Electrochemical Measurement of the Concentration Depth-profile of Cr near the Surface of Fe-Cr Alloys

Tetsutaro Ogushi*

*Technical Research & Development Laboratories, Nippon Kinzoku Co., LTD.

This work is concerned with the electrochemical measurement of the concentration depth-profile of Cr near the surface of Fe-Cr alloys. In Fe-Cr alloys, the steady current density ($I_{t,p}$: mA/cm$^2$) in the transpassive region increases with Cr concentration, suggesting that Cr concentration can be evaluated from the measurement of $I_{t,p}$. When $I_{t,p}-Q$ (Coulomb/cm$^2$) curves of Cr-depleted Fe-Cr alloys are measured at $+1.400$ V vs S.C.E. (transpassive region) in 1 mol·dm$^{-3}$ H$_2$SO$_4$ (25°C, air open), $I_{t,p}$ increases gradually according to the dissolution in the transpassive region, and finally reaches a constant value depending on Cr concentration of matrix. From this $I_{t,p}-Q$ curve, the concentration depth-profile of Cr can be obtained by converting $I_{t,p}$ into Cr concentration and $Q$ into depth.

I. Introduction
The concentration depth-profile of Cr near the surface of Fe-Cr alloys plays a very important role in the corrosion and oxidation resistance. In order to produce high quality Fe-Cr alloys, speedy and exact measurement of the concentration depth-profile of Cr must be made and the production process must be properly controlled.

Only qualitative measurement of the degree of Cr-depletion can be made using the Ferric Chloride Spot Test$^1$ and more quantitative information needs to be obtained.

The present work is concerned with a new method for measurement of the concentration depth-profile of Cr near the surface of Fe-Cr alloys. This method is based on electrochemistry and gives some fairly quantitative information.

2. Principle
The steady current density ($I_{t,p}$: mA/cm$^2$) of Fe-Cr alloys in 1 mol·dm$^{-3}$ H$_2$SO$_4$ (25°C, air open) at $+1.400$ V vs S.C.E. (transpassive region) increases with Cr concentration (Fig. 1$^2$).

The test specimen is immersed in 1 mol·dm$^{-3}$ H$_2$SO$_4$ and then the electrode potential is fixed at $+1.400$ V vs S.C.E. and the $I_{t,p}-Q$ (Coulomb/cm$^2$) curve is measured. If a Cr-depleted zone is present, $I_{t,p}$ increases gradually according to the dissolution in the transpassive region, and finally becomes a constant value depending on Cr concentration of matrix. In this $I_{t,p}-Q$ curve, $I_{t,p}$ is converted into Cr concentration by Fig. 1 and $Q$ into depth by equation (1) if the current efficiency of dissolved metallic ions is about 100%.

$$D=10^4\left(\frac{dQ}{dQ}\right)\left[0.0000898 \left(\eta_{H^+} \right)^{+} + 0.000193 \left(\eta_{Fe^{+++}} \right)^{+}\right]$$

(1)
3. Experimental and Result

Commercial cold-rolled SUS 430 (thickness 0.5 mm) and three standard Fe-Cr alloys with different Cr concentration (Fe-9% Cr, Fe-13% Cr, Fe-17% Cr) were studied in this work. The chemical composition of these alloys is shown in Table 1.

Cr-depletion treatment of SUS 430 specimens was carried out by heating them in an air-opened siliconite furnace (790°C, 60 sec), and after cooling them in air, removing the oxide film by anodic polarization in 5 wt% HNO₃ (+1.600V vs S.C.E., 70 sec). After this treatment, SUS 430 specimens were immersed in 1mol dm⁻³ H₂SO₄ (60°C) for various time length (0 sec, 30 sec, 60 sec and 180 sec) in order to remove the Cr-depleted surface layer, and then the ıₜₚ-Q curves were measured in 1mol dm⁻³ (25°C, air open) by polarizing the specimen at +1.400V vs S.C.E. (transpassive region). Fig. 2 shows that ıₜₚ increases with immersion time and Q, representing the profile of Cr concentration near the surface of Cr-depleted SUS 430.

The ratio of Cr/(Fe+Cr) dissolved in 1mol·dm⁻³ H₂SO₄ (60°C) for various time length (0 sec, 30 sec, 60 sec and 180 sec) in order to remove the Cr-depleted surface layer, and then the ıₜₚ-Q curves were measured in 1mol·dm⁻³ (25°C, air open) by polarizing the specimen at +1.400V vs S.C.E. (transpassive region). Fig. 2 shows that ıₜₚ increases with immersion time and Q, representing the profile of Cr concentration near the surface of Cr-depleted SUS 430.

The ratio of Cr/(Fe+Cr) dissolved in 1mol·dm⁻³ H₂SO₄ versus Q was measured by chemical analysis and the results are summarized in Table 2. Cr⁶⁺ ions were analyzed by diphenylcarbazide method and Fe³⁺ ions by O-phenanthroline method. Table 2 shows the gradual increase of the ratio of Cr/(Fe+Cr) from 14.59% to 16.01% with increasing amount of Q. Within experimental errors, this result agrees with the variation of Cr concentration in the surface layer of Cr-depleted SUS 430. In table 2, the amount of charge (Q) measured by chemical analysis is almost equal to...
the amount of \( Q \), showing that the generation of 
\( \text{O}_2 \) does not occur and the current efficiency of
dissolved metallic ions is about 100\%, hence \( Q \)
can be converted into \( D \) (depth) by equation (1). 
In Fe–12\% Cr alloys
\[
D \equiv (10^4)(1/7.7)Q \left[ (0.0000898)(0.12 \times 6)/(0.12 \times 6 + 0.88 \times 3) + (0.000193)(0.88 \times 3)/(0.12 \times 6 + 0.88 \times 3) \right] ^{0.22 Q} \ldots (2)
\]
and in Fe–17\% Cr alloys
\[
D \equiv (10^4)(1/7.7)Q \left[ (0.0000898)(0.17 \times 6)/(0.17 \times 6 + 0.83 \times 3) + (0.000193)(0.83 \times 3)/(0.17 \times 6 + 0.83 \times 3) \right] ^{0.21 Q} \ldots (3)
\]
From equation (2) and (3), equation (4) is obtained
for Fe–(12~17\%) Cr alloys.
\[
D \equiv 0.22Q \ldots (4)
\]
The concentration depth-profile of Cr (Fig. 3), 
therefore, is obtained by converting \( I_{\text{t,p}} \) into Cr 
concentration by Fig. 1 and \( Q \) into \( D \) (depth) by 
equation (4).

4. Summary
If Cr-depleted zone is present in Fe–Cr alloys,
the current density \( (I_{\text{t,p}}: \text{mA/cm}^2) \) measured in
1 mol·dm\(^{-3}\) \( \text{H}_2\text{SO}_4 \) (25\°C, air open) at +1.400 V 
vs S.C.E. (transpassive region) increases gradually 
according to the dissolution in the transpassive 
region.

From this \( I_{\text{t,p}}-Q \) (Coulomb/cm\(^2\)) curves, the 
concentration depth-profile of Cr is obtained 
by converting \( I_{\text{t,p}} \) into Cr concentration and \( Q \) 
into \( D \) (depth).

Acknowledgment
The author is grateful to Dr. Tatsuhiko Noda 
for his advice on the preparation of this note.
(Received September 28, 1982)

References
1) R. V. Trax & J. C. Holzwarth: Corrosion, 
16, 271t (1960).
2) R. Oliver: Comite' International de Termo-
dynamique et de Cinetique Electrochimiques 