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Preparation of black-colored thin films from silica sol containing dissolved metal nitrates by the sol-gel method

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Black-colored SiO_2-based films, containing colorant inorganic spinel crystals such as Cu_2MnO_4, $CuMn_2O_4$, $CuMnCrO_4$, $CuMnFeO_4$ or $CuMnCoO_4$, were prepared from a silica sol containing dissolved metal nitrates using the dipping-withdrawing technique. The inorganic colorants were formed in the SiO_2 matrix of the films by heat-treatment at temperatures from 600 to 660°C. The black-colored coating films were uniform and transparent with a low haze value (less than 1.0%) and with a thickness of 100–800 nm in the SiO_2-(Cu-Mn-Cr-O) system, for which the colorant was the spinel crystal of $CuMnCrO_4$. The visible light transmittance of the colored films was controlled in a relatively wide range of 15–65% by changing the film thickness or the colorant concentration in the coating solution. Optimization of the composition of the coating solution and the preparation conditions gave black-colored films with excellent durability and visible light transmittance of about 25%, which is similar to that of deeply black-colored glasses commonly produced by the melting method. For example, a black-colored film with a visible light transmittance of 24.6% and a film thickness of 160 nm was obtained from a coating solution with a nominal composition of $36SiO_2 \cdot 64CuMnCrO_4$. The durabilities of the glasses with black-colored coatings against scratching, abrasion and chemicals are good enough for the practical applications.

1. Introduction

Several kinds of colored glass plates have been produced from molten glasses containing transition metal ions such as iron, chromium, cerium and others corresponding to the desired color. Recently in the application of automotive windows, a deeply black-colored glass also called "deeply gray-colored glass" has been used as it offers privacy and design features. Such a glass is commonly produced by the melting method. In the present recycling system for colored glass plate, used glasses and cullet should be classified by color. In the case of deeply colored glass plate, in particular, the cullet can only be used for production of glass plate with the same color. This causes problems of high cost and low efficiency in the glass production process. It is difficult to produce various kinds of colored glass plate, that meet the customers' requirments of wide variations in color and depth of color and designs of glass products tend to be limited.

Colored glasses produced by the coating method have much greater flexibility in terms of production than those made by the melting method. For example, color and the depth of color (i.e. visible light transmittance, Tv) can be easily controlled by changing the kind of colorant, the concentration of the colorant or the film thickness of the coating. Therefore, the coating method can be suitable for production on the small scale and with wide color-variation. Moreover, the coating method can reduce the volume of colored cullet and it can be used for the production of common glass plate, because the concentration of colorants is 10–100 ppm which is much less than that of the colored cullet produced by the melting method. The coating method to produce various colored glass plate, thus, has a great advantage in terms of recycling and greater high flexibility of production.

Sol-gel methods are well known as one of the most promising technologies to obtain new functional products, and have been studied for more than two decades. It has been used to produce films with various properties on glass. Some successful results have already been reported including protective coatings [1], fine-patterned films for waveguides or gratings [2], anti-reflective glass [3, 4], water-repellent glass [5, 6], hydrophilic mirrors [7] and colored glass using organic colorants [8, 9].

In this paper, black-colored thin films from the SiO_2-(Cu-Mn-X-O) (X = Cr, Fe, Co) system coated on glass substrates have been prepared from silica sols containing dissolved metal nitrates by the sol-gel method. The composition of coating solutions and the preparation conditions necessary to obtain black-colored coating films, in which spinel crystals are precipitated as a colorant have been investigated. The optical, mechanical and morphological properties of the black-colored films have been characterized and the preparation conditions have been finally optimized in order to minimize the film thickness to give a visible light transmittance of about 25%, which is very similar to that of deeply black-colored glass commonly produced by the melting method.

2. Experimental

2.1. Preparation of coating solutions

Chemical grade tetraethoxysilane (TEOS) was used as the raw material to give the SiO_2 matrix. Metal nitrates used were chemical grade $Cu(NO_3)_2{\cdot}3H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_2{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ (Kishida Chemicals). These were dissolved in ethanol.

Fig. 1 shows the flow chart for the preparation procedure for a coating solution consisting of TEOS, water containing 1 mass% nitric acid, ethanol and metal nitrates. At first, a silica sol was prepared by mixing TEOS, water containing 1 mass% nitric acid and ethanol, stirring for 4 h at room temperature and then standing for 12 h. The molar ratio of water to TEOS was 8, and the TEOS concentration was adjusted to be 1.5 $mol{\cdot}kg^{-1}$ by the addition of ethanol. For example, the required weight of TEOS, water with 1 mass% nitric acid and ethanol were 31.3, 21.7 and 47.0 g, respectively, when 100 g of the silica sol was prepared.

Next, a coating solution was prepared from the mixture of the silica sol, ethanol and metal nitrates for each metal in the composition $(100-y)SiO_2{\cdot}y$(Co-Mn-X-O), where the concentration of an oxidation product of $Cu_pMn_qX_rO_4$ ($p+q+r=3.0$), y, ranged from 10 to 80 mol%, and X corresponds to the metals mentioned above. The content of SiO_2 in 1.0 kg of the coating solution was adjusted to be 0.1–0.8 mol, by the addition of ethanol, which is defined here as a SiO_2 concentration in a unit of $mol{\cdot}kg^{-1}$. In the case of the preparation of 100 g of the coating solution with a SiO_2 concentration of 0.7 $mol{\cdot}kg^{-1}$ for the composition $80SiO_2{\cdot}20CuMnCrO_4$ (mol%, $y=20$, $p=q=r=1.0$, X = Cr), 46.67 g of silica sol prepared above, 37.08 g of ethanol, 4.23 g of $Cu(NO_3)_2{\cdot}3H_2O$, 5.02 g of $Mn(NO_3)_2{\cdot}6H_2O$ and 7.00 g of $Cr(NO_3)_3{\cdot}9H_2O$ were mixed together and then stirred at room temperature for 1 h, until all the metal nitrates that had been added were completely dissolved. Table I shows the batch composition of 100 g coating solutions as nominal compositions of the films for typical samples.

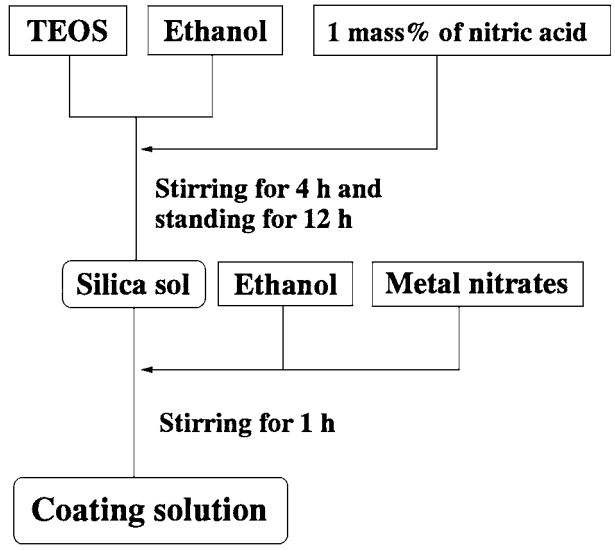

Figure 1 Preparation procedure for a coating solution.

A dried coating solution was examined over a temperature range from 25 to 800°C by using a DTA-TG analyzer (Rigaku, Model TAS-100).

2.2. Coating procedure

Coating films were formed by a dipping-withdrawing technique on a clean soda-lime-silica glass substrate (100 mm × 100 mm × 2 mm in thickness) under a relative humidity of 50% at 23°C. The withdrawing speed was in the range 1 to 8 $mm{\cdot}s^{-1}$. The wet films were heated at 350°C for 10 min and finally heat-treated at 450–700°C for 5 min.

TABLE I Batch composition of the coating solutions as nominal composition of films for typical samples

Nominal composition of films (mol%)	Concentration of SiO_2 in coating solution ($mol \cdot kg^{-1}$)	Batch composition of 100 g coating solutions (g)						
		Silica sol	Ethanol	$Cu(NO_3)_2 \cdot 3H_2O$	$Mn(NO_3)_2 \cdot 6H_2O$	$Cr(NO_3)_3 \cdot 9H_2O$	$Fe(NO_3)_2 \cdot 9H_2O$	$Co(NO_3)_2 \cdot 6H_2O$
$80SiO_2{\cdot}20CuMnCrO_4$	0.8	53.34	28.09	4.83	5.74	8.01	0.00	0.00
$84SiO_2{\cdot}16CuMnCrO_4$	0.8	53.34	32.52	3.68	4.37	6.10	0.00	0.00
$80SiO_2{\cdot}20CuMnCrO_4$	0.7	46.67	37.08	4.23	5.02	7.00	0.00	0.00
$36SiO_2{\cdot}64CuMnCrO_4$	0.1	6.67	76.82	4.30	5.10	7.12	0.00	0.00
$80SiO_2{\cdot}20CuMn_2O_4$	0.7	46.67	39.06	4.23	10.05	0.00	0.00	0.00
$80SiO_2{\cdot}20CuCr_2O_4$	0.7	46.67	35.10	4.23	0.00	14.01	0.00	0.00
$80SiO_2{\cdot}20CuMnFeO_4$	0.7	46.67	37.02	4.23	5.02	0.00	7.07	0.00
$80SiO_2{\cdot}20CuMnCoO_4$	0.7	46.67	38.99	4.23	5.02	0.00	0.00	5.09

2.3. Characterization of colored thin films

The color of the films was observed with the naked eye and visible light transmittances (Tv) and haze values (H) were measured by using a hazemeter (Nippon Densyoku Kogyo, NDH-20D). The visible light transmittance (Tv) was calculated as an average of transmittances calibrated by the sensitivity of the human eye at each wavelength, as described in JIS R3106. The film thickness was measured by using a thickness meter (Sloan Tech., Dektak-3030). The surface morphology and cross sections of the films were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4500).

The precipitated crystal phases in the films were examined by using an X-ray diffractometer (XRD) with Cu K_α (Rigaku, Model RINT-1500), using an accelerating voltage of 40 kV, a current of 200 mA and a scanning range of 2θ from 10 to 70 degrees.

To evaluate the durability, resistance tests such as a pencil hardness test, a scratch test, an abrasion test and a chemical durability test were carried out. The pencil hardness test was done as described in JIS K-5400, the scratch test involved scrubbing the film surface 10 times by hand using steel wool, in the abrasion test the film was rubbed with a canvas cloth as a friction material (refer to JIS L3102-1206), and in the chemical durability test a drop of 1.0 $mol \cdot l^{-1}$ hydrochloric acid aqueous solution was put on the film at room temperature for 10 min.

3. Results and discussion

3.1. Black-colored film formation region of the SiO_2-(Cu-Mn-X-O) system

Figs 2–4 show the black-colored film formation regions for the systems SiO_2-(Cu-Mn-Cr-O), SiO_2-(Cu-Mn-Fe-O) and SiO_2-(Cu-Mn-Co-O), respectively, where the SiO_2 concentration was kept at 0.7 $mol \cdot kg^{-1}$ and the concentration of $Cu_pMn_qX_rO_4$ ($p + q + r = 3.0$) in the coating solutions was 20 mol%. For all the coating films plotted in these figures, the withdrawing speed and final heat-treatment condition were 6 $mm \cdot s^{-1}$ and 600°C for 5 min, respectively. In these figures, the symbols of solid circles, open squares and open triangles indicate colors of black, partially black with bronze and bronze, respectively, where the condition of "partially black with bronze" corresponds to films in which black-colored areas can be observed on bronze films.

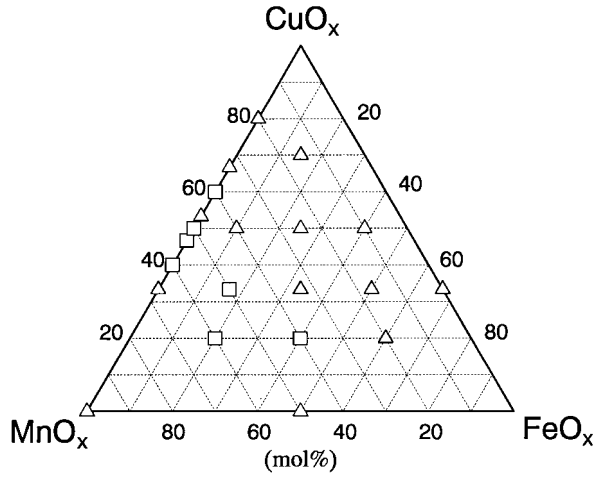

Figure 3 Black-colored film formation region in the system SiO_2-(Cu-Mn-Fe-O), where the SiO_2 concentration of the coating solution was 0.7 $mol \cdot kg^{-1}$ and the concentration of an oxidation product of $CuMnFeO_4$ was constant at 20 mol%.

In the SiO_2-(Cu-Mn-Cr-O) system, the thickness of the films obtained ranged from 450 to 500 nm. The films were transparent and their haze values ranged from 0.1 to 0.4%. In this system, black-colored films are obtained in a relatively wide range of the composition of the oxidation product, $Cu_pMn_qCr_rO_4$ ($p + q + r = 3.0$); 33–67 mol% for CuO_x (1.0–2.0 for p), 22–50 mol% for MnO_x (0.67–1.5 for q) and 9–34 mol% for CrO_x (0.27–1.0 for r). The black-colored film formation region was spread from the composition of $CuMnCrO_4$ ($p = q = r = 1.0$) which is the stable spinel-type crystal (JCPDS No. 20-0352) to Cu-rich compositions.

In the SiO_2-(Cu-Mn-Fe-O) and the SiO_2-(Cu-Mn-Co-O) systems, the thickness of the films obtained

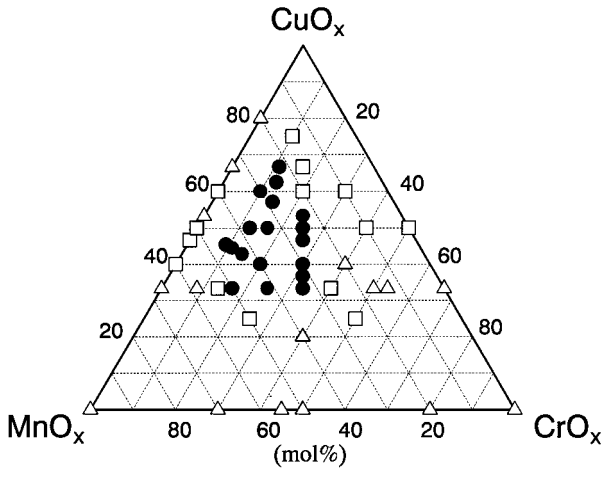

Figure 2 Black-colored film formation region in the system SiO_2-(Cu-Mn-Cr-O), where the SiO_2 concentration of the coating solution was 0.7 $mol \cdot kg^{-1}$ and the concentration of an oxidation product of $CuMnCrO_4$ was constant at 20 mol%.

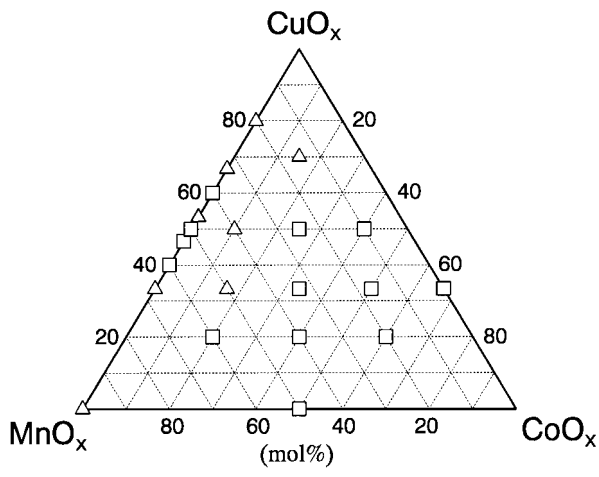

Figure 4 Black-colored film formation region in the system SiO_2-(Cu-Mn-Co-O), where the SiO_2 concentration of the coating solution was 0.7 $mol \cdot kg^{-1}$ and the concentration of an oxidation product of $CuMnCoO_4$ was constant at 20 mol%.

TABLE II Composition dependence of color and chemical durability of the films in the $Cu\{Mn_qCr_{(2-q)}\}O_4$ system, where q changes from 0 to 2.0

q	Color	Chemical durability
0	Bronze	Good
0.2	Bronze	Good
0.4	Bronze	Good
0.6	Bronze	Good
0.8	Partially black	Good
1.0	Black	Good
1.2	Black	Good
1.4	Black	Poor
1.6	Partially black	Poor
1.8	Bronze	Poor
2.0	Bronze	Poor

also ranged from 450 to 500 nm. The films were transparent and their haze values ranged from 0.1 to 0.3%. However, no black-colored films were obtained in either system, although the composition of $CuMnFeO_4$ is the stable spinel-type crystal (JCPDS No. 20-0358) which is well known as an inorganic black colorant.

The differences in the black-colored film formation regions in these three systems must relate to the difference in crystallization temperatures for the black-colored spinel crystals. In the systems SiO_2-(Cu-Mn-Fe-O) and SiO_2-(Cu-Mn-Co-O), partially black with bronze-colored films were obtained. Therefore, it is assumed that the crystallization temperatures in the Cu-Mn-Cr-O system are lower than those of the Cu-Mn-Fe-O and Cu-Mn-Co-O systems.

Table II shows the composition dependence of color and chemical durability of the films obtained in the SiO_2-$Cu\{Mn_qCr_{(2-q)}\}O_4$ system, where q changes form 0 to 2.0. In this table, the words "good" or "poor" in the "Chemical durability" column indicate that the color and appearance of the film did not change after the chemical durability test or did change, respectively. High chemical durability is attained in the composition range of q from 0 to 1.2, i.e. the Cr-rich compositions in this system. The black-colored films, however, are obtained in the composition range of q from 1.0 to 1.4. It is easy to form black-colored films in Mn-rich compositions. Therefore, in order to obtain black-colored films with high chemical durability, the composition of $CuMnCrO_4$ ($q = 1$) is appropriate and the optimum conditions for preparation of the films are investigated in the next section.

TABLE III Color, visible light transmittance, Tv (%), and haze value, H (%), of the films obtained by heat-treatments from 450 to 700°C of $80SiO_2 \cdot 20CuMnCrO_4$ (mol%)

Temperature (°C)	Color	Tv (%)	H (%)
450	Bronze	59.8	0.9
500	Bronze	59.8	0.2
550	Partially black	32.4	0.2
600	Black	32.1	0.2
630	Black	35.7	0.2
660	Black	39.4	0.2
700	Gray	44.7	11.8

3.2. Black-colored films of the system SiO_2-$CuMnCrO_4$

Table III shows color, visible light transmittance, Tv (%), and haze value, H (%), of the films obtained by heat-treatments at 450, 500, 550, 600, 630, 660 and 700°C for the composition $80SiO_2 \cdot 20CuMnCrO_4$ (mol%). Black-colored films are obtained in the temperature range from 600 to 660°C, of which Tv and H are about 32–40% and 0.2%, respectively. The films heated at temperatures lower than 550°C are not black but bronze, for which Tv is about 60%. The film heated at 700°C becomes less black (gray) and hazy; Tv and H increase up to 44.7% and 11.8%, respectively. The increase in Tv and bleaching of the black color, with increasing temperature indicates that the spinel crystal precipitated by heat-treatment is possibly influenced by Na^+ ions diffusing from the glass substrate at such a high temperature.

Fig. 5 shows the X-ray diffraction patterns of the films obtained by heat-treatments at 450, 500, 550, 600, 630, 660 and 700°C, respectively. In the XRD patterns of the films heated at 500°C or lower, no obvious peaks can be observed except for a typical halo pattern for an amorphous material. In the XRD pattern of the film heated at 550°C, a small peak due to the spinel-type crystal of $CuMnCrO_4$ ($2\theta = 35.7°$) is observed, and its intensity increases with increasing heat-treatment temperature. For heat-treatment temperatures from 600 to 700°C, the peaks due to a spinel-type crystal of $CuMnCrO_4$ at 30.1, 35.7, 43.2, 57.5 and 62.8 degrees are observed, as indicated by solid circles in the figure. Therefore, the colorant in black-colored thin films obtained in the SiO_2-$CuMnCrO_4$ system is mainly $CuMnCrO_4$ precipitated in a SiO_2 matrix. However at 700°C, the peak at around 35.7 degrees shifts to a slightly lower angle than that of the films heated at lower temperatures. This means that a lattice constant of the crystal slightly changes. As shown in Table II, the color of the film heated at 700°C also became gray, and Tv and H greatly increased. The lower-shift of diffraction angle of the film heated at 700°C therefore relates to the diffusion of Na^+ ions from the glass substrate into the crystal phase. However, it was found that Na^+ ions played an important role in obtaining black-colored films, because only bronze-colored films were

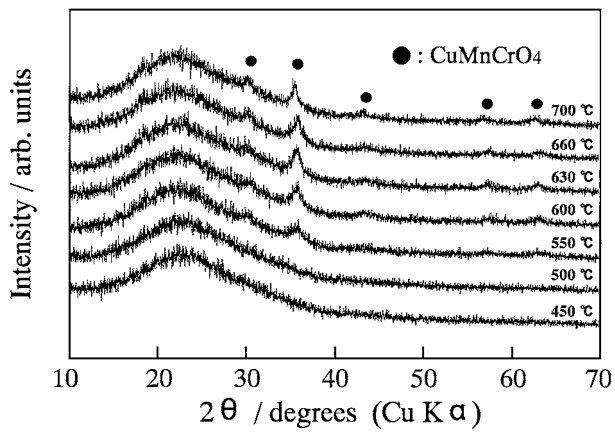

Figure 5 X-ray diffraction patterns of the films obtained by heat-treatments at 450, 500, 550, 600, 630, 660 and 700°C, respectively.

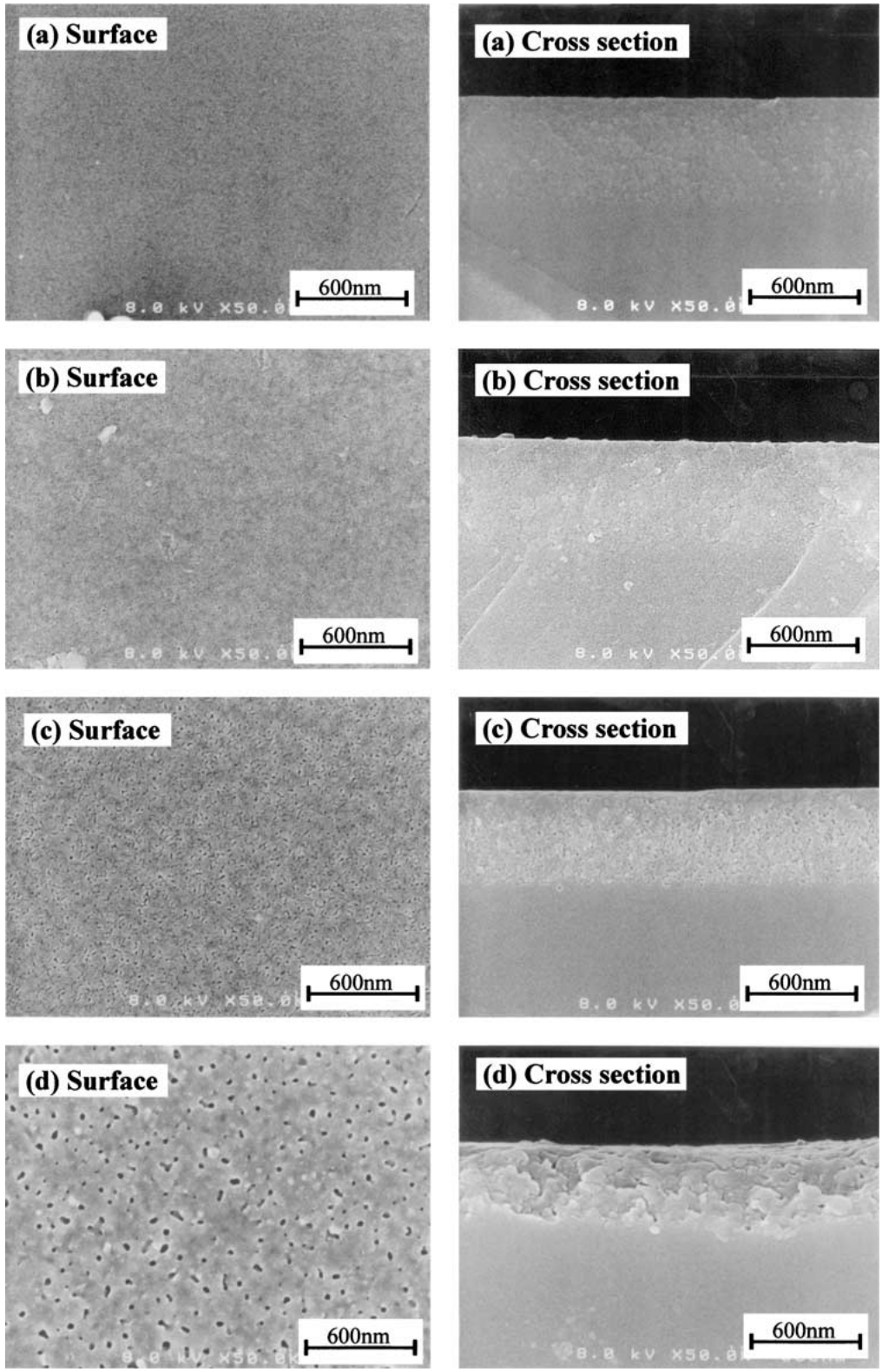

Figure 6 Surface and cross sectional SEM micrographs of the films of $80SiO_2 \cdot 20CuMnCrO_4$ (mol%), which were obtained by heat-treatment at (a) 450, (b) 550, (c) 600 and (d) 700°C, respectively.

obtained when using fused silica as a substrate with heat-treatment at 630°C. Further study is now underway to investigate the behavior of Na^+ ions during the heat-treatment of the coating films and will be reported elsewhere.

Fig. 6a–d show surface and cross sectional SEM micrographs of the films of $80SiO_2 \cdot 20CuMnCrO_4$ (mol%), which were obtained by heat-treatments at 450, 550, 600 and 700°C, respectively. At a temperature of 450°C, a thin film with a flat and uniform surface is observed. At 550°C, very fine crystals are precipitated in the film and small pores are observed on the surface, formed by decomposition products such as CO_2 and NO_x from the gel film. These gases were detected by the DTA-TG measurements for the coating solution dried at 50°C for 6 h as shown in Fig. 7; a weight loss of about 4% is observed in the temperature range from 450 to 600°C. As the heat-treatment temperature increases,

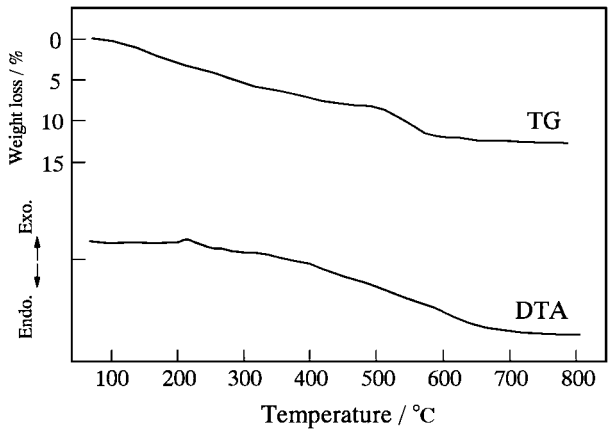

Figure 7 DTA-TG curves of the coating solution dried at 50°C for 6 h, of which nominal composition was $80SiO_2 \cdot 20CuMnCrO_4$ at a SiO_2 concentration of 0.8 mol·kg^{-1}.

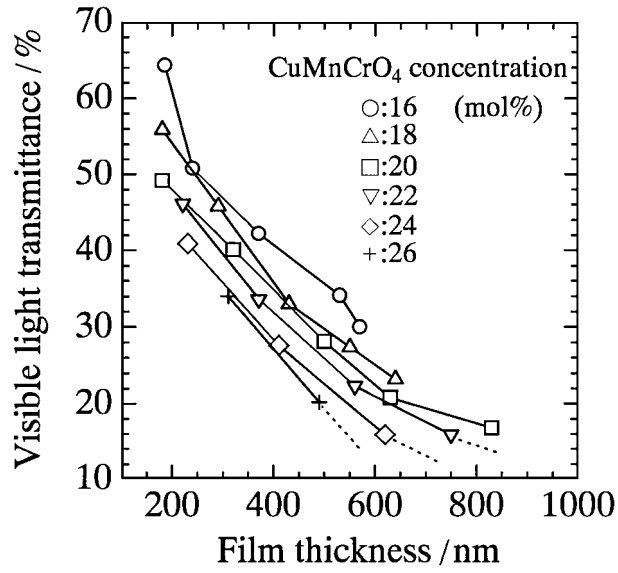

Figure 8 Relationship between visible light transmittance and thickness of the films in the system $(100 - y)SiO_2 \cdot yCuMnCrO_4$, where y ranges from 16 to 26 mol% at a SiO_2 concentration of 0.8 mol·kg^{-1}.

these pores and the crystallite size become larger, because film shrinkage and crystal growth of $CuMnCrO_4$ have occurred. The pores and the crystallite size became large enough to scatter visible light and the haze value of the film heated at 700°C increased to 11% to become a hazy film. Moreover, at 700°C, the interface between the film and a glass substrate becomes rough and unclear, indicating that reaction at the interface has occurred during the heat-treatment. This reaction of the film with the glass substrate affected the crystal phase of the black colorant and thus the color of the film was bleached from black to gray. Therefore, the optimum heat-treatment temperature to obtain the black-colored films is 600°C.

Next, methods of obtaining a black-colored thin film with visible light transmittance (Tv) of about 25%, which can be used as a similar product to deeply black-colored glass commonly produced by the melting method are investigated. It is sometimes preferable to make films as thin as possible in order to avoid any problems accompanying the shrinkage of films during the heat-treatment process or in order to attain high mechanical properties of the resultant films.

Fig. 8 shows the relationship between visible light transmittance and thickness of the films with the composition of $(100 - y)SiO_2 \cdot yCuMnCrO_4$, where y ranges from 16 to 26 mol% at a SiO_2 concentration of 0.8 mol·kg^{-1}. In this figure, the film thickness changed by changing the withdrawing speed in the range 1 to 8 mm·s^{-1}. In the cases of $y = 22$, 24 and 26 mol%, the number of the plotted points are four, three and two, respectively, because uniform thin films were not obtained at larger withdrawing speeds by the dipping-withdrawing method; that is, it becomes more difficult to obtain uniform thicker ones, because the film thickness increases with the inorganic content.

Black-colored thin films with a wide range of visible light transmittance, Tv, from 15 to 65% are obtained and Tv can be controlled by changing the withdrawing speed or the $CuMnCrO_4$ concentration; the films with lower Tv can be prepared by increasing the withdrawing speed, which is equivalent to increasing the film thickness, or by increasing the $CuMnCrO_4$ concentration. For example, a black-colored film with a visible light transmittance of 25% and a thickness of about 500 nm can be prepared from a coating solution with a $CuMnCrO_4$ concentration of 22 mol%.

Fig. 9 shows the maximum $CuMnCrO_4$ concentration introduced into the film against the SiO_2 concentration of the coating solution, where the maximum $CuMnCrO_4$ concentration is described for uniform black-colored films with a haze value less than 1.0%, obtained at a withdrawing speed of 6 mm·s^{-1}. It is clear that the maximum $CuMnCrO_4$ concentration increases with decreasing SiO_2 concentration of the coating solution, indicating that a lower SiO_2 concentration is preferable to increase the $CuMnCrO_4$ concentration for deeper coloration.

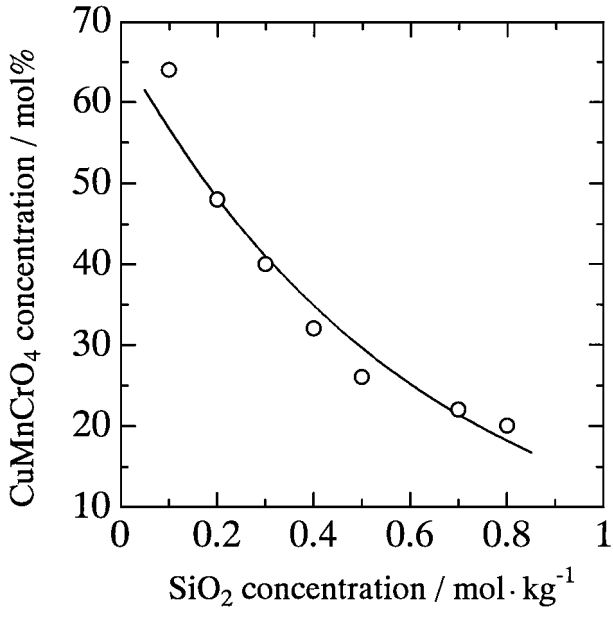

Figure 9 Maximum $CuMnCrO_4$ concentration in the film against the SiO_2 concentration in mol·kg^{-1} of the coating solution in the case for uniform black-colored films with a haze value less than 1.0%, obtained at a withdrawing speed of 6 mm·s^{-1}.

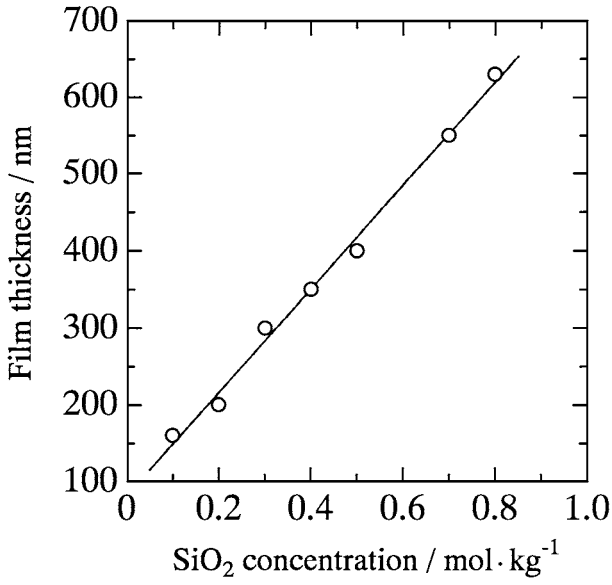

Figure 10 Film thickness of the black-colored films obtained from the coating solutions with SiO_2 concentrations of 0.1–0.8 mol·kg^{-1}, of which the visible light transmittance ranged from 20 to 30%.

Fig. 10 shows the film thickness of each black-colored film obtained from the coating solution with a SiO_2 concentration of 0.1–0.8 mol·kg^{-1}, and with the required $CuMnCrO_4$ concentration to give visible light transmittances of about 25%. The film thickness linearly decreases with decreasing SiO_2 concentration of the coating solution, in spite of the increase in the $CuMnCrO_4$ concentration of the films. Therefore, for the preparation of the thinner black-colored films with deeper color, the $CuMnCrO_4$ concentration in the coating solution rather than the film thickness should be increased.

The possible reasons why a deeper colored film was obtained from a coating solution with a lower SiO_2 concentration and a higher $CuMnCrO_4$ concentration are explained as follows. First, solubility of the metal nitrates in the solvent (ethanol) is very high. Secondly, the dipping-withdrawing method is more suitable for the formation of thinner films. Finally, the metal nitrates added to the coating solution form fine crystals of $CuMnCrO_4$, which do not contribute much to the increase in film thickness. It is thus considered that deeper coloration is easier to achieve by increasing the colorant concentration rather than by increasing the film thickness. As a result, black-colored films with a visible light transmittance of 24.6% and a film thickness of 160 nm were obtained from the coating solution with a nominal composition of $36SiO_2 \cdot 64CuMnCrO_4$ (mol%) at a SiO_2 concentration of 0.1 mol·kg^{-1}.

Table IV shows, as an example, the optical properties and durabilities of the film of $36SiO_2 \cdot 64CuMnCrO_4$ (mol%). The color, visible light transmittance, haze value and thickness of the film are black, 24.9%, 0.9%, and 160 nm, respectively. The pencil hardness is over 9H and the other resistances of scratch with steel wool, abrasion with canvas cloth and chemical resistance with acid solution are good, indicating that the appearance and optical properties of the film after each test did not change. Therefore this black-colored film has great potential in various practical applications such as architectural or automotive windows.

TABLE IV Optical and durability properties of $36SiO_2 \cdot 64CuMnCrO_4$ film obtained by heat treatment at 600°C

Item	Property
Color	Black
Visible light transmittance, Tv (%)	24.9
Haze value, H (%)	0.9
Film thickness (nm)	160
Pencil hardness	>9H
Scratch resistance with steel wool	Good (no peeling)
Abrasion resistance with canvas cloth	Good (no change)
Chemical (acid) resistance	Good (no change)

4. Conclusion

Black-colored films were prepared by coating a silica sol containing dissolved metal nitrates in the systems SiO_2-(Cu-Mn-Cr-O), SiO_2-(Cu-Mn-Fe-O) and SiO_2-(Cu-Mn-Co-O), and the following results were obtained.

(1) It was found that the spinel crystal $CuMnCrO_4$, an inorganic colorant, was easily precipitated in the SiO_2 matrix by heat-treatments at 550° or higher in the SiO_2-(Cu-Mn-Cr-O) system and uniform and transparent black-colored films were obtained:

(2) The visible light transmittance of the films ranged from 15 to 65%, and was controlled by changing the film thickness or the colorant concentration in the coating solution.

(3) For the preparation of the thinner black-colored films, with deeper color and a light transmittance of Tv = 25%, a lower SiO_2 concentration and a higher $CuMnCrO_4$ concentration in the coating solution were preferable. As a result, black-colored film with a visible light transmittance of 24.6% and a thickness of 160 nm was obtained from a coating solution with a nominal composition of $36SiO_2 \cdot 64CuMnCrO_4$ (mol%) at a SiO_2 concentration of 0.1 mol·kg^{-1}.

(4) The durabilities of the black-colored glass obtained against scratching, abrasion and chemicals were good enough for practical applications.

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