Mendeleev Commun., 2004, 14(2), 58–59

Effect of the strain sign in corrosion under stress

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10.1070/MC2004v014n02ABEH001875

A difference in corrosion rates on the concave and convex sides of a bent carbon steel plate exhibits the mechanochemical effect of the strain sign as a new discovery in the field of corrosion under stress.

As a result of contact interactions between metals or alloys and their environment, corrosion (*e.g.*, the rusting of iron) includes heterogeneous oxidation of a metal or another component (an anode process) accompanied by reduction of one or more components of the environment (a cathode process). Typical examples of anode and cathode processes are the anode dissolution of iron ($Fe = Fe^{2+} + 2e$) and the formation of hydrogen ($2H^+ + 2e = H_2$), respectively. Corrosion under stress is usually studied as the rate of anode dissolution of a bent metallic plate in a corrosive medium (typically, hydrochloric or sulfuric acid). In the case when both the sides of a bent plate dissolve simultaneously, the total corrosion rate was found to increase almost linearly with strain.[1] The goal of this work was to find a difference in the corrosion rates on the concave and convex sides of a bent metallic plate, which is the effect of the strain sign in the phenomenon of corrosion.

We studied the rate of anode dissolution of various elastic steel samples (other than stainless steel) in a 35% aqueous solution of hydrochloric acid. The samples were rectangular plates (strips) 0.15–0.8 mm in thickness. One of the plate sides was prevented from dissolution by coating it with a lacquer. The dissolution rate was determined from the time dependence of the sample mass. As an example, Figure 1 displays the time dependence of mass loss for a bent plate of carbon steel. The slope mirrors the corrosion rate, which is larger for the concave side of the plate (curve *1*) than that for the convex side (curve *2*). Importantly, such observations should be carried out at the initial stage of corrosion. The further development of corrosion leads to the cracking of the convex side whose real area increases and can cause the inversion of the strain-sign effect, so that the convex side corrodes faster than the concave one. Such an inversion is illustrated by Figure 2 for another sort of steel. The fact that the inversion of the strain-sign effect is caused by cracking is confirmed by the subsequent destruction of a steel sample in the experiment. Thus, the strain-sign effect can be treated as a mechanochemical phenomenon only at the initial stage of corrosion. Here we show, however, that the effect is real and can be clearly recognised.

The effect observed can be explained in terms of chemical thermodynamics and the theory of elasticity. The rate of physicochemical process is determined by chemical affinity, which is a combination of the chemical potentials of substances participating in the process. For the above reaction $Fe = Fe^{2+} + 2e$, the affinity is $A = \mu_{Fe} - \mu_{Fe^{2+}} - 2\mu_e$ where μ_{Fe} is the chemical potential of iron at a solid surface, $\mu_{Fe^{2+}}$ is the electrochemical potential of the ferrous ion in solution, and μ_e is the electrochemical potential of the electron. According to this expression, the larger is the chemical potential of iron at the solid surface, the faster is the process of corrosion. Gibbs[3] was first to show that the chemical potential of a solid is determined by the density of free energy, which, in turn, is always higher in a state of strain. Therefore, a strained metal should always corrode faster than the same metal in the absence of strain. The theory of elasticity derives the elastic energy to be proportional to the square of strain and, hence, to be independent of the strain sign. However, this is true only in the case when an initial state is defined as possessing no stresses and strains, which is the principal postulate of the theory of elasticity. There are no initial states of this kind in real nature because of the existence of surface tension (not speaking about the atmospheric pressure). Every piece of metal has its own surface tension as a surface stress; therefore, any corrosion is always corrosion under stress. When stretching a metal surface, the surface tension should be added to the surface stress created. By contrast, the surface tension should be subtracted from the surface stress created by surface compression. In this way, surface tension produces an additional effect, linear in strain, which causes a difference in corrosion rates for the concave and convex sides of a bent metallic plate. A similar effect was already observed in dissolving a bent single-crystal plate of potassium chloride in water.[4] Here, we report evidence for the strain-sign effect on surface chemical reactions.

Carbon steel plates or strips with polished surface, carbon tetrachloride as a degreasing agent, and a poly(vinyl chloride) lacquer were used to prepare test samples. The experimental cell is shown in Figure 3. The plate sag was regulated with a drive screw, creating a sag of 1 mm per revolution. The cell was made of Teflon. In the experiment, the cell with a bent plate installed was immersed in hydrochloric acid. The plate surface was oriented vertically to prevent the adhesion of hydrogen bubbles, which would decrease the effective surface area. After

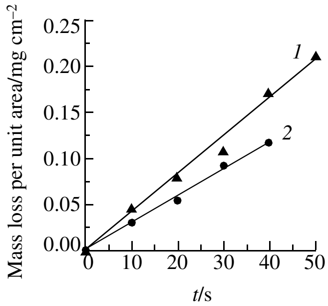

Figure 1 The time dependence of the mass loss on the (*1*) concave and (*2*) convex sides of a bent plate steel (0.45% C and 0.01% S) immersed in a 35% solution of hydrochloric acid. The plate parameters are as follows: thickness, 0.5 mm; width, 24 mm; length, 43 mm; and deflection amount, 1.5 mm. Every point is the average of five measurements (scattering was within no more than 6%).

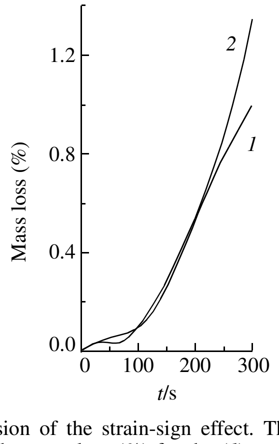

Figure 2 The inversion of the strain-sign effect. The curves depict the time dependence of the mass loss (%) for the (*1*) concave and (*2*) convex sides of a bent plate of steel (0.675% C and 0.023% S) immersed in a 35% solution of hydrochloric acid. The plate parameters are as follows: thickness, 0.16 mm; width, 12 mm; length, 40 mm; and deflection amount, 5 mm.

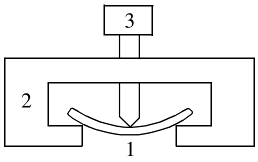

Figure 3 The experimental cell for investigating corrosion under stress: (1) test specimen, (2) cell body, and (3) drive screw.

a certain exposure, the sample was separated from the cell, washed and dried for weight control. In principle, the contact of the screw tip with the concave surface slightly decreases the surface area (although introducing a corresponding correction would only strengthen the effect observed). To avoid this inconvenience, the simplest detent shown in Figure 4 was also used in experiments with thinnest plates allowing manual bending.

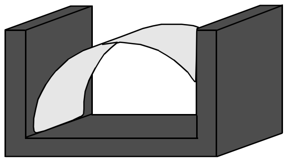

Figure 4 The simplest detent for fixing a bent plate.

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Received: 15th December 2003; Com. 03/2201