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Development of XAFS/XRD simultaneous measurement technique at high temperatures

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1 Introduction

In order to increase the energy efficiency of gas turbine engines used in aircrafts, it is necessary to operate at a temperature higher than the current temperature. Evaluate methods of the properties of structural materials used at ultrahigh temperatures such as gas turbine blades of engines are required, and it is essential to have a technique to accurately measure changes in structure and chemical state proceeding under these conditions. Thus, *in situ* measurement technique at ultra-high temperature is required. As various type of reactions, such as diffusion of main component, phase transition, and precipitation of minor phases, are expected, the combination of complemental analytical techniques is inevitable. Considering these requirements, we are developing a technology to measure simultaneously a short-range structure obtained by XAFS and a long-range structure obtained by diffraction measurement at ultra-high temperature up to 1500 °C. We have developed a prototype *in situ* furnace to investigate elemental technologies for spectroscopic measurements at extremely high temperatures, and have been accumulating XAFS measurement techniques at high temperatures [1]. Here we report the development of the in situ the furnace for spectroscopic / diffraction measurement and typical results of XAFS / XRD measurements.

2 Experiment

The XAFS / XRD simultaneous measurement furnace was developed based on an infrared furnace (gold image furnace) which is not susceptible to properties of material such as a thermal conductivity of the sample as a heating method. In order to simulate the operating condition of an aircraft engine, we aimed at measurement at 1500 °C for regular use. The heating area in the cell is about 10 × 10 mm at the sample position, which is sufficiently larger than the X-ray beam irradiation area. Figure 1 shows photographs of the novel ultra-high temperature XAFS/XRD furnace under development, which is installed at the beam line of synchrotron facility. For heating experiments, a sintered plate of $Yb_2Si_2O_7$ (8 × 8 mm, t = 0.5 mm) was used as a sample. Measurements of Yb LIII absorption edge (8944 eV) and diffraction (8046 eV) were carried out at KEK PF BL-15A1, at which semi-micro beam (about 20 μm) can be utilized. XAFS was measured by detecting the fluorescence from the sample with a silicon drift detector (SDD) or Lytle detector from the direction of 90° with respect to the X-ray optical axis. For the XRD measurement, the required angular range was measured in multiple steps using PILATUS 100k installed in a goniometer. The camera length was 200 mm. The spot diameter of the irradiated X-ray beam on the sample was estimated to be about 0.2 (vertical) × 0.1 (horizontal) mm. This is because the beam spread in the lateral direction is deviated from the focal position, and the beam spread in the longitudinal direction is caused by tilting the specimen. Temperature rise was carried out under continuous gas (air, N_2) flow.

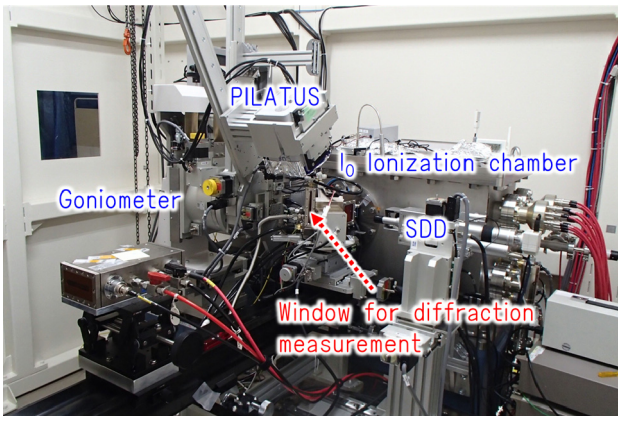

Fig. 1. Set-up of the measurement system at PF BL-15A1.

3 Results and Discussion

As a result of the heating test, it reached 1500 °C at a heating rate of 500 °C min^{-1}. The stability is ± 3.9 °C when kept at 1500 °C for 30 min, which is considered to be sufficient heating performance for spectrum measurement at ultra-high temperature. Figure 2.a shows XAFS oscillations measured with various temperatures.

From the XANES spectra of $Yb_2Si_2O_7$ around Yb LIII edge, no energy shift of spectrum was observed before and after heating, showing that the valence of Yb does not change. The radial structure functions which are obtained by Fourier transform of EXAFS oscillation with a range of k = 1-12 × 10 nm^{-1}. Because EXAFS oscillations changed reversibly during heating cycles, it means that no irreversible structural change is caused during heating cycles. Since the oscillation cycle has not changed and only the decrease in oscillation intensity, which is considered to be due to the increase of Debye-Waller factor accompanying temperature increase, is observed, it suggests that the local structure around Yb does not change.

Figure 2.b shows the diffraction patterns obtained, where each image is a part of Debye-Scherrer ring covering the diffraction angles of 2θ = 4 to 46°. Because of the small beam size, the XRD measurements are sensitive to change of grain growth, which is expected at high temperatures. However, the distinct change was not observed, showing that no severe grain growth was

observed during heating under the conditions of experiments.

From the above, it was shown that simultaneous observation of XAFS and XRD at the same sample position can be measured at high temperature, and that it provide crucial information of change of structures both in short- and long- range ordering.

Now we are improving the way to hold the specimen at high temperatures and control the temperature more precisely.

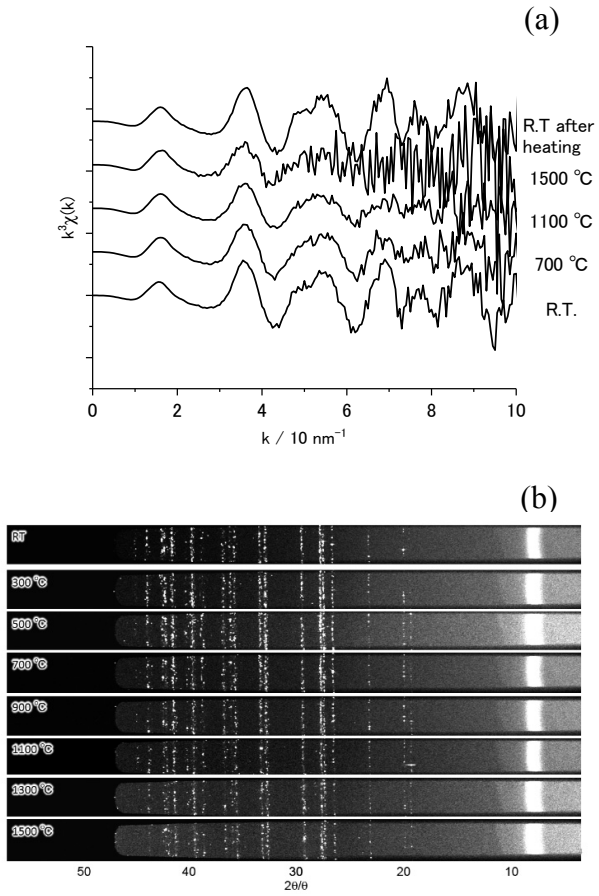

Fig. 2 (a) XAFS oscillation (Yb LIII) and (b) diffraction image of $Yb_2Si_2O_7$ sintered plate measured at various temperatures (R. T. ~ 1500 °C).

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References

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