Controlling photochromic properties of molybdenum oxide based composite films by copper addition

Hidetoshi MIYAZAKI,[†] Hiroaki ICHIOKA, Hisao SUZUKI* and Toshitaka OTA**

Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690–8504, Japan

*Graduate School of Science and Technology, Shizuoka University, 3–5–1 Johoku, Hamamatsu 432–8561, Japan

**Ceramic Research Laboratory, Nagoya Institute of Technology, 10–6–29 Asahigaoka, Tajimi, Gifu 507–0071, Japan

MoO₃ based photochromic composite films were fabricated using a Mo-IPA methanol solution and a transparent urethane resin, and the photochromic property of the films was controlled by copper addition. All the composite films colored by UV–vis light irradiation, and bleached in placing a dark room. The initial color of the films changed from blue to transparent by Cu addition to the composite film, and Cu addition caused acceleration of the bleaching speed of the composite films with the Cu/Mo ratio of higher than 0.5.

©2014 The Ceramic Society of Japan. All rights reserved.

Key-words : Photochromic property, Composite film, MoO₃, Copper

[Received August 21, 2013; Accepted October 30, 2013]

1. Introduction

Photochromic materials show a reversible photosensitive property by light irradiation and interception of light, and these materials are silver chloride based glasses,^{1)–3)} tungsten oxide based films or composites^{4)–9)} and molybdenum oxide based film.^{10),11)} The photochromic property of the MoO₃ based materials appear by means of reduction of Mo⁶⁺ to Mo⁵⁺ or Mo⁴⁺ by UV–vis light irradiation, thereby the MoO₃ color changes from transparent to blue or brown.

Hinokuma et al. reported fabrication of Mo-IPA using metal molybdenum powder and H₂O₂.¹²⁾ The resulting Mo-IPA has an empirical formula MoO₃·nH₂O₂·mH₂O where n and m depended on the extent of removing of H₂O₂ in the precursor solution. In previous, we have reported fabrication of MoO₃ based photochromic composite films using an α - β - and γ - peroxyisopoly-molybdic acid (Mo-IPA) aqueous solution and transparent urethane resin.¹³⁾ However, in the previous investigation,¹³⁾ the color at the initial state and the bleaching speed of the composite films could not be controlled.

In this investigation, we fabricated molybdenum-based photochromic composite films using a Mo-IPA methanol solution and transparent urethane resin as starting materials, where the γ - Mo-IPA was employed to fabricate composite films because of its high methanol solubility. In the present study, γ - Mo-IPA called as “Mo-IPA. We evaluated coloring and bleaching properties of the resulting composite. Furthermore, the photochromic property of the composite films was controlled by addition of CuCl₂ (Cu²⁺ ions) in the films; referring the previous investigation since existence of Cu²⁺ ion affected to the photochromic property of WO₃ based composite films.⁹⁾

2. Experimental procedure

Metal molybdenum powder (particle size of 4 μ m, Kojundo

Chemical Co. Ltd.) was used as a starting material. The molybdenum powder was dissolved completely into an ice-cooled 15% H₂O₂ solution to achieve atomic molybdenum concentration of 1.0 mol/L. After reaction, the excess H₂O₂ was removed catalytically using Pt nets for 3 days, and the (γ -) Mo-IPA solution was obtained according to the previous study.¹²⁾

Mo-IPA was dissolved into methanol with the concentration of 0.01 mol/L, and subsequently CuCl₂ (Wako Pure Chemical Industries Ltd.) was dissolved into the solution with the Cu/Mo ratios of 0 to 1.0. The 1.0 mL of the resulting Cu/Mo-IPA methanol solution was mixed into urethane resin (M-40, Asahi Kasei Chemicals Corp.) of 3.3 g (volume of 3 cm³). The mixture slurry was mixed well, and degassed at 1 kPa for 60 min to expel the dissolved air in the precursor slurry. Then the precursor slurry was put between the slide glasses with film thickness of 1 mm, and the slurry was cured by UV–Vis light irradiation for 1 min using a 1 kW low-pressure Hg lamp. The resulting films were colored because of the UV–vis light irradiation. Therefore, the composite film was put into a dark room to clarify the film for 7 days.

The photochromic properties of the films were evaluated at room temperature using a UV–Vis spectrophotometer (UV-1600; Shimadzu Corp., Japan). Through the investigation, a 1 kW low-pressure Hg lamp was used for coloration of the composite films.

3. Results and discussion

Composite films were fabricated using a Cu/Mo-IPA ethanol solution and a urethane resin. **Figure 1** depicts the coloring property of the composite films with various Cu contents before and after UV–vis irradiation, and the inset photographs are the films on the paper before and after 20 min UV–vis irradiation.

The Cu un-doped film before UV–vis irradiation indicated light blue color and a broad absorption at the peaks of 630 and 790 nm. The absorption was attributed to be existence of Mo⁵⁺.^{10),11),13)} The Cu un-doped composite film after UV–vis irradiation showed broad absorption at the absorption peaks of 450 and 790 nm, and the color of those was brown. In this study, Mo-IPA methanol solution was used as the starting material.

[†] Corresponding author: H. Miyazaki; E-mail: miya@riko.shimane-u.ac.jp

[‡] Preface for this article: DOI <http://dx.doi.org/10.2109/jcersj2.122.P1-1>

Fig. 1. Transmittance spectra for composite films with the Cu/Mo ratios of (a) 0, (b) 0.1, (c) 0.5 and (d) 1.0 before and after UV-vis light irradiation. Inset photographs in respective graphs show films before and after 20 min UV-vis irradiation.

Electrons were released from the OH group or MeOH in the composites by UV/Vis light irradiation. Mo^{6+} and Mo^{5+} in the films were received electrons and reduced to Mo^{5+} and Mo^{4+} by UV/Vis irradiation, and it assumed that the color of the resulting film became brown. These photo-chemical reaction is describes as follows:

The composite films with Cu addition were transparent at the initial state, and the no absorption peaks were observed. Where, additive of Cu assumed to exist as Cu^+ or Cu^{2+} ion in the composite. The Cu addition effect on controlling of the color of the composite films was described on the later. After UV-vis irradiation, the composite films showed the broad absorption at the peaks of 450 nm and around 700–800 nm, and the color of the

Fig. 2. Transmittance spectra on bleaching for composite films with the Cu/Mo ratios of (a) 0, (b) 0.1, (c) 0.5 and (d) 1.0 after 20 min Uv-vis irradiation.

composite films became brown.

In general, the color of MoO_3 based photochromic films was transparent at initial state, and changed from transparent to blue according to reduce of Mo^{6+} to Mo^{5+} by Uv-vis irradiation.^{10),11)} Where, the composite film (at the initial state) was put into a dark room to clarify the film for 7 days. On the contrary, the results in the present work were different from the previous investigations. The results of the present work assumed to originate from Mo^{4+} or interaction with the resin polymer, but further investigations are required to explain this phenomenon.

Using the optical property of the composite films, the reaction rate constant k was estimated at the wavelength of 450 nm: the remarkable absorption peak of the films in the coloring condition. The method of calculating the photochromic reaction rate constant was described an earlier reports.^{9),13)} The reaction rate equation is described as

$$-\ln([A]/[A_0]) = kt, \quad (3)$$

where A_0 is the initial absorbance, t is the passing time and A is

the absorbance at the time t passed. The calculated reaction rate constants of the composite films with the Cu/Mo ratio of 0, 0.1, 0.5 and 1.0 were 0.122, 0.148, 0.105 and 0.0354 min⁻¹, respectively. The rate constants were very close to each other with less than the Cu/Mo ratio of 0.5, and that with Cu/Mo ratio of 1.0 was slower than that of the Cu un-doped film. The results suggested that Cu²⁺ ions did not affect as a coloring sensitizer.

A bleaching property of the films was evaluated in dark room at room temperature, and Fig. 2 presents the bleaching property of the films after 20 min UV-vis irradiation. For the Cu un-doped composite film and the composite film with the Cu/Mo ratio of 0.1, the color of the films did not return completely to the initial state color. On the other hand, the color of the composite films with the Cu/Mo ratio of 0.5 and 1.0 became to the initial state color for 120 h.

Bleaching property of all the films was observed, and the bleaching speed was much slower than the coloring speed. Regarding the bleaching property, plots of the reactions on the Eq. (3) showed no linear property. The bleaching reaction therefore was not first-order, and the rate-determining-stage was two or more steps. The rate-control factors assumed to be electron mobility in MoO₃ clusters, returning electrons from Mo⁴⁺ to matrix (hydroxyl function), and so on. Thus, the reaction constant of the films on the bleaching could not be evaluated.

To compare the bleaching speeds of the films semi-quantitatively, we calculated the half-life period of the films τ (h), where τ was the time taken from the transmittance of the sufficiently coloring state (20 min UV-vis irradiation) to the transmittance at 450 nm of the on a half of its after 120 h. The calculated half-life periods τ of the films with Cu/Mo ratios of 0, 0.1, 0.5 and 1.0 were 21.8, 29.2, 9.7 and 4.8 h, respectively. The results suggested that CuCl₂ addition with higher than Cu/Mo ratio of 0.5 caused acceleration of beaching speed of the MoO₃ composite films.

In previous investigations, the bleaching speed of the AgCl and the WO₃ photochromic composite films was accelerated by CuCl₂ addition.^{3),9)} For the MoO₃ based composite films, Cu²⁺ ion also acted as sensitizer on the bleaching of the composite films as follows:

The composite films were placed in the dark room, the equilibrium of these Eqs. (4) and (5) move to the left side. Mo in the

composite films was more oxidized by existence of Cu²⁺ ions, thereby it assumed that the bleaching speed was accelerated. As well as this speculation, the composite films without CuCl₂ addition was color because of low molybdenum valence, and the composite films with CuCl₂ addition was transparent because molybdenum kept a high molybdenum valence by existence of Cu²⁺ ions.

4. Conclusion

The MoO₃ based photochromic composite films were fabricated using Mo-IPA methanol solution and transparent urethane resin, and the Cu addition effect on the photochromic property of the films was evaluated. The initial color of the composite films could be controlled by copper addition in the films, and the color of the composite changed from blue to transparent with increase of the Cu contents in the composites. Furthermore, the bleaching speed of the composite films accelerated by Cu²⁺ ion addition with the Cu/Mo ratio of higher than 0.5. These results suggested that the initial state color and the bleaching property of the MoO₃ based composite films could be effectively controlled by Cu²⁺ ion addition.

References

- 1) W. H. Armistead and S. D. Stookey, *Science*, **144**, 150–154 (1964).
- 2) H. Miyazaki, H. Shimoguchi, H. Suzuki and T. Ota, *Adv. Mater. Sci. Eng.*, **2012**, 784202 (2012).
- 3) H. Miyazaki, H. Shimoguchi, H. Nakayama, H. Suzuki and T. Ota, *Adv. Mater. Sci. Eng.*, **854928** (2013).
- 4) Y. Shigesato, *Jpn. J. Appl. Phys.*, **30**, 1457 (1991).
- 5) Y. A. Yang, Y. W. Cao, P. Chen, B. H. Loo and J. N. Yao, *J. Phys. Chem. Solids*, **59**, 1667–1670 (1998).
- 6) C. Bechinger, M. S. Burdis and J.-G. Zhang, *Solid State Commun.*, **101**, 753–756 (1997).
- 7) N. Xu, M. Sun, Y. W. Cao, J. N. Yao and E. G. Wang, *Appl. Surf. Sci.*, **157**, 81–84 (2000).
- 8) H. Miyazaki, Y. Baba, M. Inada, A. Nose, H. Suzuki and T. Ota, *Bull. Chem. Soc. Jpn.*, **84**, 1390–1392 (2011).
- 9) H. Miyazaki, M. Inada, H. Suzuki and T. Ota, *Bull. Chem. Soc. Jpn.*, **85**, 1053–1056 (2012).
- 10) K. Ajito, L. A. Nagahara, D. A. Tryk, K. Hashimoto and A. Fujishima, *J. Phys. Chem.*, **99**, 16383–16388 (1995).
- 11) J. Scarminio, A. Loureno and A. Gorenstein, *Thin Solid Films*, **302**, 66–70 (1997).
- 12) K. Hinokuma, K. Ogasawara, A. Kishimoto, S. Takano and T. Kudo, *Solid State Ionics*, **53–56**, 507–512 (1992).
- 13) H. Miyazaki, H. Ichioka, H. Suzuki and T. Ota, *Bull. Chem. Soc. Jpn.*, Accepted.