SIMULTANEOUS AND CONTINUOUS DETERMINATION OF IRON AND CHROMIUM DISSOLUTION RATES FROM Fe–Cr ALLOYS

T. I. Shirinov, G. M. Florianovich, and Ya. B. Skuratnik

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A radiometric method was developed to simultaneously determine component dissolution rates of Fe–Cr alloys having various compositions. The method was used to assess Fe and Cr dissolution rates from an actively dissolving Fe–28% Cr alloy. Several seconds after the alloy contacted the solution, its components were found to dissolve in the same ratio as their concentrations in the alloy. This method was shown to be superior to other analytical procedures.

Partial dissolution rate determinations of alloy components were deemed of considerable interest in studying mechanisms of alloy dissolution [1]. This action has been found experimentally to comprise both uniform dissolution [2, 3], when all alloy components dissolve at the same rate so that their ratio in solution is equal to that in the alloy, and selective dissolution [4-6], when one of the components dissolves preferentially so that its relative concentration in solution is higher than that in the alloy. Selective dissolution of alloy components is sometimes observed after prolonged action [5]. Individual rates can be determined by taking samples of the solution continually during the reaction and analyzing them for metal ions. Often, however, selective dissolution occurs quickly [6], making sampling impractical and analysis unsuitable, even with high analytical sensitivity.

These inadequacies are overcome by radioisotope methods based on γ-radioactive electrodes. Dissolution rates can be recorded continuously as a function of increasing radioactivity in the solution.*

Developed initially for individual metals [7, 8] the method was then applied to alloys [6, 9-14] having one [6, 9, 10] and two [11-14] radioactive tags. A difficulty with alloys, not encountered with pure metals, is that spectra of two or more of the alloy components can often overlap, necessitating development of special methods and modes of calculation to interpret the results.

We developed a radiometric method for simultaneous and continuous recordation of iron and chromium dissolution rates from Fe–Cr alloys. The method is of interest primarily to clarify the dissolution mechanism of iron–chromium alloys. According to [3] Fe–Cr alloys in an active state dissolve uniformly under constant conditions, possibly through various mechanisms. On the one hand, the alloy can dissolve by successive removal of surface monolayers upon contact with the solution [15]. At practically any point in time, the ratio of dissolved iron and chromium should be equal to that in the alloy. On the other hand, a mechanism is possible [4] where one more electronegative component dissolves preferentially as soon as the alloy contacts the solution and at the same time the other component builds up on the surface. In the latter case, the alloy components begin to dissolve uniformly after a certain time, partially through mechanisms examined earlier [16, 17].

To draw conclusions on the mechanism of Fe–Cr alloy dissolution, information is required on the kinetics of reactions occurring soon after exposure to the corrodant, since selective dissolution time can be very small. Previous radiometric methods using successive sampling [18] could yield reliable results only with experiments of fairly long duration, i.e., not less than 10 min.† It had consequently been concluded that Fe–Cr alloys dissolved uniformly [3]. Continuous recordation of the iron and chromium dissolution can provide the needed kinetic information.

*Another advantage of this method is that changes in component dissolution rates with time can be determined without taking samples of the solution.

†This is due to the effect of sampling on electrochemical parameters and reduction time.

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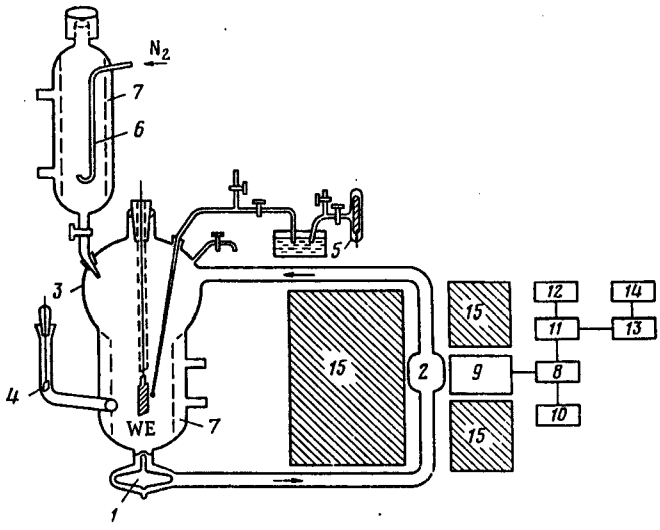

Fig. 1. Schematic of equipment for simultaneous and continuous recordation of partial dissolution rates of binary alloy components under controlled polarization (WE = working electrode).

Our use of radioisotopes was based on the work of [18] where it was shown that Fe–Cr alloy components could be determined with high sensitivity through γ spectrometry using radioactive tracers ^{59}Fe and ^{51}Cr produced by neutron activation. Emission of the ^{51}Cr isotope is characterized by a single γ line with an energy of E = 0.32 MeV (9.8%) and that of the iron isotope by three lines with E values of 0.19 (2%), 1.1 (57%), and 1.29 (43%) MeV, respectively.

Measurements were made by means of a cell (Fig. 1) in which a pump 1 circulated the solution between bulb 2 used for recording radioactivity, and main cell 3.* A platinum platelet 4 was used as an auxiliary electrode. Potentials were measured vs reference electrode 5 consisting of a palladium platelet immersed in 1 N sulfuric acid. Jacket 7 was used to thermostat the solution in the main cell and in a preliminary deaeration vessel 6.

Electrodes of Fe–Cr alloys with various chromium contents, weighed quantities of these alloys, pure iron, and pure chromium were placed in a nuclear reactor and bombarded with a neutron flux of 1.2-2.4 neutrons/cm^2 for 66-90 h. After bombardment the weighed samples were completely dissolved in hot sulfuric acid containing nonradioactive $FeSO_4$ and $Cr_2(SO_4)_3$ salts as carriers. These solutions served as standards and were used to prepare mixtures of Fe and Cr in the ratios necessary for verification of the method developed. The electrodes were welded to a platinum wire, sealed into the ground glass cell joint, and placed into the cell.

To record ^{51}Cr and ^{59}Fe in bulb 2 (see Fig. 1) we used a type USS-1 γ radiometer 8 with a NaI(Tl) scintillation counter 9 having crystal dimensions of 40 × 40. Radioactivity of ^{51}Cr was measured by differential scanning with a 30% window under a full-energy peak of 0.32 MeV, whereas ^{59}Fe was recorded by integral scanning using the upper discriminator of the above window. Recordation of relative activity in the differential channel was accomplished with a USS-1 ratemeter fitted with an EZ-1 recorder 10 and in the integral channel with a PI-4 ratemeter 11 fitted with an EZ-1 recorder 12 (or with a PP-15A scaler 13 on a BAP-3 printout connected to an ÉUM-23 apparatus 14). Lead shield 15 was used to prevent electrode radiation from penetrating the radiometer.

Thus, only the relative activity of ^{59}Fe (n_1 in pulses/sec) was measured in the integral channel.† In the differential channel, on the other hand, not only was the relative activity of the ^{51}Cr measured but also the contribution of the Compton effect for ^{59}Fe (n_3 in pulses/sec) [16]. This was the case as the value of n_2 (in pulses/sec) for the differential channel was the sum of all the values and depended on n_1, since n_3 depends on n_1.

*Circulation produced a solution exchange frequency in the cell of 12 volumes per minute with a solution volume of 100 ml.

†Here and henceforth all values of n designate specific activity taking the corresponding background into account.

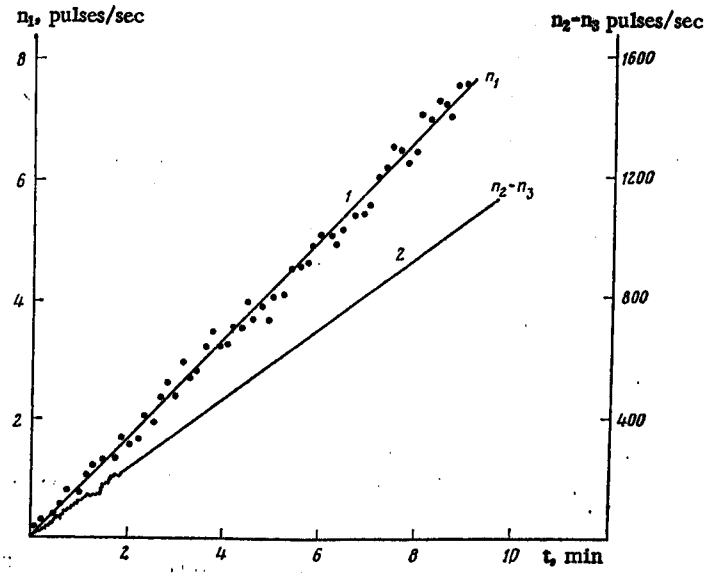

Fig. 2. Relation of the radioactivity of a 1 N H_2SO_4 solution containing ^{59}Fe and ^{51}Cr γ isotopes with respect to dissolution time of Fe–28% Cr alloy at a potential of −0.32 V and a temperature of 50°C. Points on linear curve 1 are ^{59}Fe printout results; linear curve 2, which shows initial oscillations, are results of automatic recordation of ^{51}Cr radioactivity in the differential mode.

The amount of dissolved iron P_1 (in g) is related to n_1 by the equation

$$P_1 = P_1^{st} \frac{n_1}{n_1^{st}}, \quad (1)$$

where P_1^{st} is the weight of standard iron (in g) and n_1^{st} is its measured relative activity in pulses/sec.

The amount of dissolved chromium P_2 (in g) is determined from the equation

$$P_2 = P_2^{st} \frac{n_2 - n_3}{n_2^{st}}, \quad (2)$$

where P_2^{st} is the weight (in g) of standard chromium and n_2^{st} is its measured relative activity (pulses/sec).

To find n_3 we can use the equation

$$n_3 = \frac{n_1 n_3^{st}}{n_1^{st}}, \quad (3)$$

where n_3^{st} is the relative activity of standard iron solution in the chromium channel, i.e., the amount recorded by 10 (see Fig. 1) when a standard solution of pure iron is present in the cell. Substituting (3) into (2) we find

$$P_2 = P_2^{st} \frac{n_2 - n_1(n_3^{st}/n_1^{st})}{n_2^{st}}. \quad (4)$$

To check the method we prepared mixtures containing Fe and Cr in the same ratios found in the following alloys: Fe–7% Cr, Fe–15% Cr, and Fe–50% Cr. Several different absolute amounts of iron were present in the mixture for each ratio. Determination of Fe and Cr radioactivity in these mixtures and calculation according to Eqs. (1) and (4) showed that the method could determine these elements in the above ratios with accuracies to 5% for iron and 10% for chromium.

Figure 2 shows a curve of n_1 vs time t as measured and a curve of $(n_2 - n_3)$ vs t calculated according to Eq. (4). Both were obtained by simultaneous recordation of ^{59}Fe and ^{51}Cr during anodic dissolution of Fe–28% Cr

alloy at a potential of −0.32 V (vs S.H.E.) in 1 N H_2SO_4 at a temperature of 50°C. These conditions correspond to dissolution of the alloy in an active state. It is evident from the diagram that the partial iron and chromium dissolution rates are constant with time starting from 10 sec* and continuing up to 10 min of exposure to the solution. Although uniform dissolution of iron and chromium was found earlier in experiments of more than 10-min duration [3], our results indicate that the Fe–28% Cr alloy components dissolve uniformly 10 sec after dissolution begins. Using Eqs. (1) and (2), calculated ratios of iron to chromium (P_1/P_2) for various values of t were found equal to 2.55 ± 0.25 which, considering how the data is scattered (Fig. 2), agrees well with the ratio of 2.57 for iron to chromium present in the alloy.

To assess the potentialities of the method developed, it must be realized that chromium does not interfere in the iron determination whereas the latter affects the chromium results. This is due to the Compton effect for ^{59}Fe which supplements the chromium channels with radiation approximately equal to that of ^{59}Fe in the iron channels. However, since the specific activity of chromium markedly exceeds that of iron, the latter's adverse effect would appear only when the iron content in the alloy is rather high. Thus, 1 week after bombardment the specific activities of iron and chromium differ by a factor of more than 500. This permits reliable determinations of chromium within this period with a background of at least a 200-fold excess of iron.

Sensitivity of the method with respect to iron and chromium has been reported [18].

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*The time to achieve ionization in the measurement bulb upon metal dissolution did not exceed 3 sec.