

Solubility of oxygen in $(\text{TeO}_2)_{0.78}(\text{WO}_3)_{0.22}$ glass melt

S. V. SMETANIN, G. E. SNOBATIN, M. F. CHURBANOV*

Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, 49 Tropinin St., GSP-75, Nizhny Novgorod 603950, Russia

The solubility of oxygen in $(\text{TeO}_2)_{0.78}(\text{WO}_3)_{0.22}$ glass melt at 640°C by the use of technique based on the measurement of oxygen pressure over the melt in evacuated closed system has been studied. The solubility of oxygen at pressure of 3.9×10^3 Pa over the melt is equal to $(5.6 \pm 0.6) \times 10^{-6}$ mole/cm³. A linear increase of solubility is observed in the pressure range from 1000 to 5000 Pa and the effective Henry coefficient is 5×10^8 Pa/mole/cm³.

(Received December 2, 2008; accepted January 21, 2009)

Keywords: Tellurite glass melt, Solubility of oxygen, $\text{TeO}_2 - \text{WO}_3$, Henry's law

1. Introduction

During obtaining of high-purity tellurite glasses by melting of macro-components the contact of charge and melt with air or oxidizing medium takes place. The glass-forming melt is saturated with components of gas mixture (with nitrogen, oxygen, and water vapor in case of air). The glass, produced by its solidification, contains dissolved gases. Their concentration N in glass at the given temperature should be proportional to pressure over the melt p according to Henry's law:

$$p = k \cdot N \quad (1)$$

The repeated heating of glass (heat slumping, drawing of optical fiber) in the medium with partial pressure of these gases lower than during production leads to decomposition of oversaturated solution with formation of microbubbles. As a result, the glass microhomogeneity may be deteriorated. Thus, the solubility of oxygen and other gases in the melt of tellurite glasses can be referred to the parameters which are important for selection of the optimum conditions for fabrication of glass.

The goal of the present work is to quantitatively investigate the solubility of oxygen in $\text{TeO}_2 - \text{WO}_3$ glass system with eutectic composition (78 mole % TeO_2 , 22 mole % WO_3) and fill the gap in relevant data in literature.

2. Experimental

The technique for determination of oxygen solubility is based on measuring gas pressure in the evacuated closed system during the following sequential operations, i.e., the oxygen input into system with glass sample up to the specified pressure – the glass heating and melt holding at the

given temperature – fast quenching. The quantity of oxygen, dissolved in the melt, is calculated by the difference in oxygen pressure before and after dissolution at the same temperature (an isochoric-isothermal variant of measurement).

The initial glass was produced by melting the oxides of tellurium and tungsten of special-purity grade in platinum crucible at 800°C . The preparation of reagents included their preliminary heating at $600\text{--}700^\circ\text{C}$ to remove the traces of moisture. The synthesis was carried out in box purged by dried air or oxygen with dew point -62°C . After homogenizing melting the melt was cooled in the switched-off furnace down to $630\text{--}640^\circ\text{C}$ and then poured into the mold pre-heated up to 345°C with subsequent cooling and solidification of the melt into glass. The produced samples were the plates with thickness of 7–8 mm, width of 25 mm, and length of up to 100 – 115 mm. There were no visible traces of crystallization. The concentration of water in glass, determined by IR-spectrometric analysis (by intensity of spectral absorption band near 3150 cm^{-1} in view of data [1]), was equal to 0.05 mole %.

The set-up for investigation of oxygen solubility (Fig. 1) comprises the system for input and measurement of pressure of gaseous oxygen, the vacuum pump and the quartz ampoule containing the boat with the glass sample. The ampoule was vacuum-tightly connected with the system for input and measurement of oxygen pressure. Prior to loading of sample the boat was tempered for several hours at 750°C . At the beginning of experiment the system tightness was tested and then it was evacuated to high vacuum by heating the ampoule 1 up to $200\text{--}250^\circ\text{C}$ to remove the adsorbed highly volatile impurities. With closed valve 3 the gaseous oxygen was introduced noting the pressure value by U-type oil manometer 4 (the ampoule with glass being at room temperature). Then the part of ampoule 1 with the sample of tellurite glass was heated and held for 1.5 hr at the given temperature noting the changes of pres-

sure in the system. The melt in vacuum was cooled down to room temperature by air flow at the rate of 80–100 K/min. In the blank experiment the gas was introduced into the ampoule with empty quartz boat subsequently heated up to high temperature with isothermal curing.

The solubility of oxygen N was calculated from Men-

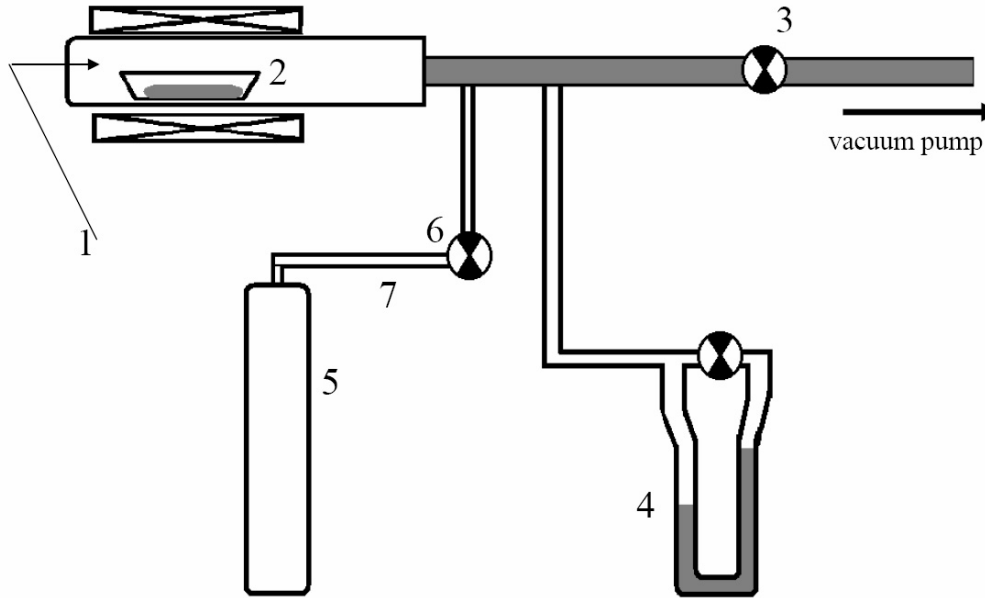


Fig. 1. Set-up for investigation of solubility of oxygen in tellurite glass melt: 1 – quartz ampoule; 2 – quartz boat with the glass sample; 3, 6 – valves; 4 – U-type oil manometer; 5 – container with oxygen; 7 – oxygen gas line.

where Δp is the decrease of pressure in the system due to dissolution of oxygen in the melt; V is the system volume determined by preliminary volumetric measurements; R is the universal gas constant; T is the ampoule temperature after quenching; m is the batch weight in the experiment with dissolution of oxygen; ρ is the glass density (assumed as equal to 6.0 g/cm³).

The change in pressure, exceeding the error of determination (± 8.1 Pa), was not observed in the blank experiment. The oxygen loss due to its dissolution in quartz glass and adsorption on the surface of the structural materials was neglected.

To account for the possible extraction of the primordially dissolved gases from the glass melt the experiments were conducted on heating the samples of tellurite glass in evacuated system. The heating conditions and maximum temperature were the same as in experiments with dissolution of the known amount of oxygen in the melt. While heating the glass up to the operating temperature the gas extraction indicated by residual pressure magnitude p_o after cooling down to room temperature took place. It also observed while heating the sample with oxygen introduced into ampoule with underestimation of pressure connected with absorption of oxygen by the melt. Thus, the magni-

delev-Clapeyron equation as the ratio of quantity of oxygen moles, dissolved in the melt, to the volume of glass by the following formula:

$$N = \left(\frac{\Delta p \cdot V}{R \cdot T} \right) \cdot \frac{m}{\rho} \quad (2)$$

tude Δp into the equation for calculation of solubility includes not only the measured difference between the initial pressure in system and pressure after cooling down to room temperature ($\Delta p'$), but also the correction term due to gas extraction from the glass melt:

$$\Delta p = \Delta p' + p_o \cdot \frac{m}{m_o} \cdot \frac{V_o}{V} \cdot \frac{T}{T_o} \quad (3)$$

(where m , V , T are batch weight of glass, system volume, temperature before and after the experiment with dissolution of oxygen, respectively; m_o , V_o , T_o are similar characteristics for test experiment). It is found that the correction value due to gas extraction is $2.4 \cdot 10^{-6}$ mole/cm³.

3. Results and discussion

The solubility was measured for pressure range of oxygen over the melt from 1000 to 5000 Pa. The results on calculation of solubility of oxygen at 640°C are given in Table 1.

The dependence of oxygen solubility upon its pressure

over the melt is given in Fig. 2. An increase in solubility from 1.2×10^{-6} to 8.5×10^{-6} mole/cm³ (or from 3.5×10^{-3} to 2.5×10^{-2} mole %) with increase of pressure in the studied range is noted. The given dependence can be approxi-

mately described by straight line. Then the Henry coefficient for gaseous oxygen, calculated from the given data, is 5×10^8 Pa/mole/cm³. This

Table 1. Solubility of oxygen in $(\text{TeO}_2)_{0.78}(\text{WO}_3)_{0.22}$ glass melt at 640°C depending upon pressure of the introduced gas

Oxygen pressure, Pa	System volume, ml	Temperature before and after melt cooling, K	Pressure drop Δp , Pa	Glass mass, g	Solubility, 10^6 mole/cm ³
1140	59.9	290	23.5	2.96	1.2
1510	56.8	300	87.9	4.53	2.6
1650	61.7	290	65.4	4.17	2.4
2180	77.4	293	24.7	2.08	2.3
2850	59.3	295	81.2	3.43	3.3
3000	77.4	294	50.1	2.85	3.4
3730	71.7	296	195.2	7.57	4.5
3740	68.6	295	96.4	4.15	3.9
3880	59.3	295	112.3	2.86	5.6
4220	59.3	292	156.2	3.10	7.3
4230	60.8	294	147.9	2.81	7.9
4320	70.8	294	78.7	1.69	8.1
4530	69.6	297	101.3	2.12	8.1
4800	69.8	294	101.0	2.13	8.2
4920	67.0	296	110.5	2.13	8.5

value is an effective one since the rate of melt cooling after dissolution of oxygen was high but finite. It is also seen from Fig. 2 that small deviations in temperature from 640°C do not affect this dependence (the difference in solubility at close pressure values does not exceed the error of measurement or is within the range of point scattering during linear approximation).

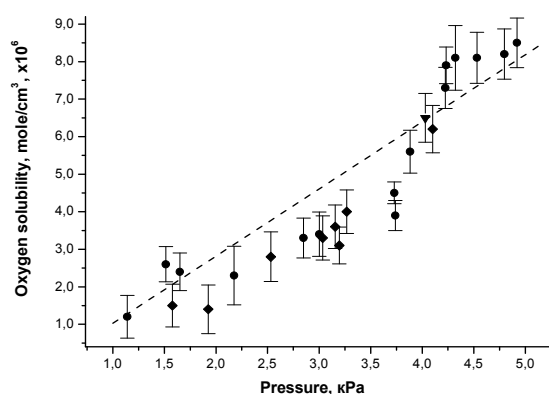


Fig. 2. Dependence of solubility of oxygen in $(\text{TeO}_2)_{0.78}(\text{WO}_3)_{0.22}$ glass upon gas pressure over the melt at the temperatures: ● 640°C, ◆ 610°C, ▼ 650°C. Dash line is guide for eye.

The obtained values for solubility of oxygen are approximately correspond to solubility of CO₂ in Na₂O – SiO₂ glass melt at 1150°C and gas pressure of 1 atm. [2]. In view of the order of magnitude they are also comparable with the solubility of non-interacting gases in silica, i.e., helium equal to 1.0×10^{-4} vol. % at 500°C and hydrogen $(0.8 - 1.0) \cdot 10^{-4}$ vol. % at temperature from 600 to 1000°C [3].

4. Conclusions

The solubility of gaseous oxygen in the melt of $(\text{TeO}_2)_{0.78}(\text{WO}_3)_{0.22}$ glass at 640°C and at gas pressure over the melt 1000 – 5000 Pa is $1.2 \times 10^{-6} - 8.5 \times 10^{-6}$ mole/cm³ ($3.5 \times 10^{-3} - 2.5 \times 10^{-2}$ mole %). The linear increase of solubility with increase of oxygen pressure proves the agreement with Henry's law. The value of the effective Henry coefficient is $5 \cdot 10^8$ Pa/mole/cm³.

Acknowledgement

The work was carried out within the financial support of Principal Scientific Schools Programme, Grant NSh 4701–2008.3.

References

- [1] B. V. Tatarintsev, A. K. Yakhkind, Optiko-mekhanicheskaya promyshlennost. No. 10, 72 (1972) [in Russian].
- [2] M. L. Pearce, Journal of American Ceramic Society. **47**, 342 (1964).
- [3] O. K. Botvinkin, A. I. Zaporozhskii, Quartz glass, Izdatel'stvo literatury po stroitel'stvu, Moscow (1965) [in Russian].

*Corresponding author: yurin@ihps.nnov.ree