Discoloration in sintered alumina ceramics from colorless to brownish yellow by ultraviolet radiation was found and its mechanism was examined. UV-induced optical absorption bands were observed around 330 and 480 nm. An intense red luminescence peak appeared around 650-690 nm upon exciting UV region, and intensity of the luminescence band decreased with duration of UV-illumination time. ESR hyperfine structures of a $^{55}$Mn$^{2+}$ appearing in the spectrum of the specimen before illumination disappeared after UV-illumination. It is concluded that the discoloration is attributed to photochemical conversion of Mn$^{2+}$ to Mn$^{3+}$ by the following reaction: Mn$^{2+} +$ Fe$^{3+} = $Mn$^{3+} + $Fe$^{2+}$. Here, Mn and Fe are contained in the specimen as trace impurities (in Refecerem concentrations of Mn and Fe are 3 ppm and 80 ppm, respectively). Extinction coefficients of visible bands in Mn$^{2+}$ are larger by 2 to 3 orders of magnitude than those of Mn$^{3+}$. Therefore, the key species of the solarization of alumina is considered to be trace impurity of Mn$^{2+}$.

Key-words: Solarization, Alumina, Discoloration

1. Introduction

Coloration phenomena in advanced ceramics are complicated problems because they may be affected by trace impurities in raw powder materials and caused by contamination in the production process. It has been found that color of sintered alumina ceramics changes from white to brownish yellow upon exposure to ultraviolet radiation. Since alumina is a typical ceramics and is most widely used ceramics, elucidation of this mechanism will be of importance in basis science as well as application. In the present work, we examine discoloration of surfaces of sintered alumina ceramic bodies by irradiation with UV light and consider the mechanism from information obtained by diffuse reflectance, photoluminescence, and electron spin resonance (ESR) spectroscopies. It is proposed that a ppm level of impurity manganese ions play a key role in UV-solarization of alumina.$^{1,2}$

2. Experimental procedures

2.1 Preparation and impurity analysis of sintered alumina
meter equipped with 60 mm dia. integrating sphere. Photoluminescence spectra from the surface were measured with a Shimadzu Model RF-5000 recording spectrofluorometer. ESR spectra were measured at room temperature with JEOL PE-3X X-band spectrometer, applying 100 kHz field modulation. The measurement was carried out for the pulverized sample before and after irradiation.

3. Results and discussion
3.1 Impurity analysis
Analytical results are summarized in Table 1. Purity of the Referceram was calculated by subtracting the sum of the amounts of the oxides of major impurities, and is 99.7%. Concentration of transition elements, which are considered to be the origin of the discoloring, are 80 ppm for Fe, 20 ppm for Ti and 3 ppm for Mn. These concentration levels are close to those in commercially available alumina ceramics.

3.2 DRS of Referceram
Figure 2 shows DRS of the Referceram before and after UV-illumination. Two broad absorption bands are induced at around 330 nm and 480 nm after illumination. Then, color of the specimen changed from white to brownish yellow, visually. The DR spectrum centered at 480 nm corresponds to the complementary pair of absorption wavelength of yellow color. ③

3.3 Photoluminescence spectra of Referceram
When specimens are excited with ultraviolet light, three emission bands peaking at 647, 677 and 690 nm appear. These emission bands are close to those in Mn-doped alumina which was separately prepared

by high purity alumina (99.99%) under a similar sintering process. No fading of coloring was observed after stopping light illumination. Intensities of emission bands around 650–690 nm decreased with UV irradiation time as shown in Fig. 3. Intensities of emission from both Mg-doped and Fe-doped aluminas were smaller by about 3 orders of magnitude than that of those of the Mn-doped alumina. This result indicates that the possibility of Mg or Fe ions as the major origin of the discoloration may be discounted. Figure 4 shows photos showing discoloration of specimen.

3.4 Changes in ESR spectra before and after irradiation
As shown in Fig. 5(a), the as-sintered Referceram shows a weak but sharp sextet signal besides intense

Fig. 2. Changes in diffuse reflection spectra of specimen before and after UV-illumination. (a) before irradiation, (b) after 3 min with Xe arc light (intensities measured by a thermopile was 500 mJ/cm² by photon flux measured with thermopile).

Fig. 3. Change in photoemission spectra with duration of UV-illumination. Spectral sensitivity was kept at constant. (a) before irradiation, (b) after 1 min, (c) after 3 min irradiation. Excitation wavelength: 325 nm.

Fig. 4. Photos of sample. White region was masked before exposure to Xe light. (a) picture in day light, (b) picture under UV-illumination in the dark.
signals\(^4\) due to Fe\(^{3+}\) located at the site of octahedral coordination. This signal is assigned to a hyperfine structure (hfs) of a divalent \(^{55}\)Mn (nuclear spin \(I=5/2\)) ion.\(^5\) After irradiation, the hfs of Mn\(^{2+}\) disappears as shown in Fig. 5(b). This result suggests Mn\(^{2+}\) is converted to Mn\(^{3+}\), which is not sensitive to ESR (Mn\(^{2+}\) with (3d)\(^4\) is paramagnetic but is not detectable except at extremely low temperatures due to rapid spin-lattice relaxation). In very high purity alumina ceramics (Mn, Fe<0.1 ppm) in which no perceptible color change was seen, ESR signals of neither Mn\(^{2+}\) nor Fe\(^{3+}\) is observable as shown in Fig. 5(c).

3.5 Discoloration mechanism

It is evident that the occurrence of a trace amount of Mn\(^{2+}\) and Fe\(^{3+}\) ions are requisite for emergence of UV-discoloration because no perceptible color change was seen for Mn and Fe-'free' alumina. When discoloration occurs upon exposure to UV-radiation, intensities of photoluminescence bands, which are close to those from Mn\(^{2+}\)-doped alumina, decrease and ESR signals of Mn\(^{2+}\) disappear. Mn\(^{3+}\) ions are ESR silent and do not emit intense photoluminescence. Thus, these results strongly suggest that Mn\(^{2+}\) is oxidized into Mn\(^{3+}\) by irradiation with UV-rays. It is already known fact that absorption coefficients\(^6\) of bands originating from d-d transitions in Mn\(^{3+}\) is larger by a factor of about 2 to 3 orders of magnitude than those of Mn\(^{2+}\). Thus, Mn\(^{2+}\) ions are oxidized into Mn\(^{3+}\) photochemically, absorption intensities are anticipated to be intensified by 2 to 3 orders of magnitude, i.e., 3 ppm of oxidized Mn\(^{3+}\) ions correspond to several hundred to thousand ppm of Mn\(^{2+}\). Since Fe\(^{3+}\) ions coexist with Mn\(^{2+}\) ions and their concentrations are much higher than those of Mn\(^{2+}\), photoionized electrons released from Mn\(^{2+}\) ions are considered to be captured by Fe\(^{3+}\) ions, which results in formation of Fe\(^{2+}\). Fe\(^{3+}\) ions in alumina occupy octahedral sites and Fe\(^{3+}\) ions prefer octahedral coordination to tetrahedral coordination. Thus, no large energy is expected in trapping an electron at the site of Fe\(^{3+}\). The following is the photochemical reaction we propose here;

\[
\text{Mn}^{2+} + \text{Fe}^{3+} = \text{Mn}^{3+} + \text{Fe}^{2+}
\]

Positions of photoemission and absorption bands induced by UV-illumination are close to those of Mn\(^{2+}\) and Mn\(^{3+}\) in alumina, respectively.

To interest, this photochemical reaction was proposed to explain deepening of purple color, which was first discovered by Faraday in the 18th centuries,\(^7\) of Mn-containing glasses. We consider that the essentially same mechanism is valid for UV-solarization of sintered alumina.

4. Conclusions

(1) Two bands centered at around 330 and 480 nm are induced in sintered alumina by UV-illumination. The 480 nm band is the origin of brownish yellow coloring.

(2) The following photochemical reaction is proposed as a mechanism of the UV-solarization.

\[
\text{Mn}^{2+} + \text{Fe}^{3+} = \text{Mn}^{3+} + \text{Fe}^{2+}
\]

Here, Mn\(^{2+}\) and Fe\(^{3+}\) ions are contained at concentration of 3 ppm and 80 ppm, respectively. Since the extinction coefficient of Mn\(^{3+}\) is by 2 to 3 order of magnitude larger than that of Mn\(^{2+}\), the formation of Mn\(^{3+}\) is contributed to the origin of discoloration.

(This paper was presented at the 4th International Conference on Ceramic Powder Processing Science, March, 1991)

Acknowledgment This work was supported in part by a grant from THE NAGAI FOUNDATION FOR SCIENCE & TECHNOLOGY to one (M.Y.) of the authors.

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