Instrumentation for *in situ* observation of growth and dissolution processes of crystals in high temperature solutions at 1600°C

Toshiya ABE*, Katsuo TSUKAMOTO and Ichiro SUNAGAWA

Institute of Mineralogy, Petrology and Economic Geology, Faculty of Science, Tohoku University, Aoba, Sendai 980, Japan

Abstract

An instrument for *in situ* observation of growth and dissolution processes of silicate crystals at elevated temperatures up to 1600°C has been newly designed. This instrument consists of a growth cell with a specially designed liquid holder, a digital temperature controller using a highly stabilized DC power unit, an optical microscopic system for *in situ* observation of the processes with transmitted light and a high resolution TV system for recording and displaying optical images. The stability of the temperature around the growing crystal has been improved to satisfy $\pm 0.3^{\circ}\text{C}$ at 1600°C in a high temperature solution of small volume ($\cong 0.06\text{ cm}^3$).

This combination makes it possible to carry out the direct observations not only of growth and dissolution processes of crystals in liquid phases at high temperatures with clarity, but also of the diffusion layers and convection around growing or dissolving crystals. This system has been successfully applied to the diopside-forsterite-silica system.

Introduction

Investigations of the growth and dissolution mechanisms of crystals in high temperature melts and solutions have important implications in both basic science and industry. Since the magmatic crystallization is regarded as high temperature solution growth (Sunagawa, 1977), such studies on silicate systems, supplemented by phase equilibrium studies, will provide a deeper understanding of the kinetics of magmatic processes.

The following methods have been employed in studies of growth and dissolution mechanisms of crystals at both low and high temperatures.

- (1) Measurements and analyses on growth rates versus supersaturation relations (Bennema, 1967 and 1969).
- (2) Detailed observations on step patterns on crystal faces (Sunagawa, 1961).
- (3) Characterizations of grown crystals (Lang, 1964; Tanner, 1976).

However, the recent studies combining these methods have revealed that the

*Present address: Department of Mineralogical Sciences and Geology, Faculty of Science, Yamaguchi University, Yoshida, Yamaguchi 753, Japan.

growth mechanisms concluded only from the measurements on growth rates were sometimes inconsistent with the observations on crystal surfaces (Van Eark *et al.*, 1980; Tsukamoto *et al.*, 1983b; Tsukamoto, 1984).

Recent *in situ* observations have made it possible to observe the movement of even monomolecular steps on crystal surfaces growing in aqueous solutions under well-controlled conditions (Tsukamoto, 1983; Tsukamoto and Sunagawa, 1985), and these observations coupled with precise measurements of growth parameters have provided a direct method to investigate these problems.

Such *in situ* studies are particularly necessary in silicate systems, since various metastable phenomena may occur more frequently in complex multicomponent systems at elevated temperatures, relevant to magmatic processes.

Kirkpatrick *et al.* (1976) have made a trial for *in situ* observations of crystallization in silicate systems. However, the images they obtained did not have enough sharpness for detailed observations and their investigations were restricted to a rather narrow temperature range and short run duration. We also have previously reported (Tsukamoto *et al.*, 1983a) a prototype *in situ* observation system workable up to 1500°C, but it has not been able to control temperature precisely. We have further improved this system, and designed a new instrument workable up to 1600°C with much better visibility and under much stabler conditions.

In this paper, the instrumentation is mainly reported with several examples of *in situ* observations in the diopside-forsterite-silica system. The detailed results will be reported in forthcoming papers.

Instrumentation

In order to carry out *in situ* observations of crystals in high temperature solutions with high visibility, the following two problems have at least to be solved.

- (1) Optical aberration due to the presence of a solution layer and glass plates above and below the crystal, which reduces sharpness of images.
- (2) Strong infrared radiation from the high temperature bodies, mainly from the heater, which reduces image contrast due to the background intensity.

In the prototype system, we utilized the heating stage of a commercial high temperature microscope (Union Co., HHS-4S) as a growth cell, of which the heating element was replaced with the specially designed loop of PtRh₂₀ wire for both heating and holding a thin liquid film. This prototype system had been successful in observing crystals growing in the silicate solution at elevated temperatures, and it had been found that the principal idea and the approaches were proper (Tsukamoto *et al.*, 1983a).

However, the ability to control temperatures was rather poor in the prototype

system because of the difficulty in measuring temperatures, and this difficulty arose from the small volume of the silicate liquid. In order to carry out the direct experiments under well-controlled conditions, we have to overcome this difficulty. In designing a new system, the following points were taken into consideration so that greater stability in controlling temperature and better visibility in observation can be achieved, although the principal idea to heat a liquid film was unchanged.

Growth cell

The growth cell was newly designed so as to enable a larger internal volume, a more sophisticated way of holding the thin liquid films and a manipulator to move a thermocouple. In Fig. 1 and Fig. 2, a schematic draft and a photograph of the growth cell installed on the stage of a microscope are shown, respectively. The thermocouple in this growth cell is mounted in such a way that the tip can be moved with the help of a micro-screw, so that both horizontal and vertical distribution of temperatures in the thin film suspended on the loop can be measured directly. Although it was feared that the temperature gradient in the liquid film might be very large, it was found that the temperature difference between the central portion and the marginal portion, except very near the heater, was about 5–10°C at about 1400°C for the diopside composition. The temperature gradient may be assumed almost negligible, if a single field

FIG. 1. Schematic draft of the growth cell. a: loop heater; b: manipulator; c: thermocouple for measuring liquid temperatures; d: fixed element for electric supply; e: element for gas supply; f: window of fused quartz; g: radiation shield and window; h: thermocouple for measuring heater temperatures.

FIG. 2. Growth cell, G, installed on a microscopic stage, S. C: condenser lens.

FIG. 3. Observation and control system for the growth cell.

of vision of the microscope, $600 \times 800 \mu\text{m}$, is considered.

Temperature measurement and control

A proper temperature control system applicable to a liquid of small volume should be designed to carry out *in situ* observations of the kinetic processes at precisely controlled temperatures.

A commonly applied control system for temperature regulation, for instance, PID system, is made for a furnace with relatively large thermal capacity. However, in the present case the thermal capacity of the liquid and the heater is so small that the stability of the heater current has a serious influence on the temperature. Thus, a perfect heat balance has to be maintained using a stabilized current before regulating the heater current to control the temperature. Otherwise due to the slight delay between measuring and controlling the temperature the resultant fluctuation of the liquid temperature may be accelerated. So the regulation of the current is necessary only when the heat balance varies gradually or when abrupt nucleation of crystals takes place releasing latent heat. This is of course possible based on employing a highly stabilized power unit. The DC power supply, instead of AC, was chosen in the present system so as to minimize the disturbance of TV image due to the alternating magnetic

fields. Necessary equipments were selected from commercially available supplements.

A systematically shown in Fig. 3, temperature is measured by a digital voltmeter (Takeda TR-6877D) employing a Pt-Rh₁₃ thermocouple, 0.075 mm ϕ , from which the data were sent to a microcomputer (Sony SMC-70G), to calibrate the measurement and to send a signal to a DC stabilized power unit (Takasago NL012-100) for controlling electric current to the heater. The microcomputer is also used to display the temperature and other data on the video image. The stability of the voltmeter and the power supply are 0.003% and 0.005%, respectively. The resolving power of the voltmeter is 0.1 μ V. Thus the stability of 0.3°C at 1600°C is guaranteed. Continuous cooling experiments are also possible using this system.

Optical system

To ensure a good resolution particularly at higher magnification, an objective lens should be newly designed so as to minimize the possible optical aberration due to the presence of liquid phase and a window glass plate. An objective lens of 20 times and long working distance 7 mm was newly designed (Olympus TS-20) in cooperation with Olympus Optical Co., Ltd. (Tsukamoto and Sunagawa, 1985), which was used in conjunction with the present system. Though this lens was mainly designed for the use of interference contrast microscopy after Nomarski by incident light illumination, this

FIG. 4. Comparison of images of a growing diopside crystal at 1290°C taken with the new objective lens (a) and a conventional objective lens (b).

FIG. 5. TV image of a growing diopside from its melt at 1380°C under polarized light, showing interference fringes due to the thickness difference. Observation under monochromatic illumination of 490 nm.

can also be used for transmission light. In Fig. 4 the corresponding images of a diopside crystal on a TV monitor taken with (a) newly designed and (b) conventional objective lenses are compared. Clearly visibility increased remarkably by the use of this objective lens.

In addition to ordinary transmission type microscopy, various optical techniques are applicable in this system, including polarization, transmission phase contrast and interference contrast microscopy. By applying these optical techniques, image contrast may be enhanced. As an example, Fig. 5 shows an image under polarized light. The equal thickness interference fringes are produced by polarized light, with which not only three dimensional image of the crystal is pictured out, but also faint growth rate can be measured precisely by measuring the fringe shift. The image contrast on a TV screen can be enhanced further by applying a real time image processor with analogue differentiation (Tsukamoto *et al.*, 1983a).

In *in situ* observation of growth or dissolution of crystals, it is also important to visualize the mass flow (diffusion boundary layer and convection flow) around a growing or dissolving crystal. For this purpose, Schlieren method (Born and Wolf, 1975) can be applied in the present experimental set up, by using a knife edge and a small pin hole in the optical path. In Fig. 6, examples of convection flow and diffusion layer around a dissolving forsterite crystal and a growing tridymite crystal are shown, respectively.

Experimental procedure

Sample preparation

Depending on the purpose and the system to be studied, different sample preparation may be adopted. As an example, description is given of the preparation procedure for the diopside-forsterite-silica system in the following.

Starting reagents (MgO: Wako, SiO₂: Wako, CaCO₃: Junsei) are mixed in a desired composition considering each ignition loss, ground and put into a rubber tube. The tube is pressed hydrostatically under 400 kg/cm² in a piston cylinder device to form a rod. A slice of 0.5 mm thick is cut from the rod, placed on the heater loop and melted by increasing the temperature gradually. In this way, the silicate liquid is prepared in the loop by surface tension. The thermocouple indicated by c in Fig. 1, which is guided with a manipulator, is inserted into the liquid film from above to measure the temperature. The other thermocouple, h, which is in contact with the heater, can be utilized for measuring the heater temperature.

In general, the liquid should be held for a sufficient time usually more than 30 minutes, to ensure homogeneous and complete melting before carrying out experiments.

Preparation of a seed crystal

Crystals do not always nucleate or it may take a long incubation time to nucleate at experimental temperatures, especially at smaller supercooling. In such cases, a kind of seeding techniques can be used to observe crystals growing or dissolving at desired temperatures.

For growth at a smaller supercooling, $\Delta T < 50^\circ\text{C}$, we can nucleate, by suddenly

FIG. 6. Two examples of Schlieren effects, (a) convection currents formed on dissolving forsterite in the liquid composition of $\text{Di}_{70}\text{--En}_{30}$ wt%, and (b) a stable diffusion layer around tridymite during growth in the composition of $\text{Fo}_{61}\text{--SiIica}_{39}$.

FIG. 7. Series of photomicrographs showing the birth of a large number of diopside crystals from a dissolving mother spherulite, S, in the liquid composition of $\text{Di}_{70}\text{--En}_{30}$ (a) at 1430°C , (b) at 1340°C , and (c) at 1330°C .

decreasing the temperature, a minute crystal on the tip of the thermocouple prior to the growth experiment. This procedure can be applied to crystals, forsterite in this studied system, which nucleate comparatively easily.

If crystals appear not to nucleate under these conditions, the following seeding technique is applicable. Firstly, the solution is substantially supercooled so that crystals can easily nucleate. Then the temperature is raised again for a moment so that a part of the liquid containing minute crystals can move slightly upwards to the tip of the thermocouple, to deposit one or a few crystals on the tip. Then temperature is raised so that crystals are dissolved to be smaller in size and number. The surviving crystal can be used as a seed on which growth experiment can be performed at a precisely controlled supercooling. This seeding technique is applicable to observations of crystals, such as diopside in the present case, which nucleate only at larger supercooling ($\Delta T > 200^\circ\text{C}$).

Observation

As a representative example of *in situ* observations at elevated temperatures, the phenomena observable under the microscope are described in the following, using the diopside-forsterite-silica system.

Although precise growth rate R versus supercooling ΔT measurements are made in general on a stably growing crystal at the tip of a thermocouple under small ΔT conditions, various dramatic scenes are also observable when a large supercooling or undercooling is realized. In these cases, crystals are not necessarily nucleated on the thermocouple. An example of such cases will be briefly explained.

Spherulites are usually formed at a large supercooling ($\Delta T > 250^\circ\text{C}$). If the temperature is increased after their formation, they dissociate into a large number of tiny crystallites, which move away quickly from the mother spherulites. Decreasing the temperature during such dissociation, the crystallites start to grow again to form prismatic crystals in the portion away from the mother spherulite. Really dramatic movements and change from dissolution to growth, or vice versa, are observed. Fig. 7 shows a series of photographs showing such a dramatic movement.

Identification of phases

During *in situ* observation, the phases may be identified by characteristic morphology and refractive index. Detailed identifications of the phases can be done on the quenched products by means of X-ray micro-diffractometry and electron probe micro-analysis. Although only a limited number of small forsterite crystals are present in the quenched sample, a very sharp diffraction pattern could be obtained by employing an X-ray micro-diffractometer (Rigaku Denki).

Since we can observe the actual process of crystals, EPMA analyses can be also made on the required portion of both crystals and the surrounding glass quenched in

the desired process.

Application

Only one example of investigations carried out using this instrument will be briefly explained.

Fig. 8 shows a temperature-time diagram of an experiment and photomicrographs of a forsterite crystal corresponding to each step which are indicated by alphabet on the diagram. Several important features can be noticed from this figure.

Firstly, forsterite nucleates freely (in fact prior to the nucleation of diopside) in the diopside stable region on the equilibrium phase diagram by Longhi and Boudreau (1980), and it continues to grow steadily in that region until diopside nucleates and grows very rapidly. The metastable nucleation of forsterite reported by Kirkpatrick *et al.* (1981) is confirmed by the *in situ* observation.

Secondly, with increasing temperature, this forsterite starts to dissolve above a certain temperature. This is confirmed by the change of crystal forms from polyhedral to rounded one. This process is reversible and thus we can determine the melting point of metastably nucleated forsterite, which is about 1305°C for the diopside composition. It was found that the melting points thus measured on different compositions lie on the extension of forsterite liquidus line. This line is taken as corresponding to

FIG. 8. Temperature-time diagram of a programmed experiment, corresponding photographs of the morphologies of a forsterite crystal, and the equilibrium phase diagram.

the solubility curve of forsterite in its metastable region, with which real ΔT value can be calculated. The determination of the solubility curve of a metastable phase, which was impossible in any of the previous experimental method, has now become possible by the present *in situ* observation system.

Details of experimental results on metastable nucleation, growth kinetics of silicates and the *in situ* observation of the growth process of GaAs in a high temperature solution will be reported in forthcoming papers.

Summary

A new instrument for *in situ* observation at elevated temperatures has been designed. This instrument consists of a temperature controller, a newly designed growth cell and a transmission microscope with an objective lens of higher magnification and long working distance.

This system has realized the *in situ* observations of not only growing and/or dissolving crystals but also diffusion layers and convection flows around the crystal. The direct observation is also useful for the study on non-quenchable materials and the kinetics of non-quenchable phase change. *In situ* observations of processes at elevated temperatures have been applied to the diopside-forsterite-silica system to study the metastably nucleated forsterite, and it has been demonstrated that this method was useful.

Acknowledgement—The authors wish to thank Mr. Matsubara, chief director in optical developing section Olympus Optical Co., Ltd. for manufacturing a new lens. Thanks are also due to members of the workshop in Research Institute for Iron, Steel and Other Metals of Tohoku University for designing the growth cell and Rigaku Denki Co., Ltd. for analyzing our quenched specimens by an X-ray microdiffractometer. This work was made by a financial support of a Grant-in-Aid for Fundamental Researches given from the Japan Ministry of Education.

References

- BENNEMA, P. (1967) *Journ. Crystal Growth*, **1**, 278-286.
- BENNEMA, P. (1969) *Journ. Crystal Growth*, **5**, 29-43.
- BORN, M. & WOLF, E. (1975) *Principle of Optics* (5th Ed.), Pergamon Press, London.
- KIRKPATRICK, R. J., ROBINSON, G. R. & HAYS, J. F. (1976) *Journ. Geophys. Res.*, **81**, 5715-5720.
- KIRKPATRICK, R. J., KUO, L. C. & MELCHIOR, J. (1981) *Amer. Miner.*, **66**, 223-241.
- LANG, A. R. (1964) *Proc. Roy. Soc.*, **A 278**, 235-242.
- LONGHI, J. & BOUDREAU, A. E. (1980) *Amer. Miner.*, **65**, 563-573.
- SUNAGAWA, I. (1961) *Amer. Miner.*, **46**, 1216-1226.

- SUNAGAWA, I. (1977) *Journ. Crystal Growth*, **42**, 214-223.
- TANNER, B. K. (1976) *X-ray Diffraction Topography*, Pergamon Press, London.
- TSUKAMOTO, K. (1983) *Journ. Crystal Growth*, **61**, 199-209.
- TSUKAMOTO, K. (1984) *Jap. Journ. Crystal Growth*, **11**, 176-190.
- TSUKAMOTO, K., ABE, T. & SUNAGAWA, I. (1983a) *Journ. Crystal Growth*, **63**, 215-218.
- TSUKAMOTO, K., OHBA, H. & SUNAGAWA, I. (1983b) *Journ. Crystal Growth*, **63**, 18-24.
- TSUKAMOTO, K. & SUNAGAWA, I. (1985) *Journ. Crystal Growth*, **71**, 183-190.
- VAN ERK, W., VAN HOEK-MARTENS, H. J. G. J. & BARTERLS, B. (1980) *Journ. Crystal Growth*, **48**, 621-634.

Received November 15, 1985; revised May 18, 1987.