On the Magnetic Properties of Sintered Iron

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Synopsis

An improved method of producing iron powder briquette from Fe(CO)$_5$ was develop-
ed. The method enables us to get iron briquette superior in magnetic properties
to any briquette produced by other industrial method. The briquette was prepared
from oxide powder, obtained by a specially arranged oxidizing apparatus for liquid
carbonyl. The oxide was reduced in hydrogen stream, and moulded to a troidal form
with the pressure of 6t/cm^2; the compact thus obtained was sintered at 450°, 800°,
900°, 1,000° and 1,100°. The superiority of the briquette in magnetic properties was
found in comparison with other briquettes, which were prepared from carbonyl iron
and electrolytic iron powder under the same condition.

I. Introduction

Carbonyl iron powder, which had been noted for an extremely pure form of iron
with the iron content of over 99.99%, was produced in a form of almost perfect
spheres, whose diameters were from one to fifteen microns. The first large scale
production was successfully done by I. G. Farbenindustrie Aktiengesellschaft in
1924.[1]

The production of iron carbonyl, from which carbonyl iron powders are made,
depends on a unique reaction as follows:

$$Fe + 5CO = Fe(CO)_5$$
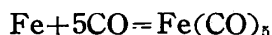
When the vapor of Fe(CO)$_5$ is heated above 200°, it will decompose into its con-
stituents. Any impurities remain in the original ore used, but some non-metallic
impurites such as carbon, oxygen and nitrogen are intermixed with the decomposed
powder.

Therefore, commercial carbonyl iron powder contains 0.01%~0.6% C, 0.1%~0.9%
O$_2$, and 0.01%~0.6% N$_2$.[2] This is the main reason why carbonyl powders have
not been used as a material for pure iron sheet or wire, in spite of their purity
and considerably old history.

Actually, there were many attempts to produce pure iron from carbonyl iron
powder by sintering or melting in laboratories, and pure iron with excellent
magnetic properties was successfully obtained by some researchers.[3] But it is
difficult to control the amount of impurites during the commercial production.

(1) W. Hieber : Z. Elektrochem. **43** (1937), 390.
(2) The specification of carbonyl iron powders : General Anilin Film Corporation. New
York (1951).
(3) F. Stäblein : Z. techn. Phys. **13** (1932) 532.
L. Schlecht, W. Schubardt, F. Duftschmidt : Z. Elektrochem. **37** (1931) 491.

In order to avoid this trouble, fine powders of iron oxide were prepared by the direct oxidation of Fe(CO)₅ and they were reduced in hydrogen stream, and then sintered to pure iron briquette of troidal form. Magnetic properties of the briquette were measured by the Ballistic method.

In comparison with the briquettes from carbonyl and electrolytic iron, it was found that the briquette produced from iron oxide had extremely superior magnetic properties.

II. Preparation of the Specimens

Mill scale was pulverized by a stamp mill and the powder, with the addition of 10% of clay in weight, was caked to briquettes and subsequently reduced at 450°. for 30 hours in hydrogen stream. The briquette was treated with carbon monoxide of 150 atm at 120° and Fe(CO)₅ was obtained in liquid.

The liquid carbonyl was oxidized by a specially arranged oxidizing apparatus, illustrated in Fig. 1. Fe(CO)₅ was heated at 80° with an evaporator A in a water bath and the vapor was led to a burner B by CO stream at the ratio of 71/min. When carbonyl vapor was oxidized into iron oxide powders at the top of B, the oxide was drawn into a fan C and separated from gas through a bag filter D. E is a receiver of the oxide powder.

The greater part of iron oxides thus obtained, was Fe₂O₃, containing about 0.16% C, whose size about 0.1 μ in diameter. The powders were roasted to pure α-Fe₂O₃ at about 600° in the air, in order to remove the carbon perfectly.

The reduction was performed in hydrogen stream at 450° for 3 hours. After cooling carefully, the reduced powder was moulded with the pressure of 6 t/cm² into a troid, 20 mm in inner- and 32 mm in outer- diameter. The troid, weighing about 10 grs, was pre-

Fig. 1. Schematic diagram of oxidation apparatus.

sintered at 450° for 3 hours in hydrogen atmosphere so as to eliminate completely the remained oxide film, in order to get sufficient strength for measurement.

The specimens were sintered at 800°, 900°, 1,000° and 1,100° for 1 to 5 hours in hydrogen atmoshpere. Carbonyl iron powder was obtained by the decomposition of Fe(CO)₅ vapor in a CO stream at 300°, and it was 2 μ in mean diameter, containing about 0.6% C and 0.9% O₂. On the other hand, electrlytic iron was pulvirized by a stamp mill and the powder size was below 325 mesh, containing 0.11% C. Moulding and sintering were carried out under the same conditions as those mentioned above.
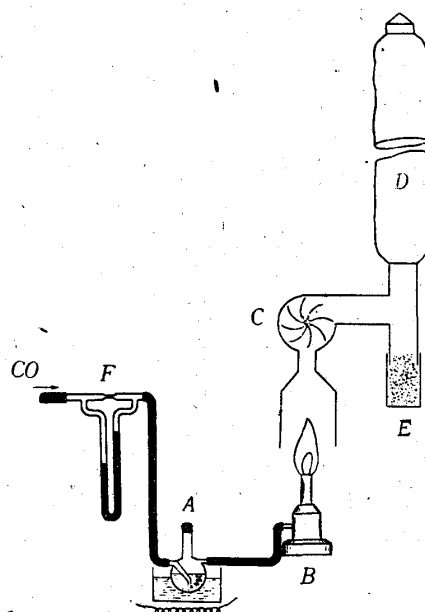
III. Experimental results

The specimens, pre-sintered at 450°, showed sufficient strength for treatment, but if they were exposed in the air carelessly, they would be oxidized at once on account of their imperfect sintering grade. So, 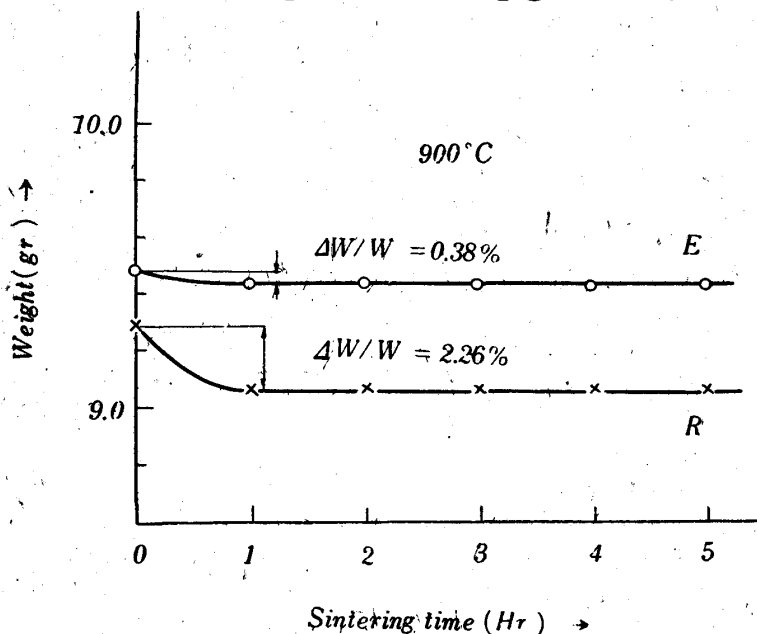after cooling carefully, changes of weight of all specimens during the sintering process were checked by a chemical balance.

The changes of the weight of specimens are plotted against the sintering time at 900° in Fig. 2. The curve E and R represent the weight of electrolytic and reduced iron troid, respectively. The diagram shows that the specimen E and R contained about 0.4% and 3% of O_2, respectively, but impurity was removed completely after sintering for an hour in both cases. The changes of specimens' density during sintering at 900° are illustrated in Fig. 3. The sintering may be completed almost within an hour at 900°, judging only from the behaviour of change in density.

Fig. 2. Weight variation of iron troids, sintered at 900°.
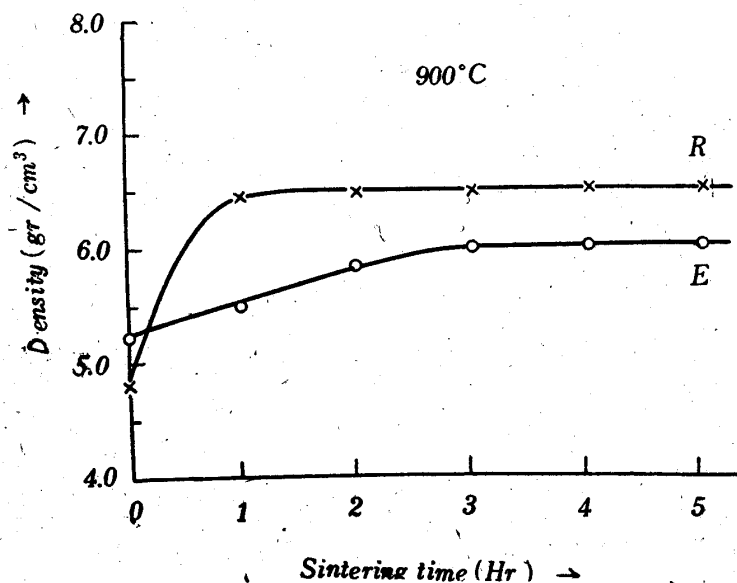 E: Electrolytic iron,
   R: Reduced iron from $Fe(CO)_5$.

Fig. 3. Density variation of iron troids, sintered at 900°.

Next, the change of magnetic properties with the sintering time, measured by the Ballistic galvanometer method, will be illustrated. μ_{max}, B_{max}, Br and Hc are respectively plotted against the sintering time in Fig. 4, Fig. 5, and Fig. 6. Except the curve of μ_{max} versus time, the changes with varying sintering time was almost complete after the sintering for 1~3 hrs.

The same observations were carried out at 800°, 1,000° and 1,100°. These results, after the sintering for 3 hrs, with which the changes were almost complete as

mentioned above, are plotted aginst the sintering temperature in Fig. 7, Fig. 8, Fig. 9 and Fig. 10; the mark ▼ represents the result of specimen C from carbonpl iron powder and the marks ● and △ show the result of electrolytic iron and hydrogen reduced iron from mill scale, respectively, observed by Lenel.[4]

The initial permeability μ_0 of specimen R was found to be about 750 after sintering at 1,100° for 3 hours.

IV. Discussion

The values of the specimen prepared from electrolytic iron powder, observed by Lenel, are plotted on the extension line of curve E in the above figures. Hence, the results on the electrolytic iron, measured in the present experiment, are considered to be reasonable. Consequently, by the improved method, namely, the direct oxide method, we can get extrmely excellent iron briquette from iron carbonyl.

In the sintering temperature between 800° and 1,100°, the changes in density and coercive force are not so remarkable (Fig. 7, Fig. 10) but the values of Br and μ_{max} increase abruptly with the rise in sintering temperature (Fig. 8, Fig. 9).

The increase of Br and μ_{max}, however, dose not mean the progress of sintering degree and they
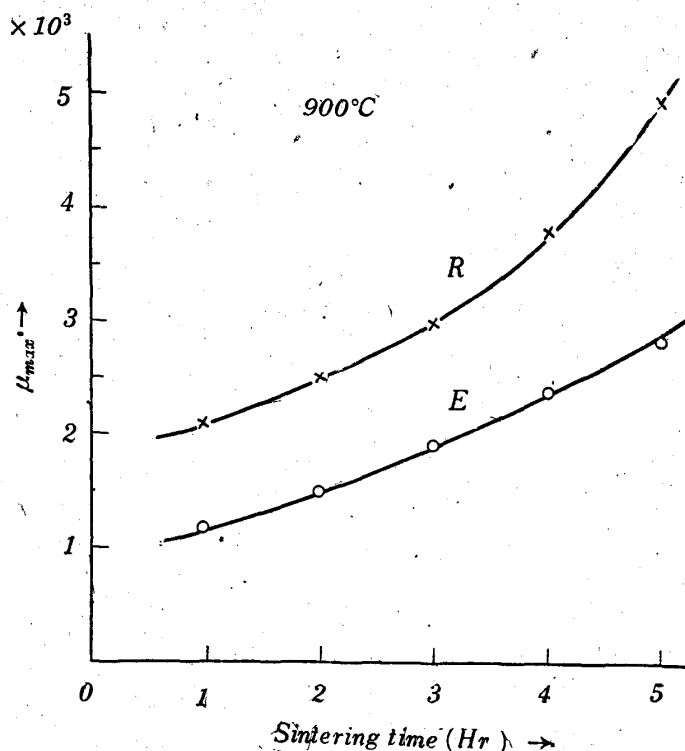

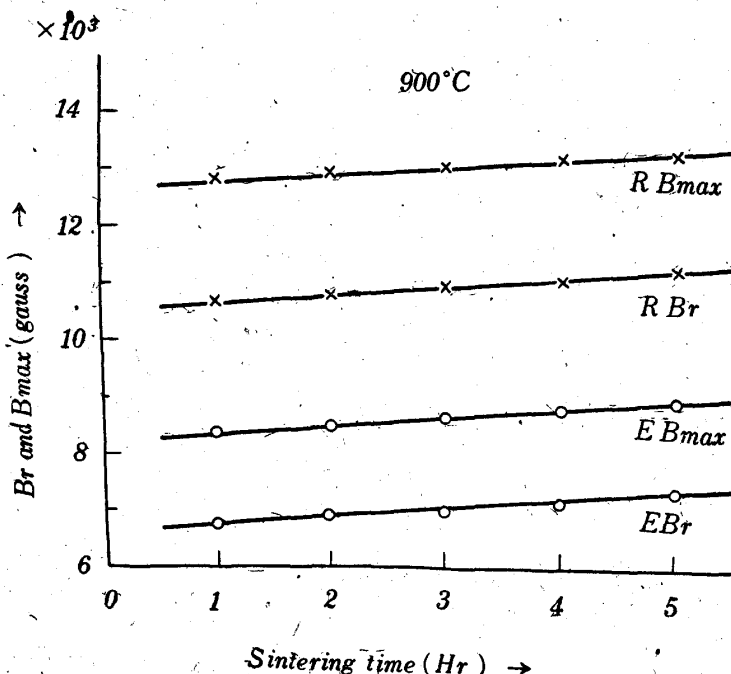Fig. 4. μ_{max} variation of iron troids, sintered at 900°.

Fig. 5. Br and B_{max} variation of iron troids, sintered at 900°.

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(4) F. V. Lenel : Trans. Am. Inst. Mining. Met. Engrs. 161 (1945), 535.

are rather affected mainly by the grain growth of sintered block.[5] The fact is noticeable in the study of sintering process by observing magnetic properties of powder compact.

All magnetic properties of specimen R are remarkablly excellent compared with those of the specimen E and C. It is mainly due to the purity of specimen R,
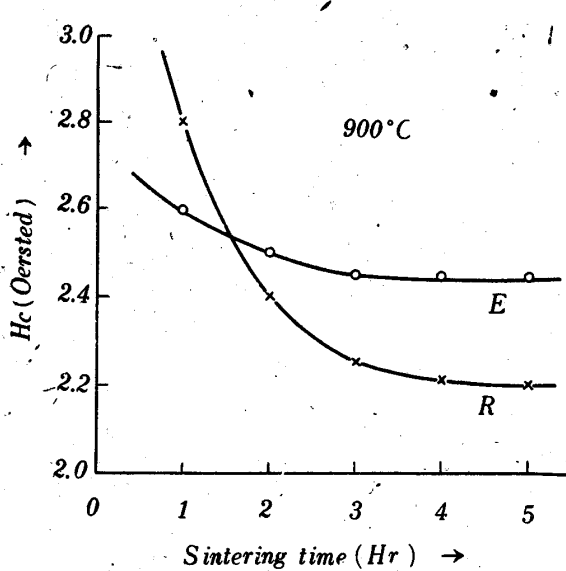

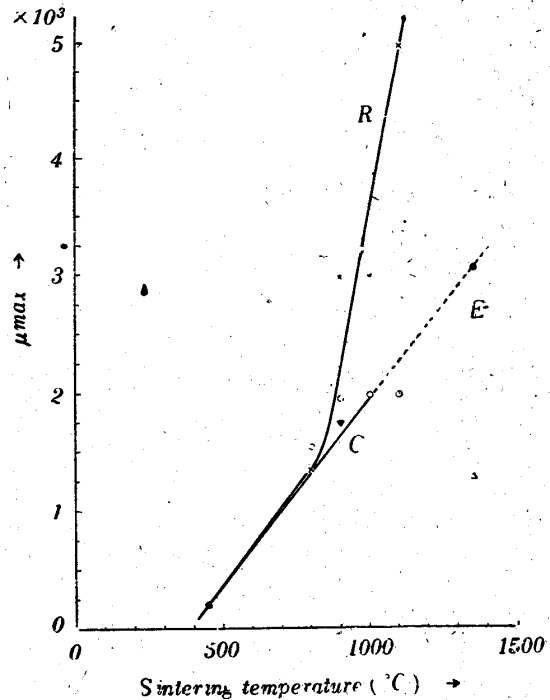Fig. 6. Hc variation of iron troids, sintered at 900°.

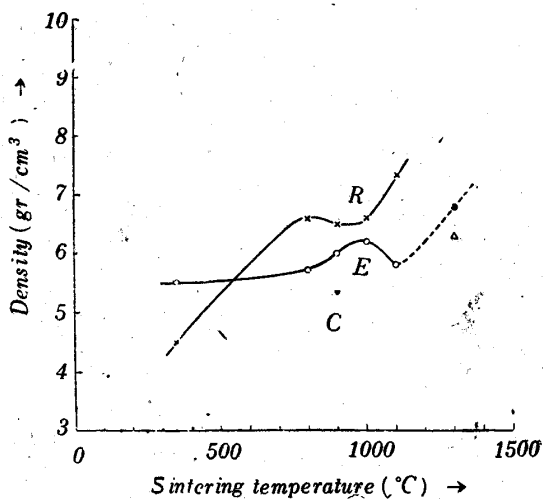Fig. 8. μ_{max} variation of iron troid, sintered for 3 hrs.

Fig. 7. Density variation of iron troid, sintered for 3 hrs.

× : Reduced iron from Fe(CO)₅
∘ : Electrolytic iron
▼ : Carbonyl iron
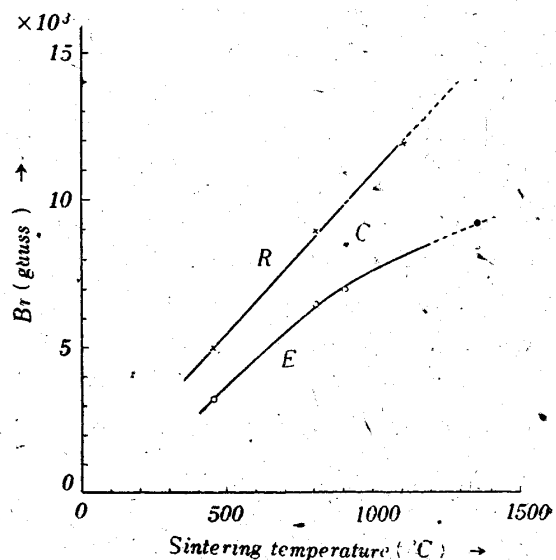• : Electrolytic iron ⎫
△ : Reduced mill scale ⎬ observed by Lenel.

Fig. 9. Br variation of iron troid, sintered for 3 hrs.

(5) There were many investigations on the effect of grain size to the magnetic properties of pure iron, i. e. K. Honda, S. Kaya, Y. Masuyama: Nature 117 (1926) 753 and K. Honda, S. Kaya : Sci. Rep. Tohoku Univ. 15 (1926) 727 etc..

but it can not be stressed too much because the sintering was not finished in the present temperature range, and the densities of R and the other specimens did not show the same value at the same sintering temperature.

When the specimens were pre-sintered at 450°, the sintering, as mentioned above, scarcely advanced and there remained in the compact various properties of fine

powder. The coercive force of the specimen R, sintered at 450°, was very large as shown in Fig. 10, for the same reason as above. And it may be explained by the recent investigations, in which the fairly great coercive force of the finely divided iron powder has been recognized theoreticaly and experimentally.[6]

The pre-sintering temperature was chosen at 450° in the experiment, in order to determin the properties of the briquette sintered at the lowest temperature as possible. But taking into consideration the pyrophoric property of the compact prepared at the lower temperature, actually it should have been chosen at about 700° in the commercial production. Then, the shrinkage of specimen R is so remarkable that an extremely gradual rise of temperature will be necessary at the beginning of the pre-sintering process.

At the sintering temperature of 900°, ρ and Hc of the specimen C were smaller than those of the other (Fig. 7, Fig. 10) and the values of μ_{max} and Br lay between the values of specimen E and R.

It might be due to the impurities, which could hardly be removed during sintering in hydrogen stream, and to the comparative difficulty of sintering, due to its spherical form and larger particle size, as compared with the powder of specimen R.
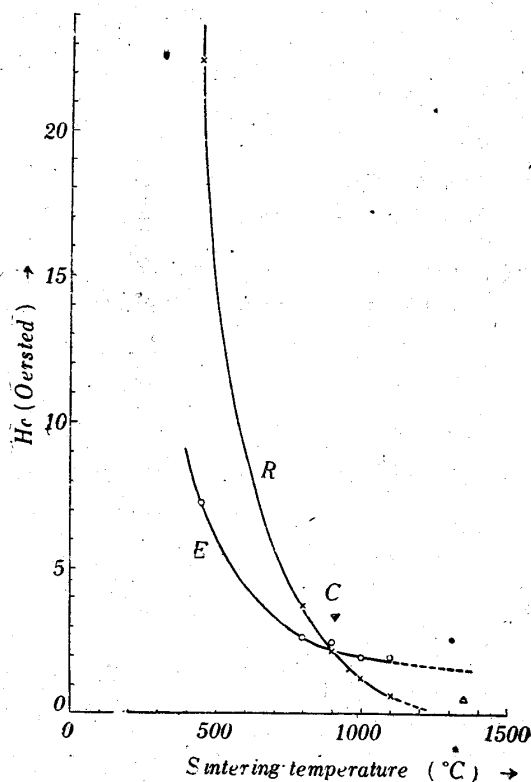

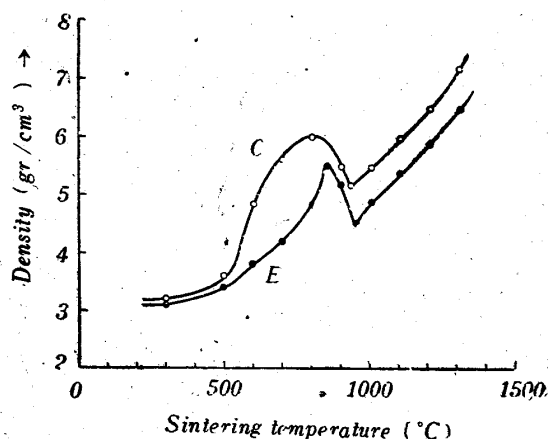Fig. 10. Hc variation of iron troid, sintered for 3 hrs.

Fig. 11. Density variation of loose iron powder, sintered for 1 hr.
C: Carbonyl iron.
E: Electrolytic iron.

(6) C. Kittel: Rev. Mod. Phys. 216 (1949), 541.
    H. Fahlenbrach: Z. des Vereins deutcher Ingenieure 92 (1950), 565.
    L. Weil: J. Phys. Radium 12 (1951), 437.

Looking over the curves in Fig. 7 carefully, we find that they have a maximum and minimum, respectively. As is shown in Fig. 11, it is noticed that the free powders of carbonyl and electrolytic iron also have both a remarkable maximum and a minimum on the curve of the change in density during sintering.

The fact is mainly due to A_3-transformation of iron, and the obscurity of the maximum and minimum shown on the curves in Fig. 7, may be attributed to the effect of stress stored by the moulding process. Consequently, the curves of magnetic properties in Fig. 8, Fig. 9 and Fig. 10 might have maxima and minima to some extent.

However, the changes of magnetic properties showed the flat curves in the forgoing figures because it was difficult to separate the effect of density from others, namely, observation error and the effect of grain growth. In other words, the deviations of measured values found on the curves in these figures are not only observation error, but the various effects, above mentioned.

Summary

Reducing the iron oxide powder in hydrogen stream, a pure iron troid was prepared and the magnetic properties were compared with those of the carbonyl iron and electrolytic iron troids, so following conclusions have been obtained:
Merits
(1) Any impurity can be removed during the improved carbonyl process.
(2) When pure iron is produced by the decomposition of $Fe(CO)_5$, a large decomposing apparatus is necessary and the control of particle size and chemical composition, etc., is very difficult, while, for the oxidation of $Fe(CO)_5$, only a small arrangement and simple operation are needed.
(3) Moulding is very easy, on account of their fine particle size and polygonal form.
(4) Without special attention, the uniformity of properties will be kept even in commercial production.
(5) Iron briquette, thus prepared, is extremely soft in mechanical and magnetic properties and worked to sheet or wire easily.
Defects
(1) Shrinkage is very large during the sintering process.
(2) Besides for sintering, hydrogen gas is necessary in excess for reduction.