

INTENSIFICATION OF ELECTROCHEMICAL PROCESSES AT THE METAL-ICE INTERFACE

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Electrochemical corrosion at the metal-ice interface has been explored in laboratory by measuring copper corrosion rates at the front of water crystallization, as well as the electrode potentials of some metals in water and in ice. The experimental data were used to test a numerically grounded model of corrosion acceleration at the crystallization front.

Design of foundations with regard to processes in frozen ground is an important engineering issue in permafrost areas. Significant damages are incurred yearly from corrosion of engineering structures associated with electrochemical reactions in which metals loose atoms – and, hence, their mechanic strength – at contacts with ice and ice-rich soils. According to expert

appraisal, corrosion of pipelines laid in permafrost is commensurate to or greater than that in the forest steppe zone [Velikotsky, 2010], though the mean annual ground temperature in the former is tens of degrees lower than in the latter. The high corrosion activity of frozen ground is due to the presence of ice and to specific physicochemical processes on its surface.

The electrochemical corrosion of metals results from half-reactions of metal oxidation at the metal-liquid interface $\text{Me} \rightarrow \text{Me}^{z+} + z\text{e}^-$ or, most often, from the oxygen reduction half-reactions ($\frac{1}{4}\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2\text{O}$) where Me is the metal, z is its oxidation degree, and e^- is the electron. In the absence of oxygen, a few metals with negative electrode potential may reduce hydrogen ions instead of oxygen reduction, namely $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2$. Corrosion

may also occur by a chemical rather than electrochemical mechanism: $\text{Me} + \text{Ox} \rightarrow \text{Me}^{z+} + \text{Red}$, where Ox, Red are the oxidized and reduced forms of the reactants, respectively.

We have explored corrosion at the metal-ice interface (where ice acts as liquid) in laboratory by measuring copper corrosion rates at the front of water crystallization and ice melting and the electrode potentials of Al, Cu, Fe, and Pb in ice. Then, on this basis, we tested a tentative model of the corrosion process.

The experimental procedure consisted in recording electrical conductivity variations in a thin metal film [Shavlov *et al.*, 2006], with the basic assumption that metal atoms involved in the redox reaction quit the electron transport process thus decreasing the conductivity. The method allowed recording corrosion while it is going on. We used thin copper films deposited on quartz or woven-glass reinforced wafers in a VUP-5 thermal vacuum evaporator. The films had a surface area of 0.5×2.0 cm, at an electrode spacing of 2 cm, a resistance about 10 Ω , and a temperature coefficient of resistance about that in copper. The average thickness of the films was 20 monoatomic layers (estimated from the amount of evaporated metal and the distance to the wafer). The films were exposed to air for more than 12 hours, whereby an oxide layer formed on their surface and the resis-

tance stabilized. The films that were exposed to air for a long time were noted to be more vulnerable to corrosion in the following tests. According to its position in the reactivity series, copper can corrode only by reduction of oxygens, the reduction of hydrogens being thermodynamically forbidden.

A prepared copper film, with a 3–4 mm drop of distilled water poured on its surface, was vacuumed in an enclosed volume. The drop partially evaporated and froze up quickly by heat loss with vapor. As the drop froze up, the film resistance increased irreversibly for ~2 %, as measured with a V7-34A ohmmeter to an error less than 0.1 %. In some tests, water was frozen with a nitrogen cryostat but the resistance change was then less prominent, possibly, because cooling was slower. See Fig. 1 (curve 1) for an empirical surface density time series $I(t)$ of the reactant copper atoms since the onset of crystallization (surface densities were calculated from the resistances of the films). The film thickness change was $\sim 5 \cdot 10^{-10}$ m, or about one monoatomic layer. Repeated tests with water freezing at the same film surface site gave more or less the same film thickness decrease. Thus, corrosion apparently developed with sufficient amounts of the initial reactants, and neither the latter nor the reaction products were involved in diffusion transport to and from the reaction front. Corrosion may be constrained by the reaction potential barrier it has to overcome. No corrosion acceleration was observed on ice melting.

Note that the irreversible conductivity decrease of the copper film on water crystallization was not due to a non-chemical process, such as mechanical disturbance of the film surface by friction on ice. Tests with noble metals (e.g., silver which is similar to copper in its mechanic properties) did not show any resistance change on water crystallization.

The measured metal electrode potentials in ice have implications for the thermodynamic efficiency of a reaction. Direct potential measurements are dif-

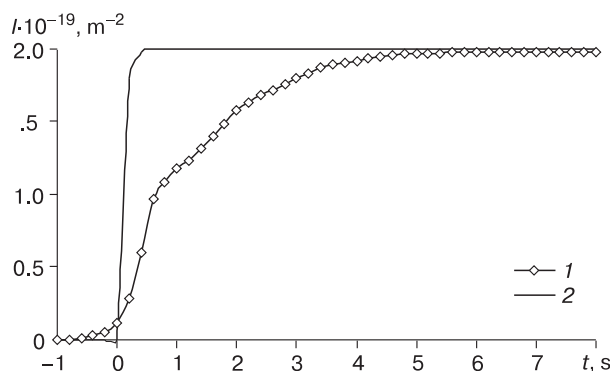


Fig. 1. Measured (1) and predicted (2) time dependences of the surface density (I) of copper atoms involved in the reaction.

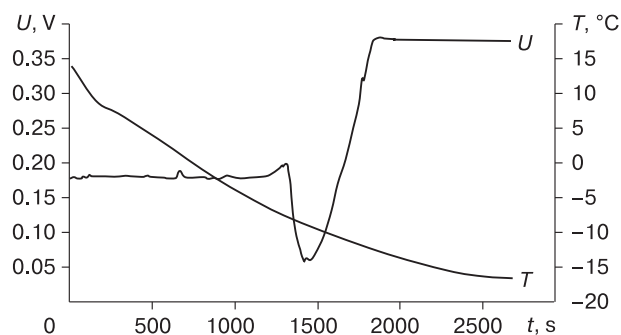


Fig. 2. Time dependences of the potential (U) of copper-lead galvanic couple and the temperature (T) of cooler during water freezing.

difficult because of hardly removable polarization of electrodes associated with their passivation and overpotential on circuit closing. Therefore, the main focus was on the behavior of voltage in galvanic couples formed by electrodes of different metals and a liquid (distilled water) as the latter froze up. Water was cooled down with a cooler connected to a flow thermostat. The potential was measured to an error of ± 10 mV; the temperature absolute error was ± 1 °C.

Figure 2 shows typical voltage and temperature time series. The galvanic couple consisted of a copper (positive) and a lead (negative) electrodes. The potential difference between the electrodes in water was 0.17 V. As the electrodes were polarized, the potential of the couple was less than that for the standard electrode potentials of 0.47 V. Cooling caused almost no voltage change. After the liquid in the space between the electrodes froze up as the cooler temperature reached -8 °C, voltage increased to 0.38 V. Voltage in the galvanic couples Cu–Al, Cu–Fe, and Fe–Pb behaved in the same way: increased by a factor of 1.5–2 as the liquid froze up. When ice melted, the potentials returned to the previous values for water.

The observed freezing-related behavior of voltage in galvanic couples indicates that the standard electrode potentials increase at the water \rightarrow ice transition. As a result, the redox reactions in ice, including corrosion, are more thermodynamically efficient than those in liquid, though the very process in ice may be slow.

The experimental data on corrosion of metals at the crystallization front was explained by nonequilibrium accumulation of ice charge carriers (ion and orientation defects) repulsed by the ice [Shavlov and Ryabtseva, 2007]. These carriers may diffuse toward the ice-metal interface where they recombine with energy release. The released energy can be further transferred to the reactants by means of collisions and used to overcome the reaction barrier, which pushes up the corrosion.

The concentration N of nonequilibrium charge carriers required to account for the experimental surface densities of the reactant copper atoms ($I = 2 \cdot 10^{19}$ m $^{-2}$, Fig. 1) was calculated as $N = I/L$, where L is the diffusion length. The obtained values were $N = 10^{25}$ m $^{-3}$ (at $L = 3 \cdot 10^{-6}$ m) for ion defects (hydrogen and hydroxide ions) and $N = 10^{28}$ m $^{-3}$ (at $L = 2 \cdot 10^{-9}$ m) for orientation defects. The latter concentration is realistic being about the equilibrium concentration of orientation defects in water while the former value can never be achieved in practice as

it is orders of magnitude in excess of the equilibrium concentration of protons in water (10^{20} m $^{-3}$). Thus, the orientation defects are the most probable corrosion agents on water crystallization.

We calculated the concentration of orientation defects at the crystallization front and the intensity of their recombination in ice and in water. At a low crystallization rate, almost all nonequilibrium defects (99.5 %) were found to be repulsed by the crystallization front and to recombine in water, and only 0.5 % recombined in ice. At fast crystallization, instead, the nonequilibrium defects recombined mostly in ice for the lack of time for repulsion. Note that the recombination energy in ice is much higher than in water (0.68 against ~ 0.03 eV, respectively) and is sufficient to overcome the corrosion barrier, which is 0.52 eV for copper. Therefore, one can expect corrosion to be the most intense at a high crystallization rate. It can exceed the isothermal corrosion already after this rate becomes faster than 10^{-7} m/s.

By the potential barrier of electrochemical corrosion we mean the energy-consuming formation of hydrogen ions, i.e., the active particles required for the reaction. We hypothesize that hydrogen ions may form during dissociation of water molecules at the account of the recombination energy of orientation defects. In the case of chemical corrosion, the reaction barrier corresponds to the energy required for overcoming short-distance repulsion in the reactants.

The discussed mechanism of corrosion acceleration is rather universal. It may account for intensification of any reactions in frozen liquid which are controlled by the capacity of overcoming the potential barrier. In addition to the corrosion issues, other applications are improving the technology of nondestructive low-temperature storage of biological preparations and medicines, or food.

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