Molten Silicates
and their Properties

Molten Silicates
and their Properties

by B. Lőcsei

Contents

Chapter I

Introduction

The rapid technical development in the 20th century has raised demands for the preparation and application of more and more new structural materials. Of the non-metallic materials, besides the various plastics, the importance of the application of glass and of other silicate products is on the increase. In the latter group belong the substances which may be classified under the collective term "molten silicates" and which up to the first half of the 1950's were exclusively the by-products of rock processing. Earlier the crystallization of glass was an undesirable source of defects in glass manufacture. For this reason the study of crystallization ability is of special importance. At the same time the efforts to avoid crystallization threw light on crystallization conditions both from the theoretical and practical aspect. The information gained in this field may be utilized for both reducing and promoting crystallization tendencies whereby methods to control crystallization ability are being evolved.

RÉAUMUR was the first to attempt a transformation of glass into a crystalline substance, but all his experiments were frustrated by the deformation of the material during the crystallization process.

In the last 20 years RÉAUMUR's old idea was brought up again, but now enriched by significant theoretical silicate chemical content to produce ceramic products by way of glass crystallization. Under the collective denomination of "molten silicates" we now understand ceramic materials produced from one or more base materials by melting. The material is molded in its liquid state like any other viscous material and converted in its bulk into a crystalline state by thermal treatment during cooling to avoid any significant change in shape, that is deformation, during thermal treatment [1].

Molten silicates may be classified into two groups:

(a) Crystallization of the first type begins at a higher temperature during molding. The thermal treatment after molding only completes this process. This type of crystallization may be considered primary crystallization from the aspect of the "thermal past" of the substance. Crystallization begins during cooling when the crystallization temperature range is primarily reached, after having reached the liquidus temperature, that is the material has cooled below the liquidus temperature.

Into this group belong mainly molten silicate products obtained by melting of rocks and slags. This method is applied primarily to the processing of basalt and diabase [2–14].

(b) In the second group belong the molten silicates called by HINZ [15] vitroceramics. These are characterized by being shaped in the glassy state

and by the fact that their crystallization begins during thermal treatment following forming at a lower temperature and proceeding towards higher temperatures where the crystallization process is terminated. This type of crystallization operation may be considered secondary, since during the crystallization process the substance reaches a second time the temperature range of crystallization. In addition, nucleators are usually added in the course of preparation. Nucleators are small quantities of additives which bring about deformation-free crystallization. This, that is nucleation kinetics, is the theoretical surplus of silicate chemistry by means of which RÉAUMUR's idea could be realized. Nucleators at the same time provide a possibility of varying the composition between wider limits and of arriving at more favorable material structures.

In this book the author could of course not attempt to discuss all the problems of vitroceramics, firstly because of only a limited available space. His analysis will refer mainly to vitroceramics in the SiO_2–Al_2O_3–CaO–MgO–Na_2O system and to the mechanism of metal sulphide nucleation. He will also report his own results with heavy metal sulphide nucleating agents and his "micro-eutectic" principle. In the discussion of general theoretical problems he will also deal with certain aspects of TiO_2 nucleation and this mainly for the sake of comparison, e.g. in the discussion of nucleation, that is of heterogeneous crystallization mechanism, he will demonstrate the control of TiO_2 nucleation by means of sulphide, selenide and telluride, respectively.

Molten silicates owe their utilization as structural materials partly to their favorable mechanical and chemical properties. In addition because of some other advantages, e.g. dielectric properties, they play an important role in many industries. The basic principles of preparation of vitroceramics were evolved in the past 20 years and the commercial manufacture of various material types was commenced in the near past.

Chapter II

Historical

It appears from the available literature that basalt melting was first performed in 1777 in France by d'ARCEL who, in the course of studying the crystallization conditions of magma, melted basalt in a porcelain crucible [3]. At the end of the 18th century the geologist GOLLOW [2] carried out also some work on the melting of eruptive rocks, and found that depending on the conditions of cooling, molten basalt will solidify to form either a vitreous or a crystalline solid. Somewhat later HALL and WATT melted basalt in a crucible and in a small rotation furnace. FOUQUÉ and MICHEL-LÉVY [1, 3] also carried out some important work in this field. They prepared synthetically a product corresponding petrographically with basalt, and thus, it was demonstrated that the method of cooling has a role in the textural structure of eruptive rocks – besides the chemical composition. They stated that "the origin of eruptive rocks is the consequence of their melting, followed by a slow cooling". Their method at the same time raises the probability of producing such synthetic materials with compositions differing from that of natural basalt and their composition number adjusted so as to give the optimum application properties to the material. FOUQUÉ and MICHEL-LÉVY did not measure temperature in their experiments and their explanations concerning the phenomena are not right because of the basic concepts of silicate chemistry at that time were not yet clarified. Obviously they did not know the laws governing the solidification of heterogeneous systems [16].

In 1837, a German scientist, BISCHOFF performed experiments on basalt melting. He poured about 350 kg of basalt melt into a clay mold and succeeded in crystallizing the melt. ADCOCK was the first taking out a patent for invention on the melting of basalt and the processing of the melt in the middle of the past century. He wanted to make glass from molten basalt, but did not envisage the difficulty that the basalt melted by blowing may not be molded because of its crystallization on heating. Thus if the ball on the blowing iron is again immersed in the melt, the already blown material will crystallize as shown by Hungarian experiments, too. In the production of large articles cooling rate was not high enough to allow the material to cool in a homogeneous vitreous state and the formation of crystal nuclei made the material brittle. This explains why was ADCOCK's invention a failure and completely forgotten [3].

The Mauritian French doctor RIBBE carried out some melting experiments with French basalts, and established the conditions for their melting and thermal treatment. Later the engineer DRIN investigated the application possibilities of the material in industry. As a result of their work the Compagnie Générale de Bazalte was founded in Paris having two factories,

one in the vicinity of Paris working with gas-heated furnaces and a daily capacity of 10 tons, the other in Auverigne with a capacity of 8 tons per day, and using electric melting furnaces [1, 6, 9].

In 1922 a basalt melting plant was established in Kahlenborn in Germany on the basis of French literature data and experience. In the 1920's the Soviet Union too began research on the melting of basalt, in 1926 GINZBURG in the Laboratory of the Rock Research Institute and FLORENSKII in the State Research Institute for Electrotechnique were working on the problem [2]. The laboratory experiments were soon followed by pilot plant trials on whose experience a factory with a yearly capacity of 5000 tons was built. The first diabase works started operation in Moscow in 1932. Experiments have shown the diabases from the Oniega district to have the most favorable technological properties. In Leningrad the Armenian andesite-basalt deposits were investigated and an appropriate technology for their processing worked out.

After World War II Czechoslovak specialists also began to be interested in molten silicates, since they had some earlier favorable experiences with molten basalt of German origin. They began their experiments in 1948 and within a few years had two plants operating with daily 16 and 10 ton capacities, respectively and today it has become necessary to plan for expansion. Poland set up a similar factory in 1954 [17–19].

In Hungary investigation of the production conditions of molten silicates began in the Glass Department of the Research Institute for Heavy Chemical Industries in 1951. Beside basalt melting experiments another type was also elaborated first on furnace slag base and later, after having clarified the role and essence of nucleation, a general process based on oxide synthesis and independent of the base material was envisaged. This work may be considered the first step in the production of vitroceramics or of ceramics produced by the nucleated crystallization of glasses. LŐCSEI and his research group have applied first in 1951, then in 1953 and 1957 for patents covering the production of secondarily crystallizing vitroceramics [20–23].

BECKER has prepared as far back as the 1930's primarily crystallizing molten silicates with high fluorine content [30, 31]. Later in 1952 WAGNER also produced crystallizing materials with high fluorine content.

STOOKEY applied in 1953 for patents covering pyroceramic and photoceramic materials which resulted from the development of photosensitive glasses. The material was prepared on lithium silicate, lithium magnesium aluminum silicate base with metal (Ag, Au, Cu) and TiO_2 nucleation [25–29]. In the Corning Works thorough research is in progress under STOOKEY's direction leading to four main types [28]. POLINSZKY and LŐCSEI have reported on the production possibilities of vitroceramics on furnace slag base [81]. In 1956 LUNGU [32, 33] published his results on a vitroceramic in the SiO_2–Al_2O_3–MgO–Na_2O system produced by fluoride nucleation. This was followed by types worked out in Great Britain as a result of the work of CLAYPOOLE, MACMILLAN, PARTRIDGE and HODGSON in the years between 1959 and 1963 [34–39].

In the Soviet Union a new type of vitroceramic material was marketed n 1960 under the trade-name "Sital" [40]. RINDONE studied the nucleation

mechanism of lithium aluminum silicate crystallization when metallic platinum is added [41].

Since 1960 research is in progress in many institutes of many countries aiming at the preparation of new vitroceramics and at the clarification of silicate chemical processes [42–68]. In 1960 HINZ and WISHMANN produced a molten silicate of microcrystalline structure from copper slag glass obtained by melting and by the addition of Cr_2O_3.

HINZ and KNUTH studied the effect of small quantities of diverse additives on the properties of pyroceramic type materials in the $Li_2O–Al_2O_3–SiO_2$ system [69].

In the Institute in Hradetz-Kralove VOLDAN is engaged in the investigation of the silicate chemical principles of vitroceramic materials and BROUKAL in that of pyroceramic soldering vitroceramics [70, 71].

In the Soviet Union vitroceramics on furnace slag base are being produced since 1962, in Poland since 1964, in both countries production is based on principles which are in agreement with LŐCSEI's experimental results [72, 73]. VOGEL and GERTH [74] and later MAURER [75] clarified many details of the nucleation mechanism and the importance of homogeneous and heterogeneous catalysis.

The study of vitroceramics received particularly great impetus in the past years both from the theoretical and the engineering aspect producing a continuous succession of new results. Interest is focused on the kinetical and thermodynamical study of nucleation [173–179]. The properties of lithium aluminum magnesium silicates nucleated with phosphates were studied by PARTRIDGE and MACMILLAN who found a new method for the processing of vitroceramics [194, 196]. The development of vitroceramics which may be used as solders is to a major part also the merit of these authors [197]. HODGSON and MACMILLAN reported on neutron absorbent vitroceramics [198]. Control of crystallization tendency and within this of crystallization rate by means of the combined application of nucleating agents is again a theoretical result which will obviously bring about an extension of the composition of vitroceramics [171].

An interesting development of the research on vitroceramics is the improved strength by surface treatment. When vitroceramics immersed in some liquid salt are subjected to heat treatment, the surface layer will shrink as a result of ion exchange and a compressive stress will develop resulting in a considerable improvement of crushing strength. KARSTETTER et al. in the Corning Works have been engaged in the study of this problem [186–193].

Another recent result is the influencing of the crystallization mechanism to form on the surface of the vitroceramic material a crystalline layer of different structure in a single operation during crystallizing thermal treatment. This is another recent solution to improve the flexural strength of vitroceramics [171].

The new possibility of coloring vitroceramics has also extended the application possibilities of these materials [181, 184]. Materials with high thermal expansion coefficients in the $SiO_2–P_2O_5–Al_2O_3–CaO–MgO$ system or vitroceramics with ZnO or BaO content can be coated with metals [180,

189]. Application to other ceramics and to metals has also opened new perspectives to these materials.

The importance of vitroceramics is indicated by the conferences on this subject such as were held in Toronto in 1961, or in Prague in 1967 in addition to a large number of national symposia. At the International Conference in London in 1968 a special section discussed the problems related to vitroceramics [181, 182, 183, 185, 195, 199]. As another sign of the importance of vitroceramics the Department of Glass Technology of the Mendeleev Institute in Moscow has changed its name to Department of Glass and Sital (vitroceramics) Technology.

Today, though vitroceramics are manufactured on the commercial scale, there are still many unsolved problems to interest the scientist, including the full possibilities of nucleation, the mechanism and kinetics of nucleation and heterogeneous catalysis, the effect of the composition of the base glass, refining of the structure, improvement of the physical and chemical properties of the materials and the revealing and extension of application possibilities.

Basic principles of molten silicate production

The production of the first group of molten silicates, that is of molten rocks, is based on the choice of a rock composition which after melting will have a crystallization ability to initiate the crystallization process in the course of molding. The low network forming and modifying cation ratio of the basalt and slag melts is in fact the primary cause of the high crystallization ability, while primary crystallization during cooling may be attributed to the presence of residual crystal nuclei in the melt [70]. This crystallization commencing at a high temperature will ensure later, when crystallization under the effect of heat treatment has been completed, the permanent molded shape of the material and its cooling without deformation or cracking.

In the case of vitroceramics on the other hand the composition of the base material has to be chosen to prevent crystallization of the melt during shaping. In this case the melt has to be solidified without crystallization. After molding a heat treatment according to a definite program will initiate the separation of the nucleating agent. This primary crystal phase, formed in the material at a lower temperature, will ensure in the course of subsequent heat treatment a deformation-free recrystallization.

Thus in both types the crystallization ability of the base material melt plays an important role to which the presence of nucleating agents contributes considerably, especially in the case of vitroceramics. The fundamental phenomena are essentially the same in both cases. The crystal residues in the rock melts – olivine, magnetite – act in fact like heterogeneous nucleating agents. The difference between the structures of the two types of materials may be interpreted from the relative values of the temperature gradient of the crystallization process and of the two parameters of crystallization tendency, namely of crystallization rate and the number of crystal nuclei. This explains that the texture of molten rocks is an agglomeration of larger single crystals that are found in vitroceramics. This appears quite clearly from the comparison of Figs 1 and 2 representing thin sections of a molten Kahlenborn basalt and a vitroceramic KM2 prepared by LŐCSEI [1] from furnace slag. The magnifications are the same ($500 \times$).

The difference is even more striking when two thin sections of the materials are compared under $1500 \times$ magnification (Figs 3 and 4). On the slide of the molten basalt diopside twin crystals crystallized by leaf-like morphology are visible. One division in the figure is 1 μm. On the slide of the material prepared from furnace slag and called "crystalline synthetic stone" (KM2) the texture of far smaller structural elements is interrupted here and there by some larger crystals [1].

FIG. 1. Structure of molten Kahlenborn basalt. Microscopic picture of a thin section in transmitted polarized light. Magnification: 400×
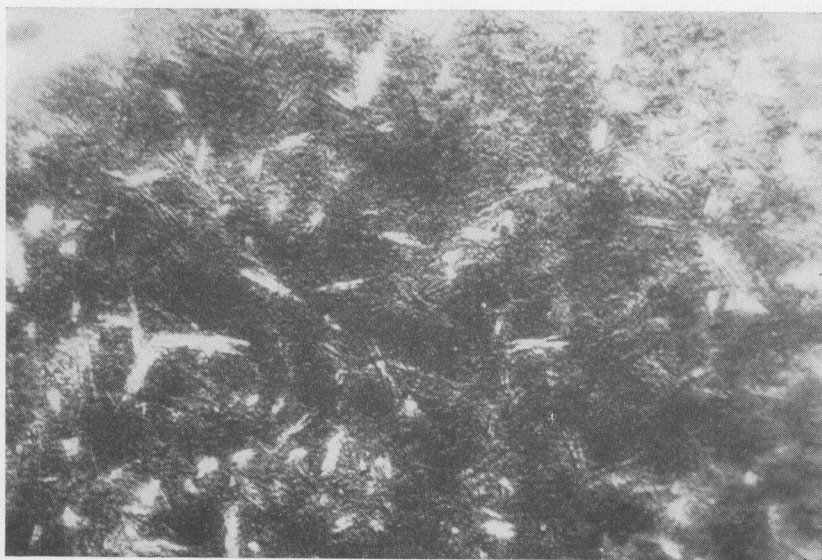

FIG. 2. Structure of a vitroceramic material on furnace slag base. Microscopic picture of a thin section in transmitted polarized light. Magnification: 400×

FIG. 3. Structure of molten Kahlenborn basalt. Picture of the same slide as in Fig. 1 in polarized light. Magnification: 1500×, 1 division: 1 μm
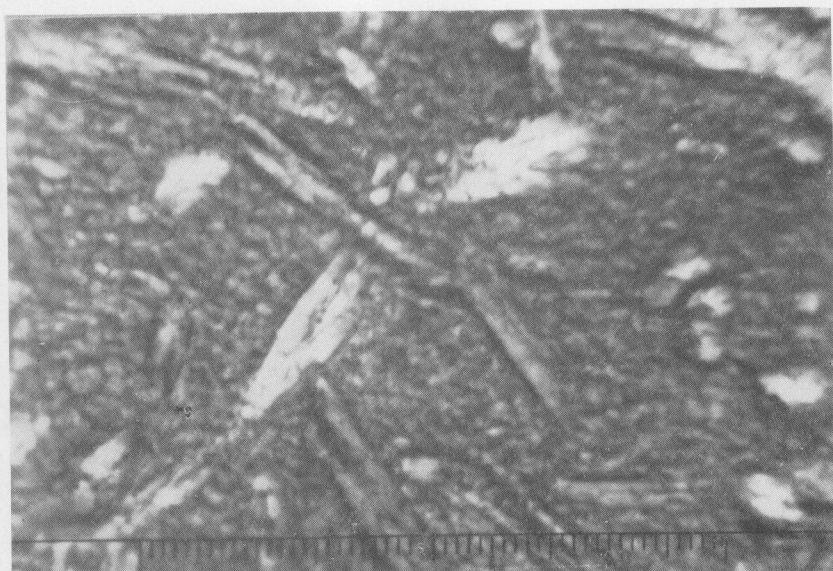

FIG. 4. Structure of a vitroceramic material on furnace slag base. Picture of the same thin section as in Fig. 2 in polarized light. Magnification: 1500×, 1 division: 1 μm

FIG. 5. Structure of Badacsony basalt. Microscopic picture of a thin section. Magnification: $400\times$, 1 division: 5 μm

The texture of vitroceramics consists of birefringent individual crystals of 0.5–3 μm dimension, the larger crystals are often sloping rod or double-rod shaped. In addition black opaque crystals of 0.5 μm diameter also appear in the texture. X-ray diffraction tests identified these latter as iron and manganese sulphide crystals, while chromium oxide crystals are also present. The larger crystals in Figs 2 and 4 have a hexagonal cross-section perpendicularly to their length, their extinction is sloping with different angles in different orientations. In this small dimension it is impossible to identify optically the minerals. Figure 4 is not a sharp picture, since the shape of the crystals is not regular. The dissolved large negative crystals with double optical axes and without preexisted faces are feldspars (Fig. 1). In Fig. 3 the leaf-like crystals form radial bunches according to the crystal form of magnetite which supports the earlier statements on crystal fragments. This characteristic crystal growth also confirms the role of magnetite as a heterogeneous nucleating agent. The development of the leaf-shaped crystals was made possible by the presence of an amorphous phase during crystallization. Well-developed crystal forms can separate from the melt only. The textures in Figs 1–4 were photographed in polarized light. Figure 5 shows for the sake of comparison a thin section of Badacsony basalt.

Beyond the circumstances of crystallization the material properties of molten silicates are also functions of the choice of the base material. The properties of vitroceramics may be varied between wide limits by the modification of their composition.