The Passivity of a Super Duplex Stainless Steel

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The passivity of a second generation duplex stainless steel (Zeron 100) has been investigated with the objective of relating its corrosion behaviour to the properties of the surface oxide. Electrochemical techniques, in particular impedance spectroscopy, have been used to characterise the electronic properties of the oxide film and the electron transfer processes. The frequency dependence of capacitance, usually observed with non-ideal systems, has been critically addressed. Potentiostatic and potentiodynamic techniques were also used to develop an understanding of the passivity phenomena on these steels.

Auger and X-ray Photoelectron Spectroscopy were employed to determine the chemical composition of the films, produced under various polarisation conditions and *in situ* Scanning Probe Microscopy (ECSTM and ECAFM) was used to observe the very early stages of corrosion.

The electrochemical results are discussed in terms of contemporary theories of the reactivity of conducting and semi-conducting oxides. The oxide on duplex stainless steels was found to be a non-ideal n-type semiconductor with a high number of carriers. Its constitution was largely dependent on the conditions under which it was produced or submitted to. When produced by polarisation in alkali it presented two regions, an inner region rich in chromium and an outer region rich in iron. When produced in acid solution, it consisted of a single region rich in chromium.

The effect of nitrogen on the passivity of the alloy was addressed. The higher nitrogen concentration (*ca*. 4 at%) in the oxide film on the austenite phase, compared to its content in the film on the ferrite phase (practically non-existent), is related to the remarkable difference in electrochemical activity between the two phases. The austenite phase is significantly more stable than the ferrite phase. If corrosion occurs, the pitting is isotropic in the austenite and anisotropic in the ferrite phase.

The electrochemical activity of the alloy was significantly dependent on the metallographic structure. The formation of the secondary phases, due *e.g.* to the heat treatment or welding, brought the breakdown potential to more negative values. The resulting localised electrochemical activity led to deep pitting, where the repassivation was extremely difficult.

Further studies are suggested that will relate to the relative importance of stochastic events in the breakdown of passivity.

The Significance of this Study for Engineering

The importance of this study for engineering application of the super duplex stainless steel, Zeron 100, is summarised below:

- Zeron 100 exhibits an excellent resistance to corrosion. This resistance is largely due to the dual phase structure. A conventional austenitic stainless steel would undergo penetrative isotropic pitting, which carries a risk, *e.g.* of stress corrosion. The austenite in the duplex structure is depolarised by the ferrite phase, which corrodes preferentially to the austenite phase. The etching of the ferrite phase, however, is not deep; it takes place laterally, and consequently, does not affect the mechanical strength. The ferrite phase can be considered as a sacrificial anode, but its corrodability is without great consequences to the phase, since it undergoes uniform corrosion.

- If, under the environmental conditions to which the super duplex stainless steel is subjected in the field, the passive film is occasionally broken, the repassivation is very easy due to the lateral mode of corrosion in the ferrite phase and to the intrinsic stability of the primary austenite phase. In working environments, electrochemical conditions are likely to fluctuate, so that aggressively anodic conditions are likely to relax, or vice-versa. However, materials containing heat affected zones, or that have received inadequate heat treatments, can undergo severe and deep corrosion. The addition of nitrogen to the new generation of duplex stainless steels is ineffective against corrosion, if secondary phases are present in the ferrite phase due to inappropriate heat treatment. Secondary austenite, without nitrogen contents is even more susceptible to corrosion than the ferrite phase. Such materials, if under stress, can also present catastrophic failures in very short exposures to the aggressive medium, because of the intrinsic brittleness of secondary phases.

- The passivity of the material can be greatly dependent on the time of exposure to the aggressive medium, since it has been seen that the electrochemical activity of the alloy increases with time of immersion in sodium chloride solutions. It is acknowledged that the correlation of short term accelerated laboratory tests to long term corrosion processes in real engineering situations is debatable.

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