STUDY OF CORROSION PROCESSES ON THE SURFACE OF STEEL BY THE METHOD OF SECONDARY ION EMISSION

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STUDY OF CORROSION PROCESSES ON THE SURFACE OF STEEL BY THE METHOD OF SECONDARY ION EMISSION

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The elementary processes occurring on the surface of steel in the initial stage of its oxidation have been insufficiently studied. Existing methods for investigating surface processes do not make it possible to obtain sufficient information about the initial stage of the oxidation process.

The successful application of the method of secondary ion emission to the study of the mechanism of heterogeneous catalytic reactions ($^{1-4}$) gave grounds to suppose that this method could also be applied to the study of the mechanism of corrosion processes. The apparatus required for studying surface processes by the method of secondary ion emission, and the essence of the method itself, are described in detail in (^{2}).

The present work contains preliminary results of an investigation of the processes occurring on the surface of steel when it is heated in vacuum (residual-gas pressure $5 \cdot 10^{-6}$ mm Hg) and in an oxygen atmosphere at a pressure of $1 \cdot 10^{-4}$ mm Hg.

The specimen studied was a steel strip with dimensions $20 \times 4 \times 0.1$ mm. According to chemical analysis, the steel contained (in %): C 0.39; Mn 0.45; Cr 0.28; P 0.016; Si < 0.01.

The strip was heated by passing an electric current through it. Its temperature was measured with a Pt—Pt-Rh thermocouple.

Secondary ions were knocked out from the surface of the strip by a beam of Ar^+ ions with energy of the order of 20 keV. Ionization of particles evaporating from the surface of the strip was carried out by means of an electron beam. Mass-spectrometric analysis of the secondary ions and of the electron-impact ionization ions was performed with a sector magnetic mass spectrometer. The mass spectrum of the secondary ions was studied after preliminary annealing of the steel strip in vacuum at a temperature of 800° for 10 hr.

In the mass spectrum of the secondary ions, positive and negative ions were observed that are associated with adsorption of residual-gas molecules on the surface of steel ($H^{\pm}, C^{\pm}, CH^{\pm}, N^{+}, O^{\pm}, OH^{\pm}, H_2O^{+}, C_2{}^{-}, C_2H^{-}, C_2H_2{}^{-}, O_2{}^{-}$).

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

These ions had previously been observed in the mass spectrum of secondary ion emission of other metals (Mo, Pt, Ag) ($^{5-7}$). A feature of the mass spectrum of this group of secondary ions, knocked out from the surface of steel, in comparison with other metals, is the considerably larger number of O^- and OH^- ions.

Another group of ions $(Fe^{\pm}, FeO^{\pm}, Fe_2{}^+, Fe(OH)^{\pm}, Fe(OH)_2{}^{\pm}, Fe_2O_3{}^+)$ is associated with the presence of chemical compounds of iron on the surface of the steel. Finally, in the mass spectrum of secondary ions, ions associated with the presence of impurities in the steel were observed $(Si^-, P^-, Cr^+, Mn^+, MnO^+, MnO_2{}^+, Cr_2O_3{}^+)$. When the temperature of the strip is raised, ions $FeCO^+$, $Fe(CO)_2{}^+$, $Fe(CO)_3{}^+$, $Fe(CO)_4{}^+$, $Fe(CO)_5{}^+$ appear in the mass spectrum of the secondary ions, and ions $Fe(CO)_5{}^+$ appear in the mass spectrum of electron-impact ionization.

Figure 1 shows the curves $J(t)$ for the dependence of the intensities of the beams of secondary ions FeO^+, Fe_2O^+, and $Fe_2O_3{}^+$ on the temperature of a steel strip that was in residual gas and in an oxygen atmosphere. Similar

curves for the ions $Fe(OH)_2^+$ and $Fe(OH)^+$ for a strip in the residual gas, and for the ions $Fe(OD)_2^+$ and $Fe(OD)^+$ in the case of a strip that had been in an atmosphere of D_2O vapor, are shown in Fig. 2. The change in the intensity of the ion beams $FeCO^+$, $Fe(CO)_2^+$, $Fe(CO)_3^+$, $Fe(CO)_4^+$, and $Fe(CO)_5^+$ with change in

Fig. 1. Dependences of the intensity of beams of secondary ions FeO^+, Fe_2O^+, and $Fe_2O_3{}^+$ on the temperature of a steel strip located in an atmosphere of residual gas (a) and in an oxygen atmosphere at a pressure of 10^{-4} mm Hg (b).

the temperature of the strip, which was in an atmosphere of residual gas, are characterized by the curves shown in Fig. 3.

The identical course of the curves for the ions FeO^+, Fe_2O^+, and $Fe_2O_3{}^+$ makes it possible to assert that these ions are sputtered from the surface oxide Fe_2O_3. The presence on the steel surface of the compound $Fe(OH)_2$ leads to the sputtering of the ions $F(OH)^+$ and $Fe(OH)_2^+$. Finally, when the temperature of the steel strip is increased, iron pentacarbonyl, $Fe(CO)_5$, is formed on its surface, from the molecules of which the ions $Fe(CO)^+$, $Fe(CO)_2^+$, $Fe(CO)_3^+$, $Fe(CO)_4^+$, and $Fe(CO)_5^+$ are sputtered.

Fig. 2. Dependences of the intensity of beams of secondary ions $FeOH^+$, $Fe(OH)_2^+$ (a) and FeOD, $Fe(OD)_2^+$ (b) on the temperature of a steel strip located in an atmosphere of residual gas or in an atmosphere of D_2O vapor, respectively.

The oxide Fe_2O_3 arises on the steel surface owing to the presence of oxygen in the residual gas (Fig. 1). However, an increase in the intensity of the ${Fe_2O_3}^+$ ion beam with increasing oxygen pressure is observed only up to a pressure of $2 \cdot 10^{-5}$ mm Hg. At oxygen pressures above $2 \cdot 10^{-5}$ mm Hg, the intensity of the ${Fe_2O_3}^+$ ion beam does not increase and, consequently, the coverage of the steel surface by this oxide does not increase. The course of the curve $I(t)$ for ${Fe_2O_3}^+$ ions can apparently be explained by competition between the processes of decomposition and formation of Fe_2O_3 oxide on the steel surface. In the temperature range 20–500°, the coverage of steel by Fe_2O_3 oxide decreases because the rate of decomposition of this oxide increases with temperature more rapidly than the rate of its formation. In the temperature interval 500–800°, the rate of formation of Fe_2O_3 oxide begins to increase with increasing temperature more rapidly than the rate of its decomposition, as a result of which the coverage of the steel by this oxide increases.

Ferrous hydroxide hydrate arises on the steel surface as a result of the presence of water vapor in the residual gas. With increasing temperature, the coverage of steel by the compound $Fe(OH)_2$ decreases monotonically and, at temperatures above 300°, is so small that it can no longer be detected from the secondary emission of $Fe(OH)_2^+$ ions. However, when the pressure of water vapor is increased to 10^{-4} mm Hg, as follows from experiments with a strip placed in an atmosphere of D_2O vapor, the coverage of the steel surface by the hydrate

iron oxide is preserved up to a temperature of 800°. The intense emission of O^- and OH^- ions observed by us is also associated with the presence of the compound $Fe(OH)_2$ on the steel surface.

Iron pentacarbonyl is not detected on the steel surface in the temperature interval 20–200°. However, as follows from the $I(t)$ curves for the pentacarbonyl group of ions*, at temperatures above 200° the coating of the steel with the compound $Fe(CO)_5$ increases monotonically. At temperatures close to 800°, evaporation of $Fe(CO)_5$ from the steel surface is revealed by the appearance of $Fe(CO)_5$ ions in the mass spectrum of gas-phase ionization by electron impact. To understand the mechanism of pentacarbonyl formation on the steel surface, the following facts may be of interest. Heating steel in residual gas leads to a decrease in the intensity of the beams of ions of the pentacarbonyl group. This effect is enhanced when steel is heated in an oxygen atmosphere. On the other hand, it was observed that in a CO atmosphere the intensity of ions of the pentacarbonyl group does not increase. These facts indicate a certain role of carbon dissolved in steel, whose oxidation is possibly a preliminary stage in the formation of iron pentacarbonyl. If this is so, then the formation and evaporation of $Fe(CO)_5$ should lead to decarburization of the steel. On the other hand, these processes lead to corrosive wear of the steel owing to the transfer of Fe

Fig. 3. Dependences of the intensity of beams of secondary ions of the pentacarbonyl group on the temperature of a steel strip in an atmosphere of residual gas. *a*—$FeCO^+$, *b*—$Fe(CO)_2^+$, *v*—$Fe(CO)_3^+$, *g*—$Fe(CO)_4^+$, *d*—$Fe(CO)_5^+$.

Figure 3: Fig. 3. Dependences of the intensity of beams of secondary ions of the pentacarbonyl group on the temperature of a steel strip in an atmosphere of residual gas. *a*—$FeCO^+$, *b*—$Fe(CO)_2^+$, *v*—$Fe(CO)_3^+$, *g*—$Fe(CO)_4^+$, *d*—$Fe(CO)_5^+$.

into the gas phase.

Fig. 3. Dependences of the intensity of beams of secondary ions of the pentacarbonyl group on the temperature of a steel strip in an atmosphere of residual gas.
a—$FeCO^+$, *b*—$Fe(CO)_2^+$, *v*—$Fe(CO)_3^+$,
g—$Fe(CO)_4^+$, *d*—$Fe(CO)_5^+$.

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named after A. M. Gorky

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* The anomalous behavior of the $I(t)$ curve for the ion $Fe(CO)_2^+$ (mass 112) is explained by the fact that this curve reflects the change in emission with temperature not only of $Fe(CO)_2^+$ ions, but also of Fe_2^+ ions, which have the same mass.