Preparation of Graphite Single-Crystal from an Iron Solution by a Temperature-Gradient Method†

Yoshihiro Sumiyoshi, Masumi Ushio,* and Sadao Suzuki
Department of Applied Chemistry, Faculty of Engineering, Gunma University, Tenjin-cho, Kiryu 376
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A graphite single-crystal with maximum dimensions of 30 mm in diameter and 0.24 mm thick was prepared from an iron solution by a temperature-gradient method. A flux of 300—500 g of electrolytical iron, 10 g of graphite powder and silicon powder of 0—5 g for the flux weight were charged in a graphite crucible. Large and thickened graphite single-crystal films of good quality were prepared at 2100 °C by repeating 4 times the heating and cooling processes. The cell parameters of the graphite single-crystal film were a_0=2.463±0.003 and c_0=6.708±0.001 Å. The optimum amount of silicon additive was 1 wt% for the flux weight. In order to increase the thickness along the *c*-axis of graphite single-crystal films, the number of heating and cooling processes should be increased.

Studies on the preparation of graphite single-crystals have been carried out by many reseachers,[1-13] in which nickel, iron, and many other metals have been used as a flux. Studies on the preparation of a graphite single-crystal from an iron melt have been reported by Austerman et al.[8] and Noda et al.[9,10] Austerman et al. synthesized graphite single-crystals by slow cooling of an iron melt which was saturated with carbon, using an electric precision furnace with a temperature gradient control. Noda et al. made graphite single-crystal films of about 30 mm in diameter and about 0.06 mm thick in which the *c*-axis was normal to the surface of the iron melt, by slowly cooling an iron melt containing 1 wt% Si.

As described in a previous paper,[1] graphite single-crystal films with maximum dimensions of 40 mm in diameter and 0.04 mm in thickness were prepared from an iron solution by a slow-cooling method. We could directly observe that the graphite single-crystal films were prepared through a heating process rather than through a slow-cooling process. It therefore appears that growth during a heating process plays an important role in the formation process of a graphite single-crystal film. The most suitable condition for preparing a large graphite single-crystal film with good quality was by using a heating rate of 6 °C min^{-1} and a maximum temperature above about 1950 °C. In addition, same crystals with a rhombohedral structure seemed to exist among the grown single crystals. The thickness along the *c*-axis for large graphite single-crystals was about 0.03—0.04 mm.

The purpose of this study was to clarify the preparative conditions for making a large single-crystal film and to elucidate the conditions under which graphite single-crystal film grows thick in along the *c*-axis, using a temperature-gradient method. Therefore, in this experiment a long, narrow graphite crucible was used, unlike that used in our previous experiment.[1] Graphite single-crystal films were prepared by a temperature-gradient method and the resproducibility investigated. The products were examined by an X-ray Laue photograph method.

† Study on Synthesis of Large Single Crystal for Industrial Use. XVII.

Experimental

A Tannman electric furnace (electric power of 1.5 kW and a maximum electric current of 1000 A) was used as a heat treatment apparatus (described in a previous paper[1]). The dimensions of the graphite heater were 400 mm long, 70 mm inner diameter and 5 mm thick. A graphite crucible (50 mm outer diameter, 10 mm thick and 180 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 installed in the graphite crucible. Temperature errors were within ±20 °C. Electrolytical iron (purity above 98%) was used as a flux. Silicon powder (99.9% pure) of 0—5 g was added to the flux as an additive agent. Graphite powder (10 g), obtained by crushing the graphite rod, was used as a nutrient.

Electrotytical iron (300—500 g) was placed into a graphite crucible with silicon and graphite powder. After heating, the wall of the graphite crucible became partially eroded. The upper part of the iron melt in the crucible was maintained at a lower temperature, while the lower part obtained higher temperature. Due to this temperature gradient thermal convection took place from the lower parts to the upper parts of the melt. Therefore, when the melt which became saturated at the higher-temperature locations moved to regions of lower temperature, the graphite was supersaturated and then deposited.

The temperature distribution at a maximum temperature of 1300 °C in the furnace is shown in Fig. 1. A Pt-Pt·13% Rh thermocouple was used for measuring the temperature distribution. The maximum measurable temperature of the thermocouple was 1600 °C, lower than the temperature of the experiment. It may be considered, however, that locations near the maximum temperature of the furnace (above 1600 °C) were the same as those below 1600 °C. In order to make use of thermal convection in the temperature-gradient method, the graphite crucible was fixed as the lower part of the melt, and was maintained at the maximum temperature. In this experiment the surface temperature of the melt for all runs was measured using a pyrometer.

A microscope with a micrometer was used for measuring the thickness of the graphite films. The grown films were uniform in thickness.

Results and Discussion

Growth of Film. In Table 1 the double circle represents the case in which a large graphite film (greater than 25 mm in diameter) was grown; the single circle represents the case in which small crystals (less than 10 mm in diameter) were prepared. As is obvious from Table 1, large films were often formed in many runs.

Graphite crystals can be classified roughly into three types: single-crystal films, small single-crystals, and fine crystals in a solidified flux, as described in a previous paper.[1]

The grown large films almost had a metallic lustre. Below these films, small graphite crystals were grown in large quantities; they were, however, directly in contact with solidified flux brick. The flux spout observed in an experiment involving cooling method[1] was not produced during this temperature-gradient method. Wrinkled patterns were mostly observed on the surface of grown films.

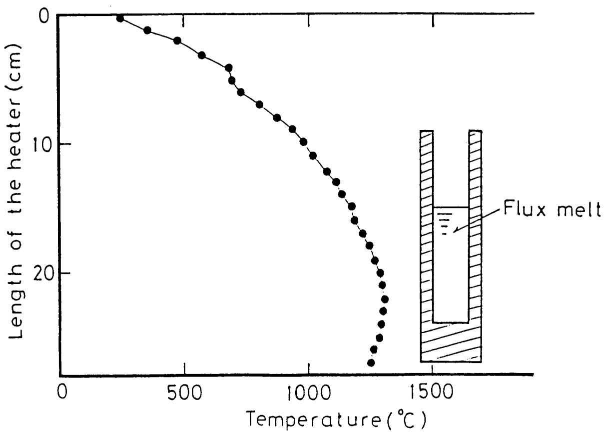


Fig. 1. Temperature distribution in an electric furnace and a position of the graphite crucible.

It was observed that the wall of the graphite crucible was much eroded and the thermal convection of the flux melt was very great.

Photographs of the films (S-2-8, S-2-15, and S-2-5) and heating curves are shown in Figs. 2 and 3, respectively. The metallic lustre of the grown films in S-2-8 was slightly faded and a wrinkled pattern on the surfaces of graphite films was observed. After repeating the heating process two times, a film with a metallic lustre and 0.16 mm thickness was prepared (S-2-15). In S-2-8, a film with a slightly metallic lustre was grown all over the surface of the flux melt. Small crystals were coprecipitated below the film.

In the case of S-2-9, the thickness of the grown film was about 0.15 mm; this film was in contact with a solidified flux. The central part of this film became depressed, perhaps caused by contact of the flux melt with the film during the cooling process.

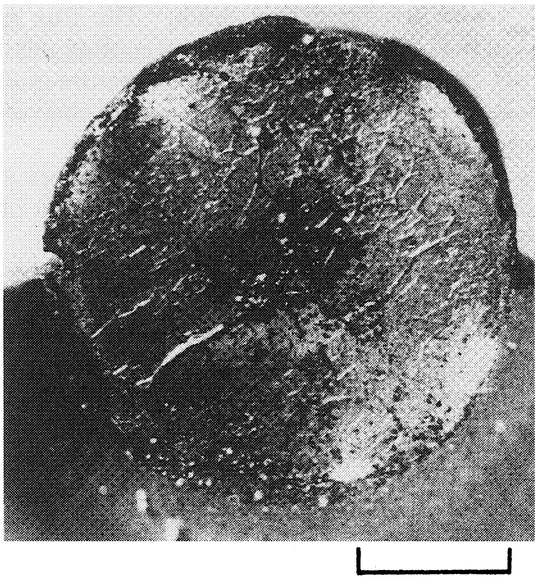
A film with a metallic lustre was grown for S-2-6. In this experiment no silicon was added to the flux melt. For S-2-7, the thickness of the film was about 0.13 mm at a maximum temperature of 2000 °C. The metallic lustre of this film disappeared upon adding 5 g of silicon.

The thicknesses of films prepared by the temperature-gradient method were 2- to 5-times larger than those produced by the previous slow-cooling method. This is because in the temperature-gradient method, which makes use of a thermal convection, it was possible for the films to come into contact with the

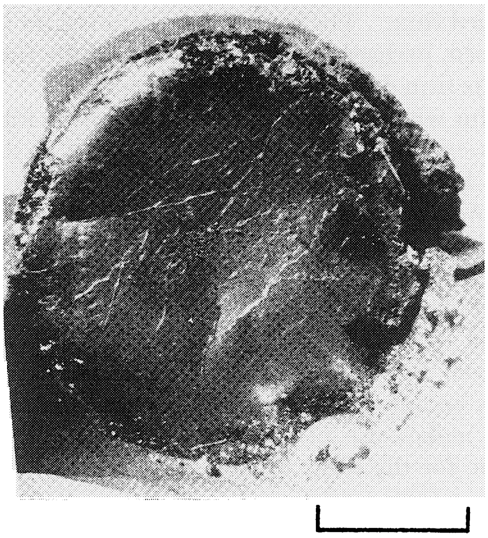
Table 1. Preparation of Graphite Single Crystal Films

Run No.	Flux (g)	Si added (g)	Maximum temperature (°C)	Heating rate (°C min^{-1})	Cooling rate (°C min^{-1})	Number of heating and cooling processes	Graphite single crystal film[b]	Tickness of films (mm)
S-2-9	300	3.0	2350	28	8	1	◎	0.15
S-2-1	309	1.5	2300	9	12	1	◎	n.m.
S-2-10	300	1.0	2250	13	4	1	◎	n.m.
S-2-8	300	3.0	2200	16	6	1	◎	n.m.
S-2-16	300	1.0	2150	3	4	1	◎	0.12
S-2-15	300	1.0	2150	2	10	2	◎	0.16
S-2-17	300	1.0	2100	5	10	4	◎	0.24
S-2-6	300	0	2000	11	6	1	◎	n.m.
S-2-7	300	5.0	2000	6	4	1	◎	0.13
S-2-5	300	1.0	1950	7	4	1	◎	0.11
S-2-14	300	1.0	1950	2	2	1	○	n.m.
S-2-11	300	1.0	1900	4	3	1	○	0.13
S-2-13	300	1.0	1800	—	—	1	◎	n.m.
S-2-12	300	1.0	1800	—	—	1	○	n.m.
S-2-3	300	1.0	1700	—	—	1	○	n.m.
S-2-4	495	1.0	1700	—	—	1	○	n.m.
S-2-2	495	1.0	(1950)[a]	—	—	1	◎	n.m.

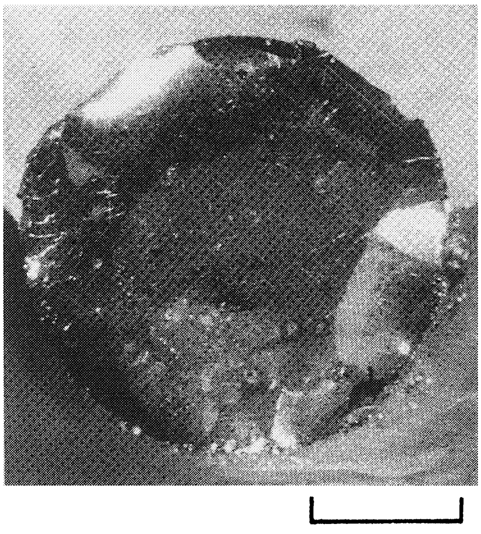
a) Estimated temperature. b) ◎; A large graphite film greater than 25 cm in diameter was grown. ○; A small crystal less than 1 cm in diameter was grown. n.m.; not measured.



(a) S-2-8



(b) S-2-15



(c) S-2-5

Fig. 2. Grown graphite single-crystal films. (a) S-2-8, (b) S-2-15, (c) S-2-5.

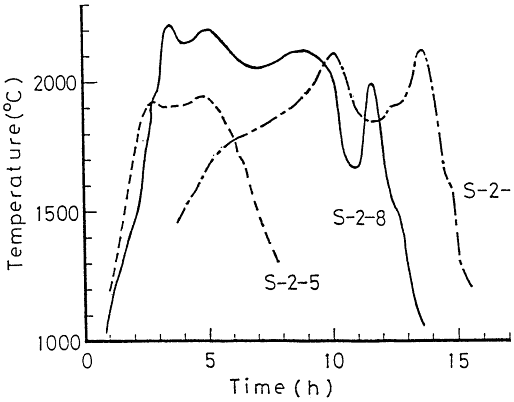


Fig. 3. Heating curves during the growth of graphite single-crystal films.

liquid surface for a long time. The depth of the flux melt was about 7 to 8 cm. Thus, the films continued to grow, and it can be assumed that large, thick graphite films were thus prepared.

The results of an attempt to increase the number of heating and cooling processes are shown in Fig. 4. In a case of S-2-16, the maximum temperature and heating rate were the same, or almost the same as that of S-2-15, expect that its cooling rate was slower and heating process took place only once. The thickness of the film was slightly thinner than that of S-2-15.

For S-2-17, heating was repeated four times. The maximum thickness of a grown film was about 0.24 mm. Comparing the growth conditions of S-2-17, with those of S-2-15 and S-2-16, it appears that the maximum temperature (ranging between 2100 and 2150 °C) and heating rate (within 5 °C min^{-1}) were almost the same. Furthers the silicon quantities (1.0 g) were also the same, though the number of the heating processes was different. As is evident from these results, we could prepare films with thick layers by increasing the number of heating and cooling processes. The reason for this may be that since the films prepared by the first heating come into contact

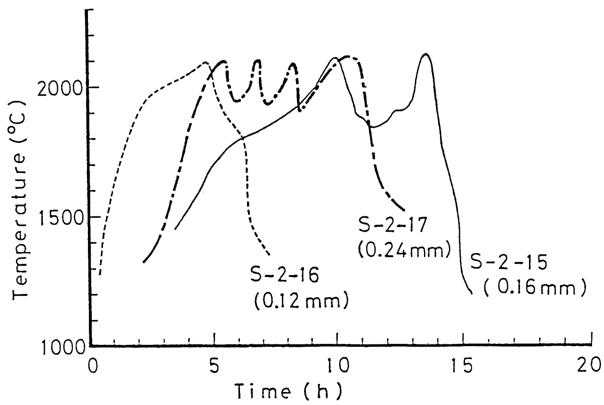


Fig. 4. Relationship between thickness of graphite single-crystal films and the number of heating and cooling processes.

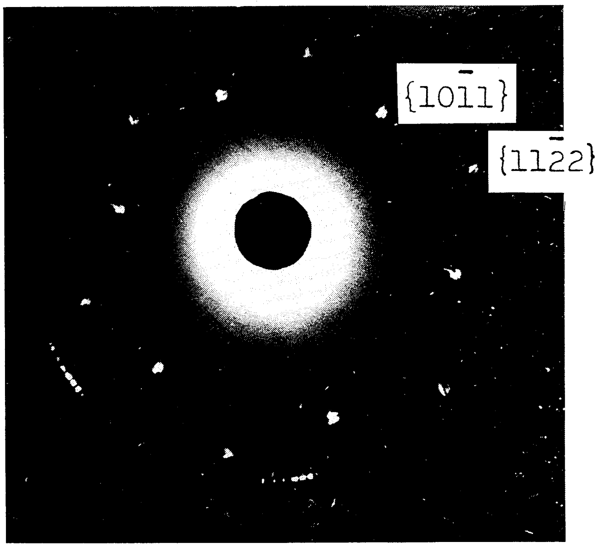


Fig. 5. Laue photograph of graphite single-crystal film for S-2-17.

with the surface of the melt, the grown films play the role of a seed for further growth.

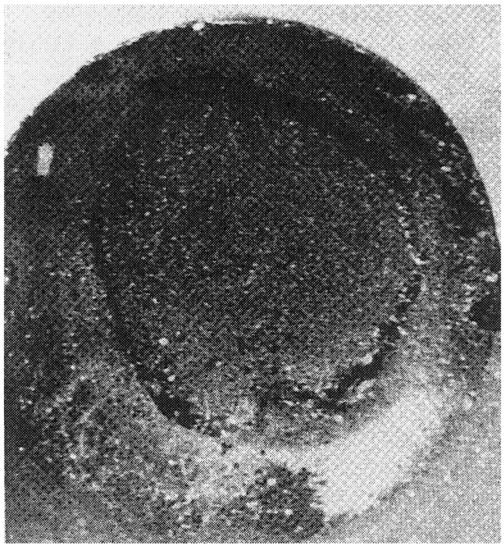
In the temperature-gradient method, the bottom of the melt attained the maximum temperature and the surface of the melt attained the lowest temperature. Therefore, the films formed on the upper part during the first heating process did not dissolve and the crystal growth of these films was promoted further by very small graphite crystals which were deposited. Further, since it was believed that repeated heating helped annealing while promoting a rearrangement of the structure, thick graphite films with good quality could be prepared by increasing the number of heating cycles.

Laue X-Ray Photograph. A Laue X-ray photograph of S-2-17 is shown in Fig. 5. Judging from the spots of hexagonal symmetry the grown single-crystal of graphite film appeared to have good quality. Laue spots show a 6-fold axis of symmetry of {10$\bar{1}$1} and {11$\bar{2}$2} groups. Indexing of the spots was achieved using the Gunomon projection method. The unit cell parameters (a_0 and c_0 values of a graphite film for S-2-17) were 2.463±0.002 and 6.708±0.001 Å respectively, and agreed well with the unit-cell parameters of a natural graphite crystal.[14)]

Effect of a Silicon Addtion. Silicon promotes graphitization for steel engineering and increases the difference in the eutectic temperature between graphite and cementite.[15)]

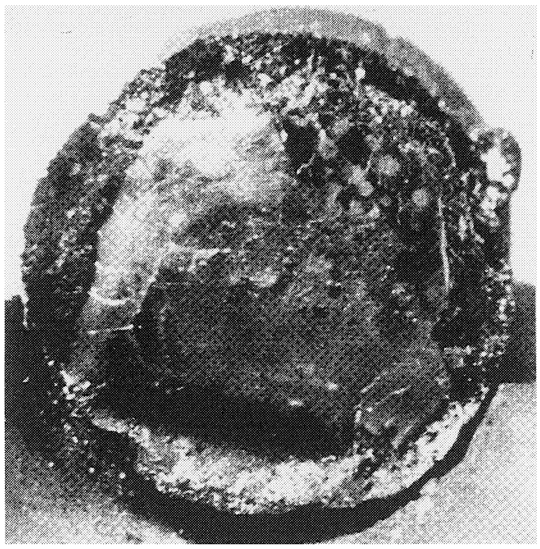
On the other hand, it seems that silicon decomposes a cementite and playes the role of a growth nucleus. If a silicon nucleus exists, heterogeneous nucleation occurs. Accordingly, a silicon nucleus plays an important role in promoting the decomposition of cementite.

The amounts of silicon additives studied ranged from zero to 5 g to the flux amounts. The most suitable silicon amount for a film to grow with a metallic lustre close to that of a natural graphite single crystal was about 1 g. The metallic-lustre effect due to the addition of silicon while growing films is shown in Figs. 2 and 6.



S-2-6

Si 0 g



S-2-7

Si 5 g

Fig. 6. Effects of silicon additions on metallic lustres. For silicon content of 1 g and 3 g, see the photographs of S-2-5(c) and S-2-8(a), respectively in Fig. 2.

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