THE STUDY OF COPPER RUBY GLASS

CAMELIA CĂPĂŢÎNĂ

University "Constantin Brâncuşi" of Tg-Jiu, Faculty of Engineering, Geneva, No 3, 210152, Gorj, Romania

E-mail: cam@utgjiu.ro

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The tendency of removing Cd from the production of red glasses comes from its toxicity. One of the alternatives is the copper ruby glass, but in this case, the formation of colloidal aggregates of CuO demands the use of efficient reductants. The paper focuses the development of copper ruby glass in the presence of Cu–Sn alloy. The study deals with the effect of melting temperature, holding time, and a subsequent heat treatment on the formation of CuO aggregates. The measurement of spectral transmission of prepared glasses showed that increasing melting temperature and holding time bring more intensive glass color indicated by an increase in the amplitude of the absorption maximum. Subsequent heat treatment of glass samples in the temperature interval 530-570°C makes an increase of absorption maximum with increasing temperature. Prolonged time of heat treatment at 570°C brings more intensive color up to 90 minutes. During longer heating the oxidation of CuO prevails, which leads to the color degradation.

INTRODUCTION

The red color in glasses, used for the both decorative and technical reasons, is relatively more difficult to obtain than the other colors, although, as a rule, any coloring agents from the three traditional categories: ionic, molecular, and colloidal, may be used. The difficulties are related to the high energy domain (green–blue–violet) that has to be attenuated or removed from the visible spectrum of glass in order to be red in transmission.

Few ions usually used in glass industry have electronic transitions in the corresponding regions and their presence in glass needs less usual compositions (glass basicity) and special redox conditions, sometimes difficult to be achieved in industry. For this reason, for centuries, red color in glass is based on ruby containing the molecular and colloidal colorants. From the first category the most frequently used is cadmium ruby, obtained from cadmium sulphides, cadmium selenides or sulfoselenides. From the second category Au, Ag and Cu in elemental state are used; the latest more frequently because it is cheaper [1, 2]. The ruby obtained by means of these substances and elements is a composite containing colloidal nano-aggregates, amorphous or crystalline, having dimensions around 50 nm [3].

The red glasses of the copper ruby type regained the interest of many researchers due to the present general tendency to eliminate the products containing toxic or potential harmful substances. The cadmium toxicity lead to the necessity to eliminate substances based on cadmium chalcogenides from the current production. Consequently, the attention was focused on copper ruby, a non toxic and relatively cheap substitute.

Although the copper ruby is known and has been used for a long time, the possibility of its continuous and large scale production leads researches to clarify some technological aspects that are not yet enough understood and managed. This situation is a result of the fact that the formation colloidal nano-aggregates involves subtle redox processes and delicate heat treatments essential for the color development, is not yet enough comprehended to assure the efficient control of the technological process.

We have performed a research work in order to accumulate data and knowledge and allow industrial application of the copper ruby glass. Some of the obtained results are presented in this paper.

Copper ruby

The metal dispersed to atoms do not color glass. For obtaining the red color, heat treatment for the color development is applied, when the copper atoms form colloidal aggregates, which grow depending on temperature and time. The coloring mechanism is mostly based on the light scattering and absorption by colloidal aggregates. Light scattering is described by the Rayleigh equation [1, 2]:

$$I_D = \frac{\pi \cdot V^2}{\lambda^4 \cdot r^2} \varepsilon_r^2 (\Delta\varepsilon_r - 1) \sin^2 \alpha \qquad (1)$$

where V is the particle volume, λ the wavelength of the incident light, ε_r relative dielectric permittivity, r the distance from the particle to the point where the light intensity is measured, and α the angle between the scat-

tered light fascicle and the incident one. It may be noticed that, beside the parameters related to the measuring conditions, the scattering is strongly influenced by the wavelength of the incident light.

The scattering is more intensive in shorter wavelengths, in the UV–blue–green domain respectively. The wavelengths corresponding to yellow–red domain of the visible spectrum mostly pass through the glass. When the concentration and the dimension of colloidal particles increase, the glass may become opalescent or even opaque.

EXPERIMENTAL

The copper ruby glass composition and the raw materials are presented in table 1. The copper quantity of 0.8 % was introduced in form of a Cu–Sn alloy.

The individual batches were melted in platinum crucibles placed in electric furnace for 90, 150 and 210 minutes. The samples for the measurement of absorption spectra having the shape of discs with a diameter of 25 mm and a thickness of about 1-2 mm were obtained by pressing a drop of melt in a metallic form. Pressed discs were then thermally treated at a temperature of 570°C for 90 minutes.

The main glass property - the spectral transmission - was measured by two-beam spectrophotometer Shimadzu UV 160 A, in the range 400-1100 nm.

Table 1. The composition of copper ruby glass.

Component	Concentration (wt.%)	Raw material	Concentration (wt.%)
SiO_2	72.86	Quartz	61.96
B_2O_3	1.14	H_3BO_3	1.49
Al_2O_3	0.5	Al_2O_3	0.42
Na_2O	9.70	Na_2CO_3	13.97
K_2O	5.06	K_2CO_3	6.45
CaO	9.38	$CaCO_3$	14.38
Fe_2O_3	0.03	Cu–Sn Alloy	1.33
Cu	0.8	Cu–Sn Alloy	
Sn	0.53	Cu–Sn Alloy	

RESULTS AND DISCUSSION

Figure 1 [2, 3] presents the absorption spectra of the copper ruby glasses, which were prepared at single melting temperature at varying time. Presented curves indicate increasing absorption intensity with increasing holding time; from A = 1.1 mm^{-1} for 90 minutes to A = 2 mm^{-1} for 210 minutes, resulting in the red color intensification. In addition, the increase o in the melting time brings a shift of the maximum to lower wavelength from 566 to 563 nm. The positive effect of longer holding time can be explained by deliberating of elemental tin from presented alloy, which can easily react with oxygen coming mainly from surrounding air to form tin oxide. This reaction protects elemental copper from the oxidation to Cu^{2+} and makes possible the formation of Cu^0 aggregates during subsequent heat treatment.

Figure 2 [2,4] presents the absorption spectra of the glasses melted at 1450°C for 210 minutes. The additional heat treatment of the color development was done for 130 minutes at temperatures 530°C, 550°C and 570°C.

The information provided by spectra presented in figure 2 is summarized in table 2. The important increase of the light absorption corresponding to the copper colloidal aggregates with the increase of heat treatment temperature could be explained by the decrease of glass melt viscosity allowing the copper atoms to form numerous aggregates, therefore influencing the intensity of ruby glass color. The increase of the temperature brings the increase of the Cu^0 colloidal aggregates absorption and, consequently, the color intensification, but may also cause the elemental copper oxidation to Cu^{2+} leading to color and quality degradation.

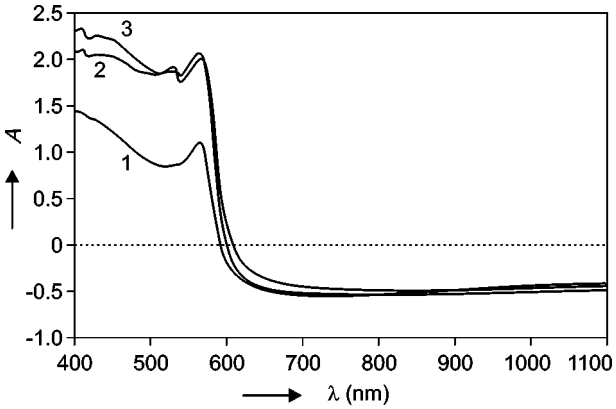

Figure 1. The absorption spectra of the copper ruby glasses melted at 1450°C for 90 min (1), 150 min (2) and 210 min (3).

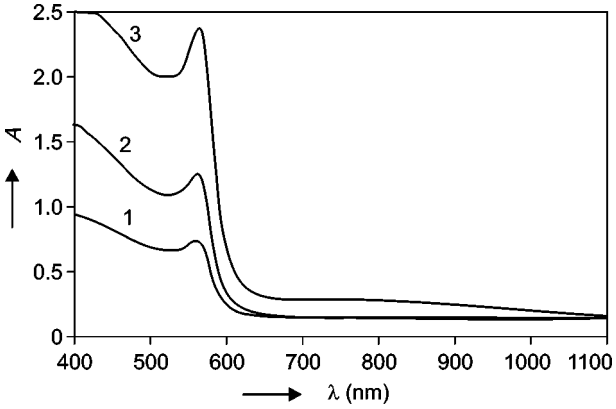

Figure 2. The absorption spectra of ruby glass additionally treated for 130 min at 530°C (1), 550°C (2) and 570°C (3).

Table 2. The influence of additional heat treatment (data obtained from spectra in figure 2).

Treatment temperature (°C)	Wavelength of absorption maximum (nm)	Absorption A (mm^{-1})
530	563	0.745
550	564	1.258
570	566	2.386

Figure 3 [2], shows the absorption spectra of glasses treated by the additional heat treatment at 570°C of different duration. The spectra indicate an increase in the dimensions of colloidal aggregates Cu^0, after which, at a new increase of the heat treatment from 90 to 130 minutes, the maximum intensity decreases. The decrease of the absorption maximum intensity of colloidal aggregates in the samples treated for 130 minutes signifies the beginning of copper oxidation to Cu^{2+} by air oxygen.

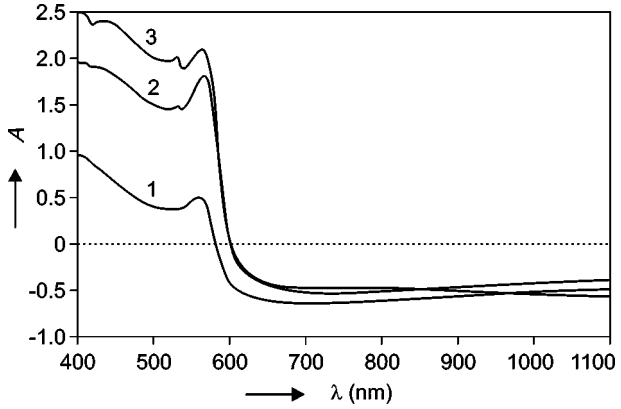

Figure 3. The absorption spectra of the ruby glass additionally treated at 570°C for 40 min (1), 130 min (2) and 90 min (3).

Presented experimental results reveal two important processes taking place during melting and additional heat treatment of ruby glass prepared by using Cu-Sn alloy:

1)Dispersion of copper alloy as Cu^0 as a result of tin oxidation in the melt, mainly occurring during melting period.
2)The concentration of copper atoms in aggregates of dimensions sufficient to efficiently scatter light during additional heat treatment.

The mutual interaction of tin and copper during melting period can be summarized by the reaction:

$$2Cu^{2+} + Sn^0 \leftrightarrow 2Cu^0 + Sn^{4+}$$

The comparison of standard oxidation reduction potentials of the pairs $Cu^{2+} \rightarrow Cu^0 = +0.15$ V, $Cu^{2+} \rightarrow Cu^+ = +0.35$ V and $Cu^+ \rightarrow Cu^0 = +0.53$ V shows Cu^+ as the most unstable oxidation form of copper. This form was therefore not considered in the reaction scheme.

Oxidation-reduction equilibria of both elements can also be examined from corresponding phase equilibrium diagrams. Figure 4 presents the phase diagram of the binary system CuO–SnO_2 [5] corresponding to the oxygen concentration in the air. Figure 5 shows the diagram of the binary system Cu_2O–SnO_2 [6] determined at very low oxygen partial pressure.

In both cases, tin is presented in maximum oxidation state Sn^{4+}, which points out the obvious oxidation tendency to attract air oxygen. It is especially evidenced in the diagram presented in figure 5, where, at very low oxygen pressure, copper is stable in the form of Cu^+, whereas tin is maintained as Sn^{4+}. This fact illustrates that tin "protects" copper against oxidation. At higher partial pressure of oxygen, copper begins to oxidize to Cu^{2+} only when the whole tin is in the oxidizing state Sn^{4+}.

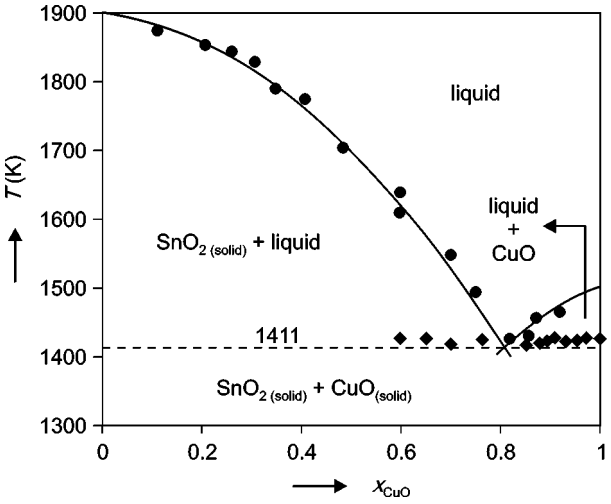

Figure 4. The phase diagram of CuO–SnO_2 system in air; x_{CuO} - molar ratio of CuO.

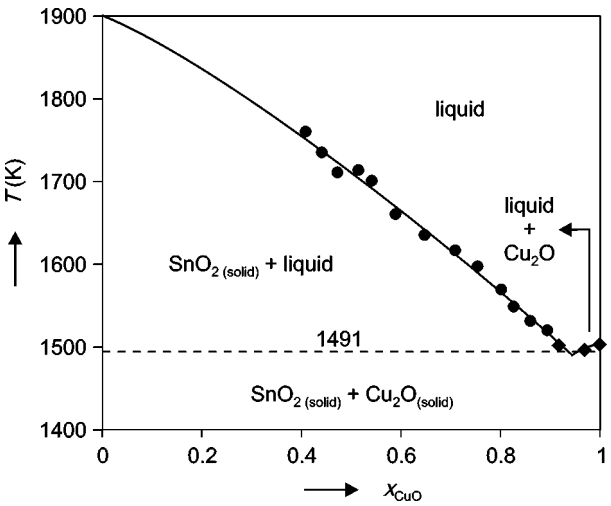

Figure 5. The phase diagram of Cu_2O–SnO_2 system at a partial pressure of oxygen of 2.78×10^{-4} atm; x_{Cu2O}-molar ratio of Cu_2O.

CONCLUSION

To obtain the copper ruby, we used a Cu–Sn alloy, providing both a copper source and a reducing environment (Sn^0). The influence of technological parameters such as melting time, temperature and period of heat treatment can be explained by gradual oxidation of Sn^0 to Sn^{4+} and prevention of Cu^0 oxidation to Cu^{2+}. Under these circumstances and at an appropriate heat treatment of the glass, Cu^0 forms colloidal aggregates determining red color of copper ruby.

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STUDIE MĚĎNATÉHO RUBÍNOVÉHO SKLA

CAMELIA CĂPĂŢÎNĂ

University "Constantin Brâncuşi" of Tg-Jiu, Faculty of Engineering, Geneva, No 3, 210152, Gorj, Romania

Snaha odstranit Cd z produkce červeně zbarvených skel vychází z toxicity tohoto prvku. Jednou z alternativ je měďnaté rubínové sklo, ale v tomto případě tvorba koloidních agregátů Cu^0 vyžaduje použití účinných redukovadel. Článek se zaměřuje na vývoj měďnatého rubínového skla za přítomnosti slitiny Cu–Sn. Studie se zabývá účinkem tavicí teploty, doby prodlevy a následného tepelného zpracování na tvorbu Cu^0 agregátů. Měření spektrální propustnosti připravených skel ukázalo, že rostoucí tavicí teplota a doba výdrže vede k intenzivněji barevnému sklu, což je doloženo zvyšujícím se absorpčním maximem. Následné tepelné zpracování vzorků v teplotním rozmezí 530-570°C s dobou výdrže do 90 minut vede k intenzivnější barvě. Při delším ohřevu převažuje oxidace Cu^0, což vede k degradaci zabarvení.