Transactions of the Materials Research Society of Japan 33[4] 829-832 (2008)

X-ray Absorption Fine Structure Analysis of Ag and Zn in the Glaze of Anti-bacterial Ceramics

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X-ray absorption fine structure (XAFS) analysis was applied to identify the chemical state of silver and zinc in the glaze of anti-bacterial ceramics. Anti-bacterial ceramics for example tile and sanitary ware are very important from the view point of hygiene. Ag and Zn have been known as inorganic anti-bacterial agents for a long time, and are widely used as raw materials for the anti-bacterial ceramics. These anti-bacterial agents were incorporated into the amorphous alminosilicate glaze. The anti-bacterial activities of the ceramics were confirmed by film covered method using *Staphylococcus aureus*. Ag K-edge XAFS analysis showed that the chemical state of Ag atoms in the Ag-glaze were monovalent, and the Ag-O bond length was increased compared to that of Ag_2O. Zn K-edge XAFS analysis showed that the chemical state of Zn atoms in the Zn-glaze were quite similar to that of Zn_2SiO_4.
Keyword: XAFS, silver, zinc, ceramics, anti-bacterial

1. INTRODUCTION

Recently, anti-bacterial products such as textile, plastic article and tile are widely spread from the view point of hygiene. Anti-bacterial products inhibit bacterial propagation on the surface and prevent biofilm, smell and scale. As an inorganic anti-bacterial agent, silver, zinc and copper have been well known for a long time. Ag is especially used because of its high activity, broad anti-bacterial spectra, durability and low toxicity for human.

Although anti-bacterial mechanism of metal elements has not been clarified yet, two hypotheses for anti-bacterial mechanism were proposed. One is 'dissolved ion theory', which means that metal elements dissolve and attack the respiratory chain of bacteria. The other is 'reactive oxygen species theory', which means that metallic elements behave as catalysts and generate reactive oxygen species that attack bacteria. Anti-bacterial activity of Ag-doped ceramics was reported to be attributed to the hydroxyl radical[1-3]. Anti-bacterial activity of ZnO was explained the generation of peroxide on the ZnO surface[4].

In the case of sanitary ware and interior wall tile, the anti-bacterial agent is added to the glaze that is made of amorphous alminosilicate. The chemical state of Ag and Zn in the glaze is very important to control anti-bacterial effect. However, it is difficult to determine the chemical state of Ag and Zn because of the small content of these elements and the existence of interference elements.

An X-ray absorption fine structure (XAFS) analysis is able to determine the local structure of the particular element in amorphous state. XAFS spectrum consists of two regions. One is X-ray absorption near edge structure (XANES) and the other is extended X-ray absorption fine structure (EXAFS). XANES provides the information about valence of the absorption elements and crystal structure of specimens and EXAFS provides the information about bond length and coordination number around the absorption elements.

To clarify the anti-bacterial mechanism of the glaze of anti-bacterial ceramics, the XAFS analysis applied to determine the chemical state of Ag and Zn in the glaze.

2. EXPERIMENTAL METHOD

2.1 Sample preparation

A sample of the glaze containing Ag as anti-bacterial agent (Ag-glaze) was prepared by the actual manufacturing process of sanitary ware. The raw material suspensions including mixture of glaze and Ag metal were sprayed on a slip-casted green body of sanitary ware, followed by the sintering at 1200°C in the air.

A sample using Zn as anti-bacterial agent (Zn-glaze) was obtained by cutting off an actual product of interior wall tile.

The cross sectional optical microscopic image of the sanitary ware is shown in Fig. 1. The thickness of the glaze layer was about 500 μm. The

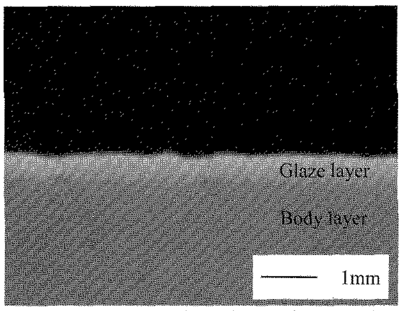

Fig.1 The cross sectional optical microscopic image of sanitary ware. The upper bright part is glaze layer and the lower dark part is body layer.

compositions of the glaze were identified by X-ray fluorescence analysis. Main components of both glazes were SiO_2 and Al_2O_3. The Ag content of Ag-glaze was lower than identification limit. From the electron probe microscope analysis, Ag_2O content was about 0.08 mass%. The Zn content of the Zn-glaze was about 15 mass% (convert to ZnO). XRD results of the both glaze showed no Ag_2O or ZnO peak, suggesting that Ag and Zn existed in amorphous alminosilicate.

2.2 Anti-bacterial test

ISO film cover method was applied for an anti-bacterial test[5]. *Staphylococcus aureus* IFO 12732 was used for the test. Bacterial suspension including *S. aureus* with cell concentrations in the range of $2\text{-}5\times10^5$ CFU/ml was prepared, and it was dropped on the sample surface. Then, the sample surface was covered by a polyethylene film. After incubation for 24 hours at 35°C, the viable cell count of *S. aureus* on the sample surface was measured by colony count method.

2.3 XAFS measurements

Ag K-edge XAFS measurements were performed at BL01B1 line, SPring-8, Hyogo, Japan. The Ag-glaze samples with the size of 50mm×50mm×10mm were used for XAFS measurements. The spectra of foil of Ag metal, Ag_2O and AgO were also measured as references. Ag K-edge XAFS spectra of Ag-glaze, Ag_2O and AgO were measured in fluorescence mode with a multi element SSD. Foil of Ag metal was measured in transmittance mode with ion chamber detector.

Zn K-edge XAFS spectra were measured at BL12-C, Photon Factory of the High-Energy Accelerator Research Organization, Tsukuba, Japan. The Zn-glaze sample pieces with the size of 10mm×10mm×5mm were used for XAFS measurements. The spectra of Zn metal, ZnO, Zn_2SiO_4 (willemite) and Zn^{2+} aqueous solution were measured as references. All samples were measured in fluorescence mode with an X-ray detector of the Lytle type.

3. RESULTS AND DISCUSSION

3.1 Anti-bacterial test

The viable cell count of *S. aureus* on the surface of Ag-glaze and Zn-glaze after 24 h incubation

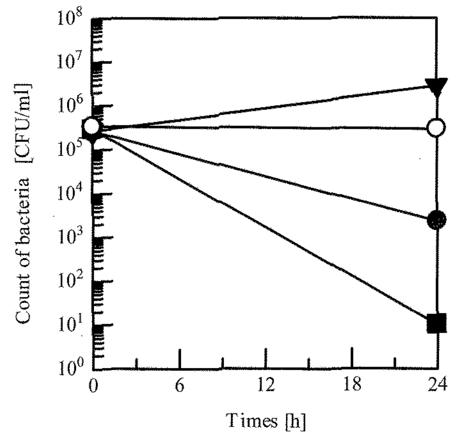

Fig.2 The count of *S. aureus* on the surface of Ag-glaze (●), Zn-glaze (■), glaze without Ag (▼) and polyethylene film (○).

was shown in Fig. 2. Polyethylene film and glaze without Ag were also described. On the surface of the polyethylene film and glaze without Ag, the count of bacteria was constant or increased. Otherwise, it decreased on the surface of Ag-glaze and Zn-glaze, resulting from the anti-bacterial activity of the Ag- and Zn-glaze. This indicates that 0.08 mass% Ag_2O and 15 mass% ZnO in the glaze contribute to anti-bacterial effect.

3.2 XAFS analysis

Ag K-edge XANES spectra of the Ag-glaze and references after normalized were shown in Fig. 3. The shape of the XANES spectrum of the Ag-glaze was different from those of the Ag metal and AgO, but similar to that of the Ag_2O. This result indicates that major components of Ag atoms in the Ag-glaze are monovalent. Figure 4 shows Fourier transforms of $k^3\chi(k)$ for the Ag-glaze, Ag metal and Ag_2O. Ag metal has a cubic closest packing structure and the Ag atom is neighbored by 12 Ag atoms with the distance of 2.88 Å. Ag_2O

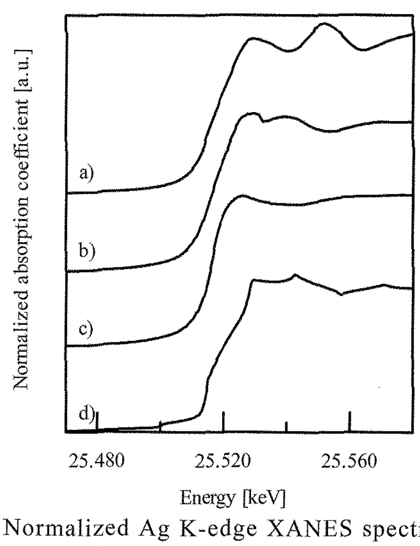

Fig.3 Normalized Ag K-edge XANES spectra for (a) Ag metal, (b) Ag_2O, (c) Ag-glaze, (d) AgO.

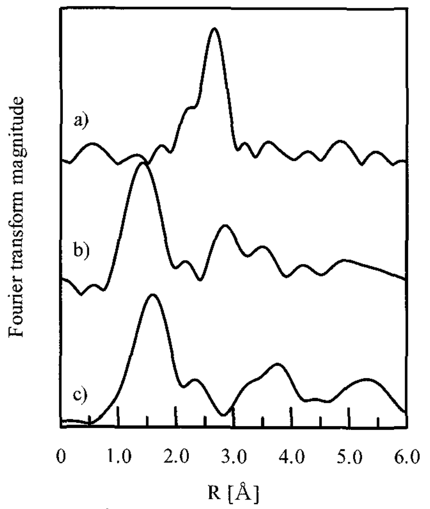

Fig.4 FTs of $k^3\chi(k)$ for (a) Ag metal, (b) Ag_2O, and (c) Ag-glaze.

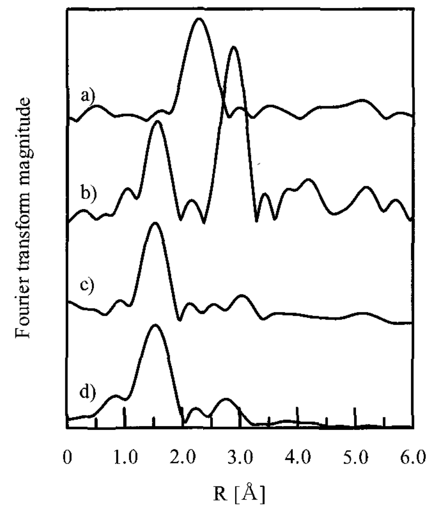

Fig.6 FTs of $k^3\chi(k)$ for (a) Zn metal, (b) ZnO, (c) $ZnSiO_4$, and (d) Zn-glaze.

is a cuprite-type structure; and the Ag atom is coordinated by two oxygen atoms with the distance of 2.04 Å. In the Fourier transforms of the Ag metal (Fig.4), an intense peak around 2.6 Å was due to Ag-Ag bonding. In the case of Ag_2O, two major peaks were observed. The first peak at around 1.4 Å was attributed to Ag-O bonding of first neighbors, and the second peak at around 2.8 Å was due to Ag-Ag bonding of second neighbors. In the Fourier transforms of Ag-glaze, only one peak attributed to Ag-O bonding was observed at 1.6 Å without Ag-Ag interaction of second neighbors. Compared to Ag_2O, Ag-O bond length was slightly increased. This indicates that Ag atoms in the Ag-glaze are isolated from crystal structure [6)] and dissolved in the glaze as Ag^+ ion.

Zn K-edge XANES spectra of Zn-glaze and references were shown in Fig. 5. In the spectrum

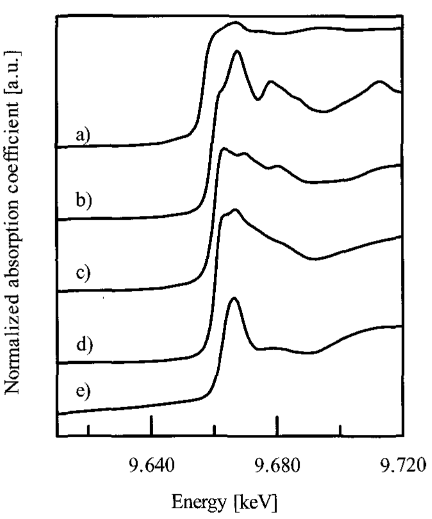

Fig.5 Normalized Zn K-edge XANES spectra for (a) Zn metal, (b) ZnO, (c)Zn_2SiO_4, (d) Zn-glaze and (e) Zn^{2+} aqueous solution.

shape of Zn-glaze was similar to that of Zn_2SiO_4. The energy of absorption edge of Zn-glaze was similar to those of ZnO and Zn_2SiO_4, indicating that Zn elements in the Zn-glaze were divalent cations and its local structure was similar to that of Zn_2SiO_4. Fourier transforms of $k^3\chi(k)$ of Zn-glaze and references except for Zn^{2+} aqueous solution was given in Fig. 6. In the spectrum of Zn metal, one distinct peak was observed at around 2.2Å attributing to Zn-Zn bonding. In ZnO the spectrum, two distinct peaks were observed. One was the peak at around 1.6 Å due to the Zn-O bonding, and the other was at around 2.8 Å due to Zn-Zn bonding. In the spectra of Zn-glaze and Zn_2SiO_4, only one peak at around 1.6 Å attributing Zn-O bonding was observed. These results indicate that Zn atoms in the Zn-glaze exist as divalent cations in tetrahedral $[ZnO_4]^{6-}$ [7, 8)].

4. CONCLUSIONS

XAFS was applied to measurement of the chemical state of Ag and Zn in the glaze of anti-bacterial ceramics. The anti-bacterial effect was confirmed by the film covered method. Ag atoms in the Ag-glaze were monovalent, and Ag-O bond length was increased compared to that of Ag_2O. In the Zn-glaze, chemical state of the Zn atoms was quite similar to that of Zn_2SiO_4. We concluded that Zn atoms exist as divalent cations in tetrahedral $[ZnO_4]^{6-}$.

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(Recieved December 28, 2007; Accepted May 13, 2008)