International Journal of Adhesion & Adhesives 29 (2009) 471–477

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

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

AFM adhesion force measurements on conversion-coated EN AW-6082-T6 aluminium

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ARTICLE INFO

Article history:
Accepted 18 September 2008
Available online 10 October 2008

Keywords:
Aluminium and alloys
Atomic force microscopy
Chemical conversion

ABSTRACT

Atomic force microscopy (AFM) has been used to measure the adhesion force between functionalised AFM tips and smooth surfaces of an EN AW-6082-T6 aluminium alloy, both before and after application of different conversion coatings. In addition, the surface of a sapphire sample was studied as a model aluminium surface. The results obtained for the sapphire surface were highly reproducible, and were used as a mean to establish proper routines for the more complex industrial surfaces. The adhesion force between a chromate conversion-coated (CCC) EN AW-6082-T6 aluminium alloy and a COOH functionalised tip was significantly increased compared to the uncoated surface, probably as a result of strong hydrogen bonding. However, the adhesion force decreased with time during the first 24 h after treatment due to aging of the CCC. Chromate-free Ti–Zr-based treatment also increased the adhesion, but the adhesion force varied significantly due to non-uniform deposition and composition of the conversion coating. The measured AFM adhesion forces correlated qualitatively with macroscopic adhesion test results obtained previously for these specific conversion coatings. The AFM technique may thus provide useful information on the adhesion behaviour of heterogeneous conversion-coated aluminium surfaces.

1. Introduction

Chromate conversion coatings (CCCs) on aluminium have been successfully used for decades to provide corrosion resistance and adhesion to paints and adhesives. Alternative pre-treatments are being developed for environmental reasons and some of them are already in use. However, their efficiency and reliability are still a matter of discussion. The formation and properties of conversion coatings on aluminium may be rather complex due to the inherent heterogeneous microstructure of commercial alloys. In particular, surface treatment processes are significantly influenced by presence of intermetallic particles exhibiting electro-chemical properties different from the aluminium matrix. Commercially available chromate-free conversion coatings are often less robust than the CCCs [1] and are in general more affected by the composition and microstructure of the substrate.

Lateral variations in the surface chemistry resulting from the subsurface microstructure may occur on conversion-coated surfaces [2]. In order to assess the influence of such variations on local adhesion to an organic coating, adhesion measurements with high lateral resolution are required. Atomic force microscopy (AFM) is particularly useful for such studies. The measured adhesion force (F_{ad}) necessary to pull a functionalised AFM tip free from the surface is interpreted in terms of the specific interaction between molecules on the AFM tip and those on the surface. In general, F_{ad} is the sum of several forces [3]:

$$F_{ad} = F_{el} + F_{vdW} + F_{cap} + F_{chem} \quad (1)$$

including electrostatic forces (F_{el}), van der Waals forces (F_{vdW}), meniscus or capillary forces (F_{cap}) as well as forces due to chemical bonds or acid–base interactions (F_{chem}). A significant electrostatic contribution may occur on insulators and at low humidity, when charge dissipation is ineffective. The van der Waals forces are always present, and the sum of these forces is in most cases attractive. At ambient conditions, a water meniscus forms between the AFM tip and the substrate due to condensation and adsorption of a water film on the surfaces. The magnitude of this interaction depends both on relative humidity and the hydrophilic nature of the tip and the sample. Depending on the chemical end groups present on the tip and the substrate, chemical bonds may form during contact.

Quantitative AFM adhesion force measurements require that measurements are performed under conditions where the

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0143-7496/$ - see front matter
doi:10.1016/j.ijadhadh.2008.09.005

electrostatic and capillary forces are minimized or can be corrected for. However, quantification is also limited by adsorption of contaminants on high-energy solid surfaces. Furthermore, surface roughness [4] and tip wear must be considered. In principle, the exact contact geometry needs to be known and procedures involving SEM or TEM are generally used to determine the tip geometry. Despite these complications, AFM force–distance curves have become an important method for studying adhesion properties with a lateral resolution at the nanometer level [3].

In the present work, we have used AFM to measure the adhesion force between functionalised AFM tips and smooth surfaces of an EN AW-6082-T6 aluminium alloy, both before and after conventional chromate and Ti–Zr-based pre-treatments. A chromated surface was examined because it represents a benchmark system for pre-treatment of aluminium. Furthermore, fundamental knowledge of the adhesion mechanisms of CCCs may be useful to develop more environmentally friendly alternatives. The Ti–Zr-based pre-treatment was chosen as a representative of a chrome-free alternative, which seems to have gained widespread acceptance industrially. Commercially available AFM tips with carboxyl (COOH) and methyl (CH_3) functional groups were used. These groups represent typical hydrophilic (COOH) and hydrophobic (CH_3) groups associated with the adhesion of organic coatings to oxidised aluminium. The AFM measurements were conducted on specimens prepared by ultramicrotomy prior to conversion coating to minimize surface roughness effects. Complementary measurements on a sapphire single-crystal surface were conducted to estimate effects of tip wear and relative humidity. The results are discussed in light of the wedge adhesion test results obtained previously for these specific conversion coatings [5].

2. Experimental

2.1. Materials, surface preparation and characterisation

The substrate materials used included a single-crystal sapphire supplied by Goodfellow, and commercially extruded EN AW-6082-T6 aluminium. Sapphire (Al_2O_3) represents an idealized aluminium surface for AFM adhesion force measurements due to its hardness and chemical stability. The RMS roughness of the sapphire was 0.089 nm, as determined from the tapping mode AFM image of a $100 \times 100\,nm^2$ area. Clean and smooth surfaces of the aluminium alloy (composition by weight 0.63% Mg, 1.0% Si, 0.53% Mn, 0.17% Fe, 0.0034% Cu, 0.016% Zn, 0.013% Ti, Al balance) were prepared by using a Reichert–Jung ultramicrotome and a diamond knife from MicroStar [6]. The ultramicrotomed surfaces were oriented parallel with the extrusion direction and generated close to the surface of the extrudate, i.e. within the 500 μm thick recrystallized layer covering the fibrous microstructure of the bulk material.

The freshly generated EN AW-6082-T6 surfaces were subsequently treated according to the following conversion coating procedures:

- *Ti–Zr-based pre-treatment*: deoxidation in 4% Alfideox™ 73 for 30 s, tap water rinsing, immersion in 4% Gardobond® X4707 (H_2TiF_6–H_2ZrF_6 solution of pH 2.9, 20 °C) for 1 min, rinsing in distilled water and air drying.
- *Chromating*: deoxidation in 4% Alfideox™ 73 for 30 s, tap water rinsing, immersion in 15 ml/l Alodine® C6100 for 3 min, rinsing in distilled water and air drying.

An uncoated ultramicrotomed specimen was included as a reference. The reference surface was deoxidised and rinsed as described above to enable an assessment of the change in adhesion force resulting from deposition of the conversion coatings.

The composition of intermetallic particles present at the surface was determined by using a JXA-8900 Superprobe electron probe microanalyzer (EPMA) operated at 15 kV. The presence of conversion coatings was confirmed by using a Hitachi S-4300 SE field emission SEM equipped with an energy dispersive X-ray analysis system (EDS).

2.2. AFM adhesion force measurements

2.2.1. General principle

The basic principles of AFM adhesion force measurements have been described and discussed in the literature [3,7]. In short, the AFM measures the deflection of a cantilever with a functionalised tip (radius about 10–50 nm) as a function of displacement of an interacting surface as sketched in Fig. 1. Initially, the distance between the tip and the surface is large (A) and there is no interaction between the two. As the surface approaches the tip, van der Waals forces start to deflect the cantilever. At a certain point, when the attractive forces become large enough, the tip jumps onto the sample surface (B). The continued movement of the surface in contact with the tip causes a deflection of the cantilever in upwards direction, represented by the diagonal line in the deflection–displacement curve. When the movement is reversed (C), the cantilever tip adheres to the surface past the point of zero deflection (D) due to adhesion forces. Eventually, the spring jumps off the surface (E) and loses contact with the surface (F). The force required to pull the tip off the surface corresponds to the adhesion force (F_{ad}) and is calculated from Hooke's law:

$$F_{ad} = k\Delta x \tag{2}$$

where k is the spring constant of the cantilever and Δx is the maximum deflection of the cantilever (difference between E and F in Fig. 1).

2.2.2. Instrumentation and tip preparation

Adhesion force measurements in this work were performed by using a Nanoscope IIIa Multimode™ AFM with commercially available carboxyl (COOH) and methyl (CH_3) functionalised tips from Bioforce Nanoscience. These probes are made by coating Si_3N_4 AFM tips with a thin gold film, which is modified with a self-assembled monolayer of thiols with desired functionality (X–$(CH_2)_n$–SH, where SH is connected to the gold surface and X is the functional end group). The spring constant of the as-received cantilevers was calibrated according to the method described by Cleveland [8], which involves attaching a known

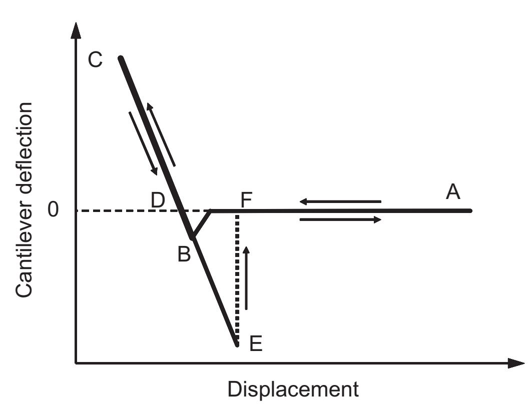

Fig. 1. Schematic curve of cantilever deflection versus displacement (distance to surface) in AFM adhesion force measurements.