

The Effects of Temperature and Potential on the Passive Corrosion Properties of Ni-Cr-Mo Alloys

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Ni-Cr-Mo alloys are considered the most corrosion resistant of the Ni base super alloys due to their high resistance to localized attack in chloride media¹. Many studies of passivation and the compositions of passive oxide films have been reported for austenitic stainless steels and Ni-Cr-Fe alloys^{2,3}. These studies show that Cr is the key element in enforcing passivity. Based on results from techniques such as x-ray photoelectron spectroscopy (XPS), this enforced passivity appears to be due to the presence of an inner oxide layer (barrier layer) rich in Cr. Similar claims have been made for the influence of Cr on the passivity of Ni-Cr and Ni-Cr-Mo alloys^{4,5}. The primary goal of this work is to determine the differences in passive behaviour of these materials and how they are influenced by the particularly important parameter of temperature.

Five alloys are currently under investigation, 625, C22, C276, C4 and C2000. These alloys can be generally grouped by their Cr content, either high or low, with C22 representative of a high Cr alloy and C276 a low Cr alloy. Potentiostatic polarization experiments were performed as a function of potential (200 mV to 700 mV vs. Ag/AgCl) and temperature (25°C to 85°C). X-Ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF SIMS) were used to determine the thickness and chemical composition of the films formed.

The currents recorded were due to dissolution with only minor increases in film thicknesses observed. Measured currents for the high Cr alloys, such as C22, were lower than for the low Cr alloys and there is a less pronounced temperature dependence for the high Cr alloys (Figure 1). Surface analysis confirmed that the passive films on all alloys consisted of a Mo, Cr and Ni oxide, with Cr present as Cr³⁺ and Mo present in several oxidation states. The films on C22 showed a distinct layered structure, consisting of an inner layer rich in Cr (Figure 2a, region II) and Ni (peak A), and an outer layer enhanced in Mo (region I). By contrast the oxide films on low Cr alloys (e.g. C276) did not show such a clear separation into layers and the relative Cr content was much lower (Figure 2b).

The point defect model (PDM) developed by Macdonald and coworkers⁶ can be used to explain the results. The increase in oxide thickness with increasing anodic potential and the low temperature dependence of the passive currents observed for C22 are consistent with an oxide dissolution rate which is low compared to the rate of creation of oxygen vacancies. The absence of a dependence of film thickness on potential and the higher temperature dependence of the passive currents on C276 are consistent with control of the overall anodic process by ion-transfer at the oxide/solution interface.

References

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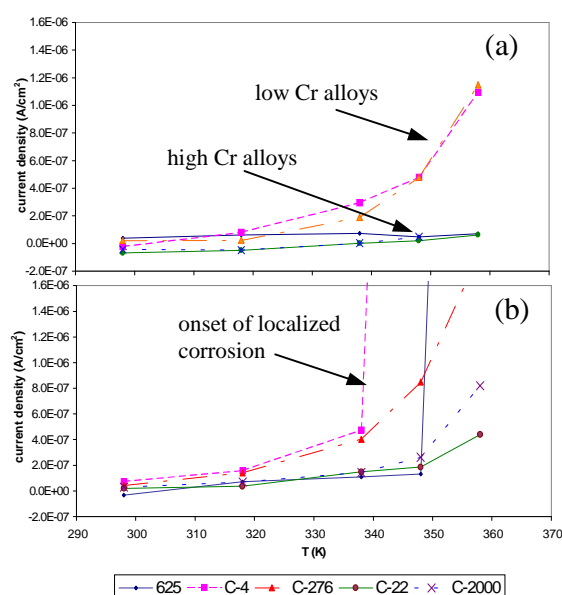


Figure 1. Passive current behaviour as a function of temperature for all five alloys at (a) +200 mV and (b) +500 mV.

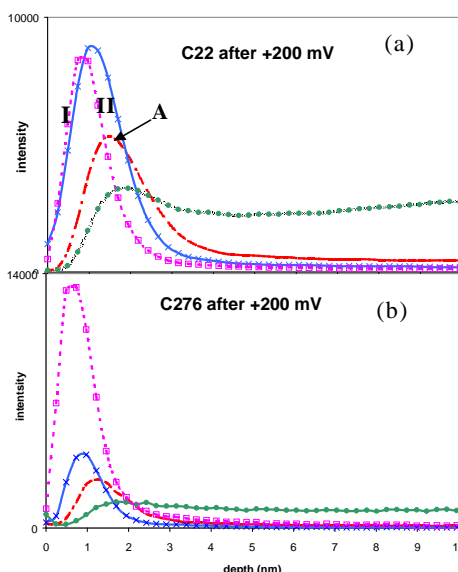


Figure 2. TOF SIMS depth profiles for C22 and C276 after polarization (and a temperature increase from 25°C to 85°C) at 200 mV.