High Resolution Electron Microscopy In Situ Observation of Dynamic Behavior of Grain Boundaries and Interfaces at Very High Temperatures

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Abstract: Two types of specimen-heating holder have been developed that allow one to observe, at near-atomic resolution, phenomena or reactions taking place at very high temperatures such as 1773K. The performance of the heating holders is described. Some typical examples of results obtained using these holders are given. These include formation of SiC through reaction between Si and C, growth of SiC, formation of a void at a grain boundary in SiC during sintering, surface reconstruction of Au deposited on Si, motion of the solid-liquid interface in Al2O3, and dynamic instability of a grain boundary in CuGa2.

Key words: in situ heating experiment, grain boundary, interface, high resolution electron microscopy, very high temperature

INTRODUCTION

In situ heating experiments have been well established and widely used in a variety of fields of materials science (see, for example, Loretto and Smallman, 1977; Butler and Hale, 1982; Fujita, 1985; Louchet and Saka, 1993; Sharma et al., 1996). However, the resolution of the in situ heating experiments carried out so far, especially at very high temperatures, has not been high enough for information at near-atomic levels to be obtained.

Recently, new specimen-heating holders, which enable one to carry out an in situ heating experiment at very high temperatures, well above 1273K, and at near-atomic resolution have been developed (Kamino and Saka, 1993; Mori et al., 1994). In this paper some typical examples of such in situ heating experiments at very high temperatures will be described.

Figure 1a and b shows the newly developed heating holders. The heating holder shown in Figure 1a has only one heating element (type 1), whereas that shown in Figure 1b has two heating elements (type 2). The latter can be used to observe reactions between more than one material. In both cases, the heating elements used are fine wires (diameter 20–30 μm) of a refractory metal such as tungsten. The heating elements are bridged across a gap of a side-entry-type specimen holder and heated by direct current from dry batteries. Usage of a dry battery as a power source is essential as it can provide a very stable current without any fluctuation, which affects the quality of a transmission electron microscopic (TEM) image.

The temperature of the heating element is calibrated either using an optical pyrometer outside the microscope or by observing the melting of a piece of pure metal such as Au or Al inside the microscope. Figure 2a shows an example of the calibration curve. A very high temperature such as...
1773K can be achieved with a very small current, e.g., 250 mA, as the thermal mass of the heating element is very small. Because of the small thermal mass, the drift of a specimen during heating is very small, as is shown in Figure 2b; this allows one to record a high-resolution electron microscopic (HREM) image on an ordinary EM film even at very high temperatures.

In addition, since the heating element has a very small physical volume and is not surrounded with a massive insulator, as in the case of an indirect-type specimen-heating holder, X-ray noise from the heating holder is so low as to make an EDX analysis possible. An example of EDX analysis is shown in Figure 3. Here, a specimen of Si was used. The noise level is very low, and up to 973K the peak of Si remains unchanged; it is not until the temperature reaches 1023K that the peak of Si broadens and a peak from the infrared appears. However, even under such circumstances, as was already mentioned, the thermal mass of the heating element is very small, and the specimen temperature can be controlled very quickly whenever required. In other words, recording of an HREM image at high temperature, say, at 1773K, and EDX analysis at room temperature can be carried out alternately during an in situ heating experiment.

The specimens of the shape of fine particles are mounted directly onto the heating elements. After mounting the specimens onto the heating elements, the specimens are blown with a blower, so that only those particles attached firmly to the heating elements are transferred into an electron microscope. In the case of the type 2 heating holder (Fig. 1b), the specimens to be observed are mounted onto heating element 1. Heating element 2 is used to deposit a metal onto the specimens mounted onto heating element 1. The distance between the two heating elements is approximately 2 mm.

Although the heating holders can be used in any type of microscope equipped with a side-entry goniometer, the particular one used mostly in this study was a Hitachi H-9000 NAR analytical microscope operated at an accelerating voltage of 300 kV. The spherical and chromatic aberration coefficients of the objective lens are 0.69 and 1.4 mm, respectively, and the point-to-point resolution is 0.175 nm. The specimen chamber is pumped with a 340 l/sec magnetic-bearing turbo molecular pump and the vacuum of the specimen chamber during the in situ heating experiment is kept between $4 \times 10^{-6}$ and $6 \times 10^{-8}$ Pa. Elemental analysis was carried out using a Kevex Delta system combined with a Super Quantum ultra thin window-type detector. TEM images were recorded on ordinary film (Fuji FG) and using a Gatan 622 high-resolution TV system. The maximum specimen tilting angle of the holder is $\pm 15^\circ$ when the heating holder is used.

**Formation of SiC through Solid State Chemical Reactions between Si and Graphite**

**Specimens**

A single crystal of Si was crushed into particles with an agate pestle and mortar. The crushed Si particles were mixed with particles of graphitized carbon and mounted on the heating element of the type 1 heating holder. The temperature of the specimens was kept slightly below the melting point of Si (1688K) (Kamino et al., 1994).

**Results and Discussion**

Figure 4 shows a series of low-magnification micrographs of an Si particle attached to a particle of graphitized carbon, which sits on the heating element (not shown). Figure 4a was taken at room temperature and Figures 4b–d were taken at 1673K. It can be seen that during heating the Si particle disappeared and at the same time the area just beneath the Si particle became darker. Figure 5 shows the diffraction pattern taken at room temperature before heating (a) and at 1673K (b). Before heating, a typical diffraction pattern from a single crystal of Si and typical Debye-
Figure 2. a: Temperature vs. heating current curve. b: Drift rate vs. time curve at 1673K.

Figure 3. EDX spectra taken on Si at various temperatures.
Figure 4. Low-magnification image of a Si particle attached to a graphitized carbon before heating (a) and after heating at 1673K (b–d). Note change in microstructure in the region inside the circles.

Figure 5. a,b: Diffraction patterns corresponding to Fig. 4a and d, respectively.
Figure 6. HREM images showing the process by which SiC is formed through a reaction between Si and graphite. (a) was taken 1 min after the temperature of the specimen reached 1673K; (b) was taken 2 min after (a) was taken. Inside a circle in (a) the lattice fringe of graphite is clearly resolved. Inside circles in (b) the lattice fringe of SiC is clearly resolved.

Scherrer rings from graphite are obtained. By contrast, after heating, extra Debye-Scherrer rings were observed in addition to those of graphite. The lattice spacings of the extra Debye-Scherrer rings were measured and it was confirmed that all the extra rings correspond to cubic β-SiC.

These changes in morphology and diffraction patterns during the in situ heating experiment show definitely that at 1673K Si atoms diffuse into graphite and react with C to form SiC.

Figure 6 reproduces a sequence of HREM images showing the process of formation of SiC. In Figure 6a the Si particles lie at the bottom left corner of the micrograph. However, most of the graphite remained unchanged. In Figure 6b, which was taken 2 min after Figure 6a, Si reacted with graphite to form SiC.

SINTERING OF SiC CRYSTALS

Cubic β-SiC particles formed during the in situ heating experiment described above were further heated at 1773K inside the electron microscope (Kamino et al., 1995). Figure 7a and b shows electron micrographs of an SiC particle after being heated for 40 min and 1 hr, respectively, at 1773K. It is evident that the crystal is growing and that many planar defects are introduced.

Figure 8a and b shows a pair of HREM images of an SiC particle heated at 1773K (taken on ordinary EM film). Figure 8b was taken 1 min after Figure 8a was taken. Approximately three layers (indicated by arrows) grew during this interval of 1 min.

Figure 9 shows an example of dynamic observations of a sequence of the crystal growth at 1773K (reproduced from a videotape). The crystal is viewed along the (110) direction and the flat surface corresponds to {111} plane of cubic SiC. Thus, the growth takes place in the direction of (111). The lattice fringes with the spacing of 0.252 nm parallel to the surface are clearly resolved. The structure of the crystal near the surface is a 3C-type cubic structure with the stacking sequence of $a^1b^1c^1a^1b^1c^1...$. In terms of the notation used usually (Fig. 9b). However, the position of molecules in the growing layer is not $b$ but $c$ (Fig. 9b-d), and the stacking sequence becomes $a^1b^1c^1a^1b^1c^1a^1...$. In other words, a stacking fault is introduced during growth. Such stacking faults are often observed during growth. For example, the step marked by the asterisk in Figure 9a is a boundary between hexagonal SiC and cubic SiC. Thus it is evident that at 1773K, during growth of SiC polytypism transformations between cubic and hexagonal SiC takes place.

When two grains meet together during growth, sintering takes place. An example is shown in Figure 10. Here, two grains of SiC grew from left to right during heating. Apparently the grain boundary in the left half of Figure 10a was free from any defects. However, the grain boundary near the growth front had an area where the density of the molecular columns was much smaller than the rest of the grain boundary and the matrices in the grains (circle in Fig. 10a). We believe that this area contained many more defects, presumably because of mismatch between the lattices of the two grains, than the matrices in the grains. The upper grain grew faster than the lower one and surmounted the less dense area (Fig. 10b–e). During this process, approximately half of the defects in the less dense area disappeared, but part of them were left behind after the growth front had passed away (Fig. 10d,f). This phenomenon is believed to be
Figure 7. Low-magnification images of a SiC particle after being heated for 40 min (a) and 1 hr (b) at 1773K.

Results and Discussion

Figure 11 shows a series of HREM images of Au clusters during deposition on an Si particle. The surface of the Si particle was covered with an amorphous native oxide layer 1.0–1.5 nm thick, formed at room temperature when the Si single crystal was crushed to particles (Fig. 11a). Native oxide is SiO (Kim and Carpenter, 1990). The deposition of Au was carried out without removing the amorphous layer using heating element 2. The formation of Au clusters could be observed after their size became as large as 0.5–1 nm (e.g., particles in Fig. 11b). The deposition of Au was stopped as the cluster grew to 6–8 nm in diameter. Then, the Au-deposited Si was heated using heating element 1 until the deposited Au clusters melted.

Figure 12 shows the change in morphology of an Si{111} surface near the melting point of Au particles. An Au particle, which could be identified as crystalline because of the lattice fringes, sits on the amorphous layer of a near-{111} surface of an Si particle in Figure 12a. The surface of Si is rather wavy and the interface between Si and the amor-

One of the mechanisms that introduces a void into a grain boundary of ceramics during sintering.

Surface Reconstruction of Au-Deposited Si

Specimens

A single crystal of Si was crushed into particles and mounted on the lower heating element 1 of the type 2 specimen-heating holder. A piece of Au was mounted on the upper heating element 2 and deposited onto the Si particles at room temperature (Kamino et al., 1997).
phous layer is not sharp. However, as shown in Figure 12b, the Au cluster has disappeared and, at the same time, the amorphous layer has disappeared, except for a few residual areas indicated by R and R'. The initially wavy surface is now transformed into well-faceted, atomically flat surfaces. It can also be noted that the contrast of the outermost layer of the faceted surface became very strong after the Au particle disappeared.

This transformation of the surface of Si from atomically rough to atomically flat proceeds as a cluster of molten Au shrinks, as can be seen in Figure 13. In Figure 13a, a large cluster of Au lies on the Si surface. It is inferred that at this stage, the Au cluster was already molten, because the lattice fringes were not observed. Also, at this stage, both the surface of Si and the interface between Si and Au were still atomically rough. However, black dotty contrasts then appeared at the left part of the interface between Au and Si, creeping to the left on the surface of Si. The interface between Si and Au and the surface of Si, both of which were now covered with the black dotty contrasts, became atomi-
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(a10). The measured distance between the two neighboring tops of the chevron is 1.54 nm; this is exactly four times the periodicity of the lattice spacing of (110) plane of Si. This HREM image can be explained by the assumption that the {001} surface is reconstructed into c(8 x 2) structure, as is schematically shown in Figure 16b.

**Solid-Liquid Interface in α-Al₂O₃**

**Experiment**

Fine particles of alumina were used. They were heated at a heating rate of 100K/hr between 1300K and 2000K. Particles steady on the heating element were selected during heating and thin areas at the edges of the particles were examined (Sasaki and Saka, 1996).

**Results and Discussion**

In the process of heating to 2000K, the (1102) and (1012) lattice fringes were clearly observed in the [0221] zone axis. When the temperature reached 2000K, very fine hemispheres were formed at the tip of a sharp edge of the sample. These hemispheres increased in size or they fused with each other. When the diameter of the droplet increased to about 50 nm, a stem-like shape started to form under each hemisphere, as shown in Figure 17. The stems continuously grew while holding the hemispheres. The stems grew along three directions, i.e., perpendicular to (1102), (1012), and (0114). During the growth, the (1102) and (1012) lattice fringes were clearly observed inside the stem, as shown in Figure 18a. The spacings and the directions of these lattice fringes coincide with those of α-alumina. On the other hand, no particular contrast was observed inside the hemispheres. The sample was tilted within a range of ±10°. However, neither lattice fringes nor diffraction contrasts were observed inside the hemispheres.

After the heating experiment, the sample was rapidly quenched to room temperature at a cooling rate of 1000K/min. The hemispheres were then transformed into faceted crystals, as shown in Figure 18b. Lattice fringes inside these faceted crystals coincide with those observed in the stem (α-alumina). From these results it can be concluded that the hemisphere is a liquid droplet of alumina.

Figure 19 presents a series of video-recorded images showing the process of formation of one monolayer at the...
solid–liquid interface. In Figure 19a, a molecularly flat solid–liquid interface is observed. The formation of the monolayer was initiated by the nucleation of a cloud-like contrast with a thickness of about 2 monolayers on the interface (indicated by double-headed arrows in Fig. 19b). The cloud-like contrast was elongated along the solid–liquid interface, reducing the thickness. When the cloud extended to a length of between 5 and 10 nm along the interface, the lattice fringes perpendicular to the interface (indicated by arrows and bar 3 in Fig. 19c) started to appear inside the cloud. These lattice fringes coincide with those observed in the stem. The cloud is transformed into an island of the monolayer with molecular steps on both sides. The island of the monolayer that had been formed on the interface extended continuously, adding new lattices on both edges until the interface was completely covered with the new monolayer (Fig. 19d). The interface covered with the new monolayer existed stably until another nucleus was created on it (Fig. 19e). The solid–liquid interface was molecularly flat over the range of more than 50 nm. The nucleation rates on the (1102) and (0014) were measured to be $2.8 \times 10^{-5} \text{ sec}^{-1} \text{ m}^{-2}$ and $3.4 \times 10^{-5} \text{ sec}^{-1} \text{ nm}^{-2}$. The velocity of the step running along the solid–liquid interface was measured to be 80 lattice fringes/sec on (1102).

The process of the formation of droplets and the growth of stems can be explained as follows. It has been observed that the surface of a solid can melt far below the bulk melting temperature for many substances. For example, in the case of lead, surface melting has been observed to take place at around 90% of the bulk melting temperature (Frenkel and van der Veen, 1983). The temperature at which the present experiment was carried out was 86–90% of the bulk melting temperature of alumina. Thus, the surface melting most likely took place in the present study. The
Figure 14. Change in the morphology of Au-deposited Si surface during thermal cycles.

Figure 15. Sequence of HREM profile-view images showing the processes of reconstruction of an Si{001} surface.

Figure 16. a: HREM profile image of chevrons on a reconstructed {001} surface viewed along (110). b: c(8 × 2) structure as viewed along the (110) direction.

Figure 17. Low-magnification micrograph of partially molten alumina particle. Molten alumina assumes hemisphere shape.
liquefied surface layer is attracted and accumulated at the tip of a sharp edge of the sample, where the surface energy is very large because of a large surface curvature. The liquid in the droplet is supercooled, so it will tend to solidify. The solidification probably takes place at the solid–liquid interface rather than inside the droplet because the heterogeneous nucleation on the solid–liquid interface should be energetically favored. This is exactly what was observed in the present study.

**Vibration of a Grain Boundary in CuGa₂**

**Specimens**

CuGa₂ has a tetragonal structure with $a = 0.283$ nm, $c = 0.5839$ nm with 3 atoms per unit cell (El-Boragoy and Schubert, 1972). Thin foil specimen of CuGa₂ was prepared by
a simultaneous deposition of Cu and Ga onto a carbon film supported by Cu mesh. This specimen was heated inside an electron microscope at 573K to synthesize the single phase of polycrystalline CuGa$_2$ and then cooled at a rate of 5K/hr; this heat treatment resulted in the growth of grains with a grain size of a few micrometers, and straight and long grain boundaries.

The specimen was observed in electron microscopes with different accelerating voltages between 200 kV and 1000 kV at a temperature range between 487K and 110K (Sasaki, et al., 1994; 1996; Sasaki and Saka, 1996).

**Results and Discussion**

Figure 20 shows a series of high-resolution images of a grain boundary observed at room temperature at an accelerating voltage of 400 kV. (001) lattice fringes are observed in the upper and the lower sides of the crystal. It is evident that the grain boundary is vibrating. No intergranular phase exists at the grain boundary: the vibration of the grain boundary proceeds in the solid–solid reaction.

Figure 21 shows the effects of accelerating voltage of the
Figure 20. Time-resolved high-resolution images of a grain boundary in CuGa$_2$, showing that the grain boundary is vibrating. Arrows indicate the position of the grain boundary in each image.

electron beam on the vibration. The flux of the electron beam was kept $2 \times 10^{23}$ e/m$^2$s. The frequency decreases as the accelerating voltage is decreased, as does the amplitude of the vibration. The vibration is closely related to flux. For instance, under a flux of $8 \times 10^{23}$ e/m$^2$s, the vibration was observed even at an accelerating voltage of 200 kV. Figure 22 shows the effect of temperature on the vibration. Surprisingly enough, the vibration diminishes with increasing
temperature: the vibration was observed between 203K and 325K.

Not all the grain boundaries examined showed the vibration. The orientation relationships between two crystals whose grain boundary vibrated were determined on about 30 grain boundaries. They are classified into two groups; a low-angle grain boundary and a grain boundary with some definite crystallographic relationship. The second group was further classified into three types; type 1, type 2, and type 3, as is shown in Figure 23.

There are two possible explanations for the vibration of a grain boundary. One is to assume that the vibration is caused by heating due to bombardment of electrons. The other is to assume that point defects produced by electron irradiation are responsible for the observed vibration.

The local heating due to a focused electron beam may give rise to a change in the internal stress near a grain boundary, which in turn may lead to the motion of the grain boundary. However, this mechanism cannot easily explain why vibration diminishes at higher temperatures.

As can be inferred from Figure 21, electron irradiation may be responsible for the vibration. Electron irradiation can produce point defects when the accelerating voltage of the electron microscope exceeds a certain threshold value. Although the type of point defects produced by electron irradiation in CuGa$_2$ is not known exactly, it would be reasonable to assume that both an interstitial and a vacancy are formed as a Frenkel pair. It would also be reasonable to assume that an interstitial can move much faster than a vacancy. Some of the interstitials and vacancies thus produced annihilate by recombining with each other, but most of the interstitials move to sinks, such as surfaces, dislocations, and grain boundaries. When an interstitial arrives at a dislocation, the dislocation climbs. A low-angle grain
boundary consists of dislocations. When interstitials arrive at a low-angle grain boundary, the low-angle grain boundary will move through the climbing motion of dislocations that comprise the grain boundary. We assume that this climbing motion is responsible for the observed vibration of a grain boundary. With increasing temperature, the concentration of vacancies in thermal equilibrium increases. This means that the probability at which interstitials produced by electron irradiation annihilate through the recombination with vacancies increases. Thus, at higher temperatures only a small fraction of interstitials arrive at the grain boundary. Thus, the vibration no longer takes place at higher temperatures.

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