SOME EXPERIMENTS WITH PEROWSKITE ($CaO \cdot TiO_2$) AND TITANITE ($CaO \cdot TiO_2 \cdot SiO_2$).

By Keizô IWASÉ and Masaji FUKUSIMA.

Received December 28th, 1931. Published March 28th, 1932.

Synopsis.

In the experimental study of the equilibrium of the system consisting of calcium silicate, $CaO \cdot SiO_2$, and titanium dioxide, TiO_2, calcium titanate, a compound belonging to the other system has often been found in the crystallized mass of a compound $CaO \cdot TiO_2 \cdot SiO_2$, calcium titanium silicate, and hence thorough investigation of the crystallization of calcium titanate and calcium titanium silicate was carried out before the determination of the equilibrium of the above mentioned system. These two compounds were synthesized from their components and their X-ray patterns were taken by the Debye-Scherrer method, and using these photographs as the standard, the condition has been fully determined in which these two compounds separate out from the melt. Microscopic study with a reflected light has also been applied for the identification of these two compounds. The stabilities of these two compounds were also investigated by several methods. Finally, the melting point of calcium titanium silicate was determined by the cooling curve method in which supercooling of the melt was prevented by seeding.

Introduction.

CaO, SiO_2 and TiO_2 unite in equi-molecular proportions to form the compound $CaO \cdot TiO_2 \cdot SiO_2$ which is also found in nature as titanite. It is considered unstable in the molten state(1) and another compound named perowskite having the formula $CaO \cdot TiO_2$ is said to crystallize out from the melt(2). On the contrary, in a paper recently published(3), no perowskite was observed in the cooled mass of molten titanite. However, in the course of the study of the equilibrium of the system consisting of $CaO \cdot SiO_2$ and TiO_2 carried out by one of the present authors, perowskite was often observed in the crystallized mass containing titanite. Hence it has been necessary to determine in what condition perowskite does crystallize out from the molten titanite and to decide whether perowskite or titanite is stable in the system consisting of the equi-molecular mixture of CaO, SiO_2 and TiO_2.

Experimental.

I. Preparation of Perowskite and Titanite. Since native perowskite and titanite were not available for the present authors, these specimens were made synthetically from their respective components. Instead of CaO, $CaCO_3$ was used because the former contains more or less moisture and is not in a suitable form for accurate weighing. $CaCO_3$ and SiO_2 (quartz sand) used here were Kahlbaum's preparation ("for analytical purpose"). TiO_2 was prepared from $TiCl_4$ as follows:—Kahlbaum's $TiCl_4$ was first treated with Na-amalgam, then it was twice distilled, once in vacuo and once in the ordinary way and in this manner the distillate coming off at 134.87°C., 745.1 mm. Hg, was collected.(4) It was then diluted with distilled water, and then it was precipitated by NH_4OH. The precipitate thus formed was thoroughly washed with hot distilled water, dried and then ignited in a platinum crucible by a platinum wound furnace at 1300°C. for 2 hours. The results of the analysis of TiO_2 thus prepared have proved that its purity is over 99%.

(1) *Perowskite* ($CaO \cdot TiO_2$). Equi-molecular quantities of $CaCO_3$ and TiO_2 were thoroughly mixed in an agate mortar by grinding them together. Then the whole of the mixture was carefully transferred to a platinum crucible and was heated to 1500°C. for 4 hours in a platinum wound furnace to let it sinter.(5) Under microscopical examination this sintered

---

(1) Doelter, Handbuch der Mineralchemie, Bd. III, 1 Teil (1918), 65; W. Eitel, Physikalische Chemie der Silikate, (1929), 325.
(2) Ibid; S. Smolensky, *Z. anorg. Chem.*, **73** (1912), 302.
(3) Fukuda, *Journ. Japan. Assoc. Mineralogist etc.* (Sendai), **5** (1931), 35.
(4) Sagawa, to be published in near future.
(5) P. Niggli, *Z. anorg. Chem.*, **98** (1916), 298.

mass was found to contain some new-crystalline product which was supposed to be perowskite. The sintered mass was again ground in an agate mortar in order to confirm the intimate mixing and then was subjected to a second sintering as before. Then by an oxy-hydrogen or an oxy-acetylene flame, the sintered mass was melted. Sometimes, a reduction took place which could be distinguished by the naked eye by the blue color of the fused mass, although care was taken not to reduce the oxides by controlling the amount of oxygen in the fusion. This bluish mass had a structure under the reflected microscope such as is shown in Photo. 1. The round grains seen in the photograph are thought to be perowskite and the dark parts distributed at the boundaries of the round grains, to be a lower oxide of titanium. It was changed to a white coloured substance by heating at a high temperature in the open air. The black spots distributed irregularly in the photograph are the holes formed in the course of polishing the specimen for microscopic purposes. In many cases, by making a careful adjustment of the nature of the flame, the reduction was prevented and homogeneous fused product was obtained, the structure of which is represented in Photo. 2. This homogeneous substance appears reddish brown and experiment by means of a picnometer points to the value 4.028 for its density. In the literature on the subject, the density of perowskite ranges from 4.02 to 4.04 and its colour is pale yellow, reddish brown or grayish black.(1) Therefore the homogeneous crystal above mentioned may safely be concluded to be perowskite. Photo. 3 shows its X-ray spectra taken by the Debye-Scherrer method. According to G. R. Levi and G. Natta,(2) the crystal lattice of perowskite was determined as pseudo-cubic.

(2) *Titanite* ($CaO \cdot TiO_2 \cdot SiO_2$). Equi-molecular quantities of $CaCO_3$, SiO_2 and TiO_2 were put into a platinum crucible and were then heated in a platinum furnace and melted. After the melt was thoroughly agitated by a platinum wire, it was then crystallized at about 1380°C. without allowing it to supercool. This was done by throwing a nucleus into the melt at a temperature not lower than 1300°C. (see IV). The crystallized mass appears light green or blue, has a density of 3.497, and is homogeneous as is shown in Photo. 4. In the literature on the subject, the colour of titanite is bluish and its density ranges from 3.4 to 3.56.(3) Therefore, this homogeneous crystal may be said to be titanite. Photo. 5 is its X-ray spectra taken as before. According to W. H. Zachariasen(4), the crystal lattice of titanite is monoclinic holohedral.

---

(1) J. W. Mellor, Compreh. Treat. Inorg. Theor. Chem., **7** (1927), 53, 54.

(2) Ibid.

(3) Doelter, loc. cit.

(4) Zachariasen, *Z. Kristallogr.*, **73** (1930), 7.

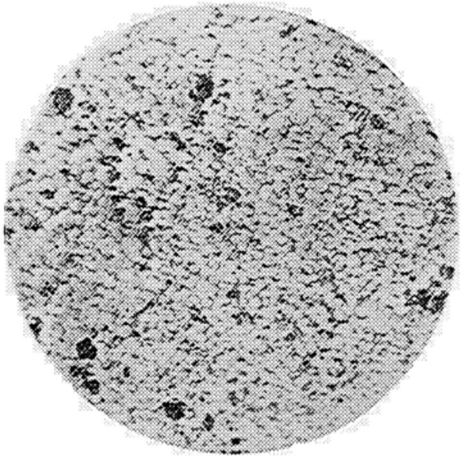

Photo. 1. Perowskite partly reduced. ×100

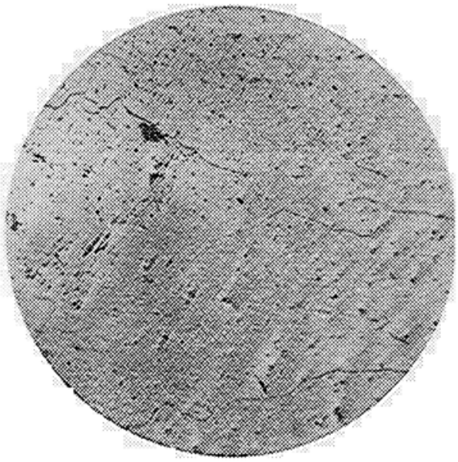

Photo. 2. Perowskite. ×100

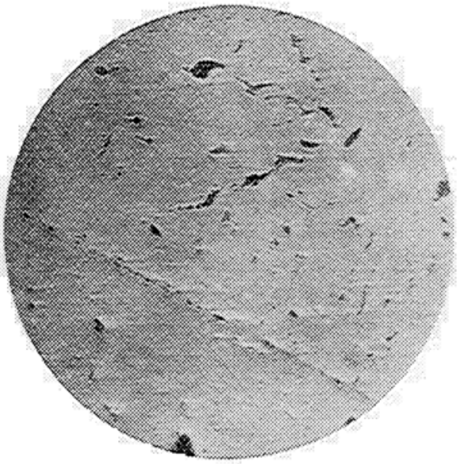

Photo. 4. Titanite. ×100

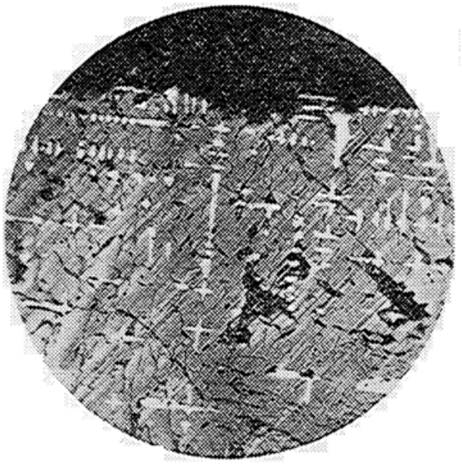

Photo. 6. Titanite, Perowskite and Silica. ×100

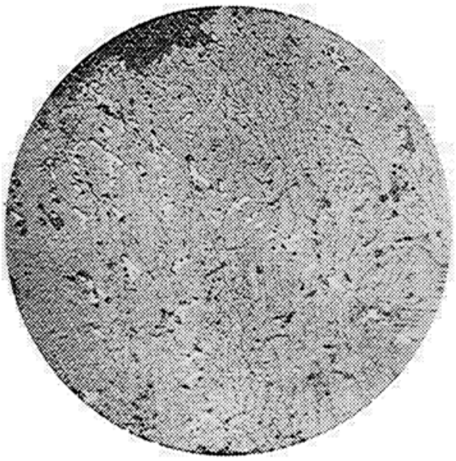

Photo. 7. Titanite, Perowskite and Silica. ×100

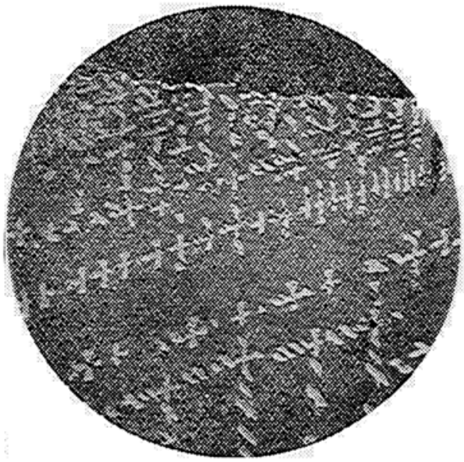

Photo. 8. Perowskite and Glass. ×100

Photo. 11. Sintered Mixture of Perowskite and Silica. ×100

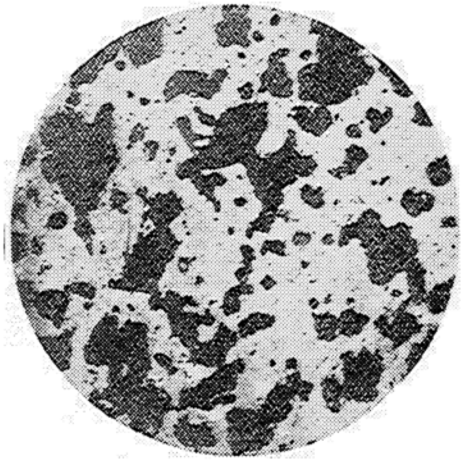

Photo. 12. Titanite from Perowskite and Silica. ×100

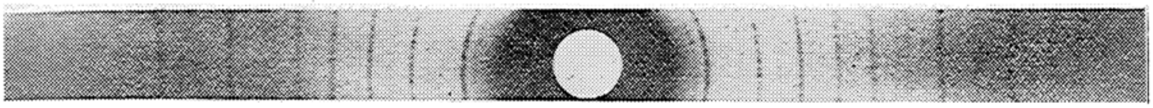

Photo. 3. Perowskite shown in Photo. 2.

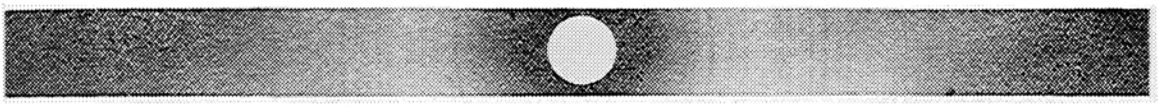

Photo. 5. Titanite shown in Photo. 4.

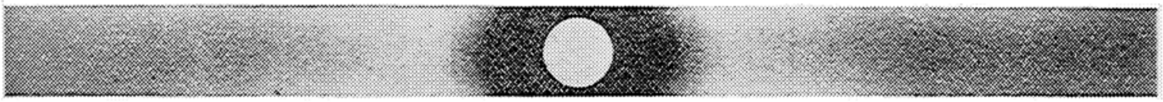

Photo. 9. Perowskite shown in Photo. 8.

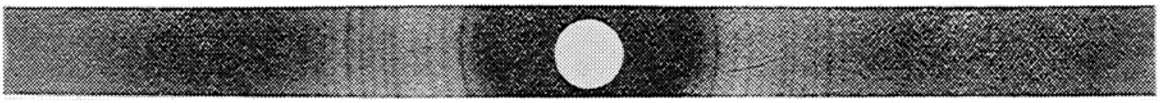

Photo. 10. Titanite shown in Photo. 6.

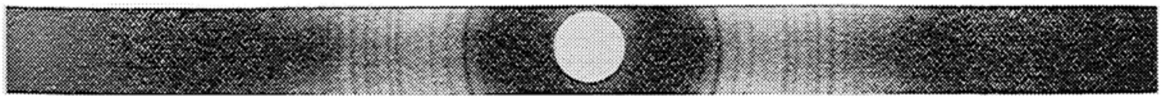

Photo. 13. Titanite shown in Photo. 12.

N.B. Anti-cathode: Copper.
Diameter of Camera: 75 mm.

II. Crystallization of Perowskite and Titanite from the Molten Titanite. As perowskite and titanite are frequently found in the crystallized mass of some silicates containing TiO_2⁽¹⁾, it is very important to study their crystallization for the investigation of the slag containing titanium formed in the smelting of the titaniferrous magnetic sand. From the standpoint of the physico-chemical conception, it is quite hard to take titanite as a component in the study of titano-silicates without making clear the phenomena of crystallization of perowskite and titanite from the molten titanite. The complete outline of the experimental results carried out by the present authors concerning this problem is as follows.

In the first place, about 2—10 gr. of titanite crystals were melted in a platinum crucible in a platinum wound furnace and the melt was solidified at various cooling rates, taking ordinary cooling curves at the same time. The solidified mass was then polished and examined under the reflected microscope. It was observed that the structure changed according to the condition of cooling, and in some cases, homogeneous products were obtained as is shown in Photo. 4, while in other cases, some light dendritic crystals were observed in it. Fig. 1 represents the cooling curves taken and Photos.

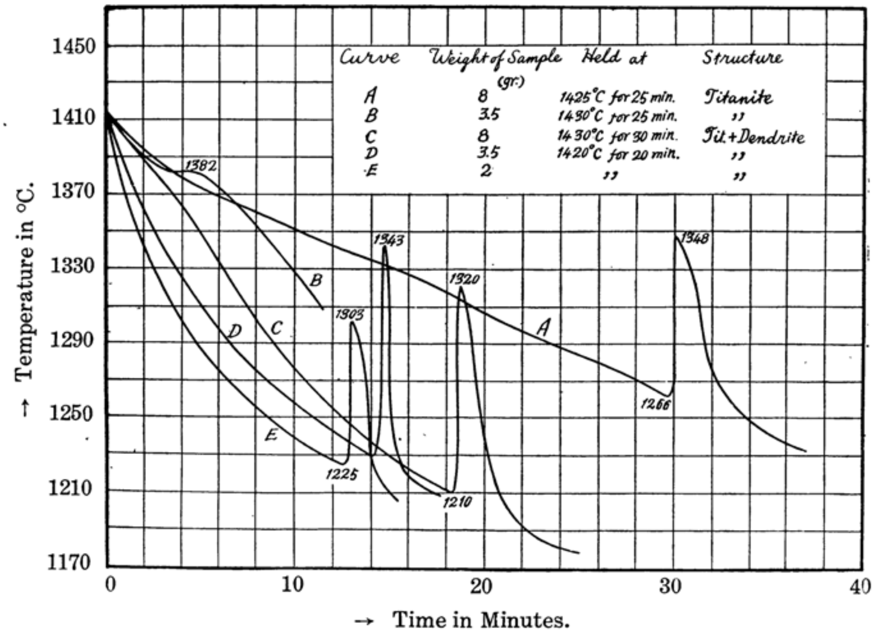

Fig. 1. Cooling Curves of Molten Titanite not Inoculated.

---

(1) Umezu and Kakiuchi, *J. Min. Inst. Japan*, **46** (1930), 994.

6 and 7 some of their structures. In the figure the heat treatment of the specimen prior to the beginning of the recording of the cooling curve and the structure of the specimen are demonstrated. By a careful study of the relation between the structure and its cooling condition represented in the curve, it has been concluded that the dendritic crystal above mentioned is formed when the melt supercools below ca. 1255°C.,(1) while when the melt solidifies above this temperature, the structure is always homogeneous. Hence, for the next experiment, the melt was carefully cooled to various temperatures and then it was quenched in ice water, together with the crucible, in order to obtain a structure consisting of the dendrite and glass, or glass only. In this experiment, 10 gr. of titanite were taken, heated to 1410°C. in a platinum crucible and melted. After keeping the melt at that temperature for about 10 minutes, it was cooled slowly to the following temperature and after certain number of minutes, it was quenched. The condition of the cooling of each melt and its subsequent structure were as follows :—

Time required for cooling from 1410°C. to the quenching temp. (min.)	Quenching temperature (°C.)	Time kept for the quenching temp. (min.)	Structure
13	1360	45	Glass
15	1330	,,	,,
20	1310	,,	,,
23	1290	,,	,,
30	1280	,,	Glass+Dendrite
35	1270	,,	,,
45	1255	30	,,
60	,,	60	,,

From this experiment it is clear that the dendrite is formed when the melt is supercooled below 1280°C. and is held at these temperatures for certain minutes. The quantity of the dendrite formed is great at the surface of the quenched mass and becomes less toward the inside. The sample whose structure is shown in Photo. 8 was photographed by X-rays and the spectra thus obtained are shown in Photo. 9 which is in good agreement with those of Photo. 3. Hence the dendritic crystals shown in Photos. 6, 7, and 8 are determined as perowskite. Thus it is clearly established that perowskite does crystalize out from the molten titanite according to the cooling

---

(1) This temperature varies according to the condition, such as the quantity of the specimen, the surface area of the melt and the cooling rate etc. (see later.)

condition of the melt. When perowskite separates from titanite, SiO_2 is left in a free state and this is clearly seen in Photos. 6 and 7. In these photographs, the ground mass is titanite, the dendrite is perowskite and the grayish lamelae or flakes are thought to be SiO_2. As the quantities of perowskite and SiO_2 are far less than that of titanite in these specimens, X-ray analysis has proved the existence of only titanite as is shown in Photo. 10. It has also been observed that the quantity of perowskite that separates from the melt increases as the cooling rate becomes slower and the degree of the supercooling becomes greater, but a structure consisting of only perowskite and SiO_2 and no titanite could not be obtained in any case, while a structure consisting of only titanite could easily be obtained when the melt did not supercool below ca. 1255—1280°C.

The apparatus for taking the cooling curves of the melt and that for quenching were as is shown in Fig. 2. The figure shows the platinum wound furnace in which the platinum crucible containing the melt is hunged by a

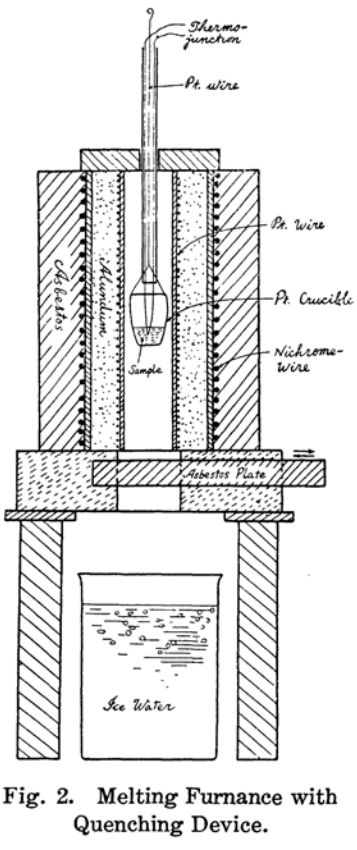

Fig. 2. Melting Furnance with Quenching Device.

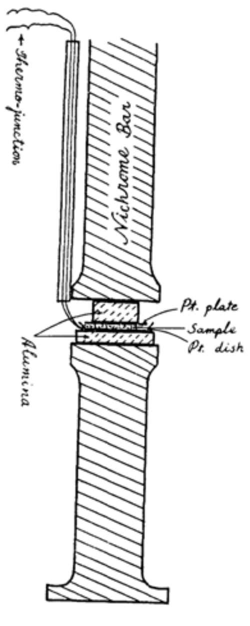

Fig. 3. Device for Heating with Pressure.

platinum wire. The hot junction of the thermo-couple dips in the melt at the point ca. 2—3 mm. apart from the surface of the melt. In the case of quenching the melt together with the crucible, the asbestos plate was pulled out and at the same time the crucible was unhooked to fall down into the ice-water in the beaker.

III. Stabilities of Perowskite and Titanite. From the results of the experiments in the preceding section and also from the general conception of the crystallization of silicates,(1) it may easily be supposed that titanite is more stable than perowskite in the system of titanite. The phenomena which support the above view have been observed in the course of the present experiment as follows:—

(1) When titanite was melted and then quenched from ca. 1390°C., an uniform glass was obtained. By annealing the glass at a temperature higher than 800°C. only titanite crystal was observed but no perowskite. The titanite thus formed remained unchanged when it was heated as follows:—

Temp. (°C.)	1160	1200	1255	1310	1365	1380
Time (Hr.)	2	2	1.5	2	2.33	2.5

(2) Although perowskite crystal was thrown into the molten titanite at about 1290—1380°C., titanite crystal was formed and no perowskite was separated.

(3) When a sample having a structure such as is shown in Photo. 7, that is, having a structure consisting of perowskite, titanite and silica, was heated at about 1310°C. for several hours, no increase of the quantity of perowskite was observed, it always melted at a temperature of about 1390 °C., and after quenching the melt thus formed in ice-water, no trace of perowskite or silica was found. This is evidence that the specimen melted completely at about 1390°C. without leaving any perowskite or silica remaining. If titanite incongruently melts,(2) the glass obtained by quenching as above mentioned should contain some crystals but this was proved not to be the case.

From these facts, it may be concluded that titanite is more stable than the mixture of perowskite and silica. In addition to this, positive proof of the above fact has been obtained by the present authors as follows. As above stated, by heating a mixture consisting of perowskite, titanite and silica in Photo. 7, no increase of perowskite or titanite was observed. But if titanite is more stable than the rest of the mixture, the quantity of titanite may be expected to increase by heating it at a high temperature. Hence in

---

(1) Doelter, loc. cit., Bd. I, 697.

(2) Eitel, loc. cit.

the next place, perowskite and silica were mixed together in equi-molecular proportion and the mixture was heated in a platinum crucible at about 1100—1300°C. in a furnace heated by carborundum bars for several hours. During the heating a massive bar made of nichrome was placed indirectly upon the content in the crucible as is shown in Fig. 3. The weight of the bar was about 7 kgr. The mixture thus heated changed more or less to titanite according to the following conditions.

Treatment	Structure
Heated at 1150°C. for 40 hours	A few titanite (Photo. 11) was formed.
Heated at 1150°C. for 40 hours and further at 1310°C. for 8 hours	Almost all the mixture changed to titanite (Photo. 12)

In Photo. 11, the brightly appearing mass is thought to be perowskite and the grayish part, titanite, and in Photo. 12, the grayish ground mass is titanite and the uncombined perowskite is seen in the middle portion of the ground mass, dark part being the void. That the grayish part in the last photograph is titanite was proved by the X-ray analysis as Photo. 13 shows.

Thus, it is decided that in the system of titanite, the mixture of perowskite and silica is less stable than titanite in the range of the temperatures experimented on.

IV. Melting Point of Titanite. As the molten silicate is apt to supercool more or less, its melting point is usually determined by the quenching method or by taking a differential heating curve of a very slowly heated specimen. But to the present authors, it seemed interesting to determine the melting points by cooling curve as is done with the metal. Therefore, the melting points of titanite and some other silicates which are apt to supercool were determined by cooling curves, throwing a nucleus(1) into the melt. The melt of titanite supercools as curves in Fig. 1 show, and the maximum point in each curve differs according to the cooling condition. By throwing glass, obtained by quenching the molten titanite, into the supercooled titanite, a very clear halting point was observed on the cooling curve as Fig. 4 shows. The quantity of glass was 0.01—0.02 gr. and it was thrown upon the melt at a position at a distance from the place where a hot junction of the platinum and platinum-rhodium thermocouple(2) lies. The crystallization of the melt begins at once by the introduction of the nucleus and when the temperature of seeding is not too low, the horizontal part on the cooling

---

(1) As a nucleus, any solid substances may be availed, for instance, MgO, Al_2O_3 and glass have proved to be effective to excite the crystallisation of the molten silicates.

(2) The couple was calibrated with melting points of the following metals; Ag (961°C.), Au (1063°C.), Cu (1083°C.) and diopside (1391°C.).

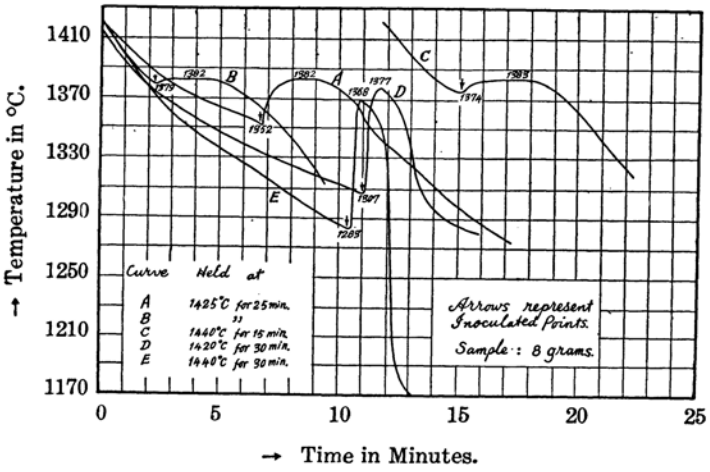

Fig. 4. Cooling Curves of Molten Titanite Inoculated.

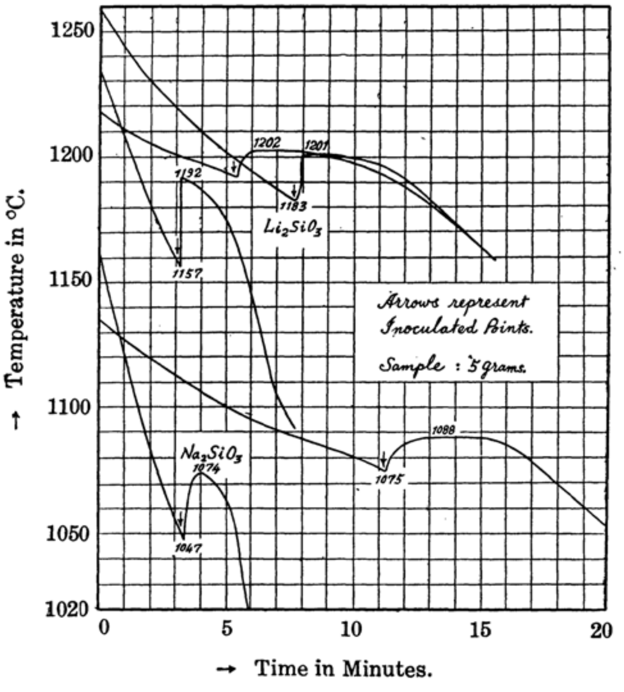

Fig. 5. Cooling Curves of Alkali silicates Inoculated.

curve lasts for several minutes, the temperature of which indicates the the melting point of titanite to be 1382°C. In the literature on the subject, the melting point of titanite is far lower than the above. On the cooling curves of molten titanite shown in M. Fukuda's paper (loc. cit.), there are found two points indicating the heat evolution of the melt. This is of course irrational and any of them can not be taken as its melting point.

Fig. 5 represents the cooling curves of Li_2SiO_3 and Na_2SiO_3 taken with seeding, which proves the superiority of seeding.

In conclusion, the present writers express their sincere gratitude to Prof. H. Shôji for the trouble of taking the X-ray photographs.

Summary.

1. Perowskite and titanite were synthesized from their respective components, using $CaCO_3$ instead of CaO.

2. Taking the X-ray spectra of these compounds as standards, the condition at which perowskite or titanite separates from the molten titanite has been fully determined.

3. Stabilities of these compounds have been determined by several methods.

4. Melting points of titanite and lithium and sodium silicates have been determined by cooling curves. Seeding was applied in this case and a very clear halting point has appeared in each case.

Research Institute for Iron, Steel and Other Metals,
Tôhoku Imperial University, Sendai.