

Transpassive Dissolution of Nickel-base Alloys in Acidic Solutions

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Transpassive dissolution of metals is a multistep process including electron and ion transport through a surface oxide film, multistep electrochemical reactions at the film/solution interface and transport of reaction products in the bulk solution. Because of transpassive dissolution, Ni-base construction materials are susceptible to general corrosion in highly oxidising environments. To control their general corrosion it is important to know the mechanism of dissolution and the parameters controlling the reaction rate. In this work we have studied the transpassive dissolution of three Ni-base alloys (Ni-15%Cr, Inconel Alloy 600 and Hastelloy Alloy C276) in oxidative acidic solutions at pHs 0 and 5 ($\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$) at ambient temperature. Electrochemical response of these materials has been determined by voltammetry, rotating ring-disc electrode voltammetry, contact electric resistance (CER) technique and electrochemical impedance spectroscopy.

Voltammetric results showed, that the transpassive dissolution starts at ca. 1.0 V (vs. SHE) at pH 0 and at 0.8 V at pH 5 on all materials. The dissolution rate is the highest for alloy C276 and the lowest for Ni-15%Cr at pH 0. In the pH 5 solution the dissolution rates are almost the same on every material. Rotating ring-disc electrode measurements showed, that the transpassive dissolution of Ni-15%Cr and alloy 600 is mostly due to the dissolution of Cr as hexavalent ions. In the case of alloy C276 also dissolution of Fe and Mo plays an important role. From the impedance spectra it is seen that for Ni-15%Cr and Alloy 600 there are three time constants in the transpassive region at both pHs (see e.g. Fig. 2 for Alloy 600 at pH 0). Also, on Alloy C276 three time constants are seen at pH 0, but at pH 5 the number of time constants is five.

In order to determine the rate controlling reaction steps in the transpassive region, a kinetic model describing the processes at the film/solution interface was developed (Fig. 1). Here we have assumed that all the applied potential is consumed by the electrochemical reactions at the film/solution interface, i.e. the potential drop at the metal/film interface and in the film is negligible. Furthermore, we have assumed that there are no appreciable concentration gradients in the film and the film is enriched in Cr with respect to the alloy substrate.

The reactions involved at the film/solution interface are: 1) oxidation of Cr(III) to Cr(VI), that further dissolves into the solution, 2) reaction of water with oxygen vacancies in the oxide film, 3) adsorption of Fe(III), Ni(II) or Mo(VI) to the outermost surface of the film and 4) dissolution of adsorbed species into the

solution. The reaction path marked with an asterisk is self-catalytic.

Because in maximum five time constants were observed in experimental results, also the model has to be able to predict all these time constants. The adsorption causing two of the time constants on Alloy C276 is due to the existence of both Fe and Mo in the film. On the basis of RRDE results for the other two alloys the model can be simplified by neglecting the adsorbed species, i.e. reaction steps k_7 , k_7^* , k_8 and k_9 .

As seen in Fig. 2, the model predicts the voltammetric transpassive behaviour of the alloy qualitatively at potentials higher than 1.2 V. The amount of Cr(VI) decreases due to its transpassive dissolution and the fraction of Ni(II) increases with increasing potential. The amount of trivalent Cr at the interface is low in the whole potential region. The model predicts qualitatively the shapes of the impedance spectra, but the magnitudes differ from the experimental results. This feature may be due to the fact that in the model all reactions at film/solution interface are assumed to be irreversible, but some of them may in reality be reversible. On the basis of the calculated parameters, it can be concluded that the transpassive oxidation of Alloy 600 at pH 0 is limited by the reactions of film growth (step k_4) and mainly by dissolution of Cr as Cr(VI) (step k_6). The rate constants of these reactions are roughly two decades lower than the rate constants of other reactions.

A general conclusion from this work is that the dissolution of Cr is a two-step reaction and mainly determines the properties of the films on the studied materials in the transpassive region. Increasing pH slows down the reactions at the film/solution interface.

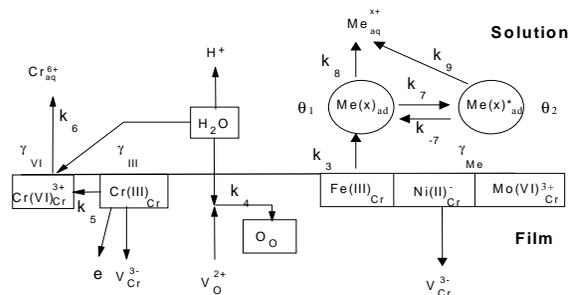


Figure 1. Scheme of the processes occurring at the film/solution interface on Ni-Cr alloys in the transpassive region

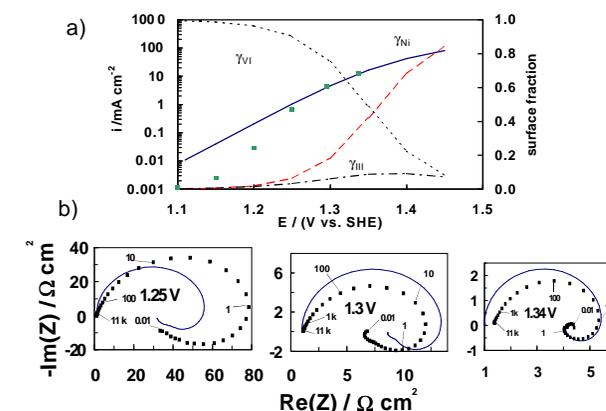


Figure 2. a) Polarisation curve of the transpassive dissolution and simulated surface fractions (γ , dotted lines) of Cr(III), Cr(VI) and Ni(II) for Alloy 600 at pH 0. b) Experimental and simulated impedance spectra of the transpassively oxidising Alloy 600 at pH 0. (simulated = solid lines)