Electrochimica Acta 56 (2011) 9588–9595

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Scanning Kelvin probe force microscopy for the in situ observation of the direct interaction between active head and intermetallic particles in filiform corrosion on aluminium alloy

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ARTICLE INFO

Article history:
Received 15 November 2010
Received in revised form 9 February 2011
Accepted 10 February 2011
Available online 17 February 2011

Keywords:
Filiform corrosion
SKPFM
Kelvin probe
KFM
Aluminium

ABSTRACT

This article presents for the first time an in situ high-resolution study of the interaction between the active head in filiform corrosion (FFC) and intermetallic particles within an aluminium alloy. For the first time direct evidence will be provided that the intermetallic particles directly determine the so far seemingly random course of the filaments. Both the segments of active filaments and the intermetallic particles (IMPs) were successfully imaged in a humid air (ca. 85% RH) environment by scanning Kelvin probe force microscopy (SKPFM) through a plasma polymer coating of about 340 nm thickness. In order to be able to do that, the experimental parameters need to be adjusted in such a way, that the width of the filaments is small enough to be well within the scan window of SKPFM (100 μm × 100 μm). Also it is important that the small IMPs can still be mapped by SKPFM through the coating. This was successfully achieved by use of a HDMSO plasma polymer film. Surface potential values in the head region of the propagating filaments were found to be 200 mV lower than the interface between intact plasma polymer and the aluminium alloy, indicating the active region. On the other hand, the surface potential values in the trailing filament tail are found to be about 250 mV higher than background, pointing out the cathodic site and superpassivation due to the accumulated corrosion products in this region. It was found that the direction of the filament is determined by the location of the IMPs nearest to the active head.

1. Introduction

Scanning Kelvin probe techniques are very powerful tools for the in situ investigation of electrochemical process at buried interfaces, such as e.g. corrosion driven delamination at the interface between an organic coating and a metal surface. The first application of the scanning Kelvin probe (SKP) in corrosion science was for studies on the fundamental mechanisms of cathodic delamination lead by Stratmann, Leng, Streckel, Hofmann and Rohwerder [1–4]. For these first studies it was sufficient to work with a resolution in the 100 μm range. Attempts to perform such studies on a nanoscopic scale are rare. In principle, with the development of scanning Kelvin probe force microscopy (SKPFM) a high resolution Kelvin probe is available for such studies. However, this method is very prone to artefacts [5]. Moreover, the experimental problems faced with trying an in situ study of cathodic delamination with nanoscopic resolution are extremely challenging. For instance, the applied coating must not be thicker than about 100 nm in order to allow the desired high resolution [6]. However, when these coatings are lifted up by the ingress of electrolyte following the cathodic delamination this seriously endangers stable imaging with the AFM tip [6]. Although in this first attempts quite interesting results were achieved, e.g. that cathodic delamination may possibly proceed in nanoscopic jumps, this work on cathodic delamination was not continued due to these considerable experimental problems. Hence, it is not surprising that in corrosion science SKPFM is currently mostly used for obtaining surface potential maps of alloy surfaces, which are widely thought to provide information on potential local galvanic elements during corrosion. Although this indeed often seems to be the case, a general correlation between surface potential maps of samples measured in air and the corrosion behaviour of the same sample immersed in a corrosive solution certainly cannot be made [5]. For obtaining reliable information about fundamental mechanisms of corrosion processes and their correlation to the microscopic phase distribution of alloy materials in situ studies are desirable. One example for this is in situ corrosion studies on magnesium alloy exposed to high humidity in absence and presence of CO_2 [7]. The potentials measured by Kelvin probe on such “dry” surface are electrochemical in nature [8] and the potential maps and especially the changes observed as a function of time provide valuable information of galvanic activity between matrix

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doi:10.1016/j.electacta.2011.02.052

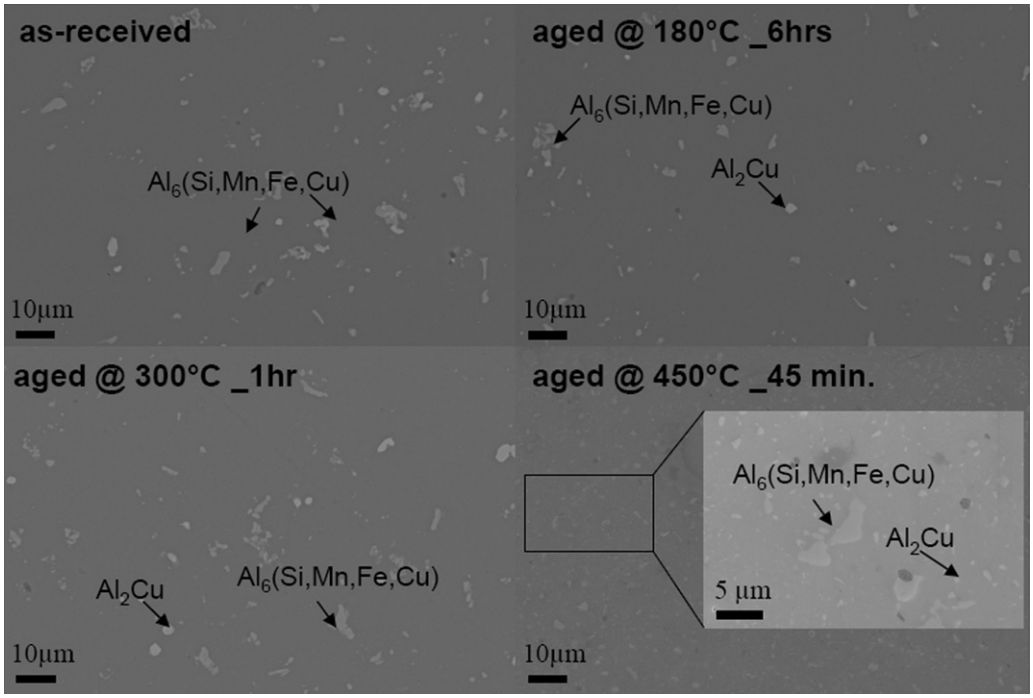

Fig. 1. SEM micrographs of the four DURAL alloy substrates used: (a) as-received, (b) aged at 180 °C for 6 h, (c) aged at 300 °C for 1 h and (d) aged at 450 °C for 45 min.

and inclusion [7]. Another example is the in situ study of cathodic delamination mentioned above [6], and studies on filiform corrosion [9]. For filiform corrosion the experimental problems should not be as severe as for cathodic delamination, as e.g. topographic changes are only locally. Leblanc and Frankel succeed in scanning over active filaments, however, their size was too large as to be able to follow their progress in situ [9]. In fact, the limited scan window in SKPFM is a considerable problem for such studies. Hence, for the investigation of filiform corrosion with Kelvin probe techniques so far most in situ studies have been carried out with the standard SKP, not with SKPFM [10–15]. In most cases the filaments observed during filiform corrosion are large enough to be accessible by standard SKP. These studies significantly helped to improve our understanding of filiform corrosion.

Filiform corrosion (FFC) was first described by Sharmann in 1944 as a form of atmospheric corrosion occurring on painted steel and

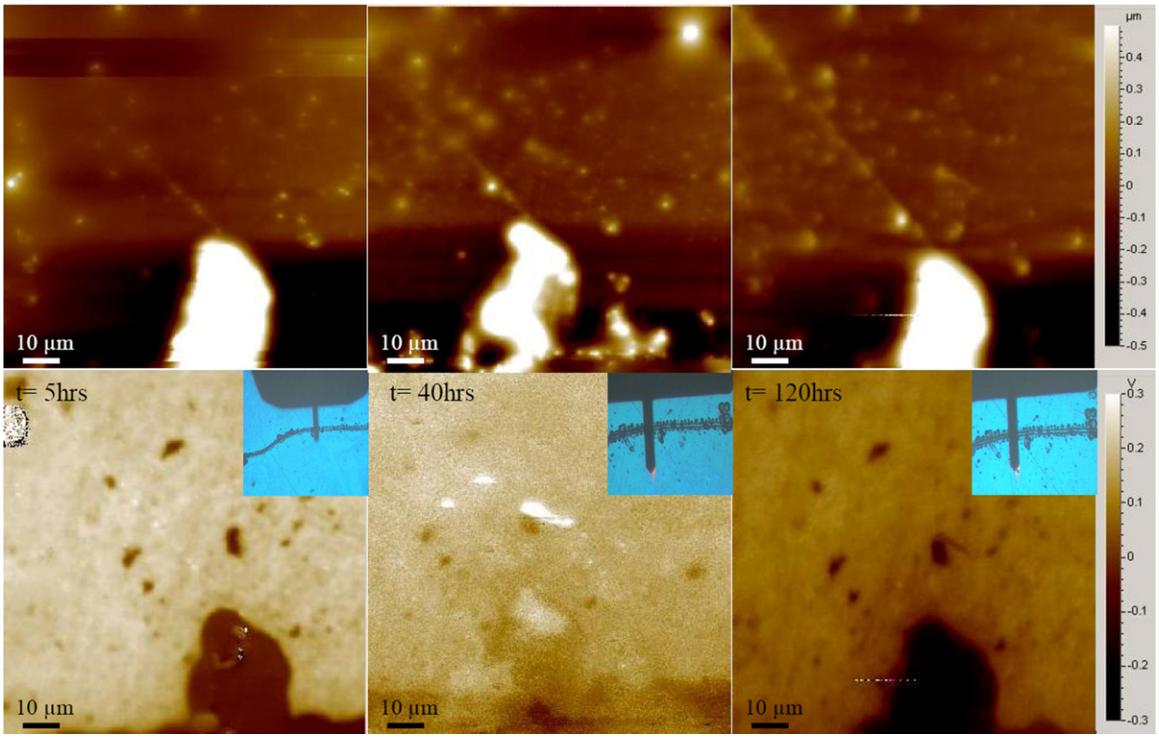

Fig. 2. Topography and surface potential images obtained during the FFC study performed on sample 1 coated with 110 nm HMDSO film. The area of the scans is 100 µm × 100 µm. Note that the topographic images on the top have a full scale range of 1 µm and the surface potential maps at the bottom have a full scale of 0.6 V.