Transactions of the Materials Research Society of Japan 25 [4] 1183-1186 (2000)

PREPARATION OF FLAT CALCITE($10\bar{1}4$) SURFACE BY THERMAL TREATMENT METHOD

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In the present experiment, a thermal treatment method was developed in order to prepare flat calcite surfaces. The prepared surfaces were confirmed by X-Ray diffraction to be ($10\bar{1}4$) planes. Furthermore, observation of the ($10\bar{1}4$) surfaces at the atomic level in an air atmosphere by atomic force microscopy revealed that no atomic step exists on the surface at a scale of approximately 600 nm×700 nm. The results of these examinations show that the newly developed thermal treatment may be considered to be a new method for the preparation of flat calcite ($10\bar{1}4$) surfaces.

Key words: Calcite, Thermal treatment, Fracture, Atomic force microscopy.

I. INTRODUCTION

Previously, the material surfaces of electric conductors and insulators were observed and imaged by atomic force microscopy (AFM) in the size range from <1 nm ~50 nm in an ambient condition, such as in air, in contact with solution or in a vacuum, in order to acquire atomic level AFM images[1]. Atomic-level observation generally requires the preparation of a surface with an atomically flat area. Typically, this kind of surface has been prepared by the mechanical cleavage method[2]. Researchers have prepared atomic level areas of mica[3], graphite[4], gypsum[5], anhydrite[6] and calcite[1,7,8,9] by mechanical cleavage. In the present experiment, a thermal treatment method is designed in order to prepare a flat calcite ($10\bar{1}4$) surface. X-Ray diffraction and AFM observation are used to examine and confirm that a flat ($10\bar{1}4$) surface is acquired. The purpose of the present study is to develop a new method by which to prepare a flat ($10\bar{1}4$) surface having a very large, atomically flat area.

II. CALCITE STRUCTURE

Calcite belongs to the $R\bar{3}C$ space group and has a trigonal unit cell with parameters of a=0.637 nm, α =46.05^0 and Z=2. For ease of understanding the structure, a hexagonal unit cell with parameters of a=0.499 nm, c=1.706 nm and Z= 6[10] is usually used. Calcite has a good cleavage property along the ($10\bar{1}4$) plane of the hexagonal unit cell. Figure 1 shows the atomic array of a ($10\bar{1}4$) surface with a surface unit cell of a=0.499 nm and b=0.808 nm. When the ($10\bar{1}4$) surface is observed from above by AFM, the black O^{2-} ions can be detected more easily than Ca^{2+} ions, because the black O^{2-} ions are positioned above the ($10\bar{1}4$) plane.

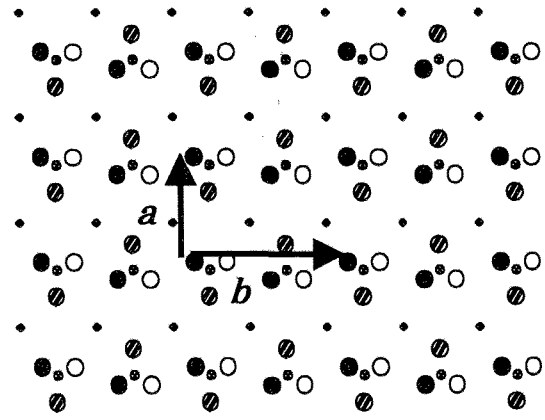

Fig. 1 Structure of the ($10\bar{1}4$) plane. a = 0.499 nm, b = 0.808 nm.
- ● Oxygen standing above the ($10\bar{1}4$) plane. Observable by AFM.
- ◆ Calcium lying in the ($10\bar{1}4$) plane. Observable by AFM.
- ⊗ Carbon lying in the ($10\bar{1}4$) plane.
- ▨ Oxygen lying in the ($10\bar{1}4$) plane.
- ○ Oxygen lying below the ($10\bar{1}4$) plane.

Ⅲ. EXPERIMENTAL

Natural pure calcite from Chihuahua Mexico was used in the present experiment. The calcite has an optical-quality rhombohedral shape. The surfaces of the calcite crystal are equivalent ($10\bar{1}4$) cleavage planes of the hexagonal structure. The calcite was cut into small samples approximately 6×6×7 mm in size along the ($10\bar{1}4$) plane using a sharp cutter and a small 100-gram hammer. The small sample was loaded in a platinum crucible having a cap and then placed into a furnace at a speed of 3600 K/minute to be thermally treated at 873 K for 1.5 hours. Next, the small sample was taken out of the furnace at a speed of 3600 K/minute to cool in air for approximately 5 minutes and then placed in a desiccator. After approximately 35 minutes, this sample began to fracture along the ($10\bar{1}4$) plane in the desiccator. The orientation of the fractured surface was confirmed using X-ray diffraction. Furthermore, the fractured surface was imaged by AFM at the atomic level in air in order to determine whether an atomic step is present on the surface.

In the present experiment, an X-ray diffractometer (RIGAKU, RINT-2000) and an atomic force microscope (SEIKO, SPA300) having a 20-μm scanner were used to confirm and examine the fractured surfaces.

Ⅳ. RESULTS AND DISCUSSION

In the present experiment, a thermal treatment method was designed for the preparation of ($10\bar{1}4$) surfaces. The calcite samples were heated 673—1073 K for 1.5 hours. The samples that were heated at 973 K and 1073 K fractured irregularly. The samples that were heated at 773 K and 673 K did not fracture. Only the sample that was heated at 873 K fractured into small hexahedrons. The fractured surface of this sample was examined by X-ray diffraction and AFM. First, the prepared surface was examined by X-ray diffraction using incident X-rays along the side orientation of the fractured hexahedron sample. Figure 2 shows the X-ray diffraction pattern. From the distance of layer A—A and B—B of this pattern, the measured periodic length along the side orientation was estimated to be approximately 1.28 nm, which is in good agreement with the periodic length along this orientation in bulk. Therefore, the fractured surface was confirmed to be a

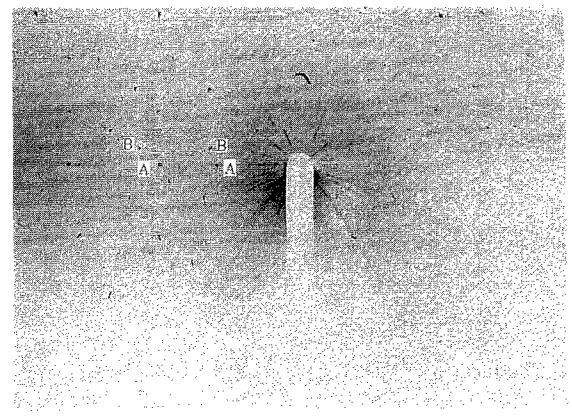

Fig. 2 X-ray diffraction pattern with the incident ray along the side orientation of the rhombohedral sample, from which the surface was confirmed to be a ($10\bar{1}4$) plane.

($10\bar{1}4$) plane. Second, the confirmed ($10\bar{1}4$) surface was examined by AFM at the atomic level. A typical AFM image is shown in Fig. 3. The figure shows an area of 600 nm×700 nm on the fractured ($10\bar{1}4$) surface, in which no cleavage step was detected. This implies that the ($10\bar{1}4$) surface was atomically flat within approximately 600 nm. This kind of area of the fractured

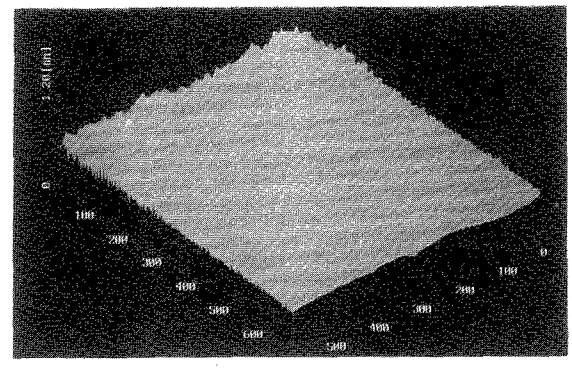

Fig. 3 AFM image of the fractured ($10\bar{1}4$) surface. Size: 600 nm×700 nm.

surface was imaged on the several-nanometer scale and a typical AFM image (Fig. 4) was obtained, in which the atomic array of the ($10\bar{1}4$) surface is visible. Figure 4 was enlarged to obtain Fig. 5. In Fig. 5 the periodical arrangement of O^{2-} and Ca^{2+} of the ($10\bar{1}4$) surface were

visible, which is in agreement with the arrangement of Fig. 1. Moreover, the image indicates the distance between the nearest bright O^{2-} sites as $a = 0.54 \pm 0.03$ nm, and the distance between the second nearest bright O^{2-} site as $b = 0.83 \pm 0.03$ nm. These findings are in general agreement with the parameters of 0.499 nm and 0.808 nm for bulk material. These images indicate that a (10$\bar{1}$4) surface having an atomically flat area over 600 nm × 700 nm is well prepared by the thermal treatment method.

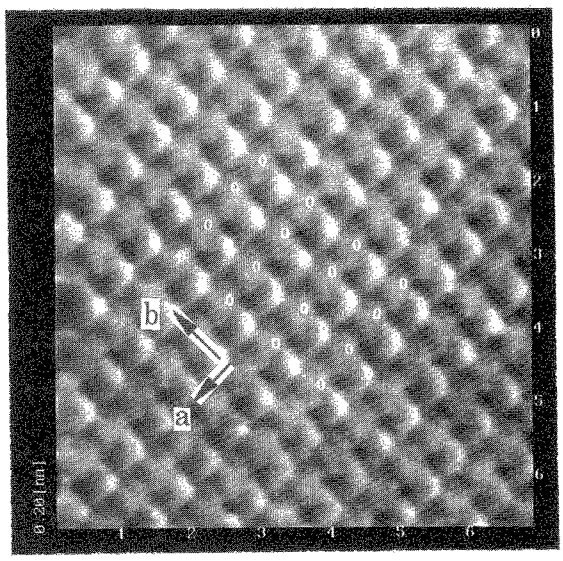

Fig. 4 AFM image of the fractured (10$\bar{1}$4) surface. Size: 6.7 nm × 6.7 nm.

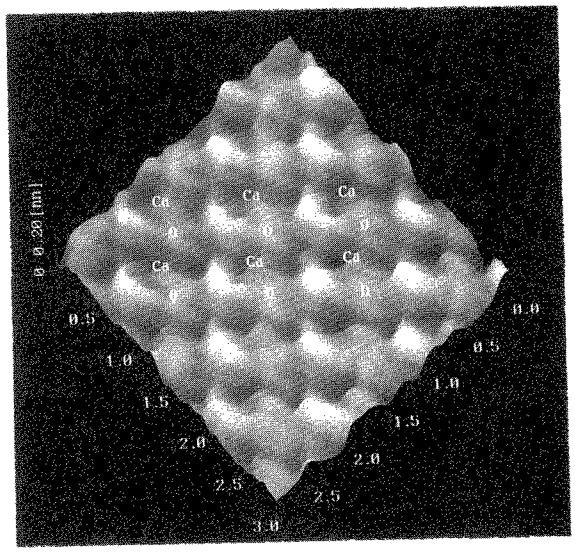

Fig. 5 AFM image of the fractured (10$\bar{1}$4) surface. Size: 3 nm × 3 nm.

Calcite is a kind of layered mineral and has a better cleavage property along the (10$\bar{1}$4) plane because this plane has the least surface free energy. In the thermal treatment method, the sample was placed into a furnace at a speed of 3600 K / min, treated at 873 K for 1.5 hours and then taken out of the furnace at a speed of 3600 K / min. The sample was then cooled in air for 5 minutes, and placed in a desiccator. The heated sample had visible white powder on the surface and was opaque. The microfracture is thought to have emanated along the (10$\bar{1}$4) plane because of rapid temperature elevation, and because of the thermal treatment at 873 K for 1.5 hours the surface of the sample and the boundaries along the microfracture were partially decomposed to become CaO. This was evident from the fact that the surface became opaque due to the white powder that covered it. The partial decomposition made the microfracture become wider. After the sample was taken out and cooled, the residual thermal stress made the microfracture continue to extend slowly along the natural cleavage plane. The extension of residual stress drove the sample fracture to slowly along the (10$\bar{1}$4) plane. The slow fracture processing made the surface energy increase slowly, gave the surface atoms enough time to adjust to a new balance and made the sample cleave exactly along the (10$\bar{1}$4) plane. Consequently, a surface with a very large, atomically flat area was acquired. Calcite surfaces were also prepared several times by the conventional cleavage method and examined via AFM in the present experiment. However, no atomic level area larger than 500 nm scale was obtained. These results suggest that the newly developed thermal treatment is a new method by which to prepare a calcite (10$\bar{1}$4) surface having a very large, atomically flat area.

V. CONCLUSION

In the present experiment, a thermal treatment method was developed for the preparation of flat calcite (10$\bar{1}$4) surfaces. The fractured (10$\bar{1}$4) surfaces were examined and confirmed to be atomically flat by

X—ray diffraction and AFM observation. The acquired AFM images showed that the fractured $(10\bar{1}4)$ surface has an atomically flat area of over 600 nm × 700 nm, on which no cleavage step exists. The experimental results indicate that the thermal treatment of the present experiment is a new method by which to prepare a very large, atomically flat area of calcite $(10\bar{1}4)$ surface.

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(Received January 24, 2000; Accepted May 6, 2000)