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In situ STM investigation of metal hydride electrodes in alkaline electrolyte during electrochemical cycles

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Abstract

For more than a decade metal hydride electrodes have been investigated by ex situ methods. In situ STM (Scanning Tunnelling Microscopy) allows investigation of single metal hydride grains during the charge and discharge process in the electrolyte. The advantage of STM measurements is its manifold analysing feasibility, e.g. surface morphology, surface conductivity and atomic forces with spatial resolution, and even sometimes atomic resolution. Samples of alloy grains pressed into a gold pellet and the polished surfaces of bulk alloys were investigated in concentrated alkaline electrolyte (6 M KOH) by means of STM. The volume expansion between the metal and the hydride was measured on a single grain in the electrolyte. This value of $\Delta V/V=14.9\%$ is very close to the value observed from X-ray diffraction measurements (15.4%). Multiphase samples show a very inhomogeneous surface conductivity. The identification of the phases with different surface conductivities is a key in understanding the hydrogen absorption mechanism in the electrolyte. ©1997 Elsevier Science S.A.

Keywords: Metal hydrides; Electrode; In situ STM

1. Introduction

Metal hydride (MH) electrodes consist of a large number of alloy grains in contact with a current collector (which at the same time acts as a supporting grid). The grain surface composition and oxidation state of surface elements [1], phase distribution [2] surface conductivity (activity) and the morphology [3] as well as the grain to grain contact [4] are crucial factors for the performance of an electrode. Due to corrosion and passivation processes, the conductivity at the grain surface changes upon cycling. A better understanding of the hydrogen absorption and the alloy degradation mechanism at the surface leads to an improvement of the metal hydride electrodes. In situ STM allows the imaging of the topology and surface conductivity during charging and discharging of the electrode.

This paper presents a detailed in situ STM investigation of single metal hydride alloy grains in an electrochemical cell during the charge and discharge process. Furthermore, the huge difference in surface conductivity of different alloy phases is demonstrated.

2. Experimental

2.1. Preparation of the sample

The alloy $LaNi_{3.5}CoAl_{0.5}$ was prepared by levitation melting as described in [5]. About 50 mg of ground alloy powder was let through a 25 μm sieve onto a thin gold pellet (0.5 mm thickness, 8 mm diameter) and then pressed with 8×10^8 Pa (4 tons). The sample was placed in a miniaturised open cell and transferred to the STM. A NanoScope III from Digital Instruments was used in the electrochemical STM mode.

2.2. Electrochemical cell

In order to do in situ STM investigation in the electrolyte we developed a miniaturized electrochemical cell (Fig. 1). The plexi-glass cell has an outer diameter of only 16 mm and consists of three connected compartments for the sample, the Hg/HgO reference electrode and for the counter electrode (Platinum wire). The miniaturized maintenance free Hg/HgO reference electrode has a diameter of 2 mm.

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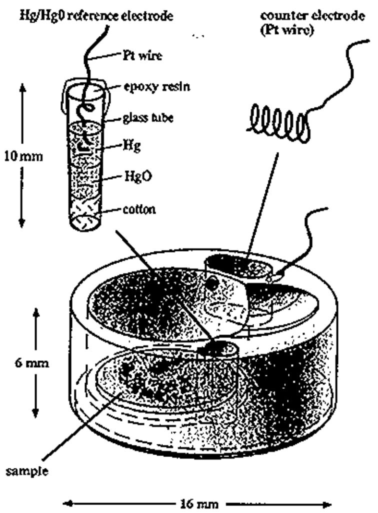

Fig. 1. Open electrochemical half cell with a Hg/HgO reference electrode and a Pt counter electrode for the extension of a commercial STM for in situ STM investigations.

2.3. *STM tips*

Special chemically stable tips are needed for the STM measurements in concentrated alkaline electrolyte. The $Pt_{80}Ir_{20}$ and $Pt_{90}Ir_{10}$ tips were etched (sharpened) using a melted mixture of 10 g NaOH and 11.7 g $NaNO_3$ [6]. An alternative voltage ($U_{\approx}$=8 V (2 kHz), U_{Bias}+6V) between the nickel cup which contains the aggressive electrolyte and the PtIr wire (diameter 0.25 mm). The PtIr wire is then brought into contact with the electrolyte and slowly moved up and down (about 3 mm) in the electrolyte. After about 20 s the end of the wire is etched so that the wire is no longer touching the electrolyte in the upper position. A final etching is performed by immersing the tip again 3 mm. After 3 s the power is switched off before retracting the tip. Cleaning the tip in kings water and an alcohol flame (several times) and finally in an ultra sound bath removes the remaining electrolyte. About 15 mm of the etched wire is cut and used as an STM tip. In order to minimise the faradaic charge transfer currents the tips are insulated with apiezon wax [7]. Our experiments have shown that the isolation is stable for several hours in concentrated 6 M KOH.

2.4. *Imaging procedure and electrochemistry*

The tip was positioned on the sample in the electrolyte with an optical microscope. The electrochemical tip potential for stable tunnelling conditions in 6 M KOH is between −950 mV and +100 mV versus the Hg/HgO reference electrode. The sample potential ranges from −600 mV (discharged state) to −900 mV (charged state). The overpotential during charge (i_{ch}=150 mA g^{-1}) is 50 mV (towards more negative potentials). Measurements on the sample were performed in equilibrium conditions at a potential of −850 mV versus Hg/HgO.

High bias voltages were used (up to 0.9 V in the electrolyte and up to 3 V in air). In our experiments, scanning with low tunnelling currents (as low as 300 pA) leads to the best images.

3. Results

Grains of the alloy $LaNi_{3.5}CoAl_{0.5}$ were imaged in the electrolyte by means of STM in the discharged and charged state (Fig. 2). Specific distances between the cracks on the surface of a single grain expanded by 4.74% upon charging. This corresponds to a volume expansion of 14.9% which is in good agreement with X-ray diffraction measurements (15.4%) [4]. The grain expands out of the gold surface. In the discharged state the highest point of the grain is 1.24 μm above the gold surface whereas in the charged state this point is 2.02 μm above the gold surface. As this difference is due to the volume expansion, the size of the grain below the gold surface has been estimated to be 15 mm. This value corresponds to the average grain size of the alloy $LaNi_{3.5}CoAl_{0.5}$ upon hydriding.

The alloy $Zr(V_{0.25}Ni_{0.75})_2$ shows two different regions on the surface (Fig. 3). EDX analyses of the surface of a polished sample of $Zr(V_{0.25}Ni_{0.75})_2$ allowed the identification of the dark and light phase to be $Zr(V_{0.33}Ni_{0.67})_{2.3}$ and Zr_7Ni_{10}, respectively [2]. The two phase sample is much

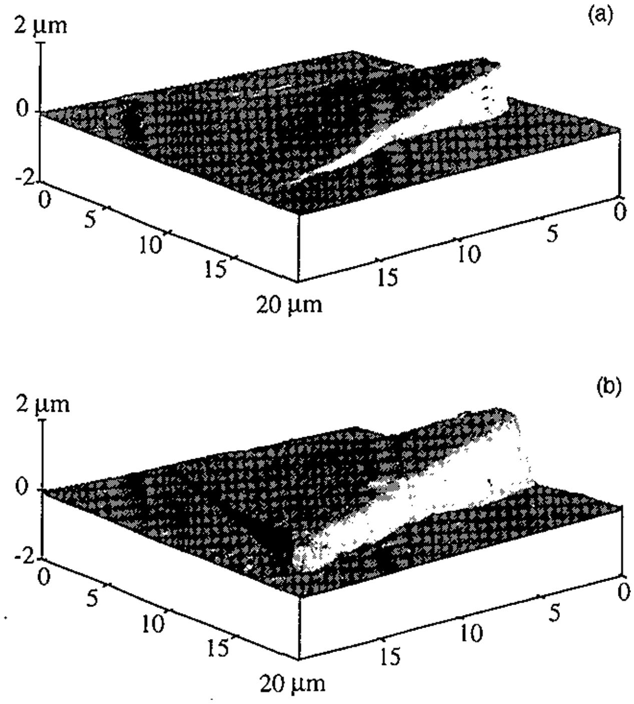

Fig. 2. A $LaNi_{3.5}CoAl_{0.5}$ grain on gold in 6 M KOH: a) the discharged and b) the charged state. The grain expands out of the gold surface due to the hydrogen absorption.

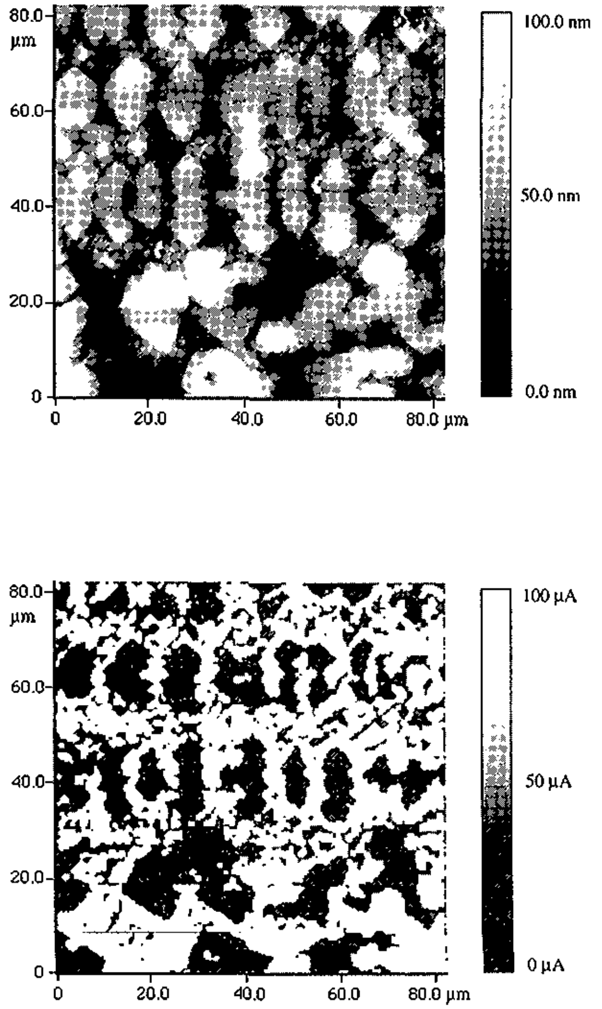

Fig. 3. a) A topographic image of the phased alloy $Zr(V_{0.25}Ni_{0.75})_2$. The light phase was found to be $Zr(V_{0.33}Ni_{0.67})_{2.3}$ and the dark phase is Zr_7Ni_{10} [2]. b) An image of the conductivity of the same region of the surface. Light means high conductivity; dark means poor conductivity.

more reactive compared to the single phase alloy $Zr(V_{0.33}Ni_{0.67})_{2.3}$. This leads to the conclusion, that Zr_7Ni_{10} catalyses the hydrogen absorption/desorption reaction. A higher surface conductivity was observed by AFM (Atomic Force Microscopy) on the Zr_7Ni_{10} phase compared to the $Zr(V_{0.33}Ni_{0.67})_{2.3}$ phase (Fig. 3b). This indicates, that the tunnelling barrier for electrons is lower on the surface of Zr_7Ni_{10} compared to the other phase. The same electron tunnelling process occurs in electrochemical hydrogen absorption reaction. The catalytic effect of Zr_7Ni_{10} can thus be explained by a higher electron transfer rate.

4. Conclusion

The mechanical volume expansion of single metal hydride grains was observed in the electrolyte upon charging the electrode. The electrochemical STM allows a local analysis of the morphology of single grains in an electrode.

The catalytic effect of a specific phase in multiphase alloys can be explained by the enhanced electron transfer rate due to the lower tunnelling barrier.

Acknowledgments

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