ON THE STRUCTURAL CHANGE OF MECHANICALLY PULVERIZED IRON POWDER DUE TO THE PROCEDURES OF ANNEALING.

By Hideki Hirata, Hidekiyo Fujihira and Eiichi Fuji.

Introduction.

During the last ten years and more, the mechanism of sintering metallic powder has been a subject of the keenest research to many investigators[1]. Nevertheless, any harmonious conclusion seems to have hardly been drawn even up to the present time. This may be mainly due to the lack of experimental results with regard to the fundamental phenomena connected with the aforesaid mechanism. The writers have, therefore, induced, by way of a supplementation of the foregoing investigations carried out concerning the sintering of various powdered metals, to set up the present experiment utilizing X-rays, to make clear the process of the structural change of mechanically pulverized iron powder due to the procedures of annealing. The experimental results thus obtained are briefly described below.

Experimental Part.

i) **Specimens:** The specimens of iron powder examined in this experiment were pulverized according to the idea of Prof. Bunsaku Arakatsu at the Fukuda Metal Powder Manufactory and the factory of the Daiwa Co., to be used in the procedure of sintering. To prepare these specimens, the stamping and bulling mills were employed. It was reported that the iron powder thus prepared was of the diameter $0.4_{mm} \sim 0.15_{mm} \sim 0.06_{mm}$ and contained less than 0.04% of C.

ii) **Outline of the Experimental Method:** The iron powder obtained as described above was heated in vaccum or in the stream of H_2, at variovs tempertures (always lower than 800°C) for 1 hour, and then cooled slowly in the furnace, before it was illuminated with X-rays. To examine the difference of the inner structure of each specimen from those of the others annealed at different temperatures, Laue photographs were taken with an ordinary Laue camera as well as with a back-reflection camera, utilizing heterogeneous X-rays containing characteristic radiations (K_α and sometimes K_β radiations) emitted Mo

1) e.g., F. Sauerwald and his co-workers, *Z. anorg. Chem.*, 122, 277 (1922); *Z. Elektrochem.*, 29, 79 (1923), 30, 175 (1924), 31, 15, 18 (1925), 38, 33 (1932); *Z. Metallk.*, 16, 41 (1924), 20, 227 (1928), 21, 22 (1929); W. Trzebiatowski, *Z. physik. Chem.*, 24, 75, 87 (1934).

Plate I. Laue Photographs of Iron Powder. (×0.61 Reductions of the Original Films)

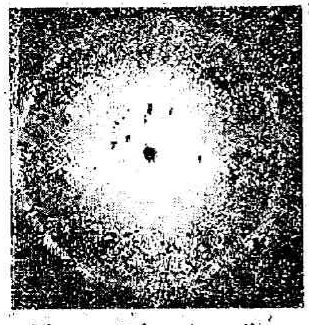

Fig. 1. Before Annealing
(L=8 cm., Mo radiation)

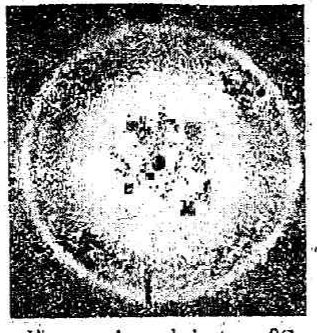

Fig. 2. Annealed at 300°C
in the Stream of H_2
(L=8 cm., Mo Radiation)

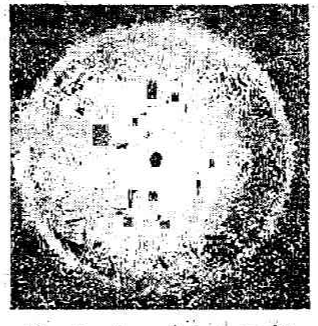

Fig. 3. Annealed at 400°C
in the Stream of H_2
(L=8 cm., Mo Radiation)

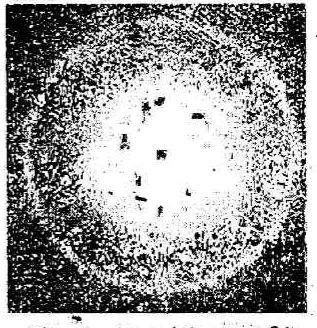

Fig. 4. Annealed at 500°C
in the Stream of H_2
(L=8 cm., Mo Radiation)

Fig. 5. Annealed at 500°C
in the Stream of H_2
(L=3 cm., Fe Radiation)

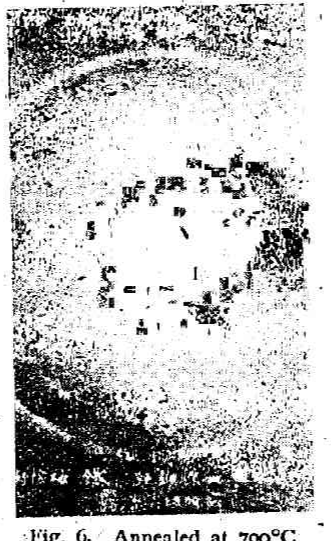

Fig. 6. Annealed at 700°C
in the Stream of H_2
(L=3 cm., Fe Radiation)

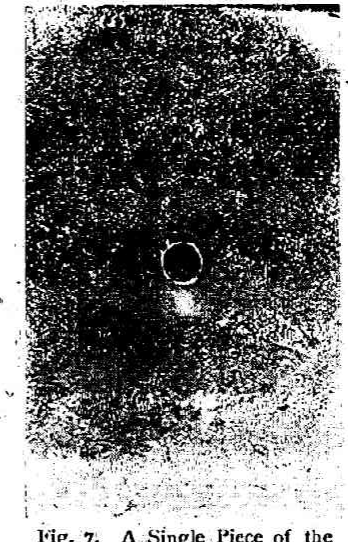

Fig. 7. A Single Piece of the
Powder annealed at 800°C in
Vacuum. (L=2.4 cm., Fe Radiation)

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Plate II. Back-reflection Laue Photographs of Iron Powder
(L=6.8 cm., Fe Radiation ×0.46 Reductions of the Original Films)

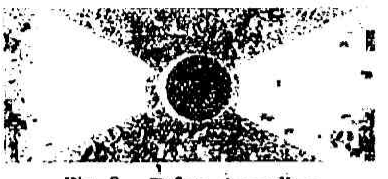

Fig. 8. Before Annealing
(Pulverized with a Bulling Mill)

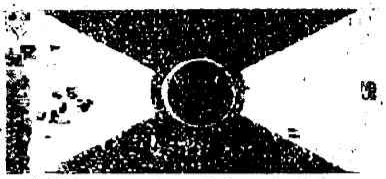

Fig. 10. Annealed at 800°C
in Vacuum

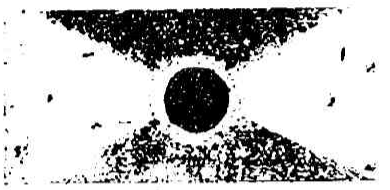

Fig. 9. Before Annealing
(Pulverized with a Stamping Mill)

Fig. 11. Annealed at 800°C in
the Stream of H_2

or Fe anticathode for the most part. In this examination, the ordinary Laue photographs were usually obtained, keeping the distance L between the specimen and photographic film 8 cm., while to take the back-reflection Laue photographs, the photographic film was always placed at a distance 6.8 cm. from the specimen.

iii) **Experimental Results:** Some Laue photographs obtained with a touch of the iron powder before annealing and those taken with that of the powder annealed at various temperatures, were reproduced in and Fig. 1~6, Plate I, and Figs. 8~11, Plate II. A set of Debye rings coming to appear in these figures, which were confirmed to correspond to (110) reflection of the characteristic radiations in the ordinary Laue photograpes and to (220) reflection sometimes accompaning the reflection from (310) plane in the back-reflection photographs, could also be observed in the diffraction patterns given rise to by a single piees of the powder not only before but after annealing, as seen in Fig. 7, Plate I. This shows us without doubt that a single piees of the iron powder was mostly of a polycrystalline structure composed of an aggregation of micro-crystals without any regularity, even after the produre of annealing.

It can be observed in Fig. 1, Plate I and Figs. 8, 9, Plate II, that each Debye ring taken with the powder before annealing was so much broadened that two rings given rise to by $K_{\alpha 1}$ and $K_{\alpha 2}$ radiations melt into one band. Such a broadening of Debye rings was somewhat reduced, as may be seen in Fig. 2, Plate I, by a simple annealing even at a temperature lower than 300°C, which is far below the recrystallization temperature of iron. Thus, we can deem that the aforesaid broadening was not due to the extreme fineness of micro-crystals (10^{-5}_{cm}~10^{-6}_{cm} in

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diameter) itself, but resulted from the largs inner strain of the crystal lattice forming the specimen, which rendered the atoms in crystals easily activatable.

Furthermore, the procedure of annealing at a higher temperature made Debye rings sharper, until an assemblage of intense spots was observed on them with the specimens annealed in the stream of H_2 at 400°C, as shown in Fig. 3, Plate I. These intense spots were especially noticed; not always becoming predominant with the rise of the annealing temperature contrary to our expectation; in Figs. 4 and 5, Plate I taken with the specimen annealed at 500°C in the stream of H_2, the aforesaid spots completely disappeared, but they were detectable again in the diffraction patterns obtained after the procedure of annealing at about 600°C, i.e., the recrystallization temperature of iron, and above 600°C became more remarkable, as may be seen in Fig. 6, Plate I or Figs. 11 and 12, Plate II. Such a tendency of the change of diffraction patterns was also observed in the case of annealing in vacuum, though not so remarkably as in the stream of H_2. From the facts above stated, we may conclude, at least with regard to the effects of the procedure of annealing in H_2, that the diameter of micro-crystals forming the powder, which mostly amounts to the order of 10^{-4} cm. before the procedure of annealing, extends partly to the order of 10^{-3} cm. by heating at about 400°C; and that, on the contrary, it remains almost unaltered when the annealing temperature is raised to about 500°C, though the growth of micro-crystals again takes place over the whole volume of each powder, up to the orher of 10^{-3} cm. in diameter by annealing the specimens at a temperature higher than 600°C for 1 hour.

Discussion of Experimental Results.

The arguments which have hitherto been advanced, lead us first to infer that the specimen of iron powder before annealing was of a polycrystalline structure partly, but considerably strained by the mechanical work of pulverization, micro-crystals of the dimension of 10^{-4} cm. in diameter arranging themselves irregularly in a single piece of the powder, irrespective to the procedure of its preparation. Furthermore, it can also be deemed, at least in connection with the structural change in the stream of H_2 that the aforesaid inner strain is gradually reduced by heating the powder even at a temperature lower than 300°C, and removed completely at the higher annealing temperature. The formation of crystal nuclei due to the heating, which begins to take place at 400°C in the parts of the powder where the inner strain is large, becomes so vigorous at 500°C that the concentration of the crystal nuclei in the aforesaid parts severely strained, grows high enough to hinder the growth of every nucleus owing to its reciprocal interference. But,

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when the annealing temperature is higher than 600°C, the so-called "Recrystallization" due to the formation and the growth of crystal nuclei can be excepted to occur throughout the whole specimen, at the thorough expense of each micro-crystal, which has hitherto existed with more or less inner strain in the power. Such a process of the change of the inner structure of iron powder, though it is considerably retarded, can also be confirmed to take place in vacuum as in the stream of H_2.

It seems rather strange in the experimental results above mentioned that the growth of crystal nuclei by heating in the specimens severely strained is interrupted in the course of varying the temperature so much as to take place in two steps. To make clear whether such a phenomomenon can also be observed or not with a specimen prepared mechanically by a different procedure, the writers repeated essentially the same X-ray examination with the specimens of iron and several alloys mechanically rolled. As the consequence of this examination, it must be especially remarked that the aforesaid phenomenon generally takes place in metals and alloys undergone by severe mechanical strain.

In conclusion, the writers wish to express their best thanks to Professor S. Horiba for the interests he has taken in this experiment, and to Professor U. Yoshida for his efficacious advices on many occasions. Their thanks are also due to Professor B. Arakatsu, who kindly supplied them with many samples required for the present investigation. Furthermore, it must be noted that the expense of this research has been defrayed from the Scientific Research Expenditure of the Department of Education.

Institute for Chemical Research (Takatuki),
Kyoto Imperial University.