

## CORROSION OF WTiN SPUTTER-COATED STEELS IN CHLORIDE SOLUTION: INFLUENCE OF THE STEEL SUBSTRATE

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The electrochemical and corrosion behaviour of WTiN coatings sputtered on three types of steels: carbon steel, chromium steel and high speed steel, HSS, has been investigated. A systematic study of the influence of the steel substrate is important in view of the expected increased wear and corrosion resistance necessary for the good service life of cutting tools [1]. The corrosion behaviour of these steel substrates in the same media has been previously studied [2,3].

Substrates were coated with films of WTiN of  $\sim 4\mu\text{m}$  thickness on one face by DC diode sputtering at a negative substrate bias in a nitrogen / argon atmosphere at a pressure of 0.3 Pa. Coatings of composition  $\text{W}_{30}\text{Ti}_{30}\text{N}_{40}$  were produced. Electrochemical measurements were carried out in 0.1 M KCl non-deaerated aqueous solution. A three-electrode cell containing a Pt foil auxiliary electrode and a saturated calomel reference electrode was employed.

Visual and SEM observation of the coated steels during the experiments shows that corrosion is essentially localised in all cases.

The corrosion potential,  $E_{\text{cor}}$ , at open circuit as a function of immersion time for the coated steels is always more positive than that of the uncoated steels, confirming that the metallic coating increases the resistance to pitting corrosion. Values become more negative with immersion time, tending to those of the respective steel substrates, which suggests that the function of the WTiN coating is primarily to protect the steel from attack by Cl<sup>-</sup>.

Polarization curves were registered in the potential range  $\pm 250$  mV from the open circuit potential. In agreement with the measurements of  $E_{\text{cor}}$  at open circuit potential, the coated steel samples present a lower rate of corrosion than the respective substrates, again demonstrating the efficiency of the protective WTiN film.

The ratio between the corrosion currents of the uncoated steels and those of the coated ones was calculated. It was found that the metallic WTiN film reduced the anodic current density up to thirty times for chromium steel. The lowest ratio was obtained for carbon steel, with a factor of around two. Coating porosity values were also calculated and were highest for coated carbon steel, in agreement with its worst corrosion resistance. Coated chromium steels had the lowest porosity, paralleling its better corrosion resistance and showing the influence of the structure of the steel substrate on the morphology of the sputtered films.

Impedance spectra were recorded at the open circuit potential after 10 min, 1 h and 4 h immersion. In all cases the general shape of the spectra and evolution with time is similar. The impedance of the substrate/WTiN system is much higher than that of the uncoated steel, even after 4 h

immersion. Electrolyte penetration through the coating and the consequent increase of substrate corrosion is reflected in the decrease of the coated system impedance with increasing immersion time (see Figure 1).

Two time constants were seen. The substrate/coating systems showed charge transfer resistance values up to 7 times larger than those of the uncoated substrates, practically independent of the type of substrate. The resistance values obtained from the time constant at high frequencies associated with the coating defects,  $R_{\text{def}}$ , are dependent on substrate type.

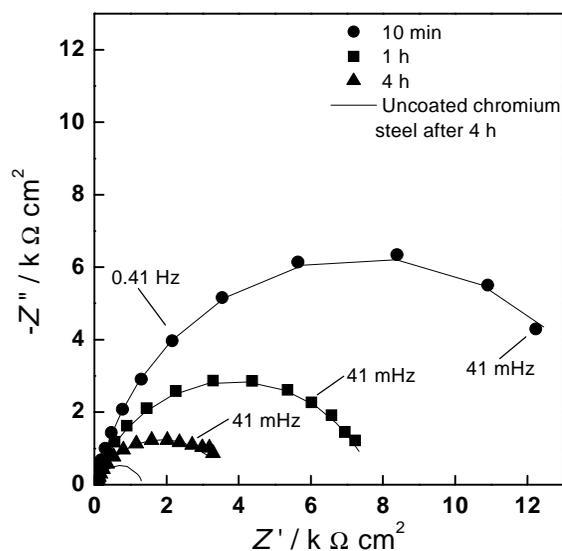


Figure 1. Evolution with time of the impedance spectra at the open-circuit potential for chromium steel/WTiN coated system in 0.1 M KCl solution. The solid lines show fitting to an equivalent circuit.

The chromium steel/coating system had the highest values of  $R_{\text{def}}$ . This suggests that these systems have a more compact coating as the result of a better interaction between the substrate and the metallic WTiN coating. Comparatively, the other steel/coating systems presented much lower  $R_{\text{def}}$  values.

Based on the overall behaviour of these systems, the following order of corrosion resistance can be proposed:

$$\text{Carbon Steel/WTiN} < \text{HSS/WTiN} < \text{Chromium Steel/WTiN}$$

The best corrosion resistance of the chromium steel/WTiN system can be associated with diffusion of Cr towards the surface during the coating deposition process forming CrN.

1. C.M.A. Brett and A. Cavaleiro, *European Federation of Corrosion Publications, Number 28* (2000), Chapter 11, p.155.
2. V.A. Alves, C.M.A. Brett and A. Cavaleiro, *J. Appl. Electrochem.*, 31 (2001) 65.
3. V.A. Alves, C.M.A. Brett and A. Cavaleiro, *Revista de Corrosão e Protecção de Materiais*, in press.

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