Stability of Ce$^{3+}$ valence state and lattice expansion of CeO$_2$ induced by high temperature annealing in vacuum

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1 Introduction

In our previous papers, we have shown that energetic ion irradiation produces oxygen vacancies in CeO$_2$ [1]. Oxygen vacancies in CeO$_2$ cause the change of the valence state of Ce atoms near the oxygen vacancies from 4$^+\rightarrow$3$^+$ as a result of charge balance [2] and the lattice expansion due to the mutual repulsion of Ce cation atoms [3]. We have also shown that the existence of Ce$^{3+}$ valence state induces the ferromagnetism in the CeO$_2$ specimens [3,4]. It is well known, however, that oxygen vacancies can be produced in CeO$_2$ more easily under the reduction process by the high temperature annealing in vacuum. In the present experiment, the stability of Ce$^{3+}$ state and the lattice expansion induced by the high temperature annealing in vacuum was investigated by using the x-ray photoelectron spectroscopy (XPS) at the BL-27A beamline of KEK-PF and a conventional x-ray diffraction method (XRD).

2 Experiment

CeO$_2$ pellet was synthesized by sintering CeO$_2$ powders at 1873 K for 12 hours in air. It was annealed at 1273 K for 1 hour in vacuum, and just after the annealing in vacuum, it was stored in an evacuated glass tube until the XPS spectra were measured. Just before the specimen was set in an XPS chamber, it was taken out of the glass tube. The specimen was left in the atmosphere only for 15 minutes before evacuating the XPS chamber. After the XPS measurement, the specimen was left in the atmosphere for 50 minutes and then the XPS spectra were measured again. The energy of x-ray for the XPS measurements was 2.2 keV. For the XRD measurement with Cu Kα x-ray, a CeO$_2$ thin film, which was deposited on an Al$_2$O$_3$ substrate by using a RF magnetron sputtering, was used.

3 Results and Discussion

The XPS spectrum (a) in Fig. 1, which was measured for the CeO$_2$ specimen without high temperature annealing in vacuum, shows typical Ce-3d peaks for Ce$^{4+}$ valence state. In the figure, the reference spectrum for the Ce$^{3+}$ valence state is also plotted (spectrum (d)) [2]. The spectrum (b) is for the CeO$_2$ specimen which was exposed to the atmosphere for 15 minutes before the XPS measurement. XPS peaks for Ce$^{3+}$ valence state can be observed as well as those for Ce$^{4+}$ state in the spectrum. The Ce$^{3+}$ state and the oxygen vacancies in the specimen, therefore, survive the exposure to the atmosphere for 15 minutes. As can be seen in the spectrum (c), however, Ce$^{3+}$ peaks completely disappear, and only Ce$^{4+}$ peaks can be observed after the exposure to the atmosphere for 50 minutes. The present experimental result clearly shows that the Ce$^{3+}$ valence state and oxygen vacancies produced by the high temperature annealing in vacuum is very unstable, and oxygen atoms in the atmosphere re-oxidize the CeO$_2$ specimen including oxygen vacancies in a very short time.

![Fig. 1: (a) XPS spectrum for CeO$_2$ specimen without high temperature annealing, (b) XPS spectrum measured after exposure to atmosphere for 15 minutes, (c) XPS spectrum measured after exposure to atmosphere for 50 minutes, and (d) reference spectrum for Ce$^{3+}$ valence state.](image-url)
time to the atmosphere, the XRD peaks gradually shift to higher angles and after the two-day exposure, the peak position is about the same as for the spectrum of the specimen before the high temperature annealing. Therefore, the exposure to the atmosphere for 2 days completely re-oxidizes the specimen.

![Figure 2: Dependence of XRD spectrum of CeO$_2$ thin film annealed at 1273 K on exposure time to atmosphere.](image)

Our previous reports show that oxygen vacancies, the accompanying Ce$^{3+}$ state and the resulting lattice expansion induced by energetic ion irradiation are much more stable than those produced by high temperature annealing in vacuum. Even after the exposure to the atmosphere for more than a few months, we could find the lattice expansion and the ferromagnetic state of CeO$_2$ irradiated with energetic ions [3,4]. The high temperature annealing in vacuum produces only oxygen vacancies, but in the case of energetic ion irradiation, not only oxygen vacancies but also oxygen interstitial atoms and the disordering of Ce atom arrangements are produced. As such complicated defects prevent oxygen atoms from moving freely in the irradiated CeO$_2$ specimens, the oxygen vacancies in the ion-irradiated CeO$_2$ can survive the long-time exposure to the atmosphere.

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References

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