USE OF A SCINTILLATION γ-SPECTROMETER TO DETERMINE LOW CORROSION RATES OF STEELS

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In many corrosion and electrochemical studies there arises the problem of measuring small amounts of metal dissolved as the result of corrosion. This refers in particular to metals dissolving at potentials corresponding to the passive state or at negative potentials, when the solution rate may be very low. Small amounts of dissolved metals must also be measured in investigations of the kinetics of the initial stages of dissolution, where each measurement is made after a very short period of dissolution.

One possible method of measuring small amounts of dissolved metal is the radiochemical method, which is based on preliminary neutron activation of the samples in a nuclear reactor, keeping them in the solution under the desired conditions for a given period of time, and then determining the concentration of radioactive corrosion products in the solution with a multichannel scintillation γ -spectrometer [1, 2].

To calculate the amount of radioactive metal which passes into the solution from the activity one can use either an absolute or relative method of measurement. In the first case the calculations are made with a special equation which takes into account the characteristics of the apparatus and the specific activity of the sample at the moment the measurements are made. The specific activity can also be calculated but requires a knowledge of the integral neutron beam. In the second case the sample is subjected to the neutron beam at the same time as a standard sample made of the same material and having the same thickness. After being activated, this sample is completely dissolved in the medium investigated and the solution obtained is used as the standard solution.

The method of relative measurement using standard samples has certain advantages as compared to the method of absolute measurements, since the calculations are much simpler and the error due to the change in the intensity of the neutron beam and self-screening of the samples during radiation (in the case of thick samples of elements with large effective thermal neutron absorption cross sections) are smaller.

We used the relative radiochemical method to obtain data on the solution rates of Fe–Cr alloys in sulfuric acid. The principal samples were alloys of Armco iron with electrolytic chromium which contained 0.1, 0.5, 4.0, 20, and 35% Cr. The same alloys were used as standard samples; samples of Armco iron and electrolytic chromium were also used as standards.

The samples were rolled into strips as thick as 0.5 mm; they weighed as much as 0.1 g. They were placed in a reactor and subjected to a neutron beam of $0.8 \cdot 10^{13}$ to $1.5 \cdot 10^{13}$ neutrons/cm^2 · sec for 20-100 h. The radioactive isotopes Cr^{51} and Fe^{59} were formed as the result of bombardment. The Cr^{51} isotope emitted one γ-line (E = 0,32 MeV) with an intensity of 9.8%; the Fe^{59} isotope emitted three γ-lines: 0.19 (2%); 1.1 (57%); and 1.29 MeV (43%).

The standard samples were dissolved completely in the heated sulfuric acid and the solutions obtained were used for calibration and quantitative calculation of the experimental results. The samples were spot welded to a platinum wire which was soldered to a special electrolytic cell; they were used as electrodes during electrochemical and corrosion tests. The electrodes were kept for a given time in the cell in a deaerated solution of sulfuric acid under a given constant potential. Then the solution was poured out of the cell and, after dilution,* was used to determine the amounts of iron and chromium with a 100-channel scintillation γ-spectrometer with a NaI(Tl) crystal 50 mm long and 40 mm in diameter.

* The solution was diluted to decrease the radiation dose to ~ 10 mCi/h. The radiation dose was checked with scintillation radiometers of the "Svet-3" or "Kristall" types.

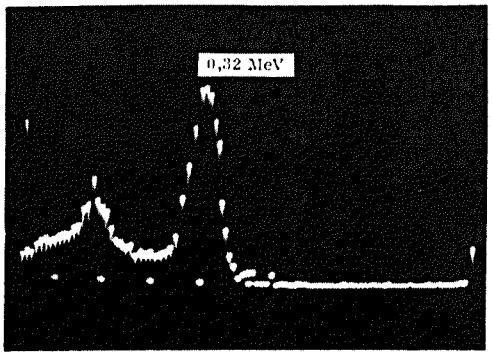

Fig. 1. The γ-spectrum of Cr^{51}.

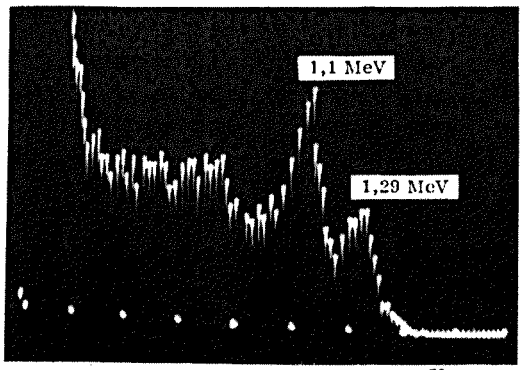

Fig. 2. The γ-spectrum of Fe^{59}.

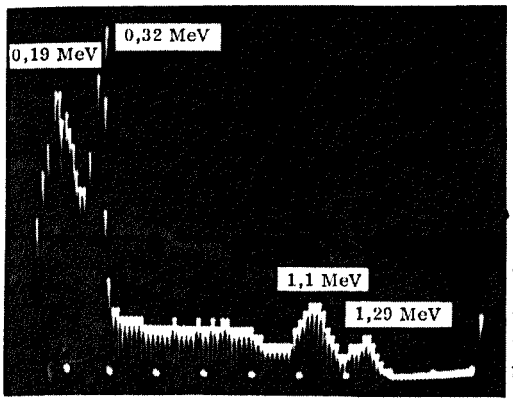

Fig. 3. The γ-spectrum of Cr^{51} anf Fe^{59} present in the solution simultaneously.

The γ-spectra of Cr^{51}, Fe^{59}, and Cr^{51} + Fe^{59} are shown in Figs. 1, 2, and 3. The smaller photo peak in Fig. 1 corresponds to the reverse scattering of γ-radiation from Cr^{51}. The peaks in Fig. 2 correspond to the 1.1 and 1.29 MeV γ-lines of Fe^{59}. The peaks in Fig. 3 characterize Fe^{59} (0.19, 1.1, and 1.29 MeV) and Cr^{51} (0.32 MeV).

The amounts of Cr were determined with the 0.32 MeV γ-line and the amounts of Fe with the 1.1 MeV γ-line. In this way we could determine the amounts of Fe and Cr separately in the same sample. The amplification coefficient of the analyzer was different for Cr and Fe. This was necessary to decrease the error due to the method of successive subtraction used when Cr and Fe were present simultaneously in the solution. Under identical measuring conditions for Fe and Cr such an error can be large because the γ-spectrum of Cr is very compressed, as can be seen in Fig. 3.

Under the conditions of our experiments the γ-background was about 1.5 pulses/min · channel in the case of chromium and 2-3 pulses/min · channel in the case of iron. This made it possible, with good statistics, to measure the chromium or iron alone in the solution with an error no greater than 5-10%. When both elements are present simultaneously in the solution the Compton "tail" of the Fe^{59} γ-spectrum is superimposed on the Cr peak. The Compton "tail" is about 50% of the Fe^{59} peak. Therefore, to determine the solution rate of Fe–Cr alloys one must use the subtraction method, and this decreases the precision in measuring the chromium. However, since the sensitivity of the method is much higher with respect to chromium than with respect to iron, one can determine the amounts of chromium rather precisely even when its concentration in the alloy is low. Thus, when the amount of chromium in the alloy is 2% it can be measured with an error of 15%. For solutions with low concentrations of Fe and Cr where the measured amounts are about three times higher than the background, the error in the measurements results from statistical scattering and does not exceed 25%.

The experiments showed that the method is very sensitive with respect to chromium and iron. For samples of these metals irradiated with a beam of $4 \cdot 10^{13}$ neutrons/cm^2 · sec for 96 h the sensitivity during 30 min of measurement with the spectrometer was $1 \cdot 10^{-10}$ g for Cr and $6 \cdot 10^{-8}$ for Fe.* These sensitivities can be increased by intensifying the neutron beam, prolonging the bombardment, and also increasing the size of the NaI crystal to a length of 80 mm and the diameter to 80-120 mm. In this case one can use the FÉU-43 and FÉU-44 multipliers.

To check this method, we compared the results of measurements of the solution rates of Fe–Cr alloys in a 0.1 N H_2SO_4 solution at different potentials by the radiochemical and photocolorimetric methods.† The measurements were made at potentials more negative than the steady potential. The results obtained for the alloy containing 4% Cr are shown in Fig. 4. This figure as well as results obtained for other alloys shows that both methods give

* These were the sensitivities in measurements made several days after irradiation of the samples.

† We measured the amounts of Fe and Cr in both cases. Under the conditions investigated iron and chromium pass into solution (in first approximation) in amounts proportional to their ratio in the alloy.

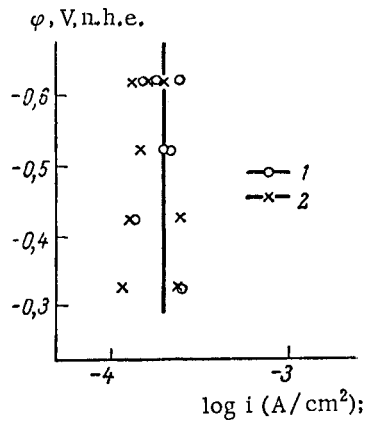

Fig. 4. Variation of the solution rate i (in units of current density) of the alloy containing 4% Cr and 96% Fe in a 0.1 N H_2SO_4 solution with the potential φ measured by the: 1) radiochemical method; 2) by the colorimetric method.

identical results. The scattering of the points on the curve characterizes the lack of reproducibility of results of electrochemical measurements and is not inherent in the method of analysis.

The results obtained are in agreement with those described in [3], where the authors give an electrochemical interpretation of the results. Here, we shall note only that the fact that the results of radiochemical and photocolorimetric analyses coincide does not mean that the methods are equivalent. It is well known that the sensitivity of the colorimetric method is $1 \cdot 10^{-5}$ g for iron and $1 \cdot 10^{-6}$ g for chromium. This shows the advantage of the radiochemical method, since its sensitivity under the conditions investigated is higher than the sensitivity of the colorimetric method by two to three orders for iron and four orders for chromium. We succeeded in determining a very low solution rate of a passive alloy (73% Fe + 27% Cr) in a 0.1 N H_2XO_4 solution at = 0.25 V (10^{-7} A/cm²) by making measurements every 30 min in a flowing solution, which would be impossible by the colorimetric method. It should be noted that the coincidence of the results of the radiochemical and colorimetric methods of analysis indicates that neutron bombardment and the activity of samples of the alloy investigated have no specific effect on the solution rate in sulfuric acid. Under the conditions in which the components of the Fe–Cr alloy dissolve in proportion to their concentrations in the alloy one can determine the solution rate of the alloy by studying the solution rate of one component only, usually chromium, since it has a larger activation cross section. In this case one must take into account the concentration of chromium in the alloy, the irradiation time, and the time between the end of irradiation and the beginning of measurements. Thus, it is reasonable to determine the solution rate by the solution rate of chromium when its concentration in the alloy is higher than 1%.

Isotope	T	t_{irr}/T	q(g)
Cr^{51}	27.8 days	0.1	$2.4 \cdot 10^{-10}$
Fe^{59}	45.1 days	0.1	$2.5 \cdot 10^{-7}$
Mn^{56}	2.58 h	5	$3 \cdot 10^{-12}$
Co^{60}	5.27 years	0.001	$4 \cdot 10^{-10}$
Ni^{65}	2.56 h	5	$2 \cdot 10^{-8}$
Mo^{99}	2.8 days	1	$1 \cdot 10^{-11}$

This method can be used to determine the corrosion rate of multicomponent iron alloys containing chromium and such elements as Mn, Co, Ni, Mo, Cu, etc. To determine the sensitivity of the radiochecmial method of measuring these components one could use, in principle, data on the sensitivity of the method of activational analysis, of which there are many in the literature. In practice, however, it is difficult to use these data because the type of measuring apparatus used is usually not indicated in such publications. The sensitivity of the method depends to a great extent on the parameters of the γ-spectrometers used.

Therefore, we calculated the sensitivity of the radiochemical analysis of Cr, Fe, Mn, Co, Ni, and Mo made with a 100-channel scintillation γ-spectrometer with a NaI(Tl) crystal 50 mm long and 40 mm in diameter.

The calculations were made with the empirical formula

$$q = \frac{4\sqrt{N_b}}{A' t_{mes} \varkappa(E_\gamma)\tau(E_\gamma)/\mu(E_\gamma) k}, \quad (1)$$

where q is the sensitivity (g); N_b is the average number of pulses per channel of the background within the energy range of the photo peak; A' is the specific activity of the sample at the moment of measurement (Ci/g); t_{meas} is the measuring time (sec); $\varkappa(E_\gamma)$ is the coefficient which accounts for the total effective recording of γ-quanta of a given energy by the NaI crystal; $\tau(E_\gamma)/\mu(E_\gamma)$ is the coefficient accounting for the fraction of the photoeffect at a given energy of γ-quanta; and k is the coefficient accounting for the geometry of measurement.

The value of the specific activity of the samples was determined by the formula [4]

$$A' = \frac{0{,}6 f\sigma}{3{,}7 \cdot 10^{10} A}\left[1 - \exp\left(-\frac{0{,}693\, t_{irr}}{T}\right)\right], \quad (2)$$

where f is the flow of thermal neutrons ($n/cm^2 \cdot sec$); σ is the effective activation cross section (barns); A is the atomic weight of the element irradiated; t_{irr} is the irradiation time (h); T is the half-life of the isotope formed (h).

The results of calculation by Eq. (1), taking into account Eq. (2) for $f = 1 \cdot 10^{13}$ $n/cm^2 \cdot sec$, k = 0.3, N_b = 4 pulses/min, and t_{meas} = 30 min are given in the table.

The comparison of the results for iron and chromium with the values of the sensitivity of the method of determining these elements found experimentally shows that the theoretical and experimental results are in rather good agreement. This work allows us to conclude that the radiochemical method can be used to measure very small amounts of corrosion products of steel, which is very important when one must measure low corrosion rates or make measurements over very short periods of time.

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