

## Ageing Effects on the Film Composition (AES, XPS) of Fe-Ni Alloys Passivated In Borate Solutions (pH : 9.2)

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In the last twenty years, passive layers structure and composition were extensively investigated in relation with the corrosion-resistant properties of metallic alloys. In order to predict the film behaviour and to optimize the alloy composition, a better understanding of the formation and growth mechanisms of passive layers is greatly needed. According to Kirchheim et al.[1], after the fast build up of precipitated precursor layers, the film grows owing to a logarithmic time law in agreement with the Mott-Cabrera model. In acidic solutions, a partial film dissolution occurs which has to be taken into account in the previous model : this may lead to a stabilization or to a decrease of the film thickness with time. A reorganization of the film constituents during ageing is also obviously expected but, surprisingly, few studies are presently reported on the subject. In this work, we shall report how the surface composition of Ni-Fe alloys (25, 50 and 75 Fe at%) may evolve during large passivation periods up to the stationary state in acid boric-borate solutions (AB medium, pH=9,2) at 0.2 V/SCE.

The analytical characterization (depth composition, chemical bondings, thickness) was performed by AES and XPS spectroscopies in association with ion depth profiling. Concurrently, passive film dissolution kinetics under small applied current intensity (potential vs time in 0,035M Na<sub>2</sub>SO<sub>4</sub> solutions adjusted to pH 3, 4 or 5) were achieved to provide complementary, fast and "in-situ" but qualitative informations about the film depth composition [2].

In a former paper [2], AES depth profiling gave the elementary composition of the passive films formed on those Fe-Ni alloys in AB medium. It briefly consists in an external nickel rich part above an inner Fe rich layer (1 to 2,5 nm) that covers the underlying metallic alloys which appears strongly Fe depleted and consequently Ni enriched. Long time ageing causes a distinct film thinning (10 to 6 layers) disclosed by quantification of the AES depth profiles. An ICP analysis of the electrolyte proves that Ni compounds preferentially dissolve during the passivation even at pH 9,2.

It was concluded that the preferential oxidation of iron - the more oxidable element - would initiate the passive film build-up and that the selective dissolution of superficial Ni species contributes to limitate the film growth during ageing.

Recently photoemission studies and film dissolution experiments furnish additional informations about those mechanisms. Clearly, XPS results validate the previous AES bilayer model with an external enriched Ni part with compounds now identified as NiOOH and Ni(OH)<sub>2</sub> above inner layers composed with mixed Fe<sup>3+</sup> and

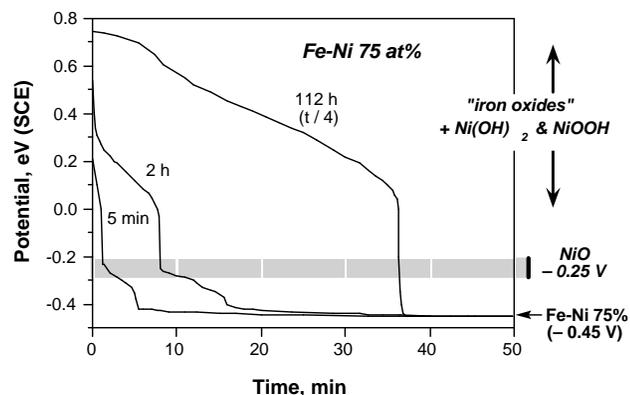
more internal Fe<sup>2+</sup> oxides. The attendance of few NiO quantities inserted with inner iron oxides at short passivation durations treatments (figure 1a) in the more Ni concentrated alloys (50 et 75 at%) is an outstanding feature for the film growth comprehension. Dissolution kinetics of passive layers display in figure 1 some potential steps occurring at - 0,25 V. They are due to the NiO dissolution reaction previously identified in thermal oxide films and in pure Ni passive layers [2]. They disappear after a long time ageing (Figure 1 at 112 h) but also in rich Fe alloys (25at%Ni) in agreement with analytical results where the thickest internal iron oxide layers were brought in evidence [2].

This seems to implicate the iron layers in a role of diffusion barrier limiting the Ni supply of the film from the alloy. So, if the Ni cation migration under the electric field towards the electrolyte (Mott-Cabrera model) cannot be compensated, this should lead to a progressive disappearance of the initial internal NiO contents with ageing. This effect is more pronounced in concentrated Fe alloys (25%Ni) where the extended iron oxide barrier seems to empede internal NiO to be depicted even after short passivation period.

In other respects, aged passive layers exhibit a clear lengthening of dissolution kinetics (Figure 1). This seems to refute the film thinning stated by AES and now confirmed by the XPS depth profiles (Figure 2). In fact, the « precursor » film obtained after a 30s passivation treatment on Fe-Ni75% alloy is thicker, widely hydrated and it contains large superficial amounts of Ni<sup>3+</sup> and Fe<sup>+3</sup> oxi-hydroxides with internal NiO contents mixed with iron oxides

(Figure 2a). Oxi-hydroxides are unstable below 0,4 V/SCE [3] ; they can be reduced into Ni(OH)<sub>2</sub> (figure 2b) or converted into Fe<sub>2</sub>O<sub>3</sub>. O-1s depth profiles - not displayed here - would also indicate that a significant H<sub>2</sub>O loss was occurring during ageing.

Those results allow to point out that, at the stationary state (t >> 10 hours), passivated Fe-Ni alloys tend to acquire the most stable thermodynamical configuration with majority Fe<sub>2</sub>O<sub>3</sub> and Ni(OH)<sub>2</sub> contents. A release of the initial incorporated water and oxi-hydroxides of the film with time should reduce the permeation rate of the electrolyte in the film. This would speak in favour of an increased duration for the dissolution kinetics and for improved protective properties of aged films.



applied current) after various ageing periods.

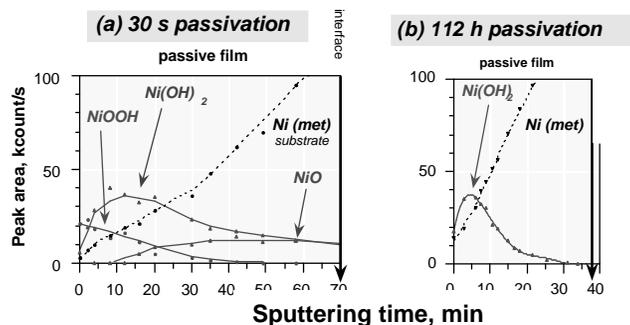


Figure 2. Ni-2p depth profiles in passive layers formed on a Fe-75 at%Ni alloy (sputter rate ~ 0.04 nm/min).

[1] J. Häfele, B. Heine and R. Kirchheim. Z. Metallkd, **83**, 395-404 (1992).

[2] F. Basile, J. Bergner, C. Bombart, B. Rondot, P. Le Guevel and G. Lorang. Surf. Interface Anal. **30**, 154-157 (2000).

[3] G. Barral, F. Njanko-Eyoké, S. Maximovich, Electrochimica Acta. **19**, 709-715 (1995).

