Micro- and Macroelectrochemical Studies of Pit Initiation at MnS Inclusions in Stainless Steels

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Introduction

The corrosion resistance of stainless steels is often limited by chemical or structural heterogeneities. Inclusions, mainly manganese sulfide inclusions, play a key role as initiation sites of pitting and crevice corrosion [1, 2]. In this work pit initiation studies were performed at MnS inclusions on 304 and 303 stainless steels. The goal was to evaluate the critical factors for stable pitting at MnS inclusions. The steels were investigated in different electrolytes and in different scales. The results of large and small scale measurements provided information about the dissolution chemistry of the MnS inclusions and allowed determining the weakest zone of MnS inclusion.

Experimental

The large scale measurements were performed in a standard electrochemical cell. The microelectrochemical cell 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 $\approx$ 10 fA enabled to detect processes occurring in the μm and nm range [3]. Additional surface analytical investigations performed before and after the microelectrochemical experiments allowed correlating localized corrosion at single inclusions with the measured currents.

Results

Pit initiation experiments on 304 stainless steels were performed in 1 M NaCl. A 100 μm microcapillary was used to study pit intiation at single MnS inclusions of different composition, structure, and size. Electrochemical measurements using capillary with a tip diameter in the range of 1 to 3 μm allowed investigation of different zones of a single inclusion. Hence, the corrosion behavior of the weakest zone of an inclusion could be determined. Figure 1a shows polarization curves measured with a 2.5 μm capillary. The investigated zones of the MnS inclusion are indicated with white circles on the SEM picture taken before the corrosion experiments (Fig. 1 b). Figure 1 c shows the AFM picture taken after the corrosion experiments. Several measurement proofed that the interface inclusion / bulk is the weakest zone. The AFM picture on the interface (spot b) indicates that a pit or microcrevice was formed on the adjacent bulk matrix, but not on the MnS inclusion. On the contrary, "nm hills" were formed at the border of the inclusion. On spot c (center of inclusion) only "nm hills" are visible, but no pits. EDX and Auger measurements indicated a high sulfur, but a low manganese content for the "hills".

To clarify the formation of the "nm hills", we performed experiments in sodium sulfate, a solution in which MnS inclusions are active but SS does not pit [1]. To obtain statistical information large scale polarization curve were measured on a 303 stainless steel rod with a high number of MnS inclusions (Figure 2a). After the corrosion experiment the surface was covered with "worm like" MnS remnants (Figure 2a). EDX and Auger measurements showed, that the "worms" contained 70% to 80% sulfur, 10% to 20% chromium and smaller amounts of manganese. The deposited film ("crust") around the "worms" contained mainly manganese, but only smaller amounts of sulfur. Several micro and macro electrochemical measurements indicated that preferential dissolution of Mn (peak A in Fig. 2a) led to sulfur rich MnS remnants. Since dissolved Mn species are more voluminous, the S rich remnant were pushed out, forming the worm like structures. The manganese rich deposit film was formed at potential above 700 mV (peak B in Fig. 2a).

Conclusions

- The interface inclusion/matrix is the weakest zone of an MnS inclusion.
- Preferential dissolution of Mn leads to sulfur rich MnS remnants in 1 M Na_2SO_4.

References

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[2] G. S. Eklund, J. Electrochem. Soc., 121, 467 (1974).

[3] T. Suter, Ph. D. Thesis No 11962, ETH Zürich, (1997).

Figures

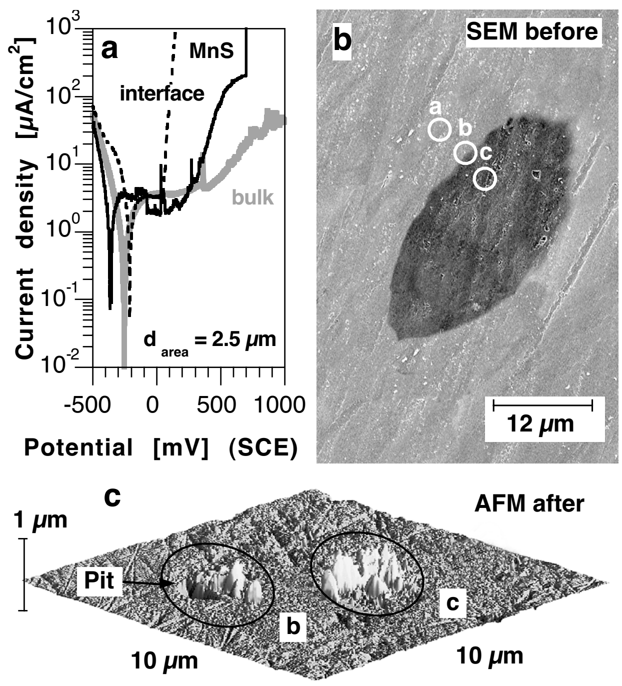

Fig. 1: Corrosion behavior of different zones of single MnS inclusion on a SS 304 plate in 1 M NaCl, a) polarization curves, b) investigated spots, c) AFM picture of the spot c and b.

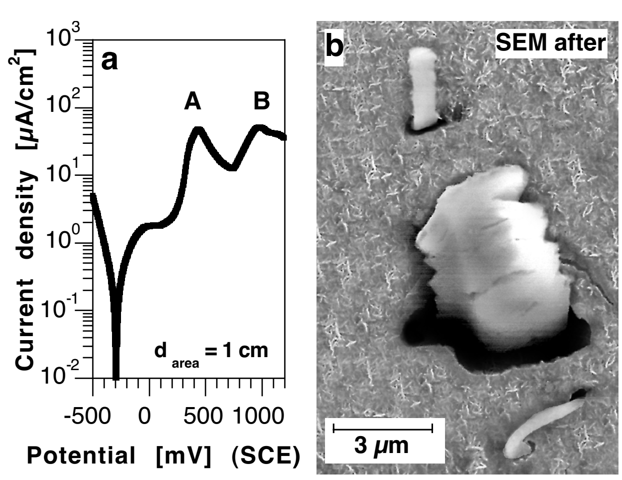

Fig. 2: Corrosion behavior of a SS 303 rod in 1 M Na_2SO_4, a) polarization curves, b) SEM picture taken after the corrosion experiment.