

Electrochemical surface treatment of glass by a lead-copper melt

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Electrochemical surface treatment of a glass by lead-copper melts was investigated and the contents of the anode elements in the glass were determined. It was shown that the glass colour changes as a function of the treatment time. The variation in the content of lead and copper in the glass was established also as function of the treatment duration. Based on the data obtained a technology for the production of new materials from glass can be developed. The surface of these materials is coloured by the ions of lead and copper.

Elektrochemische Oberflächenbehandlung von Glas mit einer Blei-Kupferschmelze

Die elektrochemische Oberflächenbehandlung von Glas mit einer Blei-Kupferschmelze wurde untersucht. Dazu wurden die Gehalte der Anodenelemente Blei und Kupfer im Glas bestimmt. Es wurde gezeigt, daß sich die Farbe des Glases in Abhängigkeit von der Behandlungszeit verändert. Außerdem wurde festgestellt, daß die Veränderung im Blei- und Kupfergehalt des Glases ebenfalls abhängig von der Behandlungsdauer ist. Auf der Grundlage der erhaltenen Daten kann eine Technologie zur Herstellung neuer Materialien entwickelt werden, deren Oberfläche durch Blei- und Kupferionen gefärbt ist.

1. Introduction

Electrochemical treatment is getting widely introduced to the technology of glass production. In the last decades the method of electrochemical treatment of a glass by metal melts has become more popular in connection with the huge technical and economic advantages over the traditional methods of glass surface treatment. Such advantages include low cost and ecological safety of the processes, small flow of the reagents and, perhaps most importantly, an opportunity for automation of the technological processes, fast adjustment and reorganization [1 and 2].

The technological development for the production of the float or thermally polished glass was the basis for development of the electrochemical processes, as the surface of tin melt forms ideal electric contacts and underlayers for hot glass sheets [3 and 4].

The technology of electrochemical glass processing by metal melts are customarily developed in two directions: processing by tin melts, and processing melts of lead, bismuth, copper and other metals including unitary, double or triple alloys in various combinations.

The electrochemical glass processing by the tin melt is applied to produce glasses with increased durability and chemical stability. Processing by melts of other metals is employed to produce glasses of specific colours, for example, for photographic masks, or glasses for architectural and construction purposes. Glass painting by metal melts with the aim of obtaining new colours, using lead-copper or other melts as the soluble anode is described in [1 and 2].

Here, we systematically investigate the effect of the treatment duration on the glass colour and the contents of lead and copper in the glass.

3. Experimental

The following experiment was carried out for this purpose. A flat glass having the usual composition [3] was

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warmed up to 700 °C and transported over 200 m between the two layers of the metal melt. The process took one hour and was carried out in a nitrogen-hydrogen gaseous environment. The top layer of the melt was comprised of 99 % lead and 1 % copper. The bottom layer was 100 % tin. Both layers were connected to a source of a constant electric current. The lead-copper melt was connected to the positive and the tin melt to the negative electrode. The lead-copper melt was the anode, and the tin melt was the cathode in the electrochemical process. The extent of the melt layer in the direction of glass transport was varied, correspondingly changing the duration of the glass processing by the melt. The contents of lead and copper in the unit area of the glass in contact with the anode were determined by the spectrometric analysis of the obtained samples. The colour of the samples was estimated visually by placing the samples on a sheet of a white paper and viewing at the 45° angle. A similar experimental procedure for the electrochemical treatment of glass by copper and lead melts, although with a slower motion of the glass tape, has been proposed in [4]. The volt-ampere characteristics and the general theory of the process are studied in detail in this reference. The results are presented in table 1 and are illustrated by figure 1.

3. Results and discussion

The data in table 1 and figure 1 show that changes of the voltage in the electrochemical cell result in changes in the contents of the soluble lead and copper in the glass. The duration of the processing also influences the contents. The trend in the concentration change of lead is quite different from that of copper.

The content of lead in the glass grows quickly in the processing interval from 0 to 0.33 s and does not essen-

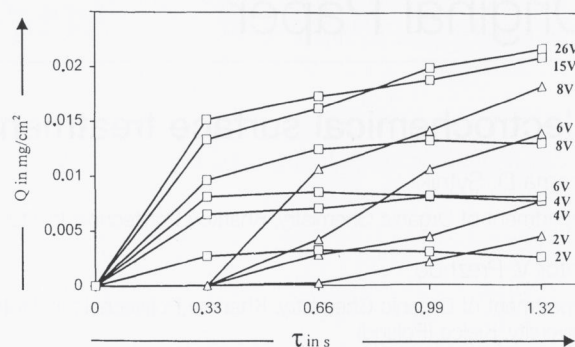


Figure 1. Relationship between the contents of dissolving elements (Q , mg/cm^2) and the duration of glass treatment by the lead-copper melt (τ , s). The copper content is denoted by Δ points and the lead content is denoted by \square points.

tially change at a further increase of the contact time with the anode voltage up to 8 V. If the anode voltage is 15 V and above, the content of lead still grows after 0.33 s, however, at a significantly smaller rate.

The content of copper in the glass practically does not grow during the processing interval from 0 to 0.33 s. When the processing time is increased from 0.33 to 1.32 s, the time dependence of the copper content is close to rectilinear for voltages up to 8 V. For voltages of 15 V and above copper does not dissolve in the glass.

Therefore, it is necessary to conclude that solubility of lead and copper in the glass is very different and depends on duration of the processing. In spite of the fact that the content of lead in the melt is 99 times larger than the content of copper, the maximum concentrations in the glass of both lead and copper are almost identical.

The colouring of the samples varies depending on the processing conditions, as evidenced by the data in table 1. With the exception of sample 5, the samples con-

Table 1. Contents of the chemical elements dissolved in the glass dependent on the time of the electrochemical surface treatment

voltage (in V) in the electrochemical cell	treatment time (τ in s), content (Q in mg/cm^2) of soluble lead and copper in the glass and colour of glass sample											
	$\tau = 0.33$ s			$\tau = 0.66$ s			$\tau = 0.99$ s			$\tau = 1.32$ s		
	Cu content	Pb content	colour	Cu content	Pb content	colour	Cu content	Pb content	colour	Cu content	Pb content	colour
2	in small proportion	0.0250	pale gray	in small proportion	0.0032	gray	0.0021	0.0030	bronze	0.0044	0.0025	bronze
4	in small proportion	0.0065	gray	0.0028	0.0070	bronze	0.0044	0.0080	bronze	0.0076	0.0076	bronze
6	in small proportion	0.0081	gray	0.0042	0.0085	bronze	0.0105	0.0081	bronze	0.0137	0.0080	bronze
8	in small proportion	0.0096	gray	0.0106	0.0124	bronze	0.0140	0.0131	bronze	0.0180	0.0128	bronze
15	in small proportion	0.0151	gray	in small proportion	0.0172	gray	in small proportion	0.0186	gray	0.0014	0.0206	gray
26	in small proportion	0.0133	gray	in small proportion	0.0161	gray	in small proportion	0.0197	gray	in small proportion	0.0214	gray

Note: in small proportion = less than 0.0001 mg/cm^2 .

taining copper are bronze in colour. The samples that do not contain copper are grey in colour. Hence, the bronze colour is determined by the copper contents, while the grey colour is determined by the lead contents. The colour intensity grows with increasing contents of the painting elements.

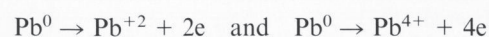
The obtained results are consistent with the theory of anodic dissolving of metals in oxide and salt melts [3] as well as in aqueous solutions of electrolytes with anodic passivity. The anodic passivity in oxygen-containing electrolytes is due to the phase boundary of the adsorbed oxygen or oxides at the anode caused by oxidation of oxygen-containing anions [5].

In the presence of the passivity the anodic dissolving becomes rather complicated especially for multivalent metals. Usually the dissolving takes place in the following sequence.

The dissolving of metals and formation of typical ions is speeded at the electrochemical potentials that are moderately shifted in the positive direction from the equilibrium potential. This region of the potentials gives the best metal activity. At a further increase of the potential the current density falls as the results of the anodic passivity. At even further increase the dissolving rate does not change, remaining very small in a wide range of potentials. This is the passivity area of the metal. In some cases a substantial growth of the applied electrochemical potential results in a secondary increase of the dissolving rate. Such region of the potentials is referred to as the re-passivity region.

The process of the anodic dissolving of lead and copper in electrolytes is particularly well investigated. Both lead and copper behave as multivalent metals.

Lead belongs to the group of metals that form passivating films and have small solubility [6]. Alloyed with tin, silver and some other metals, lead is used for production of insoluble anodes. The electric power applied to such anodes almost entirely goes into production of gaseous oxygen. The following anodic reactions are possible during the anodic dissolving of lead in electrolyte solutions:



with the standard potentials of $E = -0.126 \text{ V}$ and $E = +0.915 \text{ V}$, correspondingly. Lead is dissolved as both Pb (II) and Pb (IV) ions. The transition from the divalent to the tetravalent dissolving occurs at a more electropositive potential.

Copper belongs to well soluble metals. The following anodic reactions are present during the anodic dissolving of copper in an electrolyte:



with the standard potentials of $E = +0.51 \text{ V}$ and $E = +0.34 \text{ V}$, correspondingly. Copper is dissolved to form Cu (I) or Cu (II) ions. Contrary to lead, the transition to the maximum valence dissolving occurs at a more electronegative potential. The dissolving of copper to both Cu (I) and Cu (II) ions is possible simultaneously at an insignificant anodic polarization.

The electrochemical potentials of lead and copper can be arranged in the following order: $\text{Pb}^{+2}/\text{Pb} = -0.126 \text{ V}$, $\text{Cu}^{+2}/\text{Cu} = +0.34 \text{ V}$, $\text{Cu}^+/\text{Cu} = +0.51 \text{ V}$, $\text{Pb}^{+4}/\text{Pb} = +0.915 \text{ V}$. The highest activity is observed for lead dissolving to divalent ions. The lowest activity is of lead again, dissolving to Pb(IV) ions.

The obtained experimental data can be interpreted based on the above properties of lead and copper. The concept of the anodic dissolving of metals with the possible anodic passivity is used along with the facts that melt oscillates during the operation and that the glass is an oxygen-containing electrolyte, where oxygen-containing anions can be discharged.

It is established for practical purposes that near point A (figure 2) only lead is dissolved. This is in accordance with the fact that the divalent lead is more electrochemically active than copper. There is no anodic passivity near point A, since a certain time is required for the discharge of the oxygen-containing anions and formation of a passive layer of oxygen. After the required time has passed, the dissolving of lead stops completely even with small voltages, as the lead becomes passive. The passivation takes place because the amount of the oxygen-containing ions in glass is kept practically constant (figure 1). Note that the anode and the glass are moving with respect to each other. However, as evidenced in figure 1, the passivation phenomenon is not always observed. The dissolving rate is increased at voltages of 15 V and above. It changes little from point B to point C as demonstrated by the rectilinear content versus time of contact dependence in the range from 0.33 to 1.3 s. Apparently, the increase of the voltage leads to the re-passivation of lead.

It is reasonable to expect that lead is dissolved to tetravalent ions at the voltage of 15 V and above and to divalent ions at the voltage of 8 V and below. This expectation does not contradict the fact that copper is also dissolved in the BC re-passivation region. This allows the conclusion that passivation is not due to adsorbed oxygen but is due to an oxidic film. Adsorbed oxygen would equally passivate both lead and copper. Since lead oxides have higher activity than copper oxides, it is necessary to expect that the oxidic film consists of the former. It is known that lead oxides are P-type semiconductors [7] and, therefore, the penetration of copper ions through a film of lead oxides is natural. A smaller radius of the copper ions (about 0.9 nm) in comparison with the radius of the lead ions (about 1,2 nm) is what makes the dissolving of copper possible [8]. The

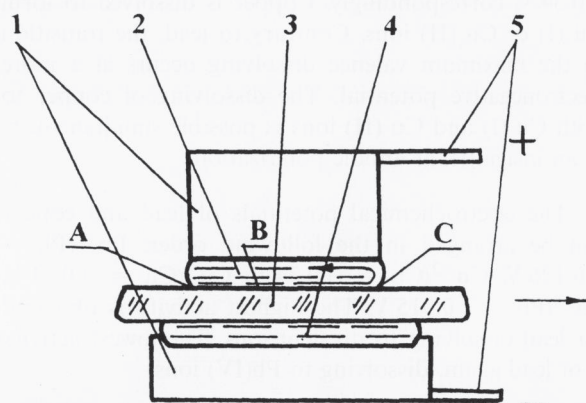


Figure 2. A conceptual sketch of the electrochemical surface treatment: 1 = the securing (fixing) elements; 2 = the lead-copper melt; 3 = the glass; 4 = tin-melt; 5 = the current supply. A, B and C are the active points of reacting melt.

ions of the tetravalent lead with the radius of about 0.78 nm have the same advantage over the copper ions (0.9 nm) in the BC region. While the tetravalent lead is successfully dissolved at voltages of 15 V and above, the dissolving of copper stops at these voltages.

In order to test the results obtained calculations of the current yields have been carried out using the Faraday law that can be applied to glasses during the temperature study. At 700 °C the glass exhibits ionic conductivity, and the anode material does not react with the glass in the absence of the electric current. According to the Faraday law

$$\Delta m = K_e q \quad (1)$$

where m is the mass of the reactive substance in mg, K_e is the electrochemical equivalent in mg/C, and q is the electric charge in C.

If more than one substance react simultaneously, their partial fractions are determined by the current yields. The current yield takes into account the fraction of the electric charge that is applied to a given electrode reaction:

$$B_T = B_{T_1} + B_{T_2} + \dots + B_{T_n} = 1 \quad (2)$$

where B_T is the total current yield, and B_{T_n} is the current yield of the i th element

$$B_{T_n} = \frac{q_n}{q_0} \quad (3)$$

with q_n being the fraction of the electric charge responsible for the n th electrode reaction and q_0 the total electric charge.

When q_n and q_0 are determined from equation (1) and substituted into equation (3), the following expression is obtained

$$B_{T_n} = \frac{\Delta m_n}{K_e q_0} \quad (4)$$

This relationship is used for the calculation of the current yields of lead and copper. The lead and copper contents Δm_n are given in table 1. The values of q_0 corresponding to Δm_n are calculated. Those of K_e are taken from the literature [9], taking into account the fact that for each of the considered elements K_e has two values corresponding to the two values of the electrochemical charges.

The calculations have shown that copper is dissolved as Cu(I) using voltages up to 8 V. The current yield is 0.7. Lead is dissolved as Pb(II) using voltages up to 8 V. The current yield of lead is 0.3. With voltages above 8 V lead can be dissolved to form Pb (IV). The type of calculations for a variety of electrochemical systems is described in detail in [2, 3 and 10].

The results obtained extend our knowledge about the electrochemical treatment of the glass surface by copper and lead melts and agree with the earlier data by other authors [4, 11 to 13].

In conclusion, the obtained experimental data, in particular the difference in the dissolving times and mechanisms for lead and copper, is successfully explained using the properties of the anodic dissolving in oxygen-containing electrolytes with the possibility of the anodic passivity. The dependencies established can be used to form a choice of the required technological parameters that guarantee production from glass of the desired new materials which are coloured on the surface by the lead and copper ions aggregated to colloidal particles.

4. References

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