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The Mechanism to Change the Strength Properties of Platinum during Hydrogenation

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Abstract

The cathodic polarization of platinum and its alloy with hafnium in a molten borosilicate glass is investigated. It is revealed that the main part of the current is spent on reducing the hydroxyl ions to hydrogen atoms. Saturation currents are found for the diffusion of H and OH^- particles in the temperature range 1200-1300°C.

Keywords: Polarization, diffusion, corrosive cracking

Platinum is widely used as crucible material in optical fiber manufacturing and monocrystals growing [1]. The strength of platinum sharply decreases at high temperatures and its ability to dissolve [2] gives rise to optical inhomogeneities in the glass and corrosive cracking of the crucible.

The reaction between platinum and molten oxides is electrochemical in nature. The reduction processes play a definite role in reducing the corrosion resistance of platinum, this determines the necessity to investigate its cathodic polarization.

In order to reveal the nature and regimes of the electrode processes, as well as to evaluate the effect of strengthening platinum, we investigated its cathodic polarization in a melt containing oxides of Si, B, Ca, and other elements in the temperature range 1200-1300°C by stationary voltammetry method.

The experimental polarization curves for different temperatures and types of electrodes do not have any points of inflection or areas of saturation currents.

The aggregate of the experimental data could be explained if we assume that the hydroxyl ions are reduced at the cathode by the reaction:

$$(OH^-) + 1e = [H] + (O^{2-}).$$

Considering the sluggish diffusion of the hydroxyl ions and hydrogen atoms, the dependence of the overvoltage on the cathodic current density can be represented in such a case by the following equation:

$$\eta = \frac{RT}{F} \ln \left[\left(1 + \frac{i}{i'_{\text{п}}} \right) \Big/ \left(1 - \frac{i}{i''_{\text{п}}} \right) \right], \qquad (1)$$

where i_n' and i_n'' are the saturation currents for the diffusion of OH^- ions and H atoms respectively. Expression (1) can be reduced to the form Y = *A* + BX and linearized in the Y—X coordinates, where

$$Y = \left[\exp\left(\frac{F\eta}{RT} \right) - 1 \right] \Big/ i, \qquad X = \exp\left(\frac{F\eta}{RT} \right), \qquad A = \frac{1}{i'_{\text{п}}}, \qquad B = \frac{1}{i''_{\text{п}}}.$$

The slope *B* of the straight line and intercept *A* on the ordinate axis characterize the saturation currents of the diffusion of hydrogen atoms and hydroxyl ions. The corresponding straight lines for commercially pure platinum, and platinum alloyed with 0.5 wt. % Hf are presented in Fig. 1, whereas the values of the saturation currents derived from them are shown in Table 1.

It follows from Fig. 1 that the experimental points fall on straight lines with a correlation coefficient of 0,98. With increasing temperature, the intercept of the lines on the ordinate axis systematically increases in length whereas the slope of the straight lines changes by a very small amount. Thus, it follows that increasing temperature has a greater influence on the diffusion of hydroxyl ions in the molten oxide than on the transport of hydrogen atoms in the metal.

Table 1. Saturation Currents for the Diffusion of Hydroxyl Ions in Molten Glass and of Hydrogen Atoms in the Metal

Electrode type	T, K	$i_{\text{п}}^{OH^-}$, mA/cm^2	$i_{\text{п}}^{H}$, mA/cm^2
Commercial purity platinum	1523	9 ± 1	$2{,}0 \pm 0{,}1$
	1473	7 ± 1	$2{,}0 \pm 0{,}1$
Platinum alloyed with 0.5 wt. % Hf	1573	14 ± 2	$3{,}0 \pm 0{,}1$
	1523	10 ± 1	$2{,}0 \pm 0{,}1$
	1473	8 ± 1	$2{,}0 \pm 0{,}1$

The values of i_n' found are independent of the nature of the cathode since it is primarily determined by the diffusion coefficient and the concentration of the OH^- particles in the melt. The small value of i_n' (from 7 to 14 mA/cm^2) indicates that the concentration of hydroxyl ions must be low in the melt, less than several hundredths of a weight percent. The appearance of OH^- in the glass is probably related to the presence of hydrated water in the starting oxides and dissolution of water vapor from air in the atmosphere. The saturation diffusion current of hydrogen turned out to be independent of not only the nature of the metal but also temperature and, probably, indicates that surface diffusion predominated over transcrystalline diffusion. The average value of i_n'' was small and was equal to

2,45 mA/cm^2. In spite of the low concentration, hydrogen can exert a negative influence on the mechanical properties of platinum due to the following reasons [3]: interactions between hydrogen and the components of the alloys forming gases (e.g., H_2O), which are responsible for the generation and development of defects; segregation of molecular hydrogen to macroscopic defects; interactions between the dissolved hydrogen and dislocations facilitating transcrystalline fracture of the sample; precipitation of hydrides, carbohydrides, hydronitrides, etc., forming inclusions; decomposition of MeH solid solution during deformation

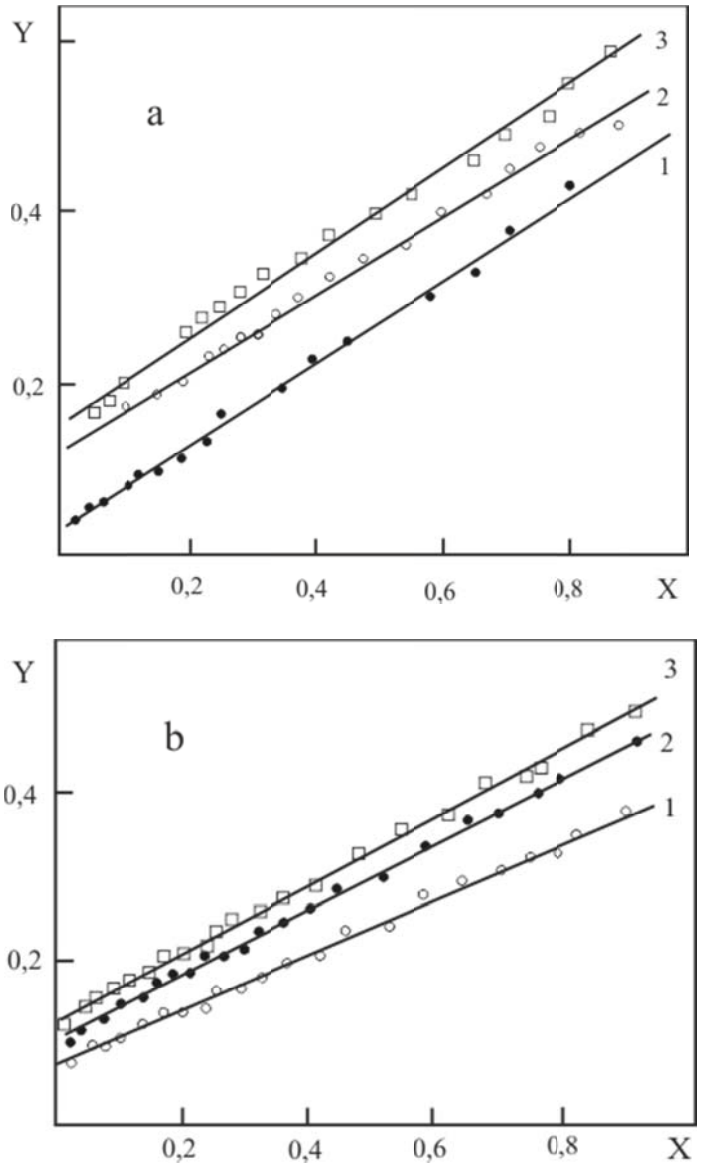

Figure 1. . Dependence of Y on X for platinum during its cathodic polarization; T = 1300 (1), 1250 (2), and 1200°C (3). Platinum: a) commercial purity; b) alloyed with 0.5 wt. % Hf.

with hydrogen gas evolution; and formation of molecules from hydrogen atoms near dislocations under the action of elastic stresses as well as thermal and electric fields.

Apparently, the aggregate of these causes also explains the sharp deterioration of the plastic properties of platinum during its cathodic polarization discovered in specially performed experiments. Cylindrical samples of platinum, of commercial purity, and its alloys were held at 1573 K for 8 hours in a molten glass for various cathodic current densities. They fractured during attempts to mechanically test them. During the analysis of transversely polished sections from the end regions of the samples, the melt was also found to have penetrated into the intercrystalline space with the cathodic current density increasing from 0 to 20 mA/cm^2 for all types of platinum. Such a penetration can indeed help in improving the wettability of the metal by the molten glass via electrocapillary effects.

Thus, cathodic reduction of hydroxyl ions from the molten glass to hydrogen atoms intensifies corrosive cracking of platinum and sharply decreases its plasticity. The limiting stage of the process seems to be the diffusion of hydrogen atoms in the surface layers of the metal and of the OH^- ions in the molten oxide. The data obtained indicate that it is possible to increase the corrosion resistance of platinum by decreasing the concentration of water dissolved in the glass.

References

[1] E.I. Rytvin, "Principles of development of high-temperature-strength and refractory platinum and palladium alloys for glass-melting equipment," in: Noble Metals and Their Applications, Tr. Inst. Fiz. Met. UNTs, Akad. Nauk SSSR, Sverdlovsk, No. 28, (1971), 284-292.

[2] V.A. Kutvitskii, V.M. Skorikov, E.N. Voskresenskaya, et al., "Kinetics of dissolution of platinum in molten Bi_2O_3 and $6Bi_2O_3$-GeO_2," Izv. Akad. Nauk SSSR, Neorg. Mater., **15**, No. 10, (1979), 1844-1847.

[3] P.V. Geld, R.A. Ryabov, and E.S. Kodes, Hydrogen and Structural Imperfection of Metals, Metallurgiya, Moscow (1979).

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