INFLUENCE OF DEFORMATION ON THE ELECTRODE POTENTIAL OF SILVER

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We showed earlier that deformation (extension) of copper wire may be accompanied by shifts of potential either in the positive or in the negative direction, depending on the electrolyte composition [1]. It was of interest to verify this result with reference to other metals, and in particular to silver, which also has a high exchange current and is less liable to oxidation by atmospheric oxygen than copper.

The method of investigation was described earlier [1]. The test specimens consisted of silver wire of Sr999.9 grade, 0.5 mm in diameter (State Union Standard GOST 7222-54).

Before the tests the specimens were annealed in vacuum at 350° for 1 h to release residual stresses. They were degreased in alcohol immediately before the experiments. The annealed wire had $\sigma_t = 15.6$ kg/mm^2 and $\delta = 20.5\%$.

The initial tests were carried out in 0.5 N $AgNO_3$ solution. As the silver nitrate solution had pH $\simeq$ 6.55, absence of an Ag_2O oxide film on the surface of the wire could be assumed:

$$\left.\begin{aligned} &2Ag + H_2O \longrightarrow Ag_2O + 2H^+ + 2e, \\ &\varphi_{equil}^{Ag_2O} = +1.22 - 0.059pH\ [2]. \end{aligned}\right\} \quad (1)$$

It follows from Eq. (1) in view of the fact that the equilibrium potential of silver in 0.5 N $AgNO_3$ solution is $\varphi_{equil}^{Ag^+/Ag} = +0.7659$ V, at pH $\leq$ 7.7 formation of Ag_2O should not occur. The results of tests in 0.5 N $AgNO_3$ solution are shown in Fig. 1. Each point on the curve is the average value from eight experiments. The deviation from the mean does not exceed 20%. It follows from Fig. 1 that the potential is shifted in the positive direction ($+\Delta\varphi$) from the equilibrium value over the entire range of deformations. In the region of elastic deformations ($\sigma_e \simeq 45\%\ \sigma_t$) $+\Delta\varphi$ increases with the load. In the region of plastic deformations $+\Delta\varphi$ remains almost constant with increase of the tensile stress. The oscillogram for silver in 0.5 N $AgNO_3$ solution is shown in Fig. 2a. It is seen that the life of the potential shift did not exceed 5 sec, and the potential always returned to the initial value. Despite the fact that the surface of silver wire is positively charged ($\varphi_{equil} > \varphi_{z.c}$, where $\varphi_{z.c} = -0.7$ V [3]), adsorption of Ag^+ ions on the wire during deformation could nevertheless be presumed. This is confirmed by observations described in the literature [4].

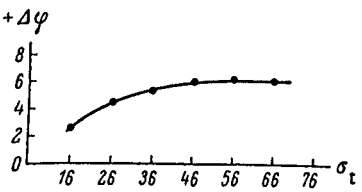

Fig. 1. Dependence of the shift of the electrode potential of silver, $+\Delta\varphi$ (mV), on the applied tensile stress σ_t (%) in 0.5 N $AgNO_3$ at pH = 6.5.

Since, as we showed earlier [1], the sign and magnitude of the shift of potential must be determined by adsorption of corresponding ions, it was decided to introduce $Na_2S_2O_3$ into the $AgNO_3$ solutions, i.e., to conduct experiments in presence of anionic complexes of the $[AgS_2O_3]^-$ or $[Ag_2(S_2O_3)_3]^{4-}$ types [5]. The corresponding oscillogram is shown in Fig. 2b.

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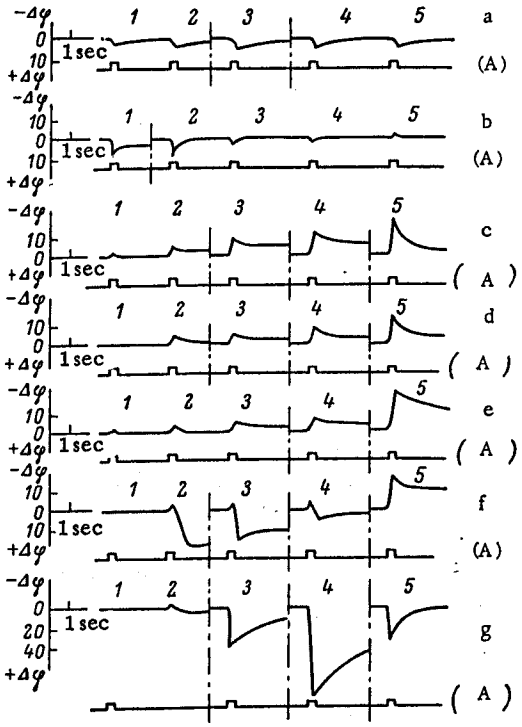

Fig. 2. Oscillograms recorded for silver in solutions. Solution concentration (normality) and pH: a) 0.5 $AgNO_3$ and 6.5; b) 0.06 $AgNO_3$ + 0.5 Na_2SO_3 and 6.0; c) 0.5 NaI and 5.85; d) 0.5 NaBr and 6.3; e) 0.5 NaCl and 6.55; f) 0.5 Na_2SO_4 and 6.0; g) H_2SO_4 + 10^{-1} g-ion NR_4^+ per liter and 0.9. % of σ_t: 1) 16; 2) 26; 3) 36; 4) 46; 5) 56. The projections on the lower horizontal lines (A) indicates the instants of application of the tensile stresses.

It follows from this oscillogram that with increase of the load from 16 to 46% σ_t the positive shift of potential ($+\Delta\varphi$) decreases from +9 to 1 mV, while in the region of plastic deformations (56 % σ_t) the shift becomes negative ($\Delta\varphi = -1.5$ mV). This shows that in the case of silver, the magnitude and sign of the shift of potential from the equilibrium value are again determined by the nature of the adsorbed ions: in the region of elastic deformations predominant adsorption of Ag^+ ions occurs; in the region of plastic deformations, when the number of active sites increases sharply, adsorption of negatively charged ions of the types $[AgS_2O_3]^-$ or $[Ag_2(S_2O_3)_3]^{4-}$, begins to have an effect, leading to decrease of the positive shift of potential and to appearance of $-\Delta\varphi$. To eliminate the influence of Ag^+, experiments were carried out in 0.5 N solutions of Na_2SO_4, NaCl, NaBr, and NaI. The corresponding oscillograms are shown in Fig. 2, c-f. It follows from these oscillograms that in solutions containing surface-active salts (NaI, NaBr, and NaCl) only negative shifts of potential ($-\Delta\varphi$) occur on application of the load, and $-\Delta\varphi$ increases with the degree of deformation. In the case of solutions not containing substances with a pronounced tendency to adsorption on silver (Na_2SO_4) the sign and magnitude of the change of potential $\Delta\varphi$ must be determined by random factors, strongly dependent on the structural features of the surface (at the atomic level) arising during extension of the metal i.e., features which escape detection.

The oscillogram in Fig. 2f shows that $-\Delta\varphi$ occurs on application of the load, but subsequently it changes to $+\Delta\varphi$. Here the potential always returns to the initial value. It is only at high plastic deformations that $-\Delta\varphi \simeq 17$ mV is observed. In every case the surface of the silver wire was positively charged, which created favorable conditions for adsorption of anions (φ_{rest} for NaI, NaBr, NaCl, and Na_2SO_4 respectively were -0.195, $+0.046$, $+0.210$, and $+0.465$ V, i.e., $\varphi_{rest} > \varphi_{z.c} = -0.7$ V). In presence of surface-active cations in solution (tetra-n-butylammonium sulfate solution) only positive deviations of potential, $+\Delta\varphi$, were observed over the enture range of determinations (Fig. 2g), confirming the foregoing.

CONCLUSIONS

1. The sign of the change of the electrode potential of silver during deformation is determined by ions which can be adsorbd on the fresh surface, rich in active sites, formed in the course of deformation.

2. Presence of Cl^-, Br^-, or I^- ions in solution tends to shift the poeential in the positive direction, whereas the presence of cations such as Ag^+ and tetra-n-butylammonium $(NR_4)^+$ favors a change in the positive direction.

LITERATURE CITED

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