**In-depth composition and conduction mechanism in the oxide film on stainless steel in a high-temperature aqueous electrolyte**

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The conduction mechanism of the oxide films formed on AISI 316L(NG) stainless steel in 0.1 M $Na_2B_4O_7$ in the temperature range 150-300 °C has been characterised by impedance spectroscopy both in metal | film | electrolyte (MFE) and metal | film | inert metal (MFM) measurement configurations. In addition, the in-depth composition of the oxide films has been estimated by ex-situ Auger Electron Spectroscopic (AES) analysis.

The impedance magnitude at low frequencies in the MFE configuration is considerably higher than that in the MFM configuration regardless of the temperature (Fig. 1). Thus the oxide film is a predominantly electronic conductor [1,2]. The two time constants observed in both types of spectra are ascribed to the oxide film electric properties (at high frequencies) and ionic or mixed conduction through it (at low frequencies). The evolution of the impedance response in both configurations with increasing temperature is non-monotonous (Fig. 1). Namely, maximum values of the impedance magnitude at low frequencies have been found at a temperature of 200 °C. The observed non-monotonous dependence of the impedance response on temperature can be explained by changes in the in-depth composition of the passive film with increasing temperature (Fig. 2). It follows from Fig. 2 that the films formed in the passive region at 150 and 250 °C are strongly Cr-enriched, whereas in the film formed at 300 °C the enrichment in Ni far outweighs that in Cr. Conversely, practically no enrichment of the alloying elements has been observed in the film at 200 °C which is in correlation with the distinct impedance magnitudes at low frequencies at this temperature.

The ability of the recently proposed mixed-conduction model for passive films [2] has been tested vs. the experimental impedance data in both configurations. The kinetic and transport parameters in the oxide film have been determined. The effect of temperature on these parameters has been discussed in terms of the particular characteristics pertinent to oxide film formation on stainless steel in a high-temperature electrolyte. It has been demonstrated that also in high-temperature electrolytes, the main corrosion-resistant barrier is constituted by a thin semiconductor layer properties of which do not drastically differ from the properties of the room-temperature passive films.

1. B. Beverskog, M. Bojinov, A. Englund, P. Kinnunen, T. Laitinen, K. Mäkelä, T. Saario and P. Sirkiä, *Corros. Sci.* 44, 1901(2002).
2. B. Beverskog, M. Bojinov, P. Kinnunen, T. Laitinen, K. Mäkelä and T. Saario, *Corros. Sci.* 44, 1923(2002).

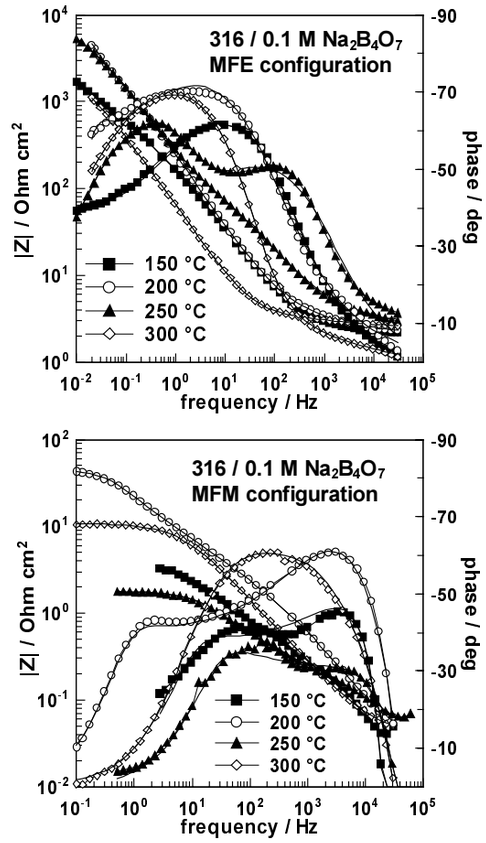


**Fig. 1.** Impedance spectra of 316 stainless steel in the passive region (-0.55..-0.45 V vs. SHE) at different temperatures in the MFE configuration (above) and MFM configuration (below).

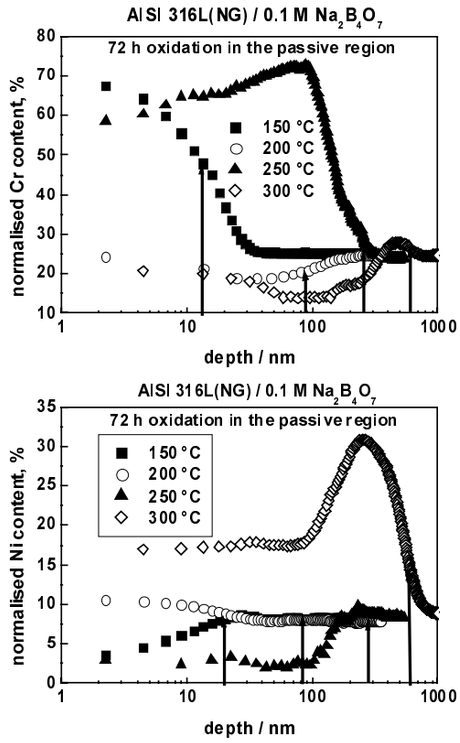


**Fig. 2.** AES depth profiles of the normalised Cr (above) and Ni (below) contents in the oxide film formed on 316 stainless steel in the passive region (-0.55..-0.45 V vs. SHE) at different temperatures. Arrows indicate the estimated position of the metal / film interface.