XANES-Analysis of Chromium Oxidation Number in Cement

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Introduction

Portland cement is manufactured by burning natural minerals that are mixed with a certain ratio. Recently, with the view to recycle of the mineral resources, wastes are used as raw materials and/or fuels. These natural minerals and wastes bring Cr in cement. The Cr is oxidized by burning and sometimes it has been a severe problem that the toxic Cr6+ were produced from the following hydration process to make cement products. But the oxidation number and distribution of Cr in clinker is still uncertain in detail. The purpose of this study is to reveal the oxidation number and its surrounding structure of Cr in clinker. As a result, the mechanism of oxidation and dissolution are revealed, and we are able to find the directions to depress the oxidation and dissolution of Cr6+ .

Experimental

Samples are portland cement clinker, silicate phase in clinker, interstitial phase in clinker and standard reagents (Cr_2O_3, CrO_2, CrO_3, K_2CrO_4). These cement samples were analyzed by XANES and compared with standard reagents to define the oxidation number. The spectra are observed by a fluorescence mode around Cr-*K*-edge, using Si(111) surfaces at BL01B1 beamline in SPring-8.

Results

As shown in Fig.1, it is concluded that Cr6+ was not recognized in all samples studied here, that is, in cement clinker, silicate phase and interstitial phase from evidence that a typical absorption peak of 5985eV from K_2CrO_4 and CrO_3 was not observed. Comparison of the slopes around 5990-6000eV suggests that the oxidation number of Cr in cement samples be close to +4.

Discussion

It has been believed that water-soluble Cr is in interstitial phase(hydrates at first) as K_2CrO_4 (or $K_2Cr_2O_7$)[1]. However, the results of this examination, it is proved that oxidation number is +4(or +5). It is expected that XANES analysis of Cr+5 reagent clarifies the exact oxidation number, and EXAFS measurements give a further information about the chemical bonding of Cr in clinker minerals.

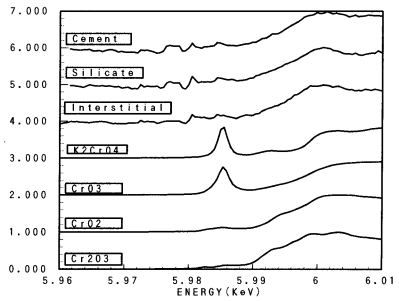

Fig.1. XANES of Cr

Reference

[1]J.F.Lee,PhysicaB2,208&209,577 (1995)

Determination of Local Structure for Ag Clusters on Si by Total Conversion Electron Yield XAFS

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It is well known that thin noble metal film exhibits anomalous light absorption in the visible and infrared regions. It increases the local electric fields near the surface. This phenomenon is not well explained by the classical theory and effective dielectric functions. The local structure of Ag clusters must play very important roles in this phenomenon. In this work, XAFS measurements were carried out to study local structures of Ag clusters.

The total conversion electron yield (TCEY) technique was applied to measure Ag *K*-edge (25.5keV) XAFS for Ag films, which were deposited on Si by electron-beam evaporation in UHV. The samples were stuck on the sample electrode with conductive adhesive tape and He gas was introduced in to CEY cell. Si(311) double-crystal monochromator was used.

Figure 1 shows the Fourier transforms of EXAFS analyzed by XANADU code.[1] All of the spectra have a strong peak at almost the same distance. It means that these clusters have *fcc* structure and almost equal interatomic distances. The intensities of |FT(r)|, however, change with the thickness of the film. The intensity is related closely with the coordination number. The coordination numbers for the first nearest atoms are plotted in Fig. 2 as a function of thickness with the expected values by calculation.[2] In the range of small thickness, the observed numbers are smaller than the calculated ones. Very thin Ag films are known to form islands at the solid surface. Since the superficies of island-shaped film is larger than that of the planar ones, we assume that this causes the decreased coordination numbers. More detailed XAFS analyses combined with structure models are in progress.

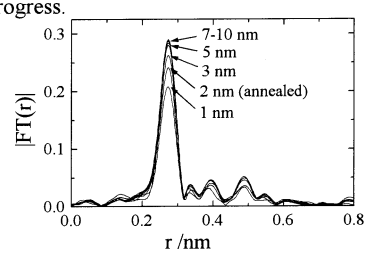

Fig. 1 Fourier transforms of Ag *K*-edge EXAFS for Ag films deposited on Si.

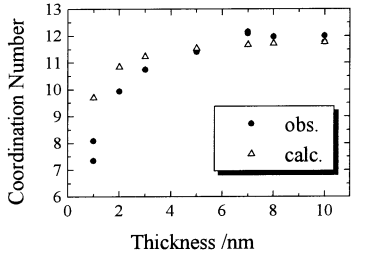

Fig. 2 Coordination number of first nearest neighbors as a function of film thickness.

References

1) H. Sakane, T. Miyanaga, I. Watanabe, N. Matsubayashi, S. Ikeda and Y. Yokoyama, *Jpn. J. Appl. Phys.* **32,** 4641 (1993).
2) E.D. Crozier, A.J. Seary, M.K. McMaus, D.T. Jiang, *J.Phys.IV France,* 7 C2, 251 (1997).