INFLUENCE OF Ni ON PHOSPHATING OF ZINC-COATED STEEL

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Phosphating of Zn-coated steel sheets get an increasing importance in the car industry. This treatment protects the surface against corrosion and improves the paint adhesion by formation of a micro-crystalline Zn phosphate layer (Fig.1). The process is complex and can be described by a series of simultaneous anodic (Eq.1) and cathodic (Eq.3-6) reactions [1].

$$Zn \rightarrow Zn^{2+} + 2\,e \quad (1)$$
$$3\,Zn^{2+} + 2\,H_2PO_4^- \rightarrow Zn_3(PO_4)_2 + 4H^+ \quad (2)$$

$$Ni^{2+} + 2\,e \rightarrow Ni \quad (3)$$
$$x\,Zn^{2+} + y\,Ni^{2+} + 2\,(x+y)\,e \rightarrow Zn_xNi_y \quad (4)$$
$$NO_2^- + 2\,H^+ + 2\,e \rightarrow NO + H_2O \quad (5)$$
$$NO_3^- + 2\,H^+ + 2e \rightarrow NO_2^- + H_2O \quad (6)$$

In this way, the Zn surface becomes partially covered by reaction products such as $Zn_3(PO_4)_2$, Ni, Zn and Ni-Zn alloys. The aim of this work is to get a better understanding about the influence of Ni deposits in relation to their catalytic properties for NO_2^- and H^+ reduction. It is well known that the presence of NO_2^- increases the rate of surface coverage by Zn-phosphate [2]. However, its reduction mechanism on the different metal phases present at the surface during the process was not sufficiently studied, in particular that for Ni. On the other hand, the formation of Ni deposits in $H_2PO_4^-$ containing solutions must also be investigated.

Conventional electrochemical techniques were used supported by SEM/EDX and X-ray Fluorescence. Experiments were performed in 0.018 M NaH_2PO_4 + 0.013 M H_3PO_4 (pH 3.2) solutions with various Ni^{2+} and NO_2^- concentrations. As electrodes, Zn-coated steel, Ni, and glassy carbon (GC) were used.

At the first stages of phosphating, the rest potential (U=-0.70 V_{SHE}) is dominated by the Zn dissolution (Eq.1). Then, a potential shift towards the Ni/Ni^{2+} value is observed for a 1.7 x 10^{-2} M Ni^{2+} concentration (Fig.2). In addition, weight loss experiment indicate a decrease of the anodic c.d. with time. Thus, these results may be interpreted in terms of microscopic elements, where two processes are considered: (i) the formation of Ni and/or Zn-Ni alloy deposits and (ii) the increasing surface coverage by phosphate crystals.

In order to compare with the reduction process occurring on Ni deposits, potentiodynamic and potentiostatic polarizations were performed on Ni electrodes under different hydrodynamic conditions. NO_2^- reduction seems to be inhibited by a passivated surface, as may be inferred from a high Tafel slope (b-factor > 120 mV dec^{-1}) and an independence of cathodic c.d. on electrode rotation. Then, the reduction rate was found to be limited by H^+ concentration according to the mechanism proposed for Pt [3,4].

$$HNO_2 + H^+ \leftrightarrow NO^+ + H_2O \quad (7)$$
$$NO^+ + e \rightarrow NO_{ads} \quad (8)$$

Formation of Ni deposits from 0.017 M Ni^{2+} + $H_2PO_4^-$ containing solutions and subsequent anodic stripping were performed on GC for different NO_2^- concentrations. A decrease of the anodic charge for $[NO_2^-]$ > 0.03 M is observed. Also, an inhibition of NO_2^- reduction can be noted when Ni^{2+} concentration is higher than that for NO_2^-. It is well known that Ni deposition takes place through adsorbed intermediates as Ni^+ or $NiOH_{ads}$ [5,6]. Thus, surface passivation and inhibition effects may be interpreted as a process where an adsorption competition between $NiOH_{ads}$, Ni^+_{ads} and NO_{ads} is established.

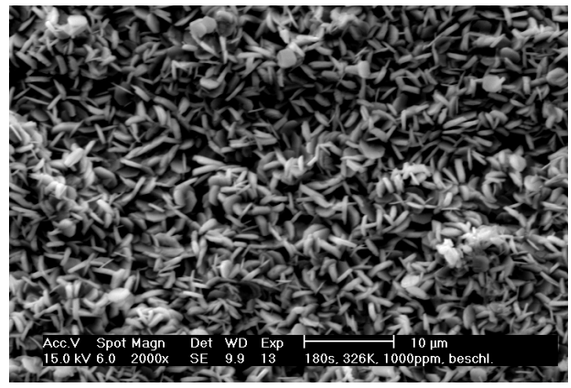

Fig. 1: SEM micro-graph of a phosphate layer obtained after 180 s phosphating. The bath contains 1,2 g l^{-1} Zn, 1 g l^{-1} Ni and 12 g l^{-1} P_2O_5. (NO_2^- and NO_3^- as accelerators).

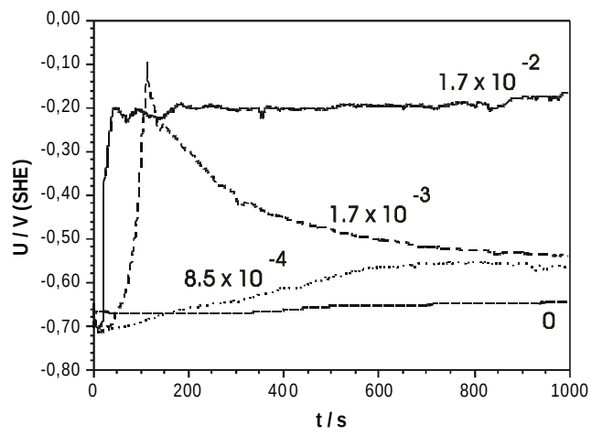

Fig.2: Rest potential evolution during phosphating of Zn-coated steel in $H_2PO_4^-$ solution for various Ni^{2+} concentrations indicated in mol l^{-1}. The solution contains 1.2 g l^{-1} Zn, NO_2^- and NO_3^-.

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