Metallurgical aspects of Corrosion Resistance of Stainless Steels

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Corrosion science is generally considered as a part of Electrochemistry, whereas corrosion Technology clearly refers to Metallurgy (as far as metals and alloys are concerned). It gave rise in the last decades to different approaches of the corrosion problems, either by academic people who generally aim to develop comprehensive models or by engineers who have to answer questions on real materials. It is intended in this talk to give some instances of metallurgical effects in localized corrosion resistance of stainless steels investigated using recent approaches developed in Corrosion science.

First, the complex effect of some alloying elements is analysed. Cu additions for instance are shown to be either beneficial or detrimental following the metal solution potential difference. Detrimental effect is observed when copper can redeposit at the pit bottom, preventing pit repassivation. At the opposite, solute Cu^{++} is beneficial, since it is able to trap the detrimental sulphur containing species provided by the Mn sulfides dissolution.

Taking advantage of a lot of consistent results already published in the literature and of some recent works performed in our teams, we discuss the detrimental effect of Sulfides inclusions and show that the sensitivity to pitting increases in the same way that the stability of the sulfides, suggesting that their role in pit initiation is simply to provide noxious sulfur species (more or less easily following the sulfur stability), which finally redeposit onto the passive film around the sulfide, resulting either in a poorer resistance to pit nucleation or in repassivation ability.

For monitoring pitting corrosion on a stainless steel regarding its metallurgical microstructure, local approaches can be used, combining scanning electrode and electrochemical micro-cell techniques . The electrochemical behaviour of single Mn sulphide inclusions was investigated, leading to a better understanding of the successive stages of inclusions activation and of key-parameters such as the onset potential for MnS dissolution and finally pitting potential. At open circuit potential the local current distribution around a pitting site can be monitored as well, allowing to locate anodic and cathodic regions and to obtain relevant information on the galvanic coupling between inclusions and the matrix. The results of these works sustain the assumption that the detrimental effect of sulfides is due to the redeposition of detrimental sulphur species around the inclusion considered as a " sulphur source". Furthermore local investigations were performed under applied stress. Microcracks in the matrix were shown to induce higher pitting susceptibility without any MnS contribution, but microcracks in the inclusion were found to enhance MnS dissolution, promoting then pit initition.

The effect of cold-working on the pitting resistance of austenitic stainless steels, more or less prone to strain induced martensitic formation, was revisited using metastable pitting transients techniques. As expected, a detrimental effect of cold-rolling was evidenced but this effect is not monotonous, showing a maximum of metastable pits initiation frequency around 20% of cold-rolling. This is not consistent with the hypothesis that martensite directly controls the pitting resistance. In agreement with the mechanochemical theory discussed by Gutman, the effect is rather due to dislocations pile-ups, which interacts in some case with martensite formation, the key parameter being assumed to be the stacking fault energy.

Despite the practical interest of cold rolled stainless steels (for use in structural devices for instance), Stainless steels sheets are generally delivered after a final "annealing" treatment (which is not strictly an annealing but rather a solution treatment), which can be performed either in oxidising conditions (needing then a final pickling treatment) or in hydrogen containing atmosphere ("Bright annealing"). The passive film developed on the final sheet and the pitting resistance strongly depends of the surface finish conditions. It was evidenced by different electrochemical investigations, particularly of metastable pitting transients. The detailed analysis of these transients allows to determine the transfer resistance and the capacity of the passive film, their evolution during long term aging, and their effect on the pitting corrosion resistance. Last, the crevice corrosion resistance was investigated using a new electrochemical device operating at rest potential, and was shown to markedly depend on the surface condition, likely via the depassivation pH, not only in the incubation stage but also in the propagation one

Those instances show clearly that new progresses in corrosion understanding can arise from detailed investigations of the metallurgical microstructure effects. To conclude, we note that temptative approaches to introduce the metallurgical characteristics in corrosion modeling, seem now possible, opening the route to a better lifetime prediction of real materials and corrosion numerical simulation in the future.