Trial Manufacturing of Heating Stage for In-situ Observation by TEM

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Abstract

Trial manufacturing of a heating stage for TEM is to realize the observation of structure image of bulk specimens at elevated temperatures. Purpose of the trial manufacturing is to obtain clean atmosphere in every in-situ observation of bulk specimen by highly resolved structure image of materials at elevated temperatures. The specimens of high temperature observation were prepared by Focused Ion Beam (FIB).

Target resolution, 0.2 nm, at 1773 K, was confirmed with Si_3N_4. Maximum resolution, 0.18 nm, was obtained at 2073 K with Si_3N_4. Phase transformation from α-Si_3N_4 to β-Si_3N_4 via liquid state was also observed during elevation of temperature.

1. Introduction

Increase of operation temperatures in fossil-fired power plants is required for higher efficiency because of the protection of natural environment by reduction of NOx, SOx, and CO_2 amounts and the preservation of fossil fuel. Higher efficiency seriously causes problems for the materials in terms of heat resistance, oxidation, and corrosion at elevated temperatures. Since the conventional metals and alloys are no longer utilized as the structural component in the advanced power plant because of deterioration of strength at elevated temperatures, intermetallic compounds and ceramics become altenative candidates for heat resistant materials. However, physical and mechanical properties and corrosion characteristics of these new materials cannot be estimated by extrapolation of those of the conventional materials.

In-situ observation by transmission electron microscope (TEM) plays an important role to characterize the structural change of the component materials at operating temperature in advanced power plants. Observation of bulk specimens has been reported by various researchers. However, previous heating stages restrict observation due to the specimen dimension or contamination from the previous experiments(1-5).

This paper describes a trial manufacturing of heating stage for high resolution TEM evaluated by structural image of Si_3N_4 at elevated temperatures. Target resolution of the heating stage is 0.2 nm at 1773 K.

2. Experimental Details

The heating stage was designed for an application of HF-2000 in which cold field emission is installed to improve brightness of electron beam, because short exposures are essential to avoid the image drift due to thermal characteristics. Power supply is prepared for both high resolution and conventional images. Direct current is supplied by dry battery in order to obtain the high resolutione image. Rectifier is installed in the temperature controller which is programmable for the various temperature profiles. The geometry of the replaceable heater made of tungsten filament is shown in Fig. 1. Thin area of specimen prepare by FIB is placed in the center of the heater as shown in Fig. 2. The dimension of the specimen is 1 mm long, 0.5 mm wide, and 0.1 mm thick. The area of TEM observation is thin enough to obtain structure image. The ceramics coating of heater is necessary to protect reaction between the specimen and the heater at elevated temperatures.

Double tilting of the specimen is required to form structure image of TEM. Fig. 3 shows mechanism of azimuthal rotation of the heater. The electrically insulated rod moves on inclined surface of the heater to tilt the specimen in azimuthal direction which enables one to obtain a proper orientation of specimen for high resolution image.

Oxidation of the specimen is also concerned for in-situ observations at elevated temperatures. The oxidation behavior of specimen can be observed by assistance of gas supply in vacuum chamber of TEM as shown in Fig. 4. The

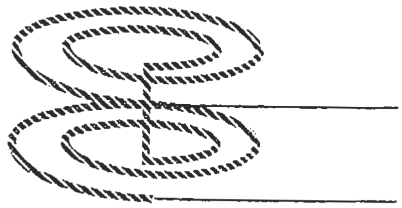

Fig. 1 Schematic view of swirled W filament for application of the heating stage

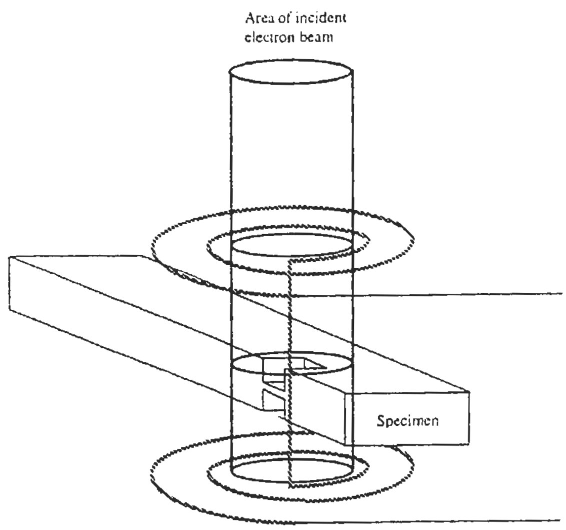

Fig. 2 Experimental position of the specimen prepared by FIB

specimen is observed before oxidation. The specimen is inserted in vacuum chamber attached to the column of TEM where oxygen diluted with inert gas is introduced in the chamber and the specimen is heated for the oxidation. Then, the specimen is placed on the previous position in TEM after oxidation of the specimen. Therefore, the specimen can be observed before and after oxidation at elevated temperatures.

Elevation of temperature as a function of voltage increase of the power supply is plotted in a vacuum bell jar for the estimation of the real temperature during heating.

A small flake of Si_3N_4 was used for the in-situ observation of structure image at various temperatures up to 2073 K.

The multi-slice method was used for the simulation of structure image of β-Si_3N_4 for the comparison of structure image obtained from TEM.

3. Experimental Results

Fig. 5 shows a high resolution image of α-Si_3N_4 whose space group is P31c at the ambient temperature.

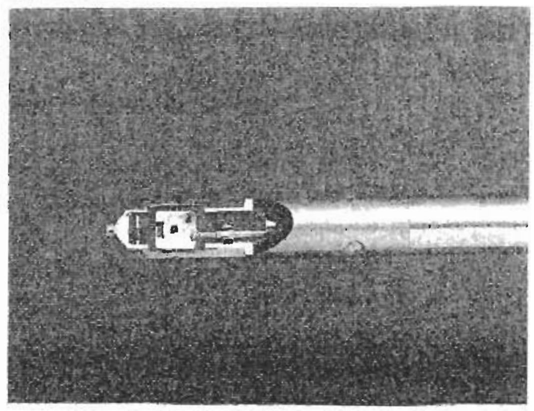

Fig. 3 Heating stage attached to translation rod for azimuthal rotation of the heating stage

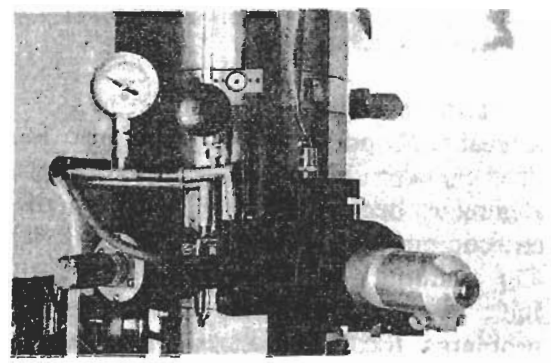

Fig. 4 Specimen oxidation chamber attached to TEM column

Fig. 6 shows a high resolution image of β-Si_3N_4 whose space group is $P6_3$ at 2073 K. Simulation image shows good agreement with the structure image of β-Si_3N_4. Resolution of the structure image was estimated as 0.18 nm for β-Si_3N_4 at 2037 K.

The transformation temperature of Si_3N_4 was not defined in this experiment. However, liquid state where nucleation of β-Si_3N_4 was observed in the transformation from α-Si_3N_4 to β-Si_3N_4 during holding temperature at 1800°C is shown in Fig. 7. The operation temperature was estimated by the trace of the master plot from the previous measurement of temperature as a function of the voltage increase. Although exposure time was limited within a few seconds because of image drift at 2073 K, the structure image showed satisfactory resolution.

4. Discussion

The space group of $P6_3$ is used for β-Si_3N_4 to interpret the structure image. It is said that the atomic site of $P6_3$ is given as follows:

(2b) 1/3, 2/3, z ; 2/3, 1/3, 1/2 + z.

(6c) x, y, z ; -y, x-y, 1/2 + z ; y-x, -x, z ;
-x, -y, 1/2 + z ; y, y-x, 1/2 + z ;

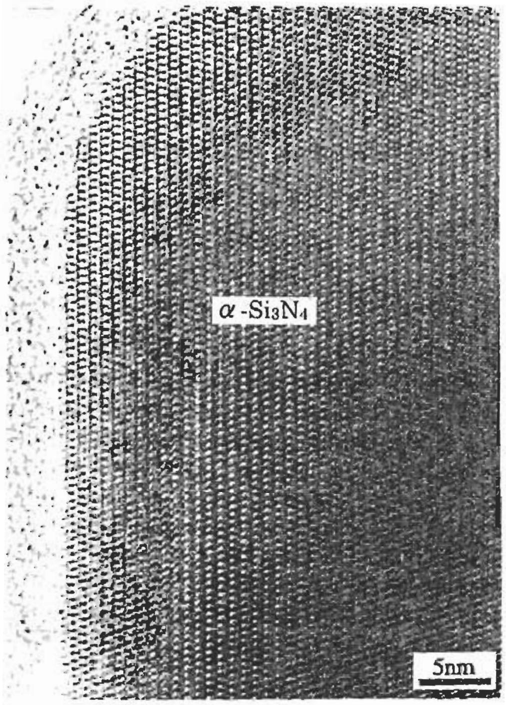

Fig. 5 Structure image of α-Si_3N_4 at ambient temperature

x-y, x, 1/2 + z.
The unit cell of β-Si3N4 consists of two subcells where N occupies (2b); z=0.739 and (6c); x=0.030, y=0.329 and z=0.250, while Si occupies (6c); x=0.769, y=0.174 and z=0.263. The lattice constant of β-Si_3N_4 is given by a_0=0.7595 nm and c_0=0.2902 nm.
The data were used for the construction of a super cell (3×3×1) for the simulated image by the multi-slice method where incident beam is parallel to c-axis. The mutual transfer function was used to construct the simulated structure image. The simulated image shows good agreement with the structure image of β-Si_3N_4 obtained by TEM at 2073 K.
It can be concluded that the structure image of β-Si_3N_4 is obtained at 2073 K with resolution, 0.18 nm.

Conclusions

The following conclusions are obtained from the trial manufacturing of heating stage for high resolution TEM evaluated by Si_3N_4.

(1) Resolution, 0.18 nm, was obtained from β-Si_3N_4 by in-situ observation at 2073 K.
(2) Transformation from α-Si_3N_4 to β-Si_3N_4 via liquid state was observed during heating.
(3) The heating stage for TEM satisfied the target resolution, 0.2 nm, at 1773 K.

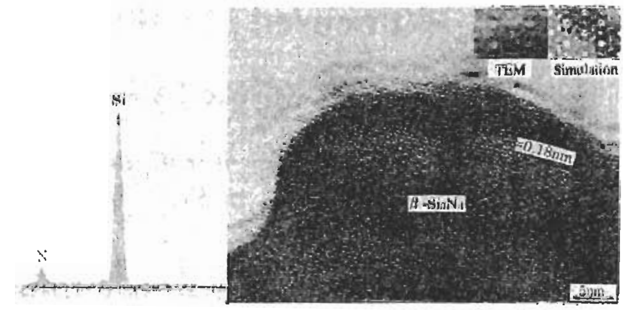

Fig. 6 Structure image of β-Si_3N_4 at 1800°C

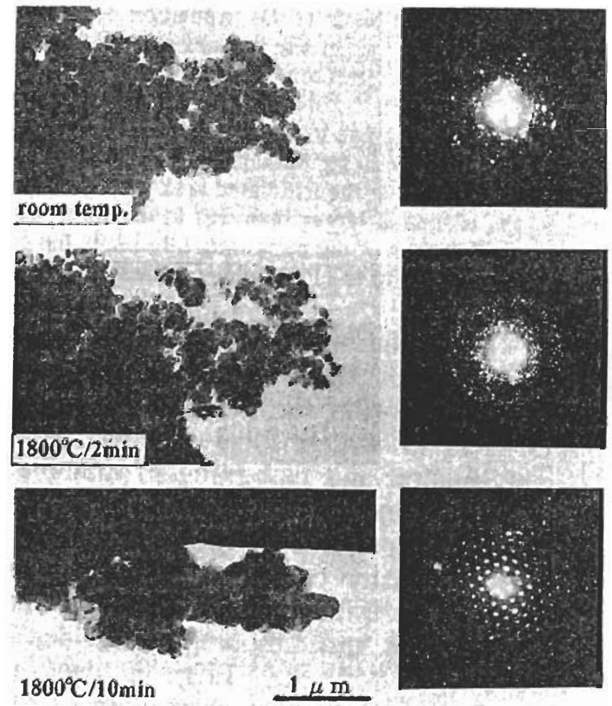

Fig. 7 Nucleation of β-Si_3N_4 from α-Si_3N_4 at 1800°C

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