODUCTION

This paper describes the changes of the magnetic properties and the microstructures of high-C, high-Cr magnet steel by various heat treatments and also describes the origin of the permanent magnetism of this steel. An abstract has already been published elsewhere [1]. In this country, high-C, high-Cr steel has been used as a tool steel e. g. as a die steel, but its magnetic properties have not been investigated as yet. The relationship between the magnetic properties of high-C, high-Cr steel and the chemical composition has been recently investigated by T. Mishima and the author [2], and the results are shown in Figs. 1~3. As shown in Fig. 3, the largest $(BH)_{\max}$ is obtained in the composition range of $\text{C} \sim 1.0\%$ and $\text{Cr} \sim 18\%$. Consequently the chemical composition of the specimen which is shown in Table 1 ($\text{C} \sim 1.0\%$, $\text{Cr} \sim 18\%$), was adopted in the present investigation. A typical demagnetization curve of this magnet steel is shown in Fig. 4.

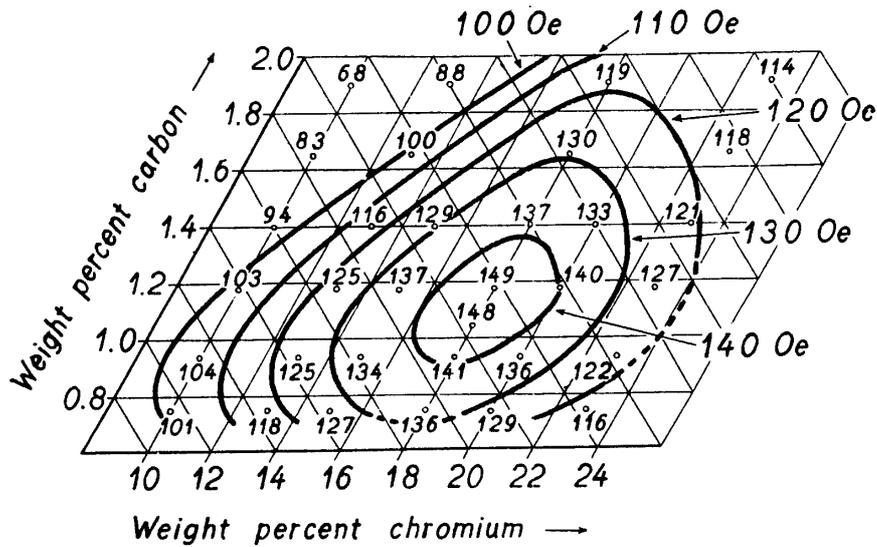


FIGURE 1. Relation between the coercive force of high-C, high-Cr magnet steel and chemical composition (Bal. Fe).

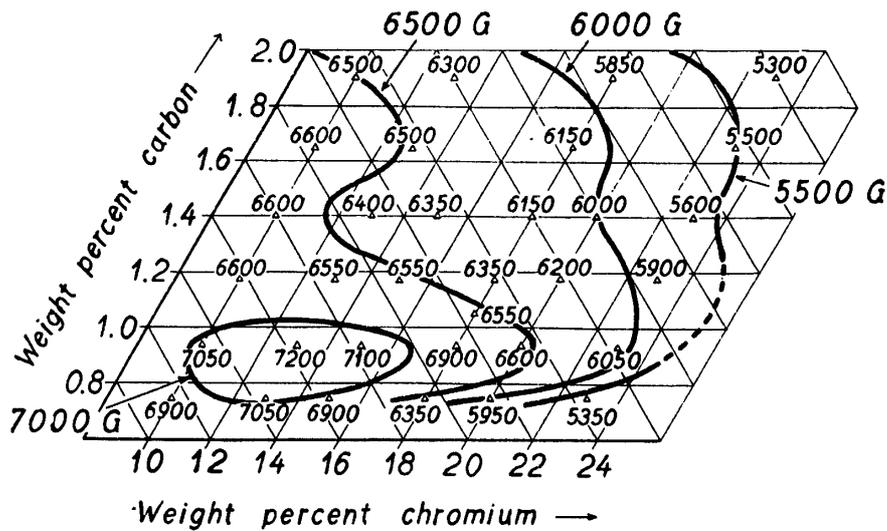


FIGURE 2. Relation between the residual induction of high-C, high-Cr magnet steel and chemical composition (Bal. Fe).

2. EXPERIMENTAL PROCEDURE

Electrolytic iron, pig iron and metallic chromium, which were crushed and mixed in the composition C=1.0% and Cr=18%, were melted in alumina crucible by a high frequency induction furnace. The melt was cast in metal mould of rod shape of 10 mm in diameter and 120 mm in length. The specimen was magnetized by an electromagnet, and the change of the intensity of the magnetization was measured by a Siemens & Halske's bal-

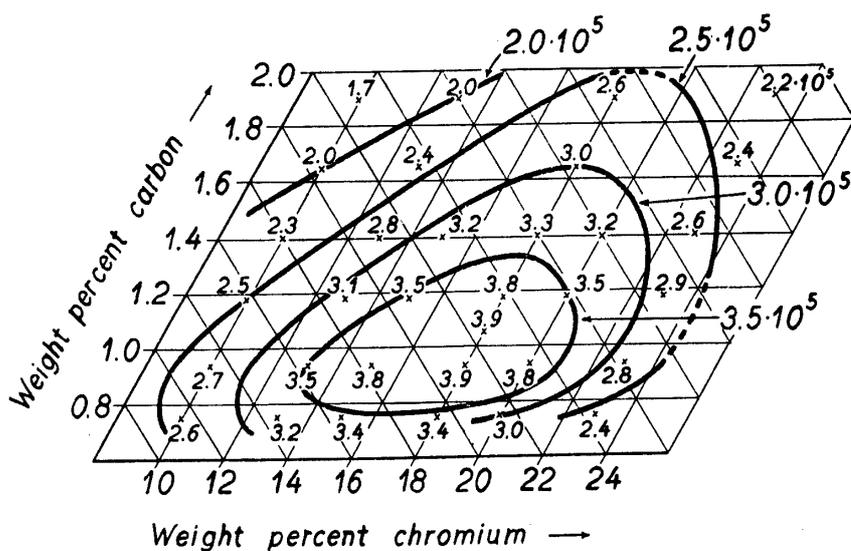


FIGURE 3. Relation between the energy product of high-C, high-Cr magnet steel and chemical composition (Bal. Fe).

TABLE 1. CHEMICAL COMPOSITION OF THE SPECIMEN (wt. %).

C	Cr	Si	Mn	P	S
0.94	17.95	0.06	0.14	0.005	0.004

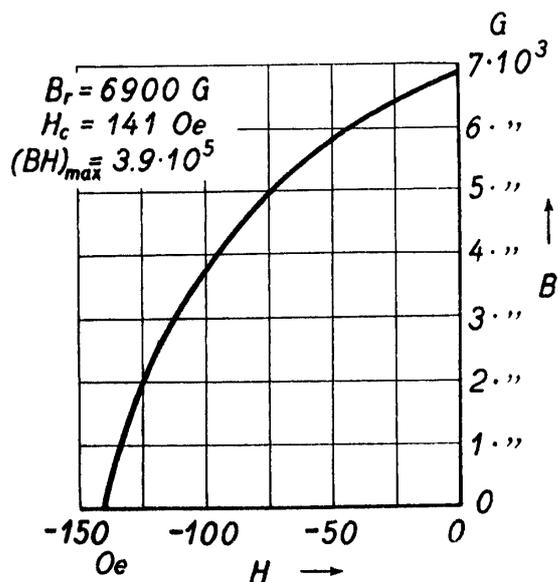


FIGURE 4. A typical demagnetization curve of the specimen. The specimen was received primary heating and additional heating for 15 mins. at 1060°C followed by air-cooling.

listic galvanometer. Vickers hardness number (V. H. N.) of each specimen was measured ten times, and the arithmetic mean was taken. The section perpendicular to the rod axis of the specimen was polished mechanically and etched by a mixture of acids (HNO_3 : HCL =2: 3) to examine the optical and electron microstructure. A triafol-carbon 2-step replica was used to examine the electron microstructure. (The electron micrographs were kindly prepared by Mr. K. Yamanouchi of The Akashi & Co.). The X-ray diffraction patterns of the specimen were also taken by a back reflection method, using Fe target.

3. THE MAGNETIC PROPERTIES AND MICROSTRUCTURES OF THE SPECIMEN THAT RECEIVED QUENCHING TREATMENT*

The magnetic properties and the microstructures of the specimen that received a mere quenching treatment will now be described. Those of the specimen that received primary heating and subsequent quenching treatment

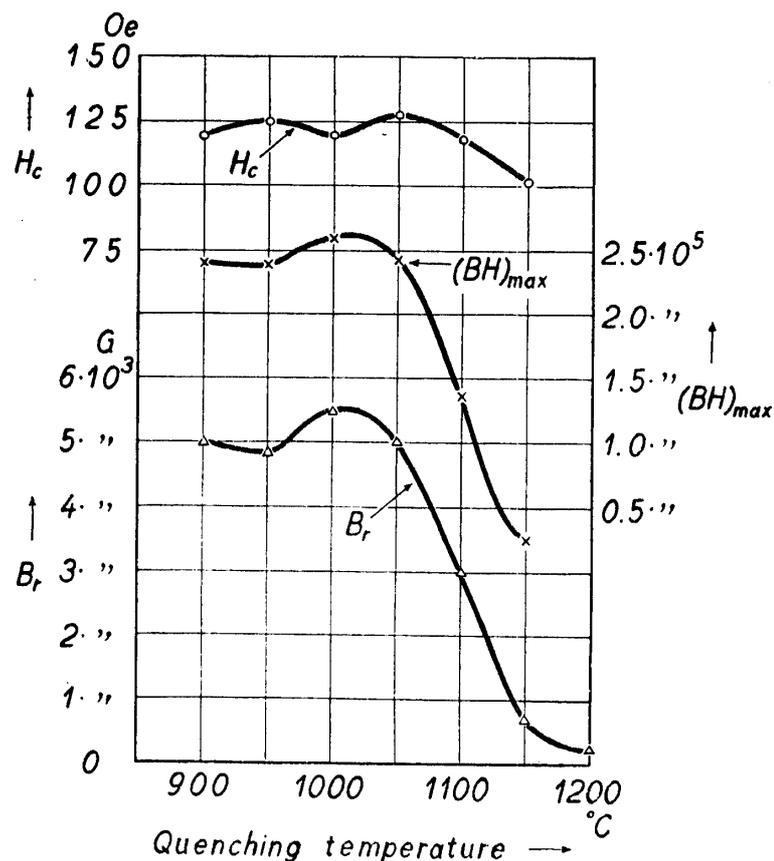


FIGURE 5. Dependence of the magnetic properties upon quenching temperature. The specimen was heated for 15 mins. at respective temperature and then air-cooled.

* In this paper, quenching treatment contains also air-cooling.

will be described in the next section.

The structure of the specimen as cast in metal mould is composed of austenite and eutectic carbides, so that the specimen as cast in metal mould is almost non-magnetic. Effect of the quenching temperature upon the magnetic properties of the specimen is shown in Fig. 5. In the case of the air-cooling, the cooling rate was $240^{\circ}\text{C}/\text{min}$. between $1000^{\circ}\text{C} \sim 600^{\circ}\text{C}$, $130^{\circ}\text{C}/\text{min}$. between $600^{\circ}\text{C} \sim 200^{\circ}\text{C}$ and $60^{\circ}\text{C}/\text{min}$. between $200^{\circ}\text{C} \sim 100^{\circ}\text{C}$. B_r and H_c of the water- or oil-quenched specimen are lower, but the hardness is higher than the air-cooled specimen. The magnetic properties of the specimen that received a mere quenching treatment are only as high as $B_r \sim 5500 \text{ G}$, $H_c \sim 120 \text{ Oe}$ and $(BH)_{\text{max}} \sim 2.5 \times 10^5$.

The structure of the specimen that was quenched from 1060°C , consists of martensite and considerable amount of retained austenite as can be seen in the X-ray pattern (see Fig. 7-b). The optical microstructure of this specimen is shown in Fig. 9-b, and the electron microstructure of this specimen is shown in Fig. 10-a.

4. THE MAGNETIC PROPERTIES AND THE MICROSTRUCTURES OF THE SPECIMEN THAT RECEIVED PRIMARY HEATING AND SUBSEQUENT QUENCHING TREATMENT

4. 1 Effect of the primary heating

Both B_r and H_c of the quenched specimen are increased considerably by the heating at $600^{\circ}\text{C} \sim 900^{\circ}\text{C}$ prior to the quenching, which heating is called primary heating in the present paper.

Effect of the primary heating temperature upon the magnetic properties of the specimen is shown in Fig. 6. Primary heating below 550°C prior to the quenching treatment has no effect upon the magnetic properties of the specimen. By the primary heating at between 600°C and 900°C , energy product of the specimen is considerably increased. But the primary heating becomes less effective above 900°C .

During the primary heating above 550°C , the austenite which has retained in as cast specimen partially decomposes. The degree of the decomposition of the retained austenite is sensitive to the primary heating temperature (between 600°C and 900°C), but it has little effect upon the magnetic properties of the specimen that received subsequent quenching treatment. Only partial decomposition of the retained austenite during the primary heating is sufficient for improvement of the magnetic properties of the specimen.

Adequate primary heating time for improvement of the magnetic properties of the specimen is about 30 mins. (10 mins. in the case of the primary heating at about 700°C). After the primary heating, the specimen was air-cooled to room temperature.

If the specimen is heated isothermally at 700°C for about 10 mins. in the

course of heating to the quenching temperature, the same effect as mentioned above is observed. Even if another heating is inserted between the primary heating and the quenching treatment, the magnetic properties of the specimen are not improved.

The effect of the primary heating upon the structure of the specimen that received subsequent quenching treatment is as follows. If the retained austenite of as cast specimen is once decomposed by the primary heating, the quantity of the austenite that retained after the quenching from 1060°C (in austenite range) decreases considerably. This can be seen in the X-ray patterns. Decrease of the quantity of the retained austenite is the reason why B_r of the specimen is increased by the primary heating.

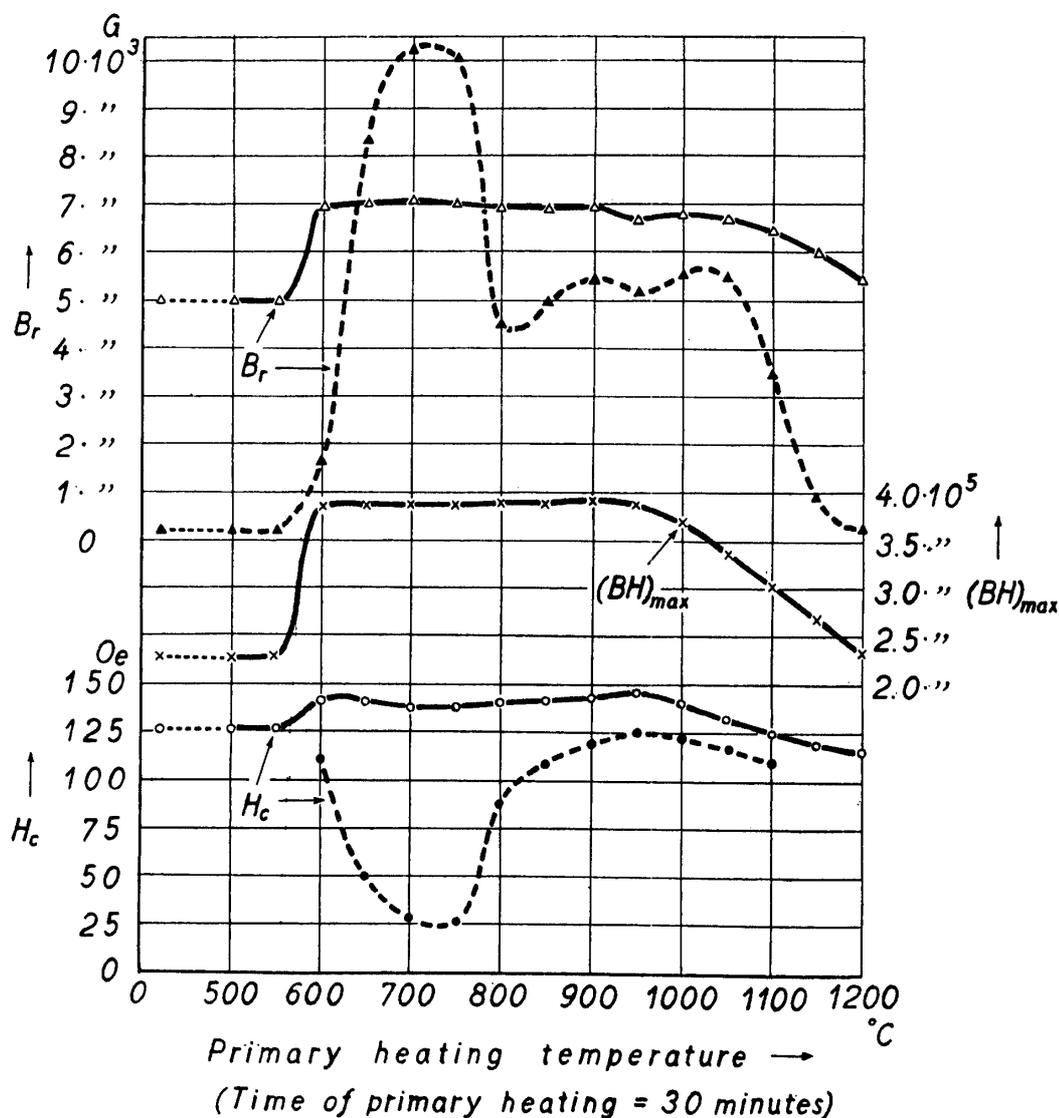


FIGURE 6. Dependence of the magnetic properties upon primary heating temperature.
 -----: primary heating at respective temperature followed by air-cooling.
 —: primary heating at respective temperature followed by air-cooling and additional heating for 15 mins. at 1060°C followed by air-cooling.

The primary heating promotes the precipitation of the fine carbides during the subsequent air-cooling from 1060°C. This can be seen in the optical and electron microstructures (compare Fig. 9-d with Fig. 9-b and Fig. 10-b with Fig. 10-a). Diameter of the precipitated fine spherical carbides is about 2000 Å and the volume fraction of them is about 10%. Smaller carbides appearing in Fig. 10-c are probably those whose cross sections are apart from the centre of the sphere. In the primary heating temperature range of 600°C~900°C, similar microstructures are obtained after the air-cooling from 1060°C.

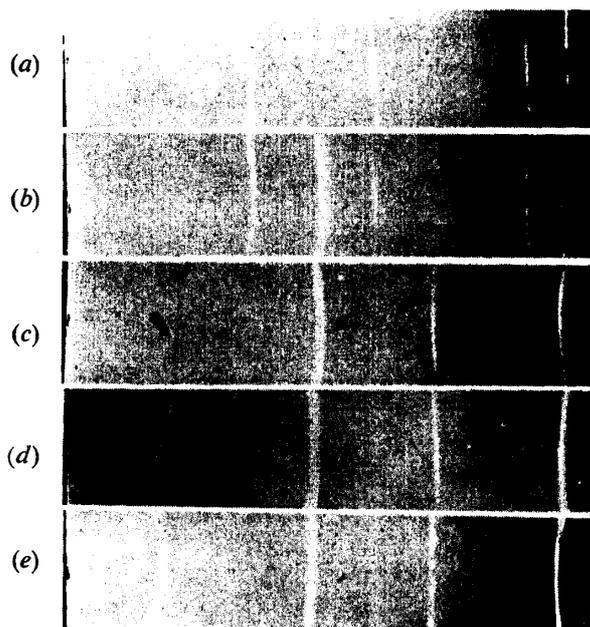


FIGURE 7. X-ray structure of the specimen (Fe target was used).

- (a) as cast.
- (b) heated for 15 mins. at 1060°C and then air-cooled.
- (c) after primary heating, heated for 15 mins. at 1060°C and then air-cooled.
- (d) after primary heating, heated for 15 mins. at 1060°C and then water-quenched.
- (e) heated for 1 hr. at 700°C.

4. 2 Effect of the quenching treatment

Dependence of the magnetic properties upon the quenching temperature is shown in Fig. 8. The highest H_c is obtained by the air-cooling from 1080°C, and the highest B_r is obtained by the air-cooling from 1020°C. The optimum heating temperature for obtaining the highest $(BH)_{max}$ is 1060°C. By the air-cooling from higher temperature than 1060°C, the quantity of the retained austenite is increased so that B_r of the specimen is much decreased. The structure of the specimen that was air-cooled from 1140°C is shown in Fig. 10-d. In the optical micrograph of this specimen, leaves of the martensite are found in the matrix of the retained austenite. In the

electron micrograph, many fine carbides are seen to precipitate in each martensite leaves. The quantity of the retained austenite of this specimen is much greater than that of the specimen air-cooled from 1060°C, but there is only a small difference of H_c between them.

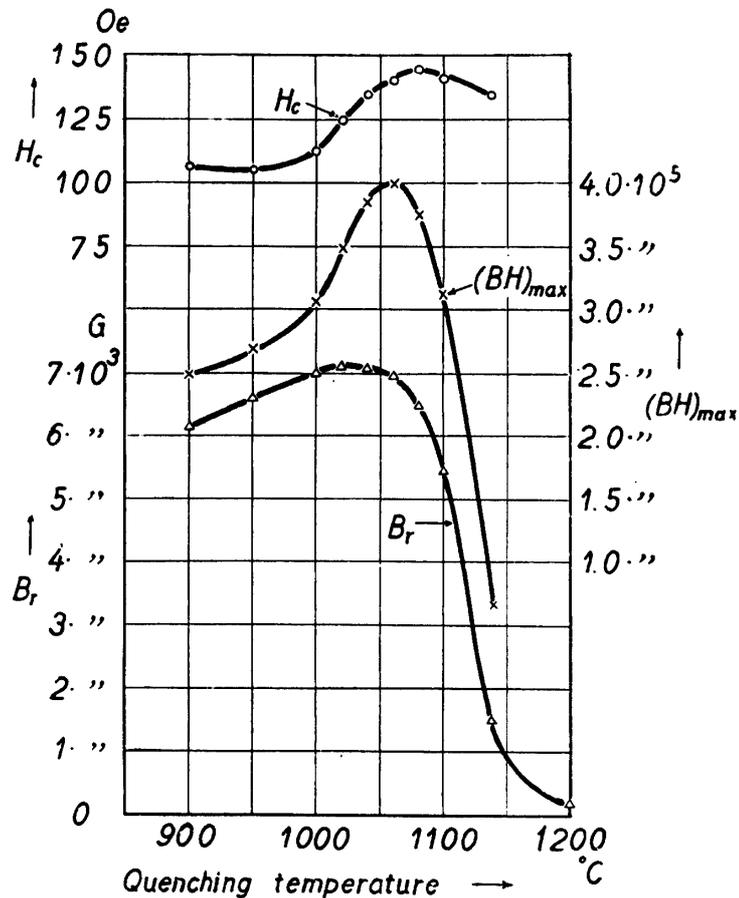


FIGURE 8. Influence of quenching temperature upon the magnetic properties of the specimen that received primary heating. After primary heating at 800°C followed by air-cooling, the specimen was heated for 15 mins. at respective temperature and then air-cooled.

TABLE 2. EFFECT OF QUENCHING TREATMENT UPON THE MAGNETIC PROPERTIES OF THE SPECIMEN THAT RECEIVED PRIMARY HEATING. BEFORE QUENCHING, THE SPECIMEN WAS HEATED FOR 30 MINS. AT 800°C AND AIR-COOLED.

Quenching treatment	B_r (G)	H_c (Oe)	V. H. N. (10 kg load)
1060°C × 10 mins., air-cooling	6850	142	659
1060°C × 15 mins., water-quenching	6300	114	736
1060°C × 15 mins., oil-quenching	6400	120	729
1060°C × 15 mins., air-cooling	6900	142	660
1060°C × 15 mins., furnace-cooling	8350	53	435
1060°C × 20 mins., air-cooling	6800	141	662
1060°C × 30 mins., air-cooling	6750	134	668

In Table 2, effect of the heating time and the cooling rate of the quenching treatment upon the magnetic properties and hardness of the specimen is shown. Effect of the cooling rate upon the magnetic properties and hardness of the specimen is as follows. Both H_c and B_r of the air-cooled specimen

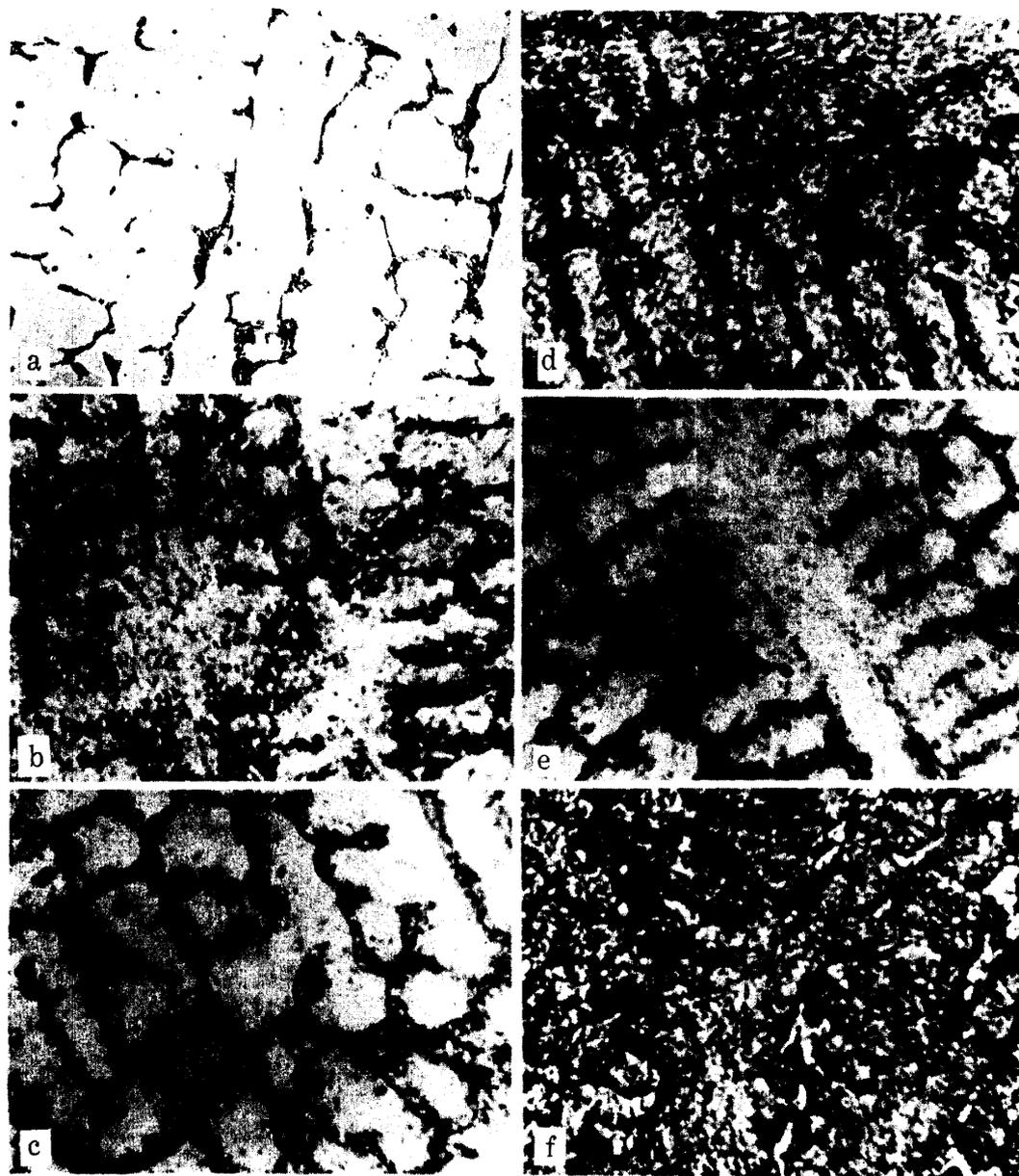


FIGURE 9. Optical microstructure of the specimen.

- (a) as cast ($\times 700$).
- (b) heated for 15 mins. at 1060°C and then air-cooled ($\times 700$).
- (c) heated for 15 mins. at 1060°C and then water-quenched ($\times 700$).
- (d) after primary heating, heated for 15 mins. at 1060°C and then air-cooled ($\times 700$).
- (e) after primary heating, heated for 15 mins. at 1060°C and then water-quenched ($\times 700$).
- (f) after primary heating, heated for 15 mins. at 1060°C and then furnace-cooled ($\times 700$).

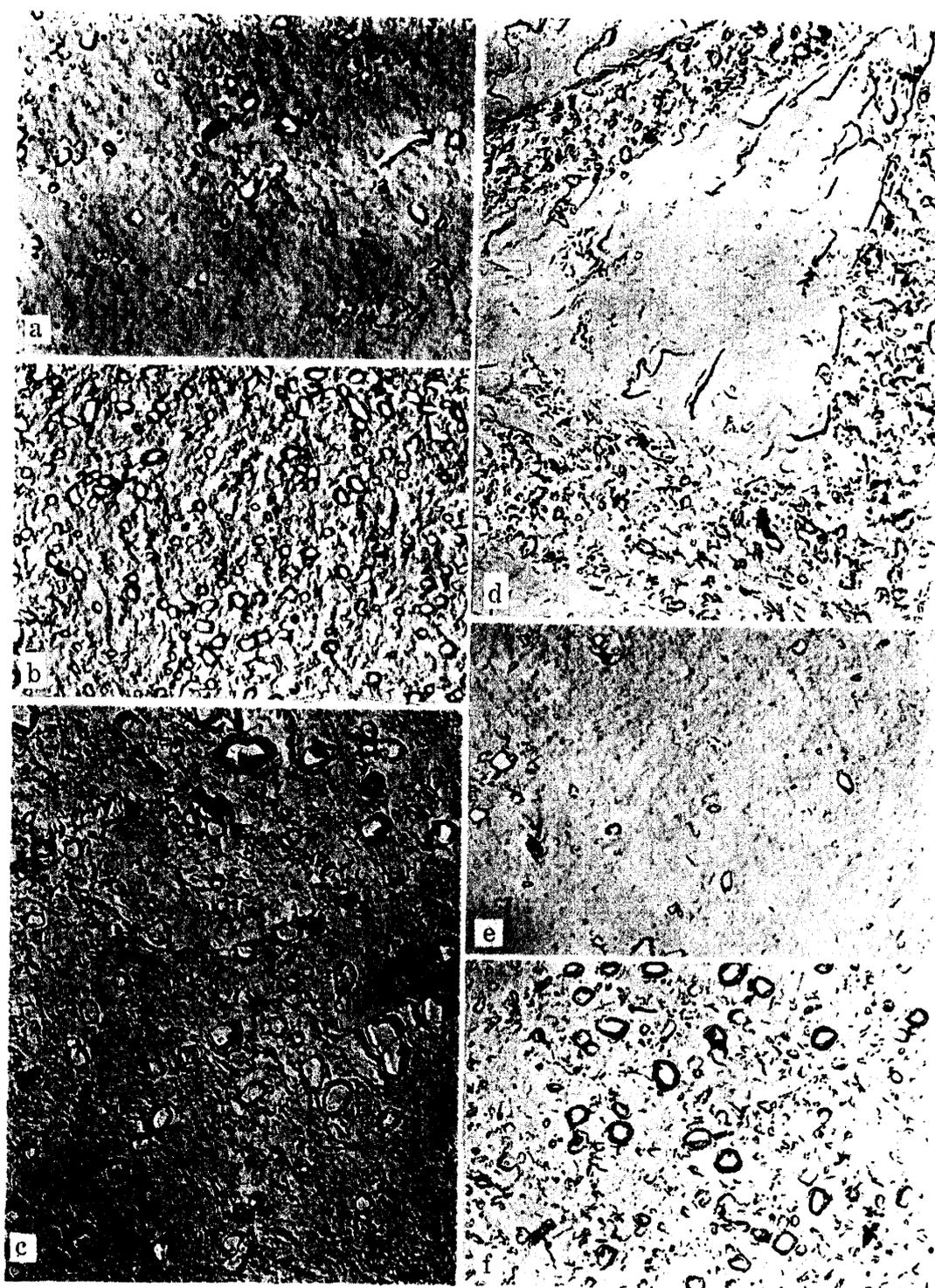


FIGURE 10. Electron microstructure of the specimen.

- (a) heated for 15 mins. at 1060°C and then air-cooled ($\times 8000$).
- (b) after primary heating, heated for 15 mins. at 1060°C and then air-cooled ($\times 8000$).
- (c) *ibid.* ($\times 20000$).
- (d) after primary heating, heated for 15 mins. at 1140°C and then air-cooled ($\times 8000$).
- (e) after primary heating, heated for 15 mins. at 1060°C and then water-quenched ($\times 8000$).
- (f) after primary heating and additional heating for 15 mins. at 1060°C followed by water-quenching, tempered at 300°C for 1 hr. ($\times 8000$).

are considerably high, whereas hardness is considerably low as compared with water- or oil-quenched specimen. During air-cooling from 1060°C, a large number of fine carbides precipitate, as shown in optical and electron micrographs. On the contrary, the precipitation is suppressed by water- or oil-quenching (see Fig. 9-e and Fig. 10-e). The quantity of the retained austenite of the water quenched specimen is nearly the same as that of the air-cooled specimen, as can be seen in the X-ray patterns. Consequently, the difference of the magnetic properties and hardness between the air-cooled specimen and the water-quenched specimen seems to be due to the dispersion of a large number of fine spherical carbides. Magnetization fluctuation in the martensite caused by the dispersion of a large number of fine carbides may increase H_c of the air-cooled specimen. Saturation magnetization of the martensite may be increased by the decrease of its carbon content, so B_r of the air-cooled specimen may be increased by the precipitation of the carbides from the martensite. By the precipitation of the carbides from the martensite, the internal stress of the martensite may be decreased, so that the hardness of the air-cooled specimen may be decreased. During the furnace-cooling from 1060°C, the austenite transforms into troostite (see Fig. 9-f), so that softening takes place which accompanies the decrease of hardness and H_c of the specimen.

Adequate heating time at 1060°C for obtaining the best magnetic properties is 15 mins., and prolonged heating at 1060°C causes the decrease of H_c and B_r of the specimen, as shown in Table 2. By the prolonged heating at 1060°C after the primary heating, the quantity of the fine carbides that appear during the subsequent air-cooling is decreased. This seems to be the reason why H_c and B_r of the specimen are decreased by the prolonged heating.

5. EFFECT OF THE SUBZERO-COOLING UPON THE MAGNETIC PROPERTIES OF THE SPECIMEN

Effect of the subzero-cooling to -196°C after various heat treatments upon the magnetic properties of the specimen was investigated, and the results are shown in Table 3. Before subzero-cooling, about 70 hrs. elapsed at room temperature. The magnetic properties and hardness of the specimen that received primary heating and subsequent air-cooling from 1060°C, are not affected by the subzero-cooling. In the case of the specimen that was air-cooled from 1060°C but did not receive primary heating, B_r and hardness are increased and H_c is decreased by the subzero-cooling. Also in the specimen quenched from above 1060°C after the primary heating, similar effect is observed by the subzero-cooling. In the specimen that was slowly cooled from 1150°C (sample E in Table 3), not only B_r and hardness but also H_c are increased by the subzero-cooling. In the case of these specimens which contain a large amount of retained austenite, martensitic transformation takes

place, so B_r and hardness of these specimens are increased by the subzero-cooling. In sample E, H_c of the martensite which is formed by the subzero-cooling is higher than that of the troostite which already existed after the slow cooling from 1150°C, so H_c of the specimen is increased by the subzero-cooling.

TABLE 3. EFFECT OF SUBZERO-COOLING TO -196°C UPON THE MAGNETIC PROPERTIES AND VICKERS HARDNESS NUMBER OF THE SPECIMEN.

Heat treatment before subzero-cooling	Before subzero-cooling			After subzero-cooling		
	B_r (G)	H_c (Oe)	V. H. N. (10 kg load)	B_r (G)	H_c (Oe)	V. H. N. (10 kg load)
(A) 800°C×30 mins., air-cooling -1060°C×15 mins., air-cooling	6900	142	660	6900	142	660
(B) 800°C×30 mins., air-cooling -1060°C×15 mins., water-quenching	6300	114	736	6350	114	738
(C) 1060°C×15 mins., air-cooling	4900	126	691	5900	124	723
(D) 800°C×30 mins., air-cooling -1100°C×15 mins., oil-quenching	2800	140	553	6000	125	737
(E) 800°C×30 mins., air-cooling -1150°C×15 mins., slow cooling	1950	73	424	5900	100	725

6. CHANGES OF THE MAGNETIC PROPERTIES AND MICRO-STRUCTURE OF THE QUENCHED SPECIMEN DURING TEMPERING

The dependence of the magnetic properties and hardness upon the tempering temperature is shown in Fig. 11. In the case of the specimen air-cooled from 1060°C after the primary heating, B_r is increased only slightly, and H_c and hardness are decreased also slightly by the tempering below 400°C. On the contrary, in the case of the specimen water-quenched from 1060°C after the primary heating, tempering between 200°C and 300°C causes considerable decrease of hardness and increase of both B_r and H_c . In the microstructure of the water-quenched specimen, dispersion of the fine carbides is scarce, but after the tempering at 300°C, many fine spherical carbides precipitate in the martensite (see Fig. 10-f). The changes of the magnetic properties and hardness of the water-quenched specimen during tempering between 200°C and 300°C seems to be due to the precipitation of the fine carbides from the martensite. In the case of the air-cooled specimen, a large number of fine carbides precipitate prior to the tempering, so that change of the magnetic properties and hardness of this specimen during tempering below 400°C is small. Diameter of the fine carbides which precipitate during tempering at 300°C after the water-quenching is larger and their number is fewer than the fine carbides which precipitate during the air-cooling from 1060°C. Higher H_c is obtained by air-cooling from 1060°C

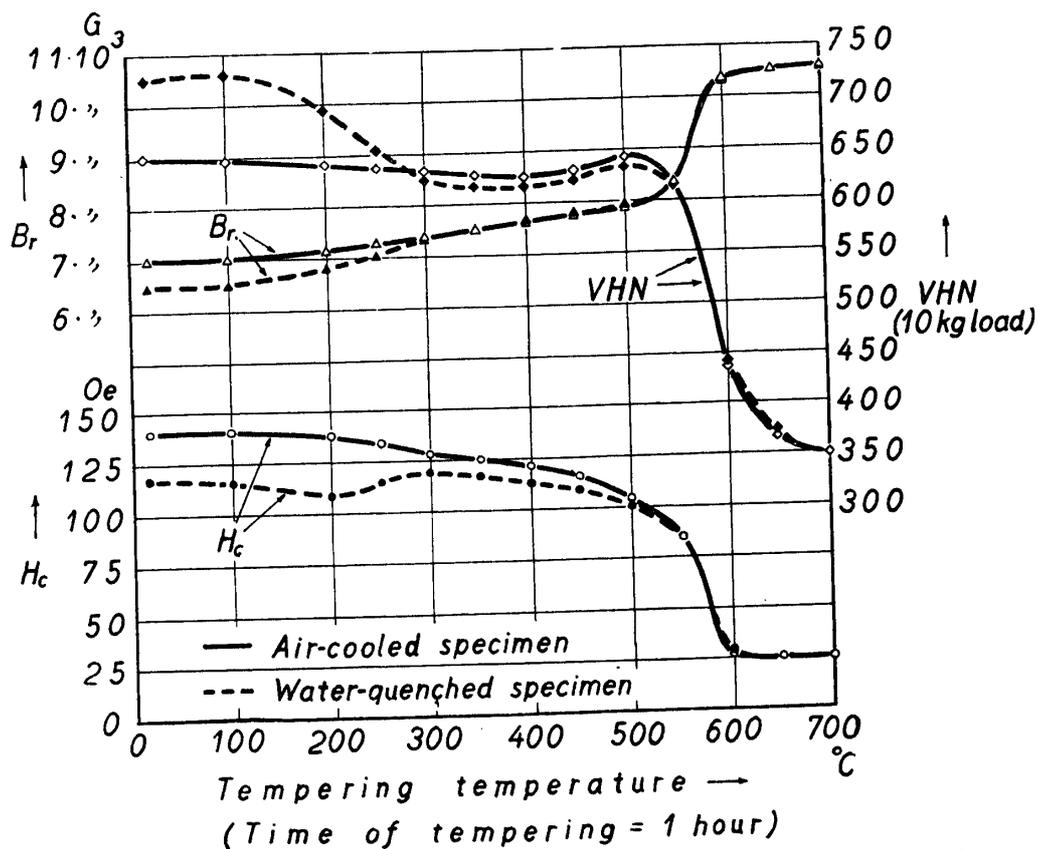


FIGURE 11. Dependence of the magnetic properties and Vickers hardness number upon tempering temperature. "Air-cooled specimen" was received primary heating and additional heating for 15 mins. at 1060°C followed by air-cooling. "Water-quenched specimen" was received primary heating and additional heating for 15 mins. at 1060°C followed by water-quenching. Each specimen was tempered for 1 hr. at respective temperature.

than by water-quenching from 1060°C followed by tempering at 300°C.

The change of the magnetic properties and hardness of the air-cooled specimen and that of the water-quenched specimen caused by the tempering above 400°C is similar. Hardness of both specimen is slightly increased by the tempering at 450°C~500°C. This effect is considered to be the result of the martensitic transformation of the retained austenite [3]. By the tempering between 550°C and 600°C, H_c and hardness of both specimen are much decreased and B_r is much increased. During tempering at 600°C, the martensite of the specimen becomes troostite, so the softening takes place.

7. EFFECT OF ADDITION ELEMENT UPON THE MAGNETIC PROPERTIES OF THE SPECIMEN

Effect of various addition elements upon the magnetic properties of the specimen containing 1.0% C and 18% Cr was investigated. The results follow.

(1) Addition elements which increase B_r but decrease H_c of the specimen

are Al, V, Ti, Si and Sn, as shown in Fig. 12. Addition of these elements decreases $(BH)_{\max}$ of the specimen.

- (2) Addition elements which decrease both B_r and H_c of the specimen are Cu, Mn, Mo and Ni, as shown in Fig. 13.
- (3) Addition element which increases H_c but decreases B_r of the specimen is W. By the addition of 1.5% W; the H_c of the specimen is increased by about 10 Oe, and $(BH)_{\max}$ is also increased slightly.
- (4) Both B_r and H_c of the specimen are increased by the addition of Co, as shown in Fig. 14. The magnetic properties of $B_r \sim 7000$ G, $H_c \sim 175$ Oe, $(BH)_{\max} \sim 5 \times 10^5$ are obtained by the addition of 5% Co and 1.5% W,

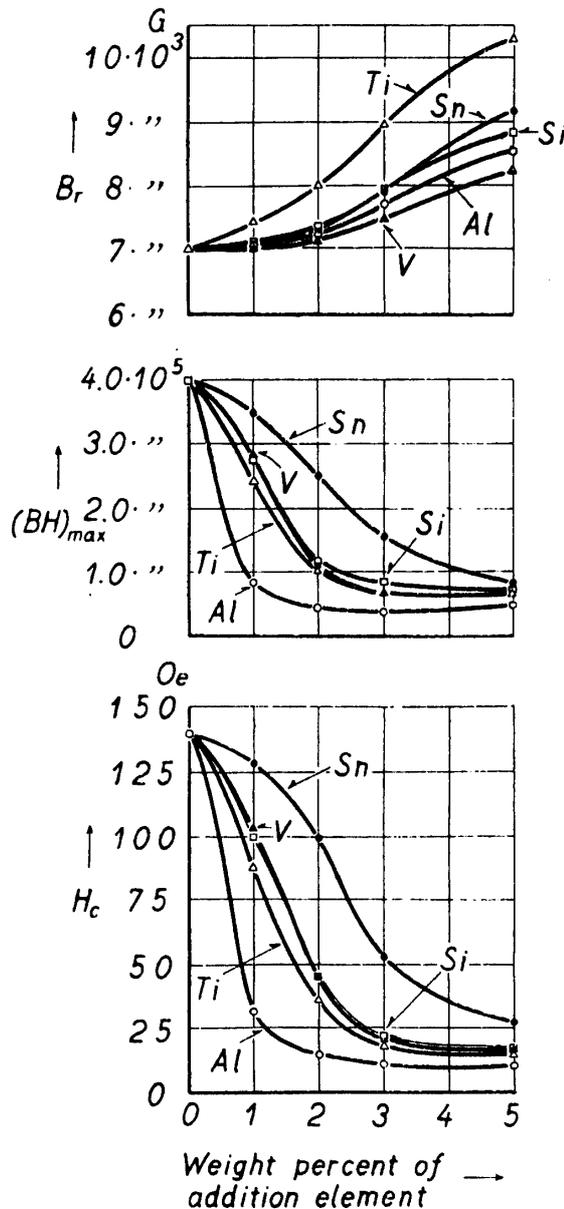


FIGURE 12. Effect of addition element upon the magnetic properties of the specimen containing 1.0% C and 18% Cr.

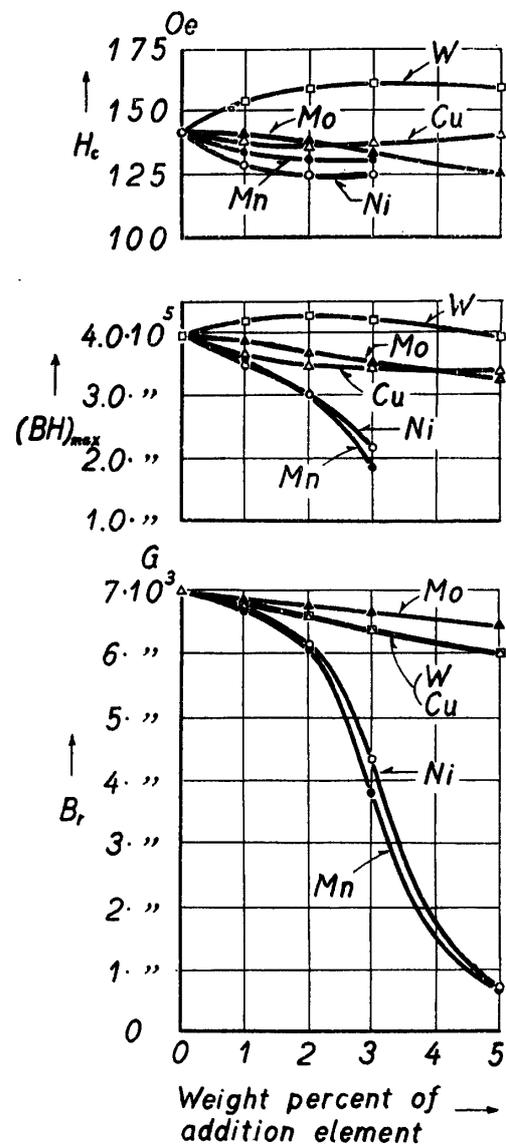


FIGURE 13. Effect of addition element upon the magnetic properties of the specimen containing 1.0% C and 18% Cr.

and $B_r \sim 7300$ G, $H_c \sim 195$ Oe, $(BH)_{max} \sim 6 \times 10^5$ are obtained by the addition of 10% Co and 1.5% W.

When two elements which have similar effect upon the magnetic properties of the specimen are simultaneously added, their effects are intensified. Even if two elements which have mutually opposite effect upon the magnetic properties of the specimen are simultaneously added, the magnetic properties of the specimen cannot be improved.

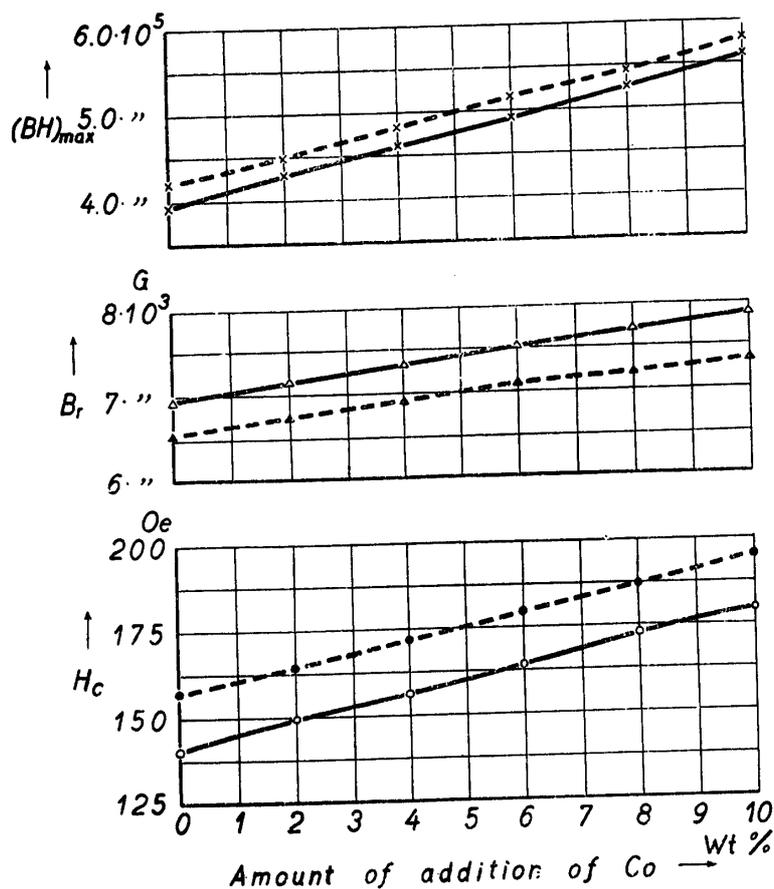


FIGURE 14. Effect of addition of cobalt upon the magnetic properties of the specimen containing 1.0% C and 18% Cr. (-----: with simultaneous addition of 1.5% W).

8. DISCUSSION

It has been hitherto considered that H_c of Cr-steel is due to the internal stress in the martensite which is formed by quenching. But, in the case of high-Cr steel of the present investigation, the highest H_c is obtained in the air-cooled specimen which is considerably softer than the water-quenched specimen. This fact cannot be explained by the internal stress theory of H_c . Néel studied theoretically how H_c is affected by the dispersion of spherical particles having spontaneous magnetization different from the matrix. According to his theory, H_c is increased by the magnetization fluctuation caused by

the dispersion of the particles, and increased proportionally with the volume fraction of the particles [4]. Dijkstra and Wert calculated the influence of the dimension of the dispersed particles upon H_c of the material and came to the conclusion that the highest H_c is obtained when the diameter of the particles is nearly equal to the thickness of the domain wall of the material [5]. The diameter of the fine spherical carbides appearing in the steel of the present study in the state of the highest H_c is about 2000 Å or less, and the volume fraction of the fine carbides is about 10%. It is probable that the magnetization fluctuation in the martensite caused by the dispersion of such fine carbides increases H_c of the specimen. When the structure of the specimen becomes troostite and softening takes place, H_c of the specimen greatly decreases. Consequently, the internal stress in the martensite may partly account for the coercive force of the magnet steel of the present study.

9. SUMMARY

High coercive force and high energy product ($B_r \sim 6900$ G, $H_c \sim 140$ Oe, $(BH)_{\max} \sim 4 \times 10^5$) are obtained in the specimen containing 1.0% C and 18% Cr. The most suitable heat treatment for obtaining the best magnetic properties of this magnet steel is primary heating at 600°C ~ 900°C and subsequent heating for 15 mins. at 1060°C followed by air-cooling. During air-cooling from 1060°C, a large number of fine spherical carbides precipitate, whereas water- or oil-quenching from 1060°C suppresses the precipitation of the fine carbides. Primary heating followed by the air-cooling from 1060°C, decreases the quantity of the retained austenite and promotes the precipitation of the fine carbides. When the specimen that was water-quenched from 1060°C is tempered at 300°C, the fine spherical carbides precipitate from the martensite. Both H_c and B_r of the specimen are increased, whereas hardness is decreased by the precipitation of the fine carbides. The coercive force of this magnet steel seems to be due to the magnetization fluctuation of the martensite which fluctuation is caused by the precipitation of the fine spherical carbides and also to the internal stress in the martensite.

The magnet steel of the present study can be forged at 800°C ~ 1000°C and also machined after the primary heating at 700°C ~ 750°C prior to the air-cooling from 1060°C. The magnetic properties of this magnet steel is further improved by the addition of Co and W.

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REFERENCES

- [1] K. Tachikawa: *J. Japan Inst. Metals*, **21** (1957) 689 (in Japanese).
- [2] T. Mishima and K. Tachikawa: Reported at the meeting of the Japan Inst. Metals, April 7, 1955.
- [3] T. Nemoto: *J. Japan Inst. Metals*, **20** (1956) 669 (in Japanese).
- [4] L. Néel: *Physica*, **15** (1949) 225.
- [5] L. Dijkstra and C. Wert: *Phys. Rev.*, **79** (1950) 979.