

The identification, mode of occurrence, and quantitative determination of crystalline phases in granulated blast-furnace slag

With Plates II-VI

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[Taken as read 14 January 1965]

Summary. This paper describes a technique for the identification and quantitative determination of crystalline phases in granulated blast-furnace slag by means of incident light microscopy on polished and etched samples. The crystalline phases (including periclase) observed in high-magnesia granulates are reported and their mode of occurrence illustrated.

DURING granulation of blast-furnace slag for the purpose of cement manufacture, the aim is to obtain a product with the highest possible glass content. This is, however, not always achieved, mainly because of insufficient chilling and the formation of crystals prior to granulation. This paper describes the mode of occurrence of these crystalline phases and the techniques applied in the Research and Process Development Laboratories of the South African Iron and Steel Industrial Corporation (Iscor) for their identification and quantitative determination. Special emphasis is given to the identification of periclase (crystalline MgO), since the literature contains no reference to this mineral as a constituent of blast-furnace slag.

The high-magnesia granulates that have been investigated originate from dolomitic burdens that are used at the Pretoria Works of Iscor. The compositions of the slags fall within the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO}$ quaternary system and the crystalline phases observed in the granulates are merwinite, monticellite, melilite, forsterite, spinel, and periclase. Metallic iron is always present in small quantities but oldhamite (CaS) is rarely observed.

The identification of crystalline phases in granulates, with the aid of transmitted light microscopy, is difficult, mainly because of the small

size of the crystals and the fact that the crystalline content of a granulate is usually low, so that some phases are present in trace quantities only. Furthermore, because periclase and spinel are both isotropic, it is frequently impossible to distinguish between these two phases and glass. During the past twenty years, incident light microscopy has been used extensively for identifying non-opaque minerals in etched polished sections of Portland Cement clinker, basic refractories, and slags. It was found that this technique could be applied equally well to granulates and that it is superior to the transmitted light technique in that it permits not only glassiness determination on a granulate but also determinations of the quantity of each of the crystalline phases present. This is important since some slag phases, notably β -dicalcium silicate and probably to a lesser extent merwinite, have no bad effect on the hydraulicity of milled granulated blast-furnace slags.

Method

Sample preparation. For the preparation of polished sections a representative portion of a granulate is ground to —30 mesh. The portion of this material that is retained on a 100-mesh sieve is then mounted in transoptic mounting powder (e.g. Perspex) in a laboratory press. Bakelite mounting powder can also be used but Perspex is preferred because it also permits, although only to a limited extent, transmitted light investigations if the layer of granulate in the mount is thin enough. The mounts are ground successively on 180, 320, 400, and 600 grit wet-grinding papers followed by 0, 00, 000, and 0000 grade dry-grinding papers. Hereafter polishing is carried out in three stages: Rough polishing at \sim 1000 r.p.m. with alpha-alumina polishing powder and water on a cotton cloth of medium nap until a well-polished surface is obtained. A 60-second polish at \sim 200 r.p.m. on a napless cloth impregnated with diamond powder of 1 micron diameter. And a final polish of 30 seconds with finest grade alpha alumina and alcohol on a Selvyt cotton cloth of medium nap at \sim 200 rpm.

The first stage gives a well-polished surface but causes extensive surface relief on some crystals, which is successfully removed during the second stage; the final polish with alpha alumina is necessary to obtain a scratch-free surface. This final polishing process should, however, not last longer than about 30 seconds, otherwise excessive surface relief will result. Alcohol is used during this stage because dicalcium-silicate, a probable slag phase, is attacked by water.

Identification and mode of occurrence of the crystalline phases

General. In granulates the crystalline phases are present in relatively small quantities and occur as small crystals enclosed in granules of glass. In unetched polished sections the various crystalline phases can be distinguished (to a limited extent) from the glass and from one another by their reflectivity, crystal form, and amount of relief. However, positive identification can only be made by treatment of the polished surface with suitable etchants.

TABLE I. Etch properties of some slag phases (successive etching)

| Phase | Etchant | | | | | |
|--------------------|---------|----|-----|------|-------|-----|
| | A | B | C | D | E | F |
| Glass | — | o | o | x-xx | x-xxx | .o |
| Dicalcium silicate | xo | xo | xxx | xxx | xxx | xxx |
| Merwinite | — | — | xx | xxx | xxx | xx |
| Monticellite | — | — | — | x | xo | o |
| Melilite | — | — | — | x | x | — |
| Forsterite | — | — | — | — | — | — |
| Spinel | — | — | — | — | — | — |
| Periclase | — | — | — | — | x? | xo |

x slightly etched
 xx etched
 xxx strongly etched

o stained
 xo etched and stained
 — no visible attack.

- A. 1 % borax in distilled water—etching time 10 minutes at room temperature (20–23° C).
- B. 10 % NaOH in distilled water—etching time 5–10 minutes at room temperature.
- C. 5% NH₄Cl in distilled water—etching time 90 seconds at room temperature.
- D. 10 % HCl in distilled water—etching time 10 seconds at room temperature.
- E. 5 % HF in distilled water—etching time 5 seconds at room temperature.
- F. Distilled water—etching time 10 minutes at boiling-point—applied after special polishing treatment as described below.

A number of different etchants have been used successfully by various investigators for the identification of phases in cement clinker, basic refractories, and slags. A large number of these etchants and others were tried on the high-magnesia granulates. It was found that successive etching with the etchants listed in table I gave the best results for distinguishing between the various phases present in the granulates.

Etching is carried out by immersing the polished surface in the etchant for the required time, washing briefly in water, then rinsing with alcohol and drying in a blast of warm air. Starting with the 1 % borax solution, the successive etching stages are carried out without repolishing between stages, except for stage F (described below) where a special polishing treatment is necessary for the identification of

periclase. This etching order must always be kept in mind when studying the effect of etchants on polished material, because, although a specific etchant may have no visible microscopical effect on a phase, it could still have an influence on the effect caused by an etchant that is applied subsequently. For example, the glass in granulates is stained and merwinite is etched by a 45-second treatment at room temperature with a 5 % aqueous solution of NH_4Cl if applied to a freshly polished surface; a 60-second treatment at 40°C is, however, necessary to obtain the same effect if the polished surface is first treated for 10 minutes in a 1 % borax solution even though the borax treatment has no visual effect on the glass or merwinite. Furthermore, the behaviour of some phases towards etchants also depends on the polishing technique. Thus, merwinite is not stained or etched by distilled water after 60 seconds if water is used as polishing lubricant during the final polishing process, whereas it is slightly stained and etched by water if alcohol is used as polishing lubricant. Clearly then somewhat different etch properties may be encountered if etching and polishing techniques other than those described above are applied.

The 1 % borax solution attacks dicalcium silicate but has no effect on any of the other phases. The NaOH treatment stains the glass but does not affect any of the crystalline phases. The intensity of coloration of the glass, however, depends largely on its composition. MgO -high glasses ($\text{MgO} > 15\%$) are distinctly coloured after a 5-min etch with NaOH at room temperature, whereas MgO -low glasses ($\text{MgO} < 10\%$) are attacked only very slightly. Longer treatments with the NaOH solution, or treatments at higher temperatures, enhance the stain on MgO -low glasses. Such treatments are, however, unnecessary if the sample is given a subsequent treatment with the NH_4Cl solution. This etchant etches merwinite and enhances the coloration of the glass. In contrast to NaOH , it stains the MgO -low glasses more readily than the MgO -high ones, with the result that a 5-min treatment with 10 % NaOH , followed by a 90- to 120-second treatment with 5 % NH_4Cl , provides a sharp distinction between glassy and crystalline regions and in addition allows the identification of merwinite.

The HCl etchant removes the stains caused by NaOH and NH_4Cl from the glass and brings out scratches on monticellite and melilite. Fine scratches also begin to show on the glass. A subsequent 3-second treatment of the same specimen with the HF etchant distinguishes between monticellite and melilite in that the former is stained whereas the latter is only slightly more etched than after the HCl treatment.

The MgO-high glasses are only slightly etched, and at places slightly stained, after the HF treatment, whereas the MgO-low ones are strongly etched by this treatment.

While the HF treatment has no effect on spinel, it causes etch pits to develop along the grain boundaries of forsterite and also a slight roughening on periclase. The roughening is, however, not sufficient to be of diagnostic value, but positive identification of periclase can be achieved by the following treatment: The specimen is first polished according to the techniques previously described; after this it is 'polished' for at least 2 minutes under moderate pressure on a dry canvas cloth, free of polishing powder and using a speed of about 1000 rpm; it is then treated for 10 minutes in boiling distilled water. This treatment, while etching the merwinite and leaving a slight stain on the glass and monticellite, has no marked effect on melilite, forsterite, or spinel: the surface of periclase is, however, roughened, etched, and stained, thus allowing its identification (plate VI, figs. 9 and 10). Polishing under moderate pressure on a dry cloth is essential, or else the water treatment will have no effect on periclase. The heat and stress developed during the dry polishing probably brings the surface of the periclase crystals into a metastable condition and the etch effect obtained is probably due to the hydration of the metastable MgO to brucite.

Detailed observations. *Dicalcium silicate* cannot crystallize from the high-magnesia blast-furnace slags that prevail at the South African Iron and Steel Industrial Corporation; it was accordingly not detected in any of the granulates investigated. Its etch properties were studied on polished sections of basic refractories and are included here because it is a probable slag phase.

Parker and Ryder (1942) recommend a one-minute etch in a 10 % MgSO_4 solution at 50° C for the detection of dicalcium silicate in the presence of other slag phases. Snow (1947) recommends a 10- to 60-second etch in distilled water to distinguish between merwinite and dicalcium silicate. It was, however, found that both these reagents also etch merwinite if alcohol is used as lubricant during the final polishing stage. A search for a more suitable reagent finally led to the 1 % borax solution. Konopicky and Trojer (1947) claim that this reagent colours tricalcium silicate but has no effect on dicalcium silicate. The author's experience on minerals that had been identified by optical and X-ray methods is that tricalcium silicate becomes iridescent and dicalcium silicate becomes brown after a 10-minute treatment with the 1 % borax solution; because tricalcium silicate does not occur in blast-furnace

slags and because none of the other slag phases is attacked, this borax reagent is exceptionally suitable for detecting dicalcium silicate in blast-furnace slags.

Merwinite has a higher mean refractive index than glass and can thus be distinguished from the glass in unetched polished sections by its somewhat higher reflectivity. Spinel and periclase also exhibit a higher reflectivity than the glass but merwinite can easily be distinguished from them, since they both stand out in relief after a 30-second polish with alumina, whereas this treatment does not bring out any relief on merwinite.

Two types of merwinite crystals occur in the granulates, subidiomorphic crystals of up to 0.4 mm in length (plate II, fig. 1) and dendritic crystallites (plate II, fig. 2). The former probably crystallized prior to granulation and the latter during granulation. This conclusion is based on microscopic observations made on blast-furnace slags with the aid of the hot-wire technique. It was found that at a slow rate of cooling merwinite crystallizes as tabular crystals but that a fast rate of cooling, such as quenching, results in the formation of dendritic crystallites (plate III, fig. 3).

Merwinite, while unattacked after the NaOH etch, is well etched after a 90-second treatment with 5 % NH_4Cl , the crystals exhibiting the characteristic twinning structure (plate II, fig. 1). This treatment leaves only a very slight stain on the larger crystallites whereas the small crystallites are stained markedly.

Monticellite occurs most commonly as skeleton crystals and as subidiomorphic to idiomorphic crystals (plate III, fig. 4), which depending on their orientation are acicular to tabular. The tabular crystals are usually six-sided in habit.

In unetched polished sections, monticellite can only be distinguished with great difficulty from the glass host owing to a close similarity in their mean refractive indices and also because of the absence of surface relief. While monticellite is not affected by the 5 % NH_4Cl reagent, it is slightly etched after 10-second treatment in 10 % HCl and surface scratches then show clearly on it. Melilite behaves similarly but a sharp distinction between melilite and monticellite can be observed after the 3-second treatment with 5 % HF. This etchant stains monticellite in various shades of brown to iridescent, whereas the melilite is not stained but etched only slightly more than after the HCl etch.

Melilite crystallizes in the tetragonal system and occurs throughout as perfect idiomorphic crystals of prismatic habit, appearing as rectangles

with a square outline in basal sections (plate IV, fig. 5). 'Peg structures', a characteristic feature of melilite, are commonly present and in the granulates these result from glass inclusions in the crystals (plate IV, fig. 5).

In unetched sections melilite, like monticellite, is only distinguished with great difficulty from the glass host. The boundaries of some crystals are marked by highly reflecting submicroscopic particles which are tentatively identified as oldhamite (CaS). In etched sections melilite is identified by a slightly etched, but unstained surface, after the 3-second treatment with 5 % HF.

The melilite present in the granulates that were investigated has a mean ω 1.653 ± 0.002 , which, according to the curves of Winchell and Winchell (1956), indicates an isomorphous mixture of more or less equal proportions of gehlenite and åkermanite.

Forsterite occurs as granular to idiomorphic crystals (plate IV, fig. 6) and can be identified in unetched sections in that it has more or less the same reflectivity as the glass host but stands out in relief; periclase and spinel also stand out in relief but have a somewhat higher reflectivity than the glass. The surface of forsterite remains unattacked after the HF treatment which, however, causes the formation of etch pits along grain boundaries (plate IV, fig. 6).

Periclase and spinel can readily be distinguished from the other slag phases in unetched sections in that both stand out in relief, have a higher reflectivity than the glass host, and occur as more or less equidimensional crystals and grains. Distinction between these two phases is, however, less easily achieved; the polished surface of spinel is smoother than that of periclase but this phenomenon is only of significance when the two phases occur next to each other in the field of observation.

In an advanced stage of crystallization distinction is made possible by the habit of the crystals; spinel then occurs as idiomorphic crystals whereas periclase always occurs as spherical grains and as skeleton crystals (plates V and VI, figs. 7-10). However, in the initial stages of crystallization both phases occur as minute spherical grains; this prevents positive identification so that etching becomes necessary.

Experiments with a great variety of etchants were carried out but without success. Treatments with strong solutions of HCl and HF do etch periclase without showing any effect on spinel, but such treatments also attack the glass host to such an extent that further microscopic observations become impossible. Selective etching of periclase was,

however, achieved by giving the sample the special polishing treatment described above.

Quantitative determination of crystalline phases

Several methods are at present in common use to carry out micro-metric mineralogical analyses on polished or thin sections. These methods are described in various textbooks on microscopy and need no further description. It should be mentioned though that the most satisfactory method of analysing materials with textures such as granulates is the linear method, which allows volume percentage determinations with the aid of a recording micrometer stage.

For micrometric analyses the ability to identify every phase encountered during traverses is essential; in the granulates this can only be achieved by selective etching. Because no single etchant will permit positive identification of all the phases present in granulates, it follows that repeated analyses on the same specimen, etched successively with various reagents, are necessary for a complete analysis. The procedure can be summarized as follows:

First the polished specimen is etched for 10 minutes in the 1 % borax solution and is then analysed for dicalcium silicate. Next, the same specimen is subjected to the 10 % NaOH and 5 % NH_4Cl etchants; this allows micrometric determinations of merwinite and dicalcium silicate (etched), of glass (stained), and of other phases (unattacked).

Thirdly, the specimen is etched in the 10 % HCl solution for 10 seconds, rinsed and dried, and immediately etched with the 5 % HF solution for 3 seconds. After this treatment the specimen is micro-analysed for monticellite (stained crystals), for melilite (scratches show on surface but no stain), for forsterite (no scratches on surface but etch pits along grain boundaries), and for periclase and spinel (not attacked, higher reflectivity than forsterite).

Finally, the sample is given the special dry polishing and boiling water treatment (described above) to etch and stain periclase. The sample is then finally microanalysed for periclase and spinel.

Micrometric mineralogical analysis is a monotonous task; it is even more so if repeated analyses have to be carried out on the same specimen. Fortunately, however, granulates usually contain only one or two crystalline phases in measurable quantities; other phases may be present, but only in traces, so that the complete procedure as outlined above is seldom necessary to determine the principal crystalline phases. It is thus advisable to examine a specimen to determine what phases are

present and then to decide which of the steps given above are necessary before starting with micrometric analyses. Furthermore, for samples that do not contain both melilite and monticellite the HF etchant is unnecessary and should be avoided. The second of the above steps is the most efficient for routine glassiness determinations on granulates.

Discussion

Primary phase determinations and investigations regarding crystalline content have been carried out on some 40 granulates in which SiO_2 varied from 32.5 to 37.6 %, Al_2O_3 from 10.0 to 12.6 %, CaO from 28.7 to 42.7 %, and MgO from 5.4 to 20.3 %. Most of these granulates were produced at an off-furnace plant that employs the intermediate agency of slag ladles. Some granulates contain only traces of crystalline phases but in others, mainly those produced at the off-furnace plant, these phases are present in quantities up to 20 % by volume.

The principal crystalline phase in a granulate is its primary phase or, for granulates whose composition falls close to the phase boundaries of the primary phase, the primary and secondary phases. This means that the conditions in the hearth and the rate of cooling of the slag in the ladles are such that crystallization takes place under near-equilibrium conditions.

The conditions under which periclase can crystallize from slags and the reasons why it has not been reported in the literature as a slag phase fall outside the scope of this paper and will be discussed in detail in a later publication. The fact that periclase does occur in some granulates is, however, of importance since it may cause unsoundness of cement made from such slags. It may be mentioned here that periclase was detected in only a few of the high-magnesia granulates, that the highest quantity observed was 2.3 % by volume, that autoclave expansion tests were carried out on all these granulates, and that even for a slag with 2.3 % by volume of periclase, the autoclave expansion after 1 hour was only 0.16 %, which is well within the expansion limitations laid down by cement specifications.

Acknowledgements. Appreciation is expressed to Drs. F. E. Malherbe and J. N. van Nierkerk for reading the manuscript; to Mr. P. A. Sterling for reproducing the photographs and to the junior staff of the Mineralogical Section of the Research and Process Development Laboratories for assistance in the preparation of polished sections. This paper is published with the permission of the Management of Iscor.

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EXPLANATION OF PLATES II TO VI

- PLATE II. FIG. 1. Twinned crystal of merwinite in a granule of glass. Etched. $\times 175$. FIG. 2. Dendritic crystallites of merwinite in a granule of glass. Etched. $\times 175$.
- PLATE III. FIG. 3. 'Hot-wire' loop holding in glass a single crystal of merwinite composed of a core formed by slow uniform growth and a rim of quench material. Transmitted light. $\times 125$. FIG. 4. Skeletal, tabular, and acicular crystals of monticellite in granules of glass. Etched. $\times 175$.
- PLATE IV. FIG. 5. Rectangular crystals of melilite in granules of glass. Note the 'peg structure' caused by inclusions of glass. Etched. $\times 175$. FIG. 6. Subidiomorphic crystals of forsterite in a granule of glass. Note the pitted grain boundaries caused by the HF etchant. Etched. $\times 175$.
- PLATE V. FIG. 7. Idiomorphic crystals of spinel and skeleton crystals of periclase in a granule of glass. Unetched. $\times 175$. FIG. 8. Skeleton crystal of periclase in a granule of glass. Unetched. $\times 175$.
- PLATE VI. FIG. 9. Crystals of periclase and spinel in a granule of glass. Unetched. $\times 175$. FIG. 10. Same field as fig. 9 after applying special treatment to etch periclase. Periclase now stained and etched, glass stained, and spinel unattacked. $\times 175$.

[*Manuscript received 23 April 1964.*]

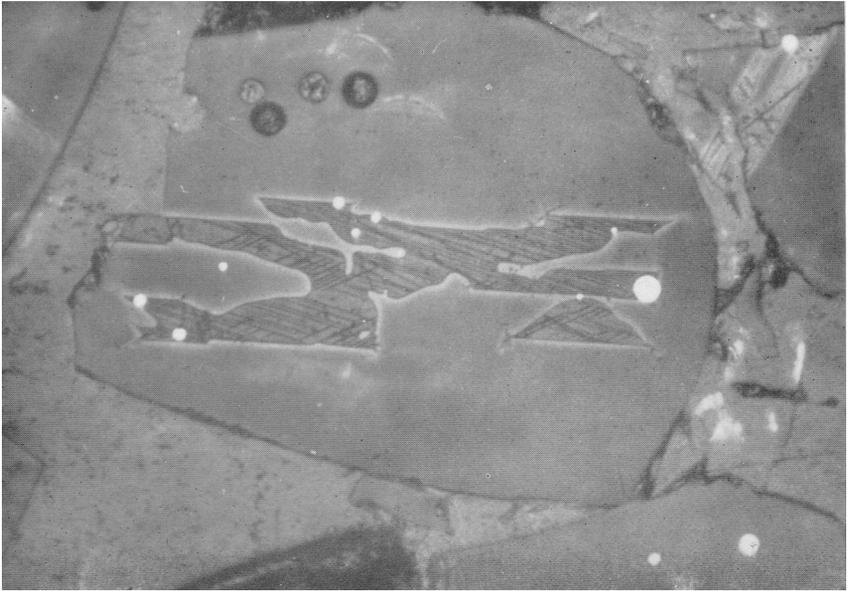


FIG. 1

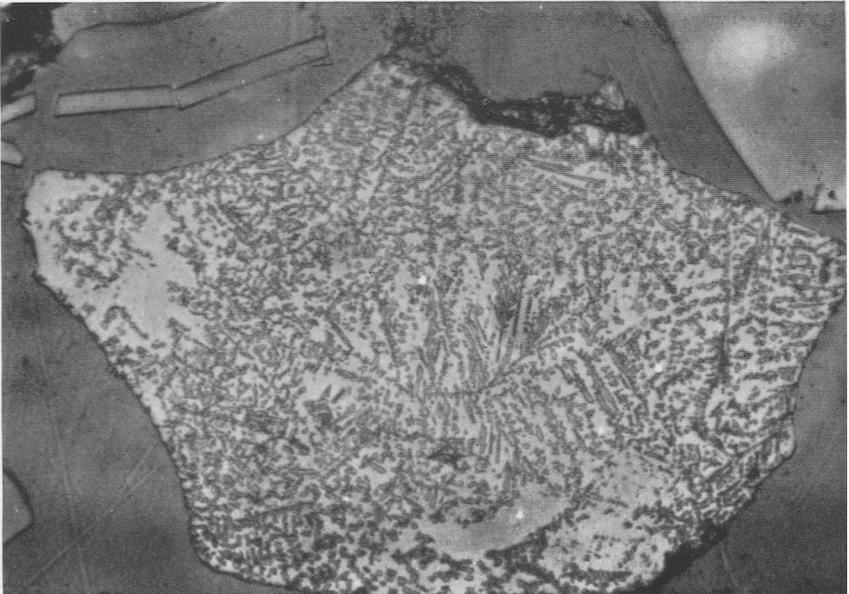


FIG. 2

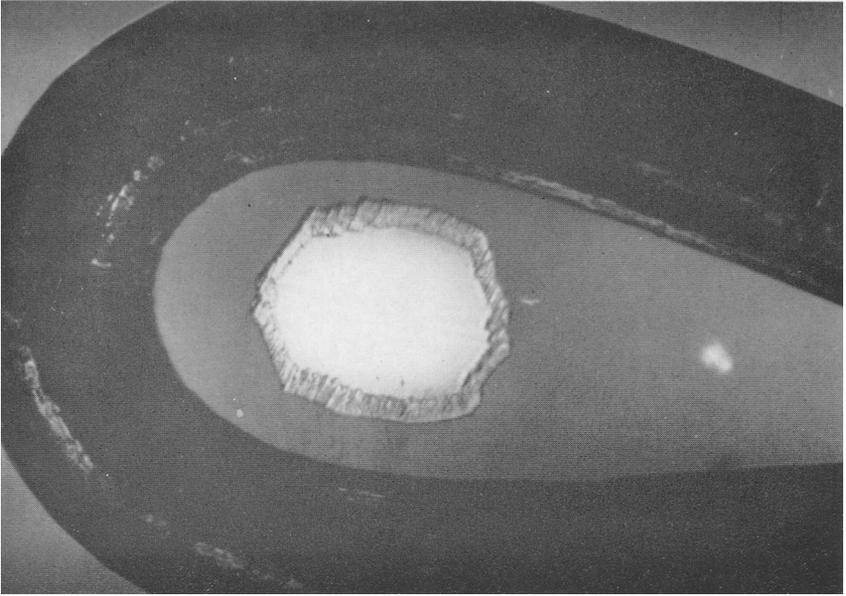


FIG. 3

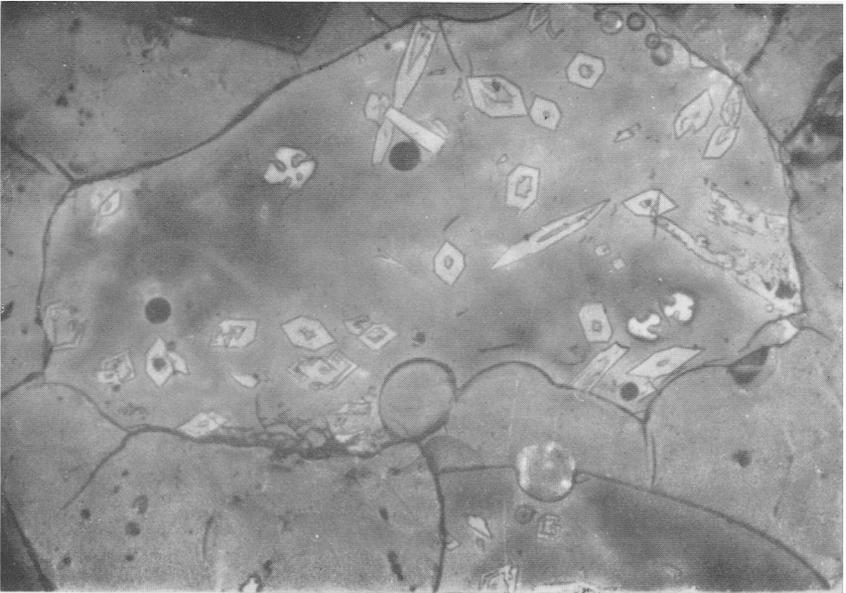


FIG. 4



FIG. 5



FIG. 6

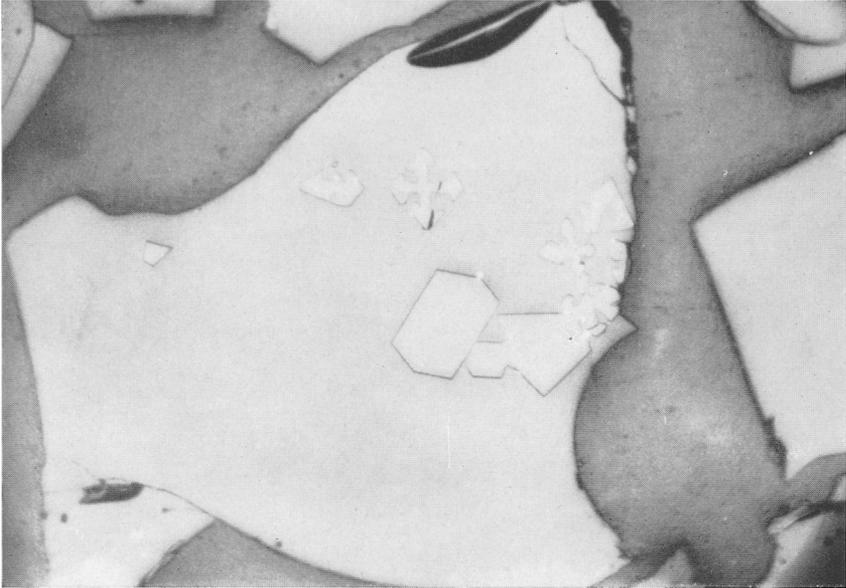


FIG. 7

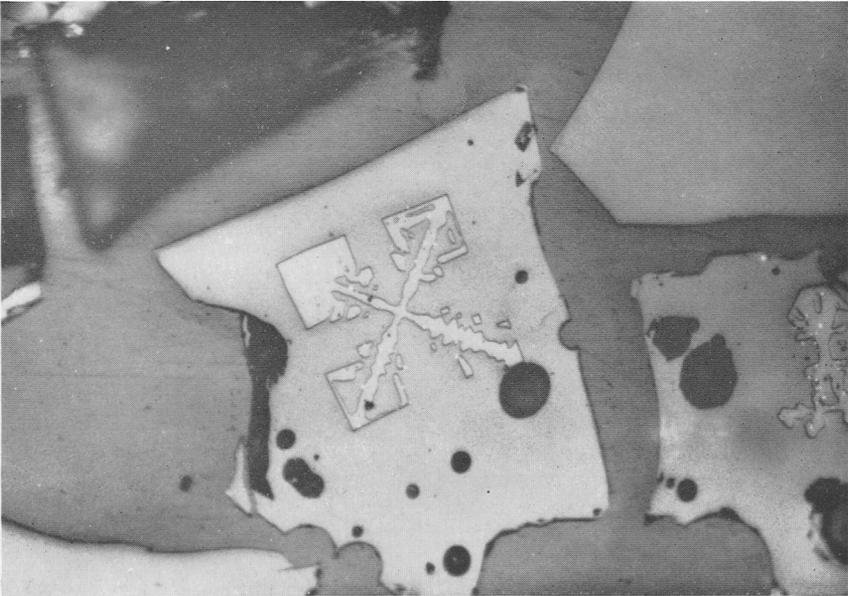


FIG. 8

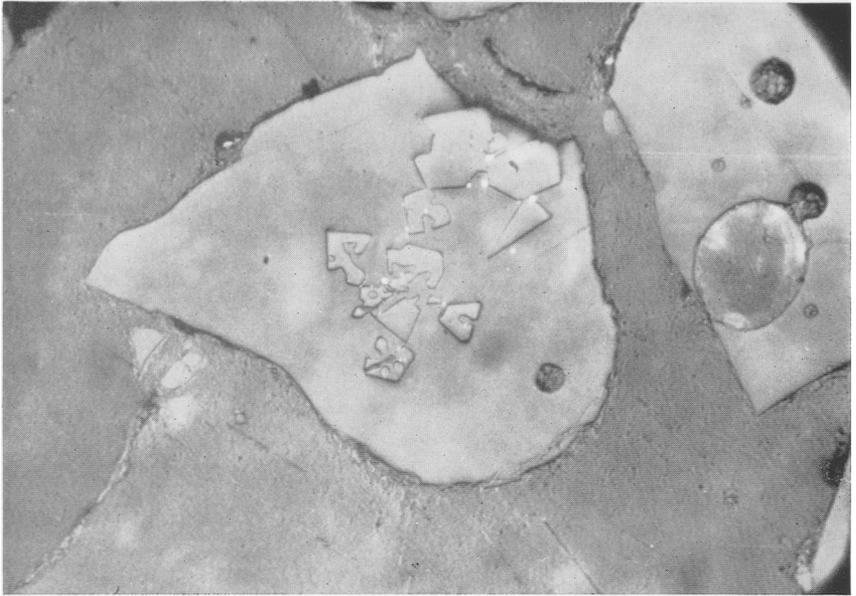


FIG. 9

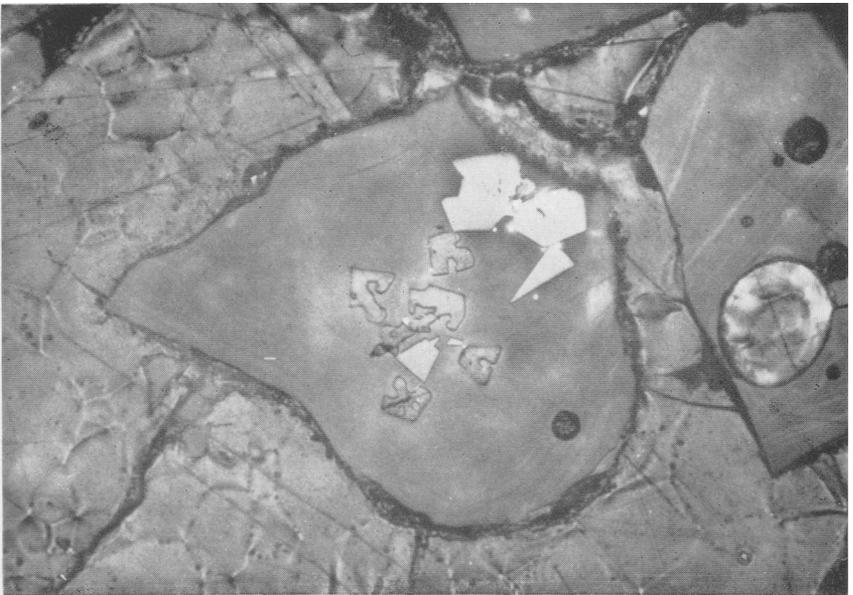


FIG. 10