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Formation of Graphite Single Crystal from Iron Solution by the Slow Cooling Method

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Graphite single crystals with maximum dimensions of 40 mm in diameter and 0.04-mm thick were prepared from an iron solution by a slow-cooling method. The cell parameters of the product were a_0=2.462±0.002 and c_0=6.708±0.001 Å. A flux of 200 g of electrolytical iron and 8 g of graphite were charged in the graphite crucible. The iron melt, saturated with carbon, was slowly cooled from maximum temperatures ranging between 1800 and 2500 °C to near 1150 °C at cooling rates ranging from 5 to 30 °C min^{-1}. Large graphite single-crystal films of better quality were formed after quick cooling rather than slow cooling. Large graphite crystal films were formed at above 1850 °C; temperatures greater than 1950 °C were needed in order to grow the crystal films with good quality. From in-situ observations through a hole, the growth of the small graphite crystals was seen to occur on the surface of the melt at about 1550 °C; these were gathered in a constant direction, initiating the incorporation of small crystals. The incorporation of the small crystals was promoted at about 1700 °C and the surface of the melt was covered with a single-crystal film. For the formation mechanism of the graphite single-crystal film, a heating process was played an important role.

In recent years, industrial carbon materials have entered the spotlight because of the following interesting properties. Such structures are unique, including amorphous carbon to graphite single crystals; the electrical resistances vary from 10^5—10^6 Ω cm, close to that of a semiconductor to about 10^{-4} Ω cm, comparable with that of a metal. The thermal conductivity of carbon materials expand from ones larger than that of the steel to ones close to that a thermal insulator. The melting point of carbon is 3800 °C and is thus a material having resistance against high temperatures.

These special characteristics are depend on the chemical bonding form of carbon atoms and the crystal structure of graphite based on the carbon atom. Therefore, in order to study such properties as chemical, physical, and mechanical, it is necessary to study the formation of graphite single crystals and to clarify the formation mechanism.

Studies on the formation of graphite single crystals have been reported by many researchers. These formation methods are as follows: (1) A method in which graphite is directly melted and then cooled while crystallizing.[1-3] (2) A method in which graphite is crystallized from a metal melt which is saturated with carbon.[4-9] (3) A method involving the thermal decomposition of metal carbides.[10-12]

In these methods, (2) is most suitable for the formation of large graphite single crystals. Nickel, iron, and many other metals are used as a flux. In these metals, since graphite is highly soluble in iron and iron is more economical than other metals, iron is used as a flux in this experiment.

Studies on the formation of graphite single crystals from an iron melt have been reported by Austerman et al.[7] and Noda et al.[8,9] Austerman et al. synthesized graphite single crystals by slow cooling an iron melt which was saturated with carbon using an electric precision furnace with a temperature gradient control. Noda et al. grew graphite single crystal films of about 30 mm in diameter and about 0.06-mm thick in which the c-axis was parallel to the surface of the iron melt, by slow cooling the iron melt with 1 wt% Si. However, the formation of these large graphite single crystal films was hard to reproduce and the formation conditions have not yet been clearly understood.

The purpose of this study was to clarify the formation conditions and mechanisms of large single crystal films and to elucidate the formation conditions under which graphite single-crystal films become thickened in the direction of the c-axis. The reproducibility was also investigated. Grown graphite single-crystal films were examined by the X-ray Laue photograph method.

Experimental

In the present experiment, carbon-saturated iron was slowly cooled from a maximum temperature ranging between 1800 and 2500 °C, to nearly 1150 °C at a cooling rate ranging between 5 and 30 °C min^{-1}.

An outline of the experimental apparatus is shown in Fig. 1. A Tunman furnace (1.5 kW, Max.current 1000 A) was used as a heating apparatus; it could obtain a maximum temperature of 2500 °C after supplying an electric current to a graphite heater. The dimension of the graphite heater was 260-mm long, 60-mm inner diameter, and 5-mm thick. The graphite crucible (40-mm inner diameter, 5-mm thick, and 50-mm high) was made from a graphite rod by machining. A graphite tube (12-mm inner diameter, 4-mm thick, and 200-mm long) used for observations was made and installed in the graphite crucible.

The surface temperature of the melt was measured using a pyrometer through this graphite tube. Temperature errors were within ±20 °C.

Iron prepared electrolytically (purity above 98%) was used

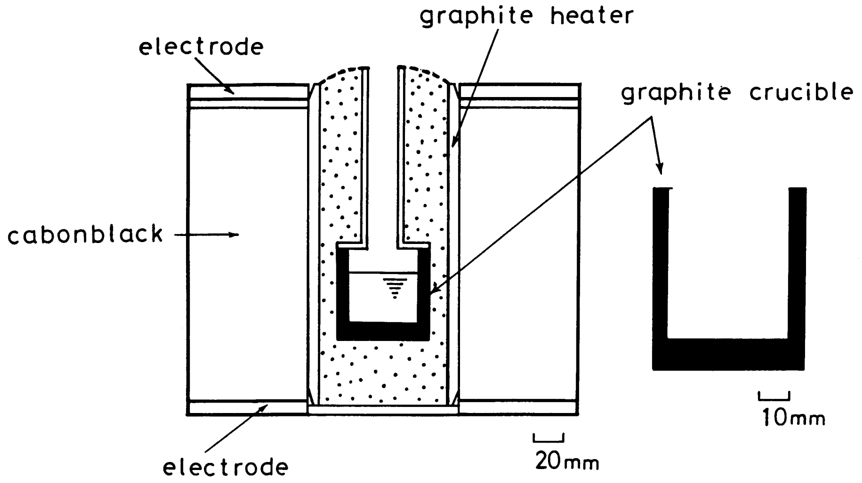


Fig. 1. Arrangement of an electric furnace for the growth of graphite single-crystal film.

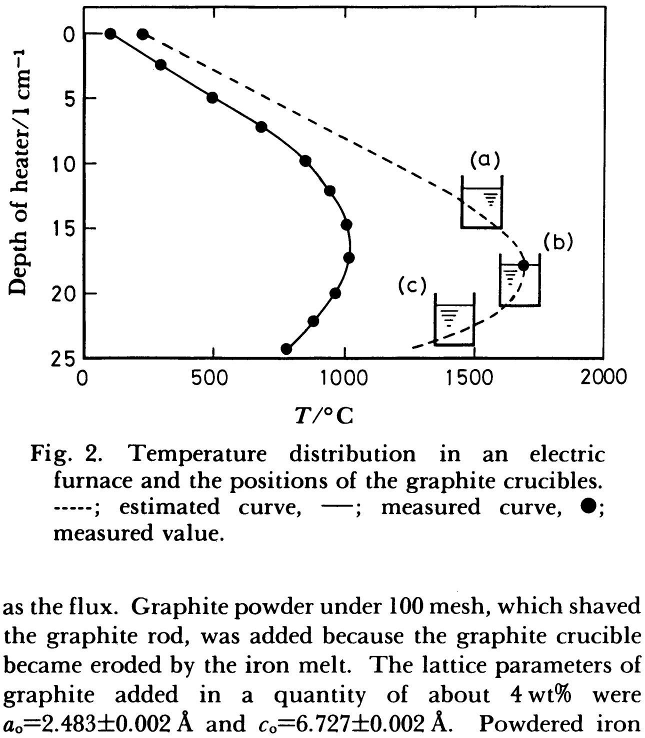


Fig. 2. Temperature distribution in an electric furnace and the positions of the graphite crucibles. -----; estimated curve, —; measured curve, ●; measured value.

as the flux. Graphite powder under 100 mesh, which shaved the graphite rod, was added because the graphite crucible became eroded by the iron melt. The lattice parameters of graphite added in a quantity of about 4 wt% were a_0=2.483±0.002 Å and c_0=6.727±0.002 Å. Powdered iron (200 g) and graphite (8 g) were charged in the graphite crucible.

The experimental process was divided into three steps: a heating process, a constant-temperature process, and a cooling process. The formation conditions of graphite single-crystal films were investigated by considering these three processes.

Temperature Distribution in the Melt. The temperature distribution in the melt significantly affected the formation of a graphite single-crystal film. However, since the graphite heater was fixed at a certain position, the required temperature distribution in the melt was obtained by varing the position of the crucible. The temperature distributions inside the graphite heater and in the melt were measured by a Pt–Pt 13%Rh thermocouple in order to determine the position of the maximum temperature in the heater. The experimental results are shown in Fig. 2. Since the limits of use of the thermocouple is below about 1500 °C, a higher temperature distribution of this experiment can be gained from measurements using a pyrometer. In an experiment involving a slow-cooling method, the crucible was placed at three positions (a, b, and c) as shown in Fig. 2. In the a-position, the lower part of the melt was located at a position of maximum temperature in the heater. On the other hand, the higher part of the melt was located as a position of maximum temperature for the b- and c-positions. In the former, the bottom of the graphite crucible was liable to erode. However, since a thermal convection current was produced in the melt since the lower part of the melt was located at a position of higher temperature, the temperature of the inside of the crucible was liable to make it uniform. On the other hand, for the b- and c-positions, the wall of the graphite crucible was liable to erode; it is therefore thought that a temperature difference between the lower and the higher parts of the melt was generated.

Results

Growth of Graphite Single-Crystal Film. The grown graphite single-crystal films can be classified roughly into the following classes: a large graphite single-crystal film, a small graphite single crystal, and a fine crystal in a solidified flux brick.

In the case of growing a large graphite single-crystal film all over the surface of the melt, it was shown the state of graphite formation as shown in Fig. 3. In this appearance, a graphite single-crystal film could be easily separated from the brick of iron flux.

In the case in which a cooling experiment was carried out at the a-position, a flux brick was created which was supposed to spout from the inside of the crucible through the center of the graphite crystal film, as shown in Fig. 4. Since it was difficult to grow a large graphite single-crystal film and to prevent this phenomenon, the graphite crucible was put in the temperature distribution at the b- and c-positions instead of the a-position. In the b- and c-positions of the crucible, solidification of the melt occured from

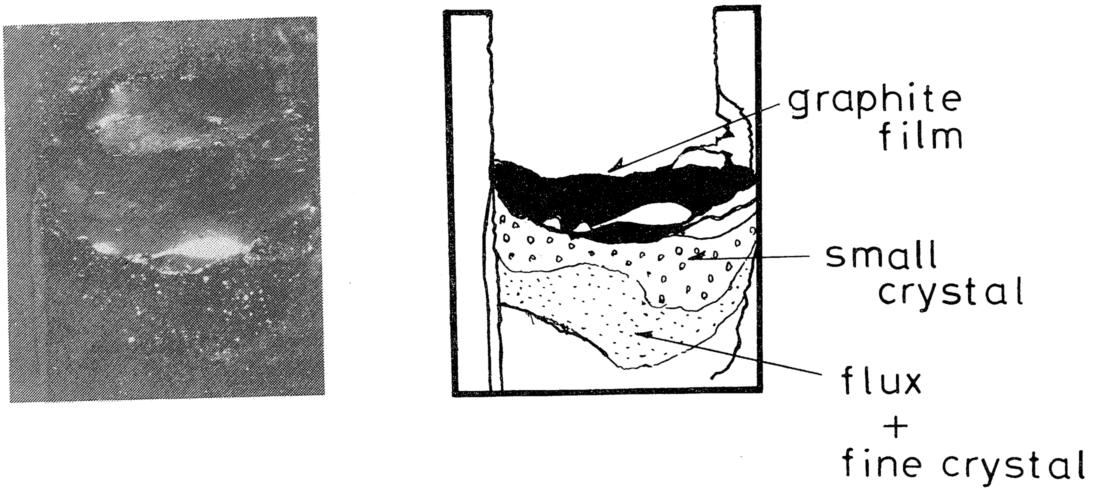
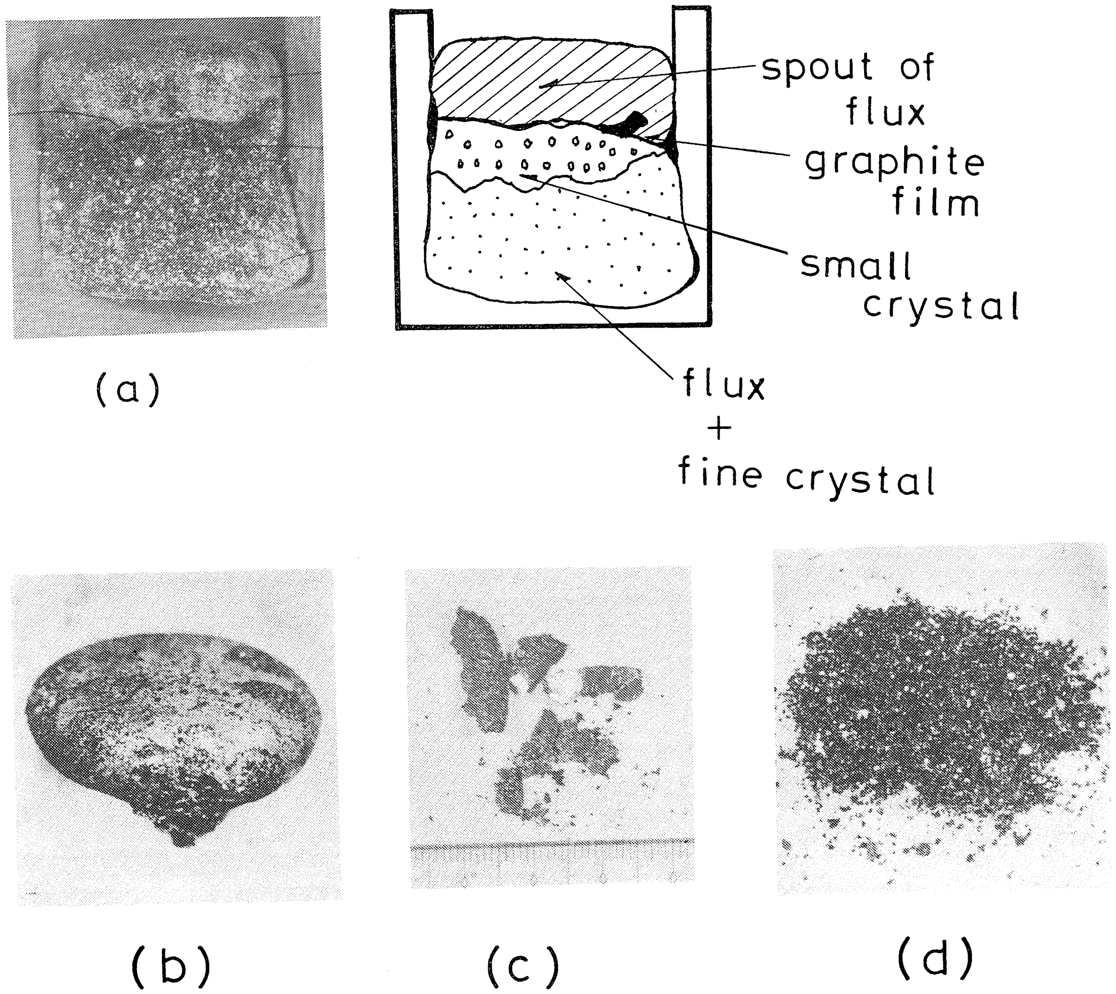


Fig. 3. Typical appearance after the growth of graphite single-crystal film.



(a)

(b)

(c)

(d)

Fig. 4. Typical appearance after the growth of graphite single-crystal film.
(a) The spout of the flux through the center of graphite single-crystal film. (b) Spout of the flux. (c) Graphite single-crystal film. (d) Small graphite crystal.

the lower part, since the temperature at the higher part was higher than at the lower part; thus, the eutectic melt was not spouted out on the graphite single-crystal film. In this case, the single-crystal film could easily be separated from the solidified flux.

The experimental results using the slow-cooling method are shown in Table 1. In this table, the heating rate results from dividing the temperature difference between 1400 °C and the maximum temperature T_m by the time (minute) taken to heat; the cooling rate results from dividing the temperature difference between the maximum temperature T_m and 1400 °C by the cooling time. In order to obtain precise values, it is necessary to use temperature-time relation curves.

In this table, the double circles represent the case in which a large graphite single-crystal film (greater than 2.5 cm in diameter) was grown; the circle represents the case in which small single crystals (less than 1 cm in diameter) were prepared. As is evident from Table 1, when the heating rate was comparatively slow, a large graphite single-crystal film could not be grown at above a heating rate of 10 °C min^{-1}. On the other hand, heating rates between 5 and 9 °C min^{-1} were closely related to the growth of graphite single-crystal films. Regarding the position of the crucible, a large graphite single-crystal film could more easily be grown at the b-position than the a-position.

Table 1. Experimental Results by the Slow Cooling Method

Run No.	Position of crucible	Flux weight g	Maximum temperature °C	Cooling rate °C min^{-1}	Heating rate °C min^{-1}	Graphite single-crystal film	Quality of graphite single-crystal film
S-1-2	a	189	1900	7	8	O	Poor
S-1-3	a	209	1950	14	9	O	Poor
S-1-4	a	213	2000	20	10	O	Poor
S-1-9	b	221	1800	10	7	O	Poor
S-1-6	b	221	1850	15	9	◎	Poor
S-1-12	b	212	1950	5	4	◎	Good
S-1-5	b	221	1950	11	9	◎	Good
S-1-7	b	221	1950	18	22	O	Poor
S-1-11	b	221	2000	5	9	O	Poor
S-1-15	b	212	2000	6	8	O	Poor
S-1-14	b	212	2000	13	5	◎	Good
S-1-8	b	221	2000	17	16	O	Poor
S-1-10	b	221	2000	20	8	O	Good
S-1-17	b	210	2050	30	6	◎	Good
S-1-16	b	216	2100	5	5	◎	Good
S-1-13	b	212	2100	9	14	O	Poor
S-1-19	b	205	2200	11	7	◎	Poor
S-1-22	c	205	1800	7	20	O	Poor

O: Small film below 1 cm dia. ◎: Large film above 2.5 cm dia. Graphite powder of 8 g was added in the graphite crucible.

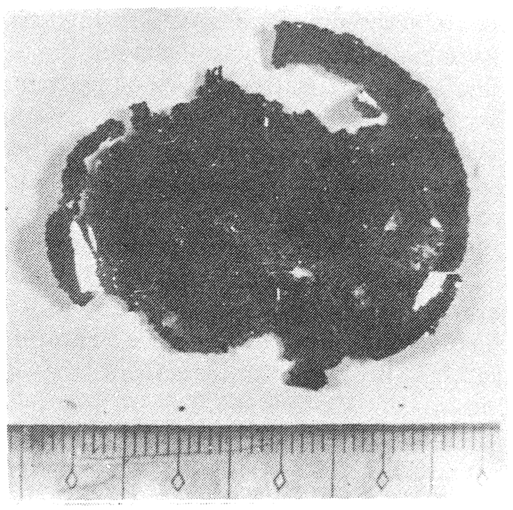


Fig. 5. Grown graphite single-crystal film for Run No. (S-1-14).

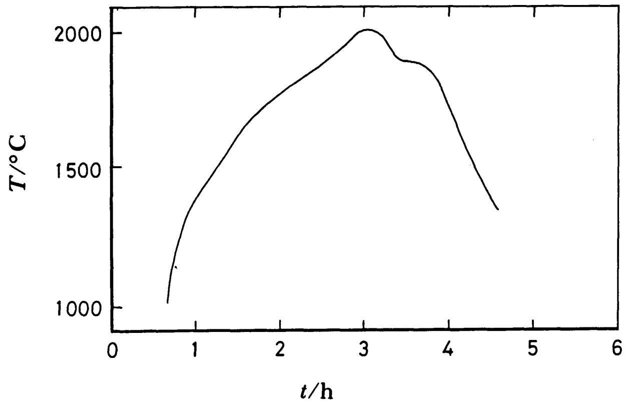


Fig. 6. A heating curve during the growth of graphite single-crystal film for Run No. (S-1-14).

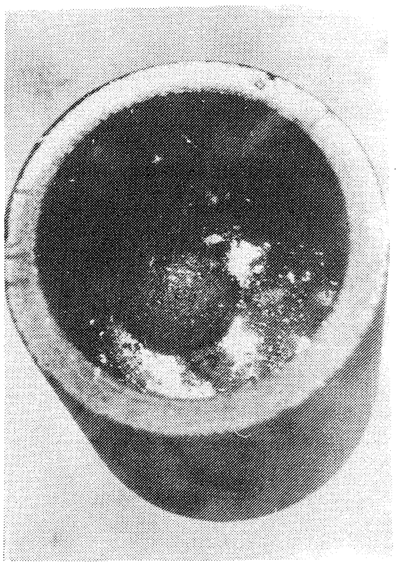


Fig. 7. An appearance of the graphite crucible just after the growth of graphite single-crystal film for Run No.(S-1-17).

The photograph of a single-crystal film obtained from Run No. (S-1-14) and the heating curve are shown in Figs. 5 and 6, respectively. A large single-crystal film with a metallic luster and the dimensions of 4 mm in diameter and 0.03_5 mm thick, could be grown. The circumference of this single-crystal film curved at a state of meniscus. The grown graphite single-crystal film had good quality, judging from the Laue X-ray pattern.

A photograph of experimental Run No. (S-1-17) and the heating curve are shown in Fig. 7. The spout of a flux melt was formed through a single-crystal film with metallic luster. This depended on quick cooling: that is, a cooling rate of 30 °C min^{-1}.

Laue X-Ray Photographs and Electron Diffraction Patterns. From a Laue X-ray photograph of the product of Run No. (S-1-5), it was presumed that the grown graphite single-crystal film had a good quality, judging from the spots of hexagonal symmetry. Though the grown single-crystal film from Run No.

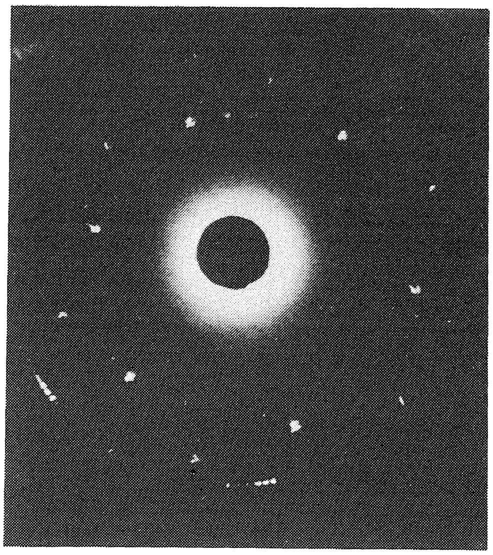


Fig. 8. Laue photograph of the graphite single-crystal film for Run No. (S-1-14).

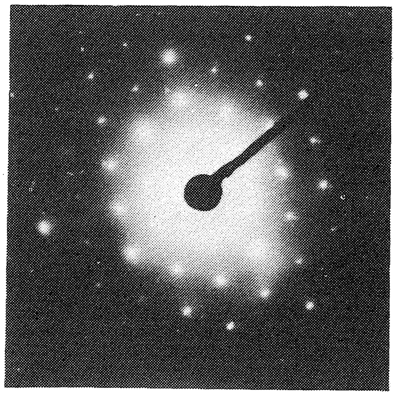


Fig. 9. An electron diffraction pattern of the graphite single-crystal film for Run No. (S-1-14).

(S-1-6) had good crystallinity, it was hard to say whether it was a single crystal from a Laue X-ray photograph and the electron diffraction pattern.

A Laue X-ray photograph and an electron diffraction pattern of the single-crystal film from Run No. (S-1-14) are shown in Figs. 8 and 9. It appears that the grown crystal had very a good quality.

Discussion

The reason that the flux spout formed above the graphite single crystal film (Fig. 4) is thought to be due to a solidification of the melt that occured from its surface. The internal pressure resulted from a contraction of iron flux upon solidifying; then, the eutectic melt of the flux plus graphite gushed out to the surface of the single-crystal film.

Formation Condition and Mechanism of a Graphite Single-Crystal Film. Graphite single-crystal films with good quality were obtained from Runs No. (S-1-5), (S-1-6), (S-1-10), (S-1-12), (S-1-14), (S-1-16), and (S-1-17), as is shown in Table 1. From these results, the formation conditions and mechanism of graphite single-crystal films are discussed in detail.

In an experiment involving the slow-cooling method, it was widely noted that the iron-flux method saturated when the graphite was cooled; it then separated the saturated graphite as crystals. This process, which separated the crystals from the iron flux, can be classified into two classes: the nucleation and the crystal growth. These two phenomena were strongly dependent on the temperature. The rate of nucleation was generally faster as the cooling rate increased, and the growth rate of crystal was faster as the temperature increased. Consequently, it is necessary to grow a single crystal in which nucleation occurs as much as possible and the crystals grow. As described above, the experimental process was thought to classified into three large steps: heating, constant-temperature and cooling processes. The correlation between these processes and the formation of a large graphite single-crystal film was investigated.

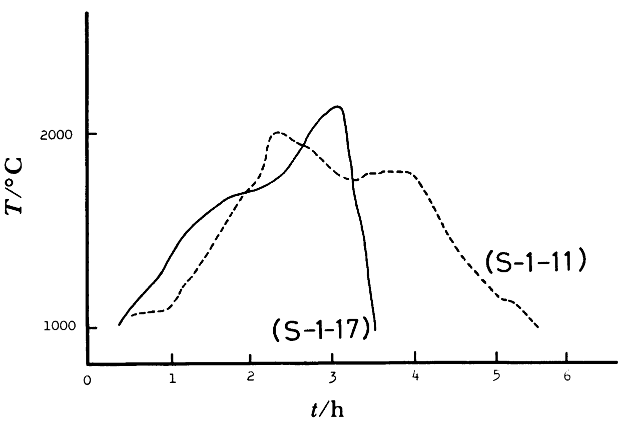


Fig. 10. Comparison of Run No. (S-1-17) quenched quickly with Run No. (S-1-11) cooled slowly.

Cooling Process. The cooling process, which was believed to be very important and a strong governing factor, was examined in terms of the cooling method. Figure 10 summarizes the results of both the temperature curves of an experiment involving rapid cooling (Run No. (S-1-17)) and an experiment involving slow cooling (Run No. (S-1-11)). Although it is generally said that for a slower cooling rate the better is the graphite single-crystal film quality, a large graphite single crystal with good quality was formed for Run No. (S-1-17), compared to Run No. (S-1-11) involving slow cooling. The assumption was compatible with these results. Note that a large

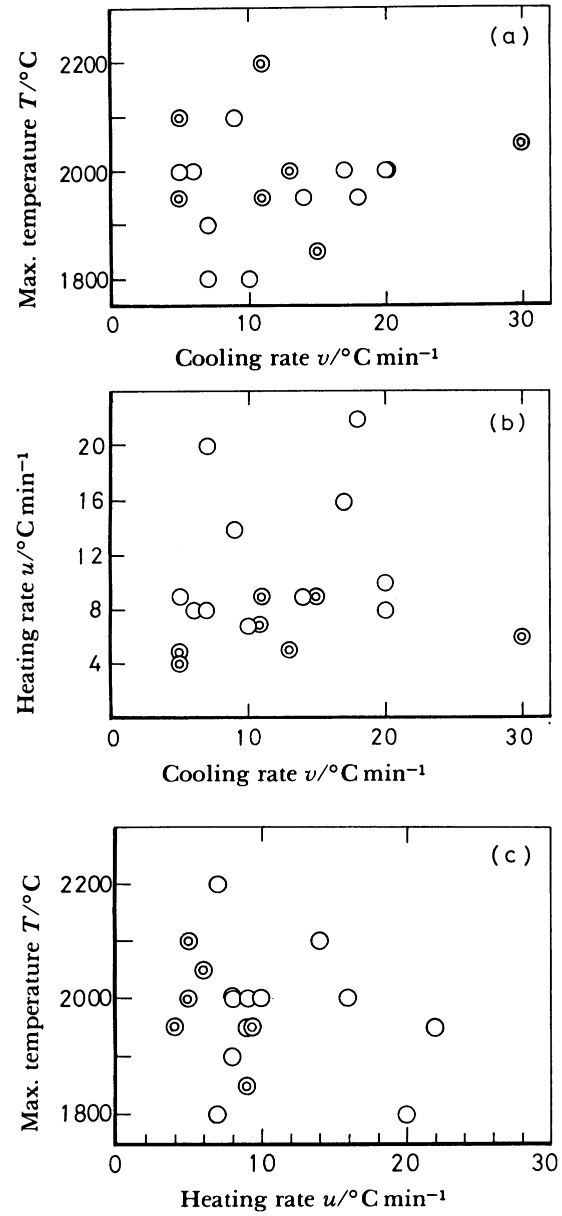


Fig. 11. Relationship among the growth ease of the graphite single-crystal film and the cooling rate, the heating rate, and the maximum temperature.
○: small film below 1 cm dia., ◎: large film above 2.5 cm dia.

graphite could be formed, even if the slow cooling was fairly well controlled. An adequate correlation based upon the cooling rate could not be found, as is shown in Fig. 11. Thus, there was little possibility of a factor which determines the formation of a graphite single-crystal film. In the cooling process, small crystals were formed below the graphite single-crystal film. Therefore, an apparatus that could control the cooling process was used; small crystals were thought to grow to some degree. A cooling process was far from a factor influenced to the growth of graphite single-crystal film.

A Constant Temperature Process. The next factor examined was the influence of the maximum temperature and its holding time. The experimental results are shown in Table 1. The influence of the maximum temperature are not shown to have a certain correlation. A large graphite single-crystal film could be formed if the maximum temperature was above 1850 °C as shown in Table 1.

We could not determine the correlation in terms of the holding time at the maximum temperature (Fig. 12). However, this constant-temperature process shows a very attractive tendency, which is obvious by comparing the temperature curves of Run No. (S-1-5) and Run No. (S-1-6), as shown in Fig. 13. In the case of Run No. (S-1-5), the temperature was held constant at a value which fell slightly from the maximum temperature (1950 °C); under this condition a graphite single-crystal film with good quality was formed. However, in Run No. (S-1-6) with a constant temperature of 1850 °C, a graphite single-crystal film of good quality could not be grown.

Generally, in the case of the type as shown in Fig. 14(a), a single-crystal film with good quality could form (Run No. (S-1-5), (S-1-14), and (S-1-16)). On the other hand, as for the temperature curve of the type shown in Fig. 14(b), Runs No. (S-1-7), (S-1-10), and (S-1-13), large graphite single-crystal films of good quality could not be formed. From these results, it appears to act as the annealing if the constant temperature, which lowered slightly from the maximum temperature, held. However, it seems to be true that another dominant factor existed.

A Heating Process. Finally, the more important factor was the heating process. The experimental results are shown in Fig. 11. In case that the heating rate was below 9 °C min^{-1}, a large graphite single crystal with good quality could form. The relation between graphite single-crystal film growth and the heating process could be determined by observing the surface of the melt from a hole. The experimental results are schematically shown in Fig. 15. It was observed that graphite single crystals rose to the surface of the melt at a temperature of about 1550 °C, and gathered in the constant direction; then, the incorporation of crystals was initiated. This incor-

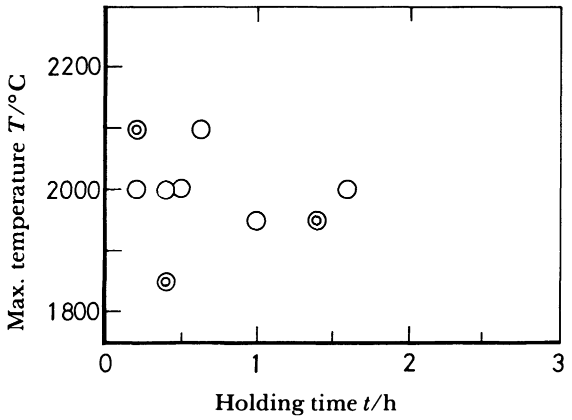


Fig. 12. Relationship among the growth ease of graphite single-crystal film and the holding time, and the maximum temperature, O: small film below 1 cm dia., ◎: large film above 2.5 cm dia.

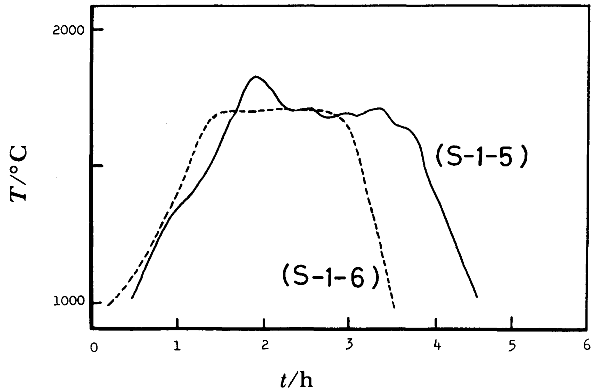


Fig. 13. Comparison of the holding times for Run No. (S-1-5) with for Run No. (S-1-6).

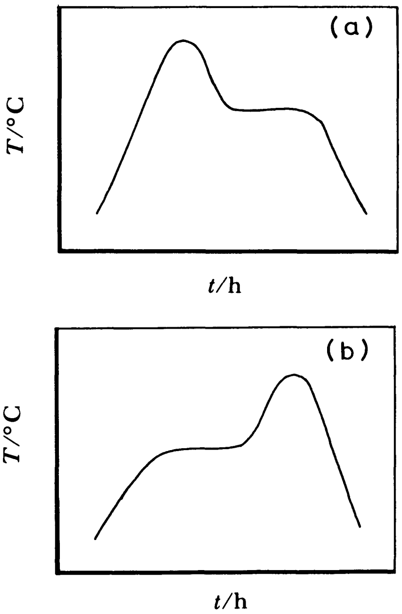


Fig. 14. Typical heating curves for the growth of the graphite single-crystal films.

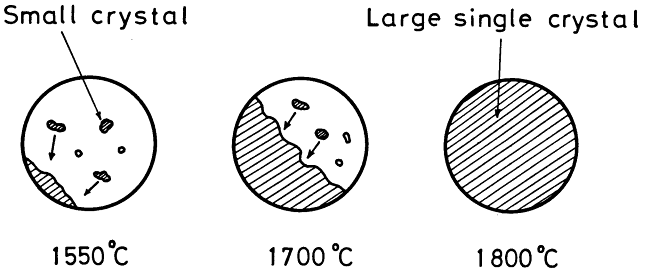


Fig. 15. Observation of the growth process of the graphite single-crystal film on the surface of the melt.

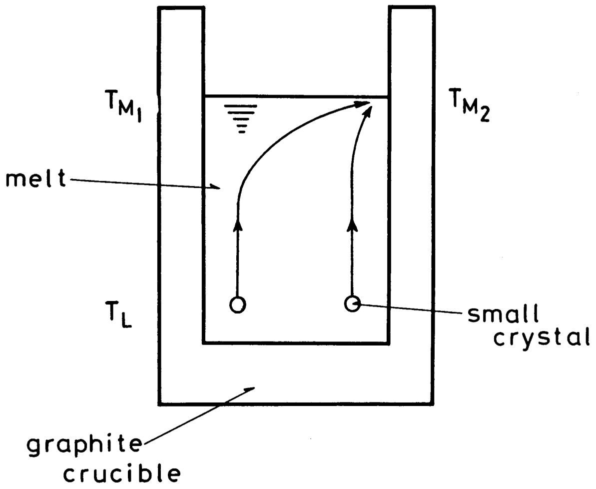


Fig. 16. The deposition process of the small graphite single crystals in the melt.

poration was promoted at about 1700 °C and the graphite single crystal covered the surface areas. Also, wrinkled patterns on the surfaces of the grown small graphite crystals were observed. These patterns were in agreement with that of a grown single-crystal film observed after the experiment. It was thus found that a single-crystal film is formed during the heating processes.

This formation mechanism of graphite single-crystal films is new and quite different from the so-called mechanism of the crystal growth by slow-cooling.

As previously stated, small graphite crystals were observed to gather in a constant direction, as is shown in Fig. 15. To investigate the cause, the temperature distribution in the horizontal direction of the graphite heater was observed. As a result, the temperature difference between sides in the central sections of the heater was several 10 °C. It seems that the graphite heater was wasted unequally during many repeated experiments; consequently, a temperature difference in the horizontal direction of the heater was produced. Accordingly, it is obvious that a temperature difference was produced in the horizontal direction in the same manner in the vertical direction as the temperature was increased.

The crystal growth of graphite is considered to be as follows. As is shown in Fig. 16, the graphite became saturated from the melt while precipitating and migrating from the lower-temperature (T_L) parts to the high-temperature (T_M) parts, owing to a difference in the specific gravities. It then floated to the surface of the melt. Then, graphite crystals were incorporated the opposite side (T_{M_2}) of the crucible wall (T_{M_1}), where the graphite heater was fairly wasted. A graphite single-crystal film with good quality was obtained by holding these incorporated crystals at a constant temperature.

From this point of view, the heating process was very significant. Therefore, the incidence of a nucleus could be slightly lowered by the decreasing the temperature difference, thus, decreasing the heating rate within 6 °C min^{-1}. It is possible that a large graphite single-crystal film with good quality was obtained by increasing the growth rate of the crystal as the temperature increased, within the scope of the heating process. In conclusion, when making use of a temperature difference in both horizontal and vertical directions, by controlling the heating rate to be 6 °C min^{-1}, and holding the maximum temperature above about 1950 °C, a large graphite single-crystal film was obtained with good reproducibility. Such hitherto performed experiments as the slow-cooling method are described; however, from a practical point of view it could be called a sort of temperature-gradient method which made use of the both temperature difference between in the horizontal and vertical directions.

Transmission Laue Photograph and Electron Diffraction Patterns. The graphite single-crystal films formed were examined by X-ray and electron diffraction methods as to whether these crystals had good quality or not.

The crystal structure of graphite has a stratified layer structure. The regular hexagonal rings of the carbon atoms are numerously linked together and make the enormous network plane. These alternate layers fall vertically above one another. Owing to the way these layers are piled, the graphite structure has two polytypes: a hexagonal system with an ABABAB structure (2H) and a rhombohedral system with an ABCABCABC structure (3R). The hexagonal system is the most common in graphite crystals with a unit cell of a_0=2.4612 Å and c_0=6.708 Å; the 3R-type unit cell is a_0=2.4612 Å and c_0=10.062 Å, by expressing it by the hexagonal cell. In the grown graphite single-crystal films with the high crystallinity, the Laue spots show a 6-fold axis of symmetry of the distinct {101} and {112} forms.

In the case of experimental Run No. (S-1-14), as shown in Fig. 8, a Laue pattern of the distinct 6-fold axis of hexagonal symmetry was obtained, indicating that a graphite single-crystal film with good quality was obtained.

The indices of these spots were evaluated by making use of a gnomonic projection method. By closely observing the Laue spots of the graphite single-crystal film for Run No. (S-1-14), it is obvious that these spots were split. When an electron diffraction photograph of the same graphite single-crystal film was taken and magnified, the spots were certainly split. In this case, the split spots of a graphite single-crystal film should be based on either twised two sheet-like networks or on the incompatibility of these networks in the a- and the b-directions. Perhaps, we suppose that the small crystals were adhered to the surface of the graphite single-crystal films.

Conversely, there was also a case in which the spots on a concentric circle were not split; the split spots appeared at the inside or outside of the circle. There is a reason that the graphite crystal was expected as a single one; however, graphite single-crystal films were piled up and the spots of the Laue photograph were split and then appeared at the inside or outside of the concentric circle, or small crystals adhered to the surface of the single-crystal film.

When we examine the Laue spots of the graphite single-crystal film curved to meniscus for Run No. (S-1-14), many spots could be recognized at the insides and outsides of the spots of 6-fold symmetry, except that of the 6-fold symmetry for {101} and {112} groups. These many spots could not index with a hexagonal system. From data of the powdered X-ray diffraction patterns, the Laue photograph, etc., we determined that these many spots corresponded to a rhombohedral structure and also that many spots on a concentric circle, except for the 6-fold symmetry, corresponded to a twisted structure like the aberration of the positions of card as a spiral stairs. There are a few cases in which a rhombohedral structure was created by a shear-stress deformation.[13]

In the present experiment, the outside circumference of the graphite single-crystal film was curved by accepting a deformation stress during the cooling time; it was also thought that a rhombohedral structure was partially created.

It is recognized that a rhombohedral structure existed several per cent in a natural graphite crystal as well as in an artificial graphite crystal with good quality. Therefore, it could be thought that the rhombohedral structure also partly existed in the large graphite single-crystal film with good quality.

Unit Cell Parameters of a Graphite Single-Crystal Film. The parameters, a_0 and c_0 values, of the graphite single-crystal film were 2.462±0.002 Å and 6.708±0.001 Å, respectively, according tô the present data from the powdered X-ray diffraction method and agreed with that of a natural graphite crystal.

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