Mechanochemical Effects in Redox Reactions with Participation of Iron

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Abstract—The processes of deposition of copper, silver, and lead from their aqueous solutions separately on the concave (contracted) and convex (stretched) sides of a bent steel plate have been investigated. The difference in the deposition rate on the opposite sides gives evidence of the existence of the mechanochemical strain sign effect in redox reactions with the participation of iron. **DOI:** 10.1134/S1070363207030115

INTRODUCTION

It is known for a long time that mechanical stresses in solids influence the rate of chemical reactions. A mechanochemical effect of the strain sigh is more delicate and is manifested, in particular, as a difference in the rate of a chemical reaction on the opposite (concave and convex) sides of an elastically bent plate, which are different only with respect of the strain sign. The effect was discovered in 1988 by the example of the simple dissolution of a monocrystalline plate of potassium chloride [1]. In contrast with the classical theory of elasticity, a thermodynamic theory of this effect [2, 3] implies the existence of an initial stress in solids in the absence of external forces. Since an initial stress is always present in the surface layer of a solid (as the surface tension), the theory predicts manifestation of the strain sigh effect for any chemical reaction with the participation of a solid, occurring at the solid surface. An experimental confirmation have already been obtained at studying corrosion of metals under stress (at dissolving bent steel plates in solutions of hydrochloric and sulfuric acids) [4-6], and also dissolving glass and silicon in an aqueous solution of hydrogen fluoride and potassium hydroxide, respectively [7]. A difference in the rate of dissolution on the concave and convex sides of a bent plate was discovered with the use of various methods: the weight method in its classical [4] and modern (with continuous measuring the sample mass in time) [5, 6, 8] variants, the hydrogen method (by measuring the volume of hydrogen formed in the course of a reaction) [5, 6], and optically (by visual observing the shift of the both opposite boundaries of a sample through a microscope) [7].

The goal of this work was the investigation of the

strain sign effect in redox reactions occurring on the surface of steel plates at their contact with solutions of the salts of other metals. The classical example of such a reaction is the interaction of iron and copper sulfate. At a contact of iron with a solution of this salt, the reaction occurs:

$$Fe + Cu^{2+} = Fe^{2+} + Cu.$$
 (1)

Here iron, a reducing agent, donates electrons:

$$Fe = Fe^{2+} + 2e.$$
 (2)

Herewith, the Fe^{2+} ions are hydrated and pass to solution. The copper ion, an oxidant, accepts electrons:

$$Cu^{2+} + 2e = Cu.$$
 (3)

The reduction of copper to the zero valence should pass via the stage of formation of a univalent ion of Cu^+ :

$$Cu^{++} + e \longrightarrow Cu^{+},$$
 (4)

$$Cu^+ + e \longrightarrow Cu$$
 (deposition), (5)

because the equilibrium potential of the reaction (4) (0.15-0.17 V) is more negative than the equilibrium potential of the reaction (3) (0.34 V) [9]. Both the elementary reactions proceed at the place of contact of iron with the solution, so that electrons pass directly from iron to copper ions.

Since the oxidizing agent, copper, (with $\phi^0 = 0.337$ V) and the reducing agent, iron, (with $\phi^0 = -0.440$ V) are located far from each other in the sequence of standard electrode potentials ϕ^0 , iron will

displace copper from an aqueous solution of its salt practically at any solution concentration. The effect i s easily visible due to a change of color of the surface of a steel plate after the deposition of copper on it. Moreover, iron possesses the same property in solutions of silver salts since $\varphi^0 = 0.799$ V for silver. The density difference is also important when working with the weight method. For this reason, not only copper sulfate and silver nitrate, but also lead nitrate solutions were taken for investigation in this work as a medium. The standard electrode potential for lead $(\phi^0 = -0.126 \text{ V})$ is less different from that for iron, but the difference is enough for realizing the process. It is of note that the reactions of deposition of metals from solutions of their salts are often used for protective coating. This also attaches a certain practical importance to this investigation.

EXPERIMENTAL

Working with steel but not with iron (as it would be appropriate in accordance with the requirement of purity of a chemical experiment) was forced by the condition of elasticity of a specimen as was implied in the theory formulated [2, 3]. There were used, in our investigations, polished plates of a rectangular shape (10×50 mm and 10×75 mm) and of a thickness of 0.3 mm made out of a high-alloy steel (of brand 05Kh22AG15N8M2F-Sh with the carbon content about 2%), a carbon steel (of brand U7a with the carbon content 0.7%), and a low-carbon steel (of brand C1010 produced by Alabama Specialty Products, Inc., USA, with the carbon content 0.1%). Following to [4-6], the lacquer XB-784 (a corrosionresistant coating) was used for the isolation of one of the plate sides. The thorough degreasing of samples with ether was performed before the experiment. Solutions of copper sulfate (CuSO₄ \cdot 5H₂O) and other salts were prepared on the base of chemically pure chemicals. Water was taken as a bidistillate. The experiment was performed at 25°C.

We investigated the process of the metal deposition on a still plate under stress in a *U*-shaped cell keeping a plate in a bent state. The cell construction was similar to that described in [4–6]. The cell with a plate was immersed in a vessel with a salt solution of a given concentration. A mass change of both the plate and the salt solution occurred in the course of a redox reaction. The measurement of this change for the plate and the solution was made separately (in different experiments) in accordance with our method of continuous registration of mass [6, 8]. We used a certain type of the "Sartorius" electronic balance (with accuracy 0.0001 g) that permitted weighing both at the classical placing a subject on the scale and at hanging it below the scale. In the first variant, the vessel with a solution was placed on the scale, and, when suspending the cell with a plate immersed from an independent support, only the changing mass of the solution was measured. In the second variant, only the cell with a plate immersed was suspended from the balance scale, whereas the solution itself rested on an independent from the balance basement. In this case, the mass change referred only to the plate itself. The registration of mass was performed with a frequency not exceeding three measurements per second. Each sample was placed in its separate solution prepared in advance.

The influence of the strain sign was established by comparing the rates of variation of the metal mass on the opposite sides of a bent plate as in [4-6]. Since the plates were slightly different in weight, we plotted, for the sake of unification, kinetic curves for the ratio m/m_0 where m is the running value of the mass of the cell with a plate and m_0 is a certain m value fixed at the beginning of the experiment (in 10 to 15 s necessary for the attainment of a stationary state). A similar ratio M/M_0 was introduced for the solution. The mass variation rate was determined from the slope of the normalized curve $m/m_0 = f(t)$ or $M/M_0 = f(t)$, where t is time. Since weighing was made at the location of the cell with a plate in the solution, it was natural that the mass measured included an increment (negative for m and positive for M) related to the action of the Archimedes' buoyancy force. However, the Archimedes' contribution for m and, moreover, for M is not very essential because of the great difference between the densities of the plate and the surrounding solution.

The variation of the plate mass in the course of a redox reaction was caused by replacing iron with a heavier metal (for example, with copper according to the reaction (1)), which naturally led to increasing the plate mass. Besides copper sulfate, salts with heavier cations (silver and lead nitrates) were tested for promoting the effect.

RESULTS AND DISCUSSIN

As is known, increasing the carbon content in the iron alloys secures transition from the plasticity to the elasticity and even brittleness of the solid phase. As was already mentioned above, we dealt with three steel samples differing in the carbon content. Let us begin with the high-alloy steel. As an example, Fig. 1 shows the curves of the relative variation in time of the cell with two different bent plates immersed in the 5% solution of copper sulfate. As it is expected, the



Fig. 1. The time (t) dependence of the relative mass m/m_0 of the cell with a plate at the deposition of copper from the 5% copper sulfate solution on the concave (l) and convex (2) sides of bent plates of the high-alloy steel.



Fig. 2. The time (t) dependence of the relative mass m/m_0 of the cell with a plate at the deposition of copper from the 10% copper sulfate solution on the concave (1) and convex (2) sides of bent plates of the carbon steel.

plate mass grows, the growth being faster at the deposition of copper on the convex side of a bent plate. If we interpret the result as a manifestation of the mechanochemical effect of the strain sign, we have to consider the surface stress at the metal/solution boundary as positive according to the theory [2, 3]. In this case, however, there is an alternative trivial interpretation. As was shown in experiments on corrosion [5, 6], the process of formation of microcracks develops on the convex side of a bent plate. As a result, the effective area of the convex surface increases causing a growth of the amount of copper deposited. Thus, the interpretation of the experimental result is not unique in this case.

Figures 2 and 3 present kinetic curves of the copper and lead deposition on bent plates of the carbon steel. Herewith, the cell with a plate (immersed in the solution) was hanged on the balance in the first case, whereas the solution itself was weighed in the second case. It is seen from the figures that the result for the carbon steel is opposite to the above result for the high-alloy steel. Now the deposition of copper and lead proceeds faster on the concave side than on the convex one. This permits the unique interpretation of the result as the mechanochemical effect of the strain sign (at a negative value of the surface stress). Moreover, one can say that the mechanochemical effect is large enough to overbear the effect of cracking on the convex side. However, Fig. 2 also exhibits a tendency of decreasing mass on the convex side that can indicate its partial destruction (abscission) at cracking. If the dominancy of the concave side is caused only by destructing the convex side, the unambiguity of



Fig. 3. The time (t) dependence of the relative mass M/M_0 of the 5.6% lead nitrate solution at the deposition of lead on the concave (1) and convex (2) sides of bent plates of the carbon steel.



Fig. 4. The time (t) dependence of the relative mass M/M_0 of the 10% copper sulfate solution at the deposition of copper on both the sides of an unstrained plate of the low-carbon steel.

interpretation again becomes problematic (concerning the deposition of copper but not lead). In addition, it strikes the eye an instability of the run of the curves $m/m_0 = f(t)$ and $M/M_0 = f(t)$ in Figs. 2 and 3 with multiple incidental deviations from a monotonic run in both directions. This nonuniformity is especially pronounced in the case of the contact of the plate convex side with the copper sulfate solution (Fig. 2). The main cause of such behavior is the surface nonuniformity that increases at the deformation. It is visually seen that copper (well distinguishable by color) is deposited in spots. This means that various accompanying reactions can occur on different parts of the surface. If we dealt with pure iron, we could speak about formation of insoluble iron hydroxide $Fe(OH)_2$. However, we would have a long list of possible processes in the presence of alloying additions in the solid phase and on its surface, in the presence

of ions Cu^{2+} , Pb^{2+} , Fe^{2+} , SO_4^{2-} , NO_3^- , H^+ , and OH^- in solution and at arising active centers on the surface as a result of strain. There is no logic to discuss these processes, the more their background does not prevent discovering main regularities even in our "dirty" experiment.

To weaken the above unpleasant secondary phenomena, we undertook experiments with the most pure (among our samples) low-carbon steel of American production. Its carbon content is such small that the steel already possesses certain plasticity. This lowers the probability of cracking at strain. The experiment with an unstrained plate in 10% copper sulfate solution exhibited a monotonic decrease of the solution weight as copper leaved the solution for the deposition (Fig. 4). The data are presented in Figs. 5 and 6 for the deposition of copper and silver on the



Fig. 5. The time (t) dependence of the relative mass M/M_0 of the 10% copper sulfate solution at the deposition of copper on the concave (1) and convex (2) sides of bent plates of the low-carbon steel.



Fig. 6. The time (t) dependence of the relative mass M/M_0 of the 10% silver nitrate solution at the deposition of silver on the concave (1) and convex (2) sides of bent plates of the low-carbon steel.

sides of bent plates from the copper sulfate and silver nitrate solutions. There are only few incidental deviations. The plot for silver is especially good, and this is understandable since silver, with its density and the standard electrode potential, is the most appropriate object for experiments with the redox reaction of its deposition on iron. Both the figures give evidence of the dominant deposition of copper and silver on the concave side of bent plates. As was already noted, this uniquely establishes the strain sign effect. In this way, the existence of the mechanochemical effect of the strain sign in redox reactions with participation of iron can be considered as proved.

We now turn to the explanation of the effect observed. As for any other chemical reaction, the rate of a redox process is determined by its chemical affinity that is a combination of chemical (electrochemical) potentials corresponding to the reaction stoichiometry. For the process of oxidation of iron, Eq. (2), the chemical affinity is

$$A = \mu_{Fe} - \mu_{Fe^{2+}} - 2\mu_e, \qquad (6)$$

where μ_{Fe} is the chemical potential of iron in the solid state at the sample surface, $\mu_{Fe^{2+}}$ is the electrochemical potential of iron ions in solution, and μ_e is the electrochemical potential of electron. The higher the iron chemical potential in the solid state, the larger is the chemical affinity and, therefore, also the rate of iron dissolution. The chemical affinity for the process of reduction of copper, Eq. (3), is

$$A \equiv \mu_{Cu^{2+}} + 2\mu_e - \mu_{Cu}, \tag{7}$$

where $\mu_{Cu^{2+}}$ is the electrochemical potential of copper ions in solution and μ_{Cu} is the chemical potential of the reduced copper in the solid state on the specimen surface. For the total redox reaction (1), the chemical affinity is given by the expression

$$A = \mu_{Fe} + \mu_{Cu^{2+}} - \mu_{Fe^{2+}} - \mu_{Cu}.$$
 (8)

We now discuss how the stress in steel plates influences the chemical affinity of the above reactions. Evidently, an artificially created stress can influence only the solid part of a system and does not touch ions located in solution. Since electrons freely move and easily equilibrate each other inside a metal, we can assume their chemical potential to be not subjected to the action of a local stress. The electrical double layer forms at the contact of a metal with water: iron ions partially pass to solution, and remaining (at the surface on the side of the solid phase) electrons create (due to their mutual repulsion) a negative stress (a positive two-dimensional pressure) in the surface monolayer and a negative contribution to the surface tension of a solid. According to thermodynamics [2, 3], this leads to an increase in the chemical potential μ_{Fe} and the chemical affinity (6). The negative surface stress is enhanced on the compressed (concave) side at plate bending, and the chemical affinity (6) becomes still larger. The situation is reverse for the stretched (convex) side. This means that the rate of transfer of iron to solution should be faster on the concave side than on the convex side of a plate.

Thus, the investigation of continuous variation of the mass of bent steel plates in aqueous solutions of salts shows that a redox reaction proceeds with different rates on the opposite sides of a bent plate (with equal in absolute value but opposite in sign strains). The mechanochemical theory explains the origin of this effect.

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