The Effect of Carbon Addition on the Magnetic Shunt Properties of M.S.Q. Alloy

The Effect of Carbon Addition on the Magnetic Shunt Properties of M.S.O. Alloy*

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Synopsis

The magnetic shunt properties of a kind of M.S.O. Alloy (31% Ni, 8.5% Cr and rest Fe) containing C from 0.019 to 0.150% were studied. The magnetization curves at 0° to 40°C were measured by the ballistic method. The dimension of specimen was 0.4 cm in diameter, 3.1 cm in length, and so the demagnetization factor N was 0.30. The experimental results on magnetic shunt properties are summarised as follows: (1) With increasing C addition, the permeability decreases at first and then increases slightly through a feeble minimum. It is assumed that the former decreasing is due to the impurity of C and the latter increasing due to the formation of $Fe_6Cr_{17}C_6$ which is speculated by the microscopic texture and the calculation. (2) The temperature coefficient of permeability becomes larger with increasing C addition, and its linearity becomes worse.

I. Introduction

The magnetic shunt alloys which have been used in the past are those which belong to Ni-Cu system[1],[2] and Fe-Ni system.[4],[3] The former are expensive and the latter have allotropic transformations and are poor in reproducibility. However, in 1948, an alloy belonging to Fe-Ni-Cr system, inexpensive and rich in reproducibility, was invented,[5],[6] which are in use in large quantities today as M.S.O. magnetic shunt alloy. It is generally thought that various kinds of impurities are mixed in when whatever materials are to be produced industrially. These impurities contain those which may spoil the property of the material. Carbon is considered to be an impurity which for the magnetic shunt property must be very careful. We should make clear the effect of carbon on the property of a magnetic material, because carbon has large effects on the magnetic materials as everyone knows. A report is made here on the results obtained by measuring the property of one of M.S.O. alloys which is composed of 31% of nickel, 8.5% of chromium, and 61.5% of iron to which 0.012 to 0.15% of carbon is added.

(1) J.E. Kinnard and H.T. Faus, Trans. Amer. Inst. Elect. Eng., **44** (1925), 275.
(2) J.E. Kinnard and H.T. Faus, ibid., **49** (1930), 949.
(3) F. Stäblein, Z. Techn. Phys., **8** (1928), 145.
(4) K. Shinba and T. Aoyagi, J. Japan Inst. Metals, **6** (1942), 145.
(5) H. Masumoto, Y. Shirakawa and T. Ôhara, ibid., **15** (1951), B–375.
(6) H. Masumoto, Y. Shirakawa and T. Ôhara, Jap. Pat. No. 178339 (1948).

II. Specimens and method of measurement

In making specimens, electrolytic iron, Sweden steel (0.2% of carbon), electrolytic nickel and metallic chromium were mixed in proper proportions, and a total of 400g of the mixture was melted in the high frequency furnace in the air. The results of analysis of the metals used, iron, nickel and chromium are shown in Table 1.

The alloys thus made were forged and lathed into bars 3.1 cm in length. Since the dimension ratio $l/D=7.8$, the demagnetization coefficient $N=0.30$. These specimens were annealed in vacuum at 1,000°C for 1 hour, furnace-cooled and used in experiments. Five kinds of specimens were made whose compositions are given in Table 2. The method of measurements are omitted here because it is nearly the same as those used in the previous study[5]. As clearly seen in the chemical analysis given in Table 2, the composition of the specimen was slightly different, nickel content being 31.01 to 30.10% and chromium 8.56 to 7.89%. Con-

Table 1. Chemical compositions of the metals used (in %)

	Cr	Al	Fe	Si	C	S	P	Cu	Mn	Ni
Electrolytic Ni	—	—	0.012	0.007	—	—	—	0.008	0.0003	rest
Electrolytic Fe	—	—	rest	0.0038	0.0047	0.0046	0.0018	0.0002	0.0071	—
Metallic Cr	rest	0.10	0.32	0.11	0.04	0.02	—	—	—	—

sequently, it is necessary to make corrections in the measured values of the property against the difference of Ni and Cr contents in order to make clear the effect of carbon on the property. Because the permeabilities of the alloys in Fe-Ni-Cr system had already been measured in detail,[5]~[7] attempts were made to correct the permeabilities against the difference of compositions by using these permeabilities. For a standard specimen, an alloy composed of 31% of nickel, 8.5% of chromium and the rest of iron was selected. In an alloy in Fe-Ni-Cr system, its permeability at 0°C and 400 Oe changes with its chromium content or nickel content if nickel content or chromium content is definite, but the rate of change is almost definite around the standard composition. Therefore, it is easy to make such corrections if we have at hand the value of $(\mu_{Cr}/\mu_{8.5})_{Ni}$ obtained by deviding the permeability of chromium content by that of 8.5% of chromium content for the case where nickel content is made definite or the value $(\mu_{Ni}/\mu_{31})_{Cr}$ obtained by dividing the permeability of nickel content by that of 31% of nickel for the case where chromium is made definite. If we assume these values to be the same for the case where the behavior caused by nickel in the permeability or by chromium content in the presence of carbon content used in the experiment is quite the same as the case where carbon content is zero, the corrected permeability value μ_n can be obtained from the measured permeability μ_m by the following equation:

(7) T. Tuno'o and T. Saito, Sumitomo Kinzoku, **9** (1957), 77.

$$\mu_n = \mu_m \cdot \frac{1}{(\mu_{Cr}/\mu_{8.5})_{Ni}} \cdot \frac{1}{(\mu_{Ni}/\mu_{31})_{Cr}} \tag{1}$$

For each specimen, the values of $1/(\mu_{Cr}/\mu_{8.5})_{Ni}$ and $1/(\mu_{Ni}/\mu_{31})_{Cr}$ are calculated from Fig. 1 and shown as the correction coefficient in Table 2. As the correction coefficients were unknown for different compositions, they were considered to be the same at high temperature as at room temperature, so we used the same values for correction in the case of high temperature.
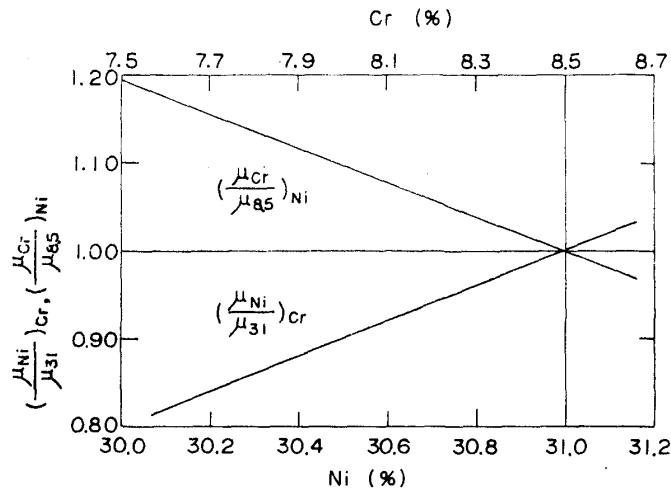

Fig. 1. Correction coefficient for elimination of permeability change due to a deviation of Ni and Cr content from the standard($=31\%$Ni and 8.5% Cr). The coefficient for Ni was obtained at the standard content of Cr, and vice versa.

Table 2. Composition of specimens used, permeability at $0°C$ in $400\ Oe$, μ_{400}^o and correction coefficient for normalizing to the standard composition (31%Ni, 8.5%Cr, rest Fe).

No. of Speci-mens	Composition (%) (rest Fe)			Permeabilty μ_{400}^o		Correction coefficient	
	Ni	Cr	C	measured μ_m	normalized μ_n	$\dfrac{1}{\left(\dfrac{\mu_{Cr}}{\mu_{8.5}}\right)_{Ni}}$	$\dfrac{1}{\left(\dfrac{\mu_{Ni}}{\mu_{31}}\right)_{Cr}}$
1	30.10	7.89	0.019	12.87	13.85	1.22_9	0.88_2
2	30.77	8.22	0.046	10.83	10.68	1.04_7	0.94_2
3	30.94	8.11	0.073	10.53	9.80	1.01_1	0.92_1
4	31.01	8.56	0.120	10.34	10.45	0.99_7	1.01_4
5	30.66	8.56	0.150	9.85	10.71	1.07_2	1.01_4

III. Results of measurement and discussion

Magnetization curves for each specimen were obtained in the temperature range $0°$ to $40°C$ at 5-degree intervals. In the standards of magnetic shunt alloys are found the permeabilities in various magnetic fields, but the examination was made here only on the property at $H=400$ Oe, because our aim was to make clear the effect of carbon on it. The measured value μ_m of permeability at $0°C$ and 400 Oe

and μ_n are as shown in Table 2. The permeabilities to be described below are all corrected values and to be designated simply μ. It is reasonable to think that carbon content is responsible for the change in the value μ. Calculating the value μ from the magnetization curve for each specimen and plotting it against carbon content will give the magnetization curves shown in Fig. 2. In order to observe the effect of carbon on the value μ, we plot μ at its respective temperature in Fig. 2 against carbon content and the results are shown in Fig. 3. As seen clearly in Fig. 3, μ suddenly lowered in value at 0°C with the increase in carbon content, reaching the minimum value around where carbon content was 0.07%. Then it gradually increased in value. The μ-t curves at high temperature are almost identical with those at 0°C. The effects of μ on carbon are two: One is that which can be observed when carbon content is small, that is, a small amount of carbon is present in solid solution as a interstitial type, preventing its magnetization; the other is the case where carbon content is large. In this case chromium carbide is formed, and nickel and iron contents increase relatively and magnetism rather becomes rich[8]. However, further increase in carbon content makes magnetism poor. Therefore, it is conceivable that μ-C curves at 0°C in Fig. 3 will show maximum where the addition of carbon is large in amount. Photo. 1 shows the microstructures ($\times$100) of specimens at room temperature. As clearly seen in the photo, with the specimen containing 0.019% of carbon, the segregation of carbide at the grain boundary is hardly observable, while it can be observed in the specimen containing 0.046% of carbon. The segregated carbide increases with
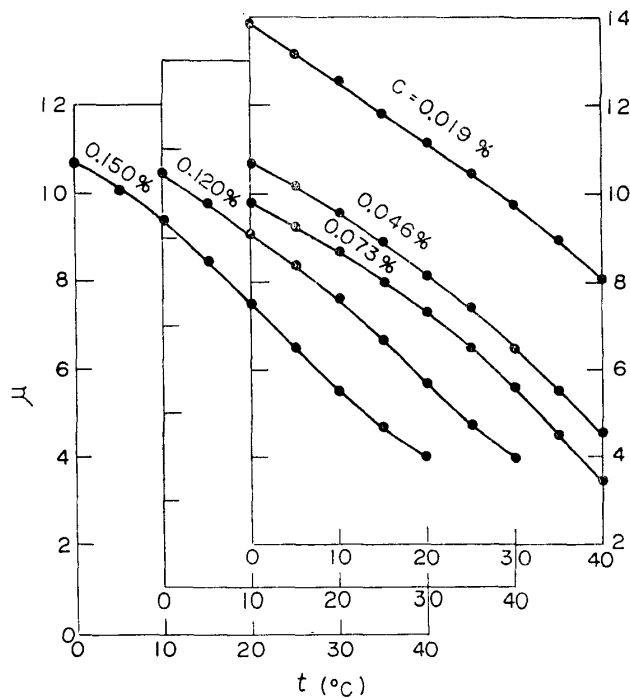

Fig. 2. μ-t curves of M.S.O. alloys with various C-contents (31% Ni, 8.5% Cr and rest Fe).

(8)   T. Tôyama, J. Japan Inst. Metals, **25** (1961), 607.
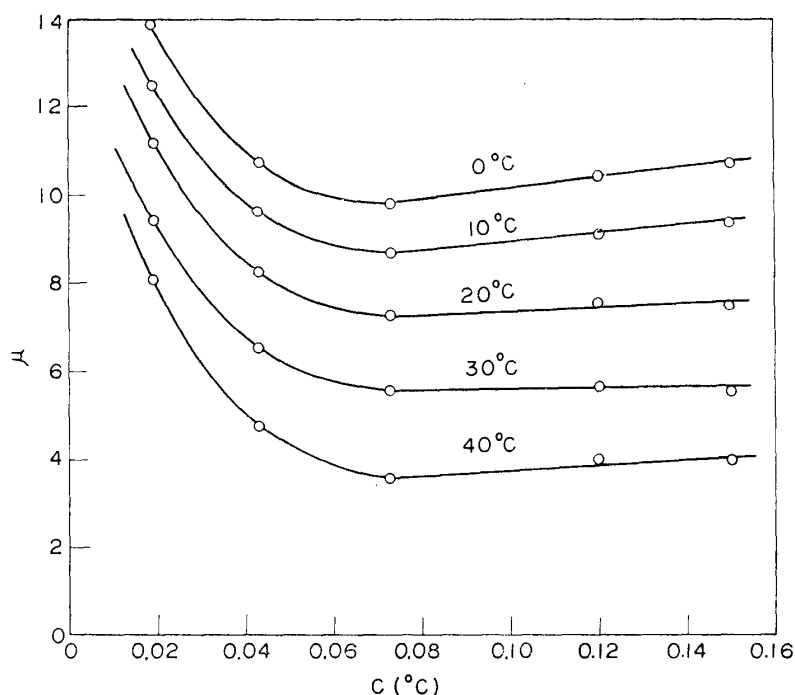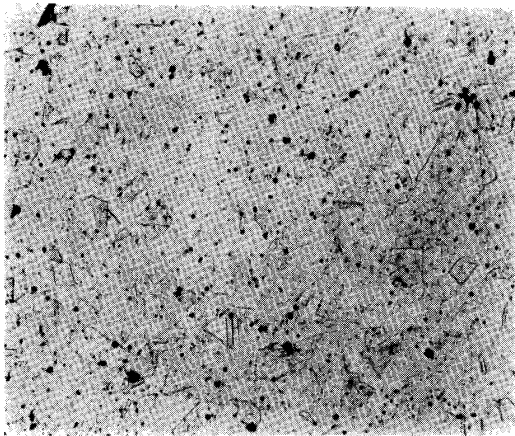
Fig. 3.   Relation between μ and C in M.S.O. alloys at constant temperature.

the increase in the additional amount of carbon.   From Fig. 3 and Photo. 1, it can be said that the critical solubility of carbon in the alloy is about 0.03%.   By conducting the following experiment on carbide, we ascertained that it was a chromium carbide containing iron, $(Fe_xCr_{1-x})_{23}C_6$.   The experiment was made by using alkali-liquid of potassium ferrocyanide[9] for etching, and from the colour shown, it was ascertained to be chromium carbide.   It was further etched in the alkali-liquid of sodium picrate[9] to ascertain that the simple substance of carbide did not exist.

Usually the examination of the composition of carbide is made by electro-deposit method[10] to take out carbide, which is studied by X-ray diffraction, but it is difficult to make use of this method for this experiment because the specimens were small in amount.   In the present experiment, x in $Fe_xCr_{23-x}C_6$, non-magnetic carbide, was selected properly and it was determined for certain by taking into consideration the lowering of μ due to the decrease of the amount of iron and the rising of μ due to the decrease of the amount of chromium, and by comparing the calculated results with the measured ones.   In calculating, we should take into account the volume of the segregated substance, but in the present experiments, we disregarded the volume of the carbide because it was small, compared with the whole volume in the case of the alloy used. μ in the alloy used containing no carbide can be obtained in the μ-C curve by exterpolating up to the solubility limit C=0.03%.   When it was determined from the μ-C curve at 0°C, μ=9.2.   The

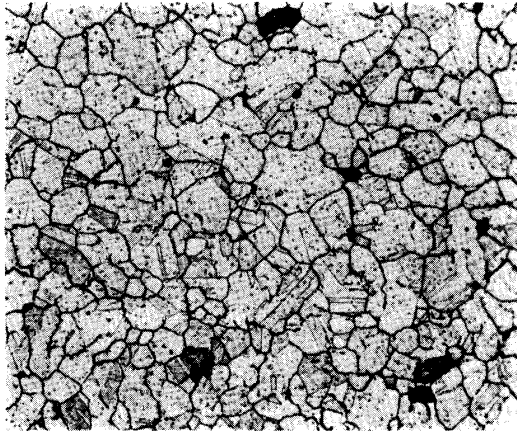(9)   T. Satô, *Microstructures of Steels and Their Explanation*, Maruzen, (1963), 252.

(10)   T. Satô, T. Kaneko and T. Nishizawa, J. Japan Inst. Metals, **19** (1955), 335.
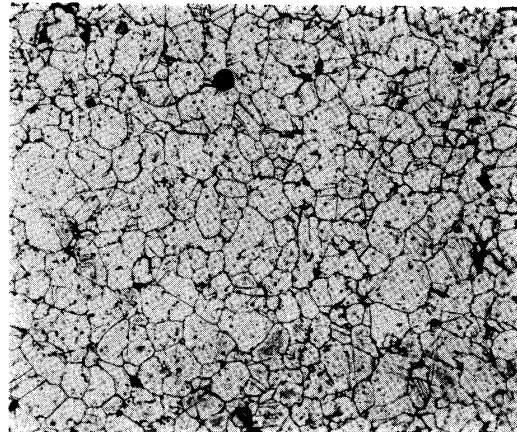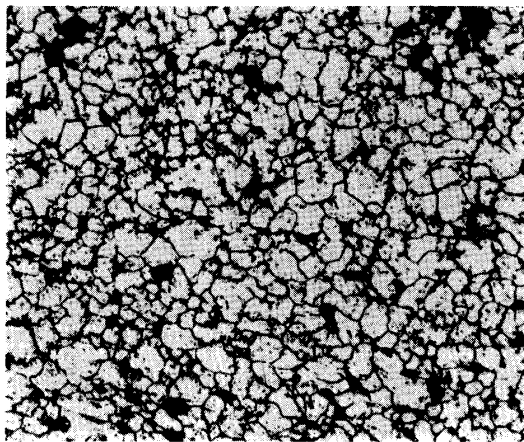
a) 0.019 %C
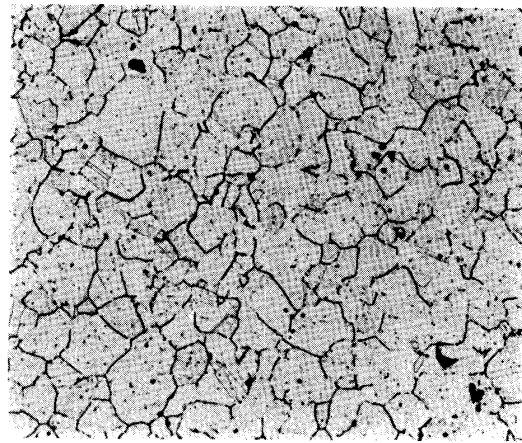
b) 0.046 %C

c) 0.073 %C

d) 0.120 %C

e) 0.150 %C

Photo. 1.   Microstructures for M.S.O. alloys annealed at 1000°C for 1 hr (etched in reagent 5% $FeCl_3$ +95% H_2O for several minutes). ($\times$ 100)
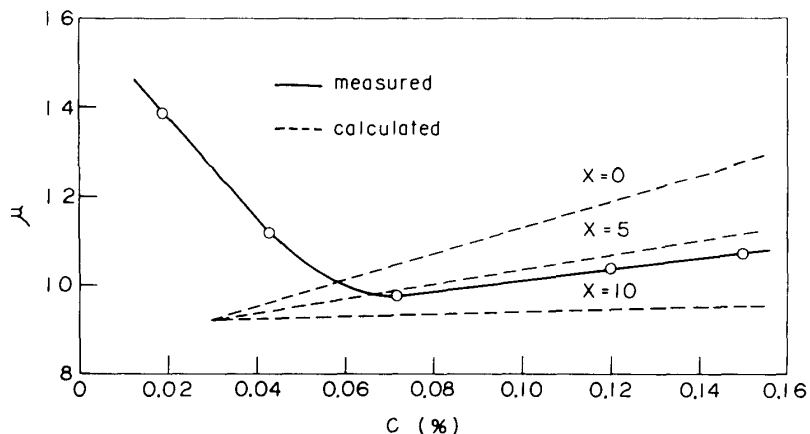
Fig. 4. Relation between μ and C in M.S.O. alloy at 0°C in 400 Oe.
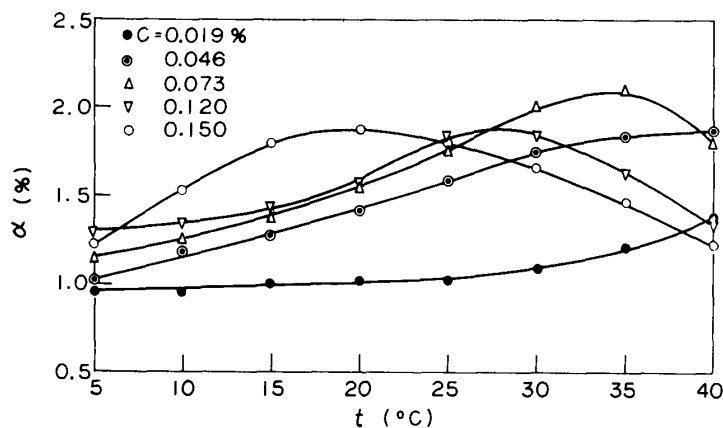

Fig. 5. α-t curves in 400 Oe for the specimens containing various amounts of C.

chromium which combined with carbon in the carbide $Fe_xCr_{23-x}C_6$ contributes to the increase of μ and the iron in the carbide contribute to the decrease of μ. Consequently, the amount of iron corresponds to the decrease of the amount of chromium. The relationship between the changed amount $\varDelta Cr$ of chromium and carbon at forming $Fe_xCr_{23-x}C_6$ can be expressed by the following equation:

$$\varDelta Cr = \frac{1}{6 A_C} \left\{ (23 - x) A_{Cr} - x A_{Fe} \right\} C$$ (2)

where A_{Fe}, A_{Cr} and A_C are the atomic weight of iron, chromium and carbon respectively. The first term in eq. (2) is the chromium which combines with 6·C and the second term is iron. If we put the permeability of the standard specimen which does not forms carbide as μ_0, μ at the time only the amount of chromium is changed by the segregation of carbide can be given by the following equation:

$$\mu = \mu_0 (1 - 0.195 \cdot \varDelta Cr)$$ (3)

where −0.195 is the inclination of $(\mu_{Cr}/\mu_{8.5})_{Ni}$ vs. Cr straight line in Fig. 1.   Substi-

tuting ΔCr in eq. (2) into eq. (3) and putting in the numerical values of the atomic weights, we have the equation (4) as follows:

$$\mu = 9.2 - (2.69\,x - 29.8) \cdot C \tag{4}$$

By ptuting $x=0$, 5, and 10, we calculated eq. (4) and obtained result shown in Fig. 4. In Fig. 4, μ-C curve at 0°C is drawn as is taken from Fig. 3. The inclination $d\mu/dC$ of the straight line where carbon content is largest in this curve was calculated to be 12.6. Therefore, if the inclination of eq. (4) is made equal to this, it will be $x=6.4$. It may be conceivable, therefore, the linear increase in permeability in the region containing 0.07% of carbon is where carbon will form carbide in μ-C curve.

In order to study the linearlity in the temperature change of μ, we calculated the temperature coefficient of μ at t°C by the following equation:

$$\alpha = \frac{\mu^{t-5} - \mu^{t+5}}{\mu^{t} \times 10} \tag{5}$$

Fig. 5 shows α in the range 0° to 40°C calculated from Fig. 2 by eq. (5) for each specimen as a function of temperature. As is clear in the figure, μ of the specimen containing 0.019% of carbon remains stable in value in the range ±5°C up to 25°C, its linearlity being the best of all. μ of the specimens containing more than 0.046% of carbon graws larger in value with the increase in carbon content, but reduces in value after passing the maximum, almost without any linearlity. The maximum of μ is a phenomenon nearly the same as Curie point, appearing linearly at lower temperature with the increase of carbon content.

It may be concluded that carbon should be prevented from mixing in as far as possible because of the linearlity which is the most essential character of magnetic shunt alloys.

IV. Conclusion

Studies were conducted on the magnetic properties of alloys made from a kind of M.S.O. alloy (31% of nickel, 8.5% of chromium and 60.5% of iron) with addition of 0.019 to 0.15% of carbon. The magnetization curves in the range from 0° to 40°C were measured by the ballistic method. The specimen was 0.4 cm in diameter and 3.1 cm in length and its demagnetization factor was 0.30. We reached the following conclusion:

(1) With the increase in carbon content, μ at first increases in value, but slightly decreases after passing the minimum. It is conceivable from the microstructures and calculations that the initial decrease in value is due to the solubility of carbon the later increase in value is due to the formation of $Fe_6Cr_{17}C_6$.

(2) The temperature coefficient of permeability increases with increasing carbon content, and its linearlity becomes worse.