Effect of Cr on the transpassive dissolution mechanism of Ni in a phosphoric acid solution

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The effect of Cr additions (10 and 20%wt.Cr) on the transpassivity of Ni in 1 M H_3PO_4 is studied by voltammetry and electrochemical impedance spectroscopy within the frames of a study of the effect of solution anion on the transpassive corrosion of nickel and its alloys.

The transpassive dissolution currents of pure Ni in 1 M H_3PO_4 are significantly smaller than those in 1 M H_2SO_4, indicating that the interaction between phosphate and Ni at the passive film / electrolyte interface is weaker than that between Ni and sulphate (Fig.1). Impedance spectra of Ni in phosphoric acid at high potentials in the transpassive region indicated the formation of a secondary film (a low frequency capacitive time constant with very high resistance values), at difference to those in sulphuric acid which exhibited second-order dynamic behaviour (impedance spectra circling the origin through all the four quadrants of the complex plane) (Fig.2).

Transpassive dissolution currents for Ni-10%Cr were also found to be somewhat smaller in phosphoric than in sulphuric acid solution (Fig.1). The increased tendency of the Ni-10%Cr alloy towards secondary passivation in 1 M H_3PO_4 in comparison to sulphate medium was observed as an extra capacitive loop in the impedance spectra at high potentials in the transpassive region (Fig. 3). In contrast, both voltammetric and ac impedance results for Ni-20%Cr and pure Cr in 1 M M H_3PO_4 point to a behaviour almost identical to that in sulphuric acid solution.

The obtained experimental results are successfully described by a modification of the kinetic model proposed for the transpassive dissolution of Ni-based alloys in sulphate and chloride solutions [1,2]. The model takes into account the dissolution of Ni as Ni(II) in two parallel reaction paths, one of which involves interaction with phosphate ions, and the dissolution of Cr featuring a Cr(VI) intermediate in the outermost cation layer of the passive film. The kinetic parameters of the model are determined by a simultaneous non-linear least squares fitting of the impedance spectra and the steady state current vs. potential curve to the equations of the model. Their relevance to transpassive dissolution is discussed in terms of cation-anion interaction at the film / solution interface.

1. I. Betova, M. Bojinov, P. Kinnunen, T. Laitinen, P. Pohjanne and T. Saario, *Electrochim. Acta* 47, 2093(2002).

2. I. Betova, M. Bojinov, P. Kinnunen, T. Laitinen, P. Pohjanne, T. Saario and M. Vilpas, *J. Electrochem. Soc.* 149, B499(2002).
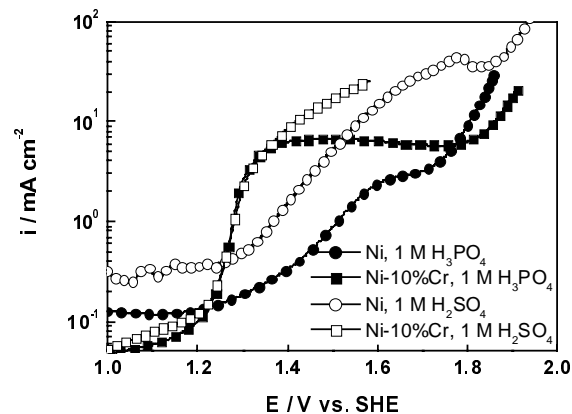
Fig. 1. Current vs. potential curves of Ni and Ni-10%Cr in the transpassive region in 1 M solutions of H_2SO_4 and H_3PO_4.
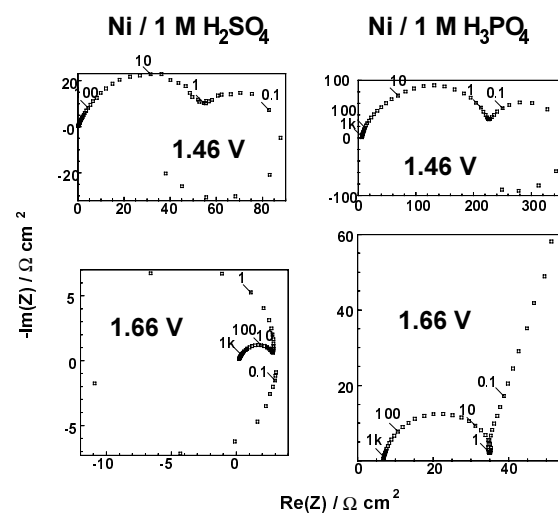
Fig. 2. Impedance spectra in the transpassive region of Ni in 1 M H_2SO_4 (left) and 1 M H_3PO_4 (right).
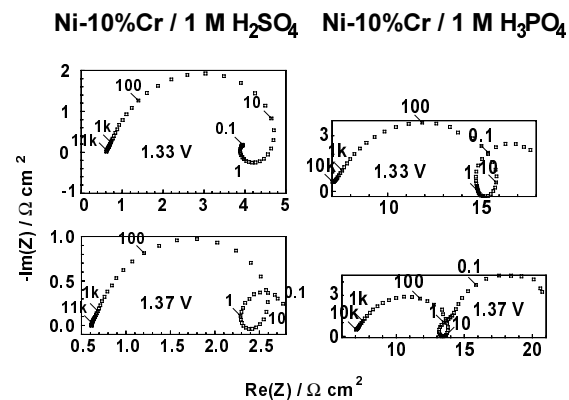
Fig. 3. Impedance spectra in the transpassive region of Ni-10%Cr in 1 M H_2SO_4 (left) and 1 M H_3PO_4 (right).