Microcell Applications on Different Systems

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Introduction
Electrochemical techniques using glass microcapillaries as an electrochemical microcell allow studying and controlling local processes on metal surfaces [1]. Due to the enhanced current resolution of the microcell technique down to pA and fA, processes in the micro- and nanometer range can easily be studied and controlled. The technique is well suited to study the corrosion behavior of microsystems and to deposit small metallic structures. Results obtained from studies of localized corrosion on different systems are presented and discussed. Furthermore some recent modifications and advancements of the microcell technique are demonstrated.

Experimental
The microelectrochemical cell used for corrosion studies consisted of a glass microelectrode (tip dia. = 1 µm - 1000 µm) filled with the electrolyte and sealed with a layer of silicone rubber to prevent leaking. The current detection limit of ≈ 10 fA enables to detect processes occurring in the µm and nm range. Different modifications of the microcells allow evaluation of additional parameters during an experiment or to perform corrosion measurements under different conditions.

Unsealed glass capillaries with a tip diameters below one micrometer were used for depositing metallic structures.

Results
Corrosion behavior of inclusions: The corrosion resistance of technical passive alloys (e.g. SS or Al alloys) is often limited by chemical or structural heterogeneities. Inclusions play a key role as initiation sites of pitting and crevice corrosion [2]. In order to study the influence of single inclusions on the corrosion behavior of an alloy, experiments were performed using capillaries with a tip diameter in the range of 20 to 100 µm. Measurements using capillaries with a tip diameter in the range of 1 µm allowed investigating different spots of a single inclusion. Hence the corrosion behavior of the weakest zone could be determined.

The results showed that the pitting potential of large scale experiments is usually fixed by the corrosion behavior of the most active inclusion whereas the pitting potential of an experiment on a single inclusion is usually determined by the weakest zone of the inclusion. It turned out that the weakest zone is always the interface inclusion/bulk. These findings are valid for stainless steels and Al alloys.

Biocorrosion: Microbially Influenced Corrosion (MIC) processes on metal surfaces are associated with microorganisms or the products of their chemical activities. Corrosion reactions are influenced by microbial activities especially when the organisms are in close contact with the metal surface forming a biofilm. Since microorganisms are almost never found in nature as pure species, samples covered with a biofilm of a microbial consortia were used. The samples, stainless steel 304, Al alloy 6082, and brass, were prepared under well controlled conditions at the institute of Plant Biology and Microbiology of the University of Zurich.

The results showed that the investigated biofilm (two weeks old) influenced the corrosion behavior of the three alloys in different ways. The biofilm decreased the corrosion resistance of the stainless steel 304 and the brass, but increased the corrosion resistance of the Al alloy 6082. On all three materials we observed that the biofilm altered the surface irregularly. Zones with different corrosion resistances could be identified. Figure 1 shows, for example, the polarization curves of three different zones on the brass sample.

Applications in Microelectronics: The determination of electrochemical properties of electronic parts with high resolution still remains a problem. Most local techniques used in microelectronics, like electrochemical AFM or SECM, require the exposure and polarization of the entire device in the electrolyte. The microcell technique allows a combination of high resolution and local electrochemical polarization without immersing the whole sample. The technique was applied for:

- quality control: By measuring the catalytic activity with microelectrochemistry the impurity level of Au connection lines could be determined.
- developing new manufacturing techniques: Glass capillaries are also a valuable tool when studying ion implanted semiconductors [3]. The implantation process is performed using a focused ion beam (FIB) and the implanted sites range between 0.1 µm and 100 µm in size. The goal is to study the electrochemical deposition behavior of different metals on these implant sites and compare them to the behavior on bulk silicon. Only microelectrochemical measurements allow us to measure exclusively on damaged zones thereby excluding any contributions from the bulk surface.
- nanoelectrochemical copper deposition: Glass capillaries with a tip diameter below half a micron were used to deposit small copper structures [4].

References

Figure

Fig. 1: Polarization curves in 0.01 M NaCl of different zones on a brass sample (diameter = 1 cm) covered with a biofilm (two weeks old).
Spot 1: no or thin biofilm
Spot 2: ‘thicker’ biofilm
Spot 3: black dots