Electrochemical stability of stainless steels modified by plasma nitriding

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Stainless steels are used as anodes for electrolytic deposition from cyanide and alkaline baths, as cathodes in anodic machining and electropolishing, or as electrodes in the Kirk grounding cells for protection against dangerous voltage. In all these applications a long-term stability is required, involving a high corrosion resistance and hardness. These goals can be achieved by surface modification, of which nitriding has found a wide application. Introduction of nitrogen to austenitic stainless steels enhances the stability of the γ phase and greatly increases the strength, hardness and wear resistance of these steels (1, 2). Nitrogen in a solid solution increases the resistance of stainless steels to pitting corrosion, and this beneficial effect is usually strongly augmented in the presence of molybdenum. The effect of nitrogen on the corrosion properties of stainless steels and the proposed mechanisms have been reviewed in Refs. (3-5). The synergetic effect of N-Mo has been reported mainly for steels with about 0.7 wt.% N and 2.5 wt.% Mo.

The objective of the present work was to examine the effects of N and Mo on passivation and susceptibility to pitting corrosion of austenitic stainless steels 00H18N10 and 00H17N14M2, containing up to 13 wt.% N dissolved in the steel crystal lattice at the near-surface region. Supersaturated solid solutions of N in these steels were obtained by plasma nitriding at 425 ^{o}C; low-temperature nitriding at 380 - 450 ^{o}C results in the formation of *S* phase, being the nitrogen expanded austenite phase (6). This phase has an increased resistance to pitting corrosion in neutral chloride solutions (6, 7) and to uniform corrosion in 0.5 M H_2SO_4 (8). However, a decreased corrosion resistance was observed in 0.1 M Na_2SO_4 acidified to pH 3.0 (9).

In the present work it was found that in a solution of 0.1 M Na_2SO_4 with added H_2SO_4 or NaOH for modification of pH, the corrosion resistance of the nitrided steels was at pH 3.0 lower than that of the unnitrided steels, whereas in the near-neutral solutions the resistance was higher. In the solution of pH 3.0 with added 0.4 M NaCl, the nitrided steels exhibited much higher resistance to pitting corrosion than that of the unnitrided steels. Electrochemical noise measurements suggested that the nucleation of unstable pits on the nitrided surface was similar to that on the untreated steel, but the growth of stable pits was strongly hindered in the presence of N and Mo. XPS analysis of surface films revealed higher contents of Fe_2O_3/Fe_3O_4 and molybdates on the N+Mo containing steels, and traces of nitrides at the steel/passive film interface.

Higher contents of these species can be related to faster anodic dissolution of nitrided steels, which was manifested by higher currents of anodic polarisation curves and lower charge transfer resistance measured with EIS. In potentiostatic transients, the initial anodic currents were for nitrided steels higher than those for the untreated steels, but after about a second the currents for the nitrided steels dropped faster. It is suggested that due to the initially faster anodic oxidation of nitrided steels, larger amounts of corrosion products were formed and they exerted an inhibiting effect.

It is proposed that the synergetic effect of N+Mo in improving the resistance to pitting corrosion of stainless steels can be related to an enhanced anodic reactivity of nitrogen-containing steels which results in a faster accumulation on the surface of the protective corrosion products, involving the Mo, Cr and Fe species.

References

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