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Research Paper

Development and optimisation of focused ion beam/scanning electron microscopy as a technique to investigate cross-sections of organic coatings

Son Ngo[a,b,*], Chris Lowe[a], Oliver Lewis[b], David Greenfield[b]

[a] Becker Industrial Coatings Ltd., UK
[b] Sheffield Hallam University, UK

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ABSTRACT

A sample of pre-painted metal was investigated using the dual beam system of a focused ion beam (FIB) and scanning electron microscope (SEM). The FIB was used to remove material (known as 'milling'), clean and 'polish' the sample exposing a cross-section of the coating. SEM was then used to investigate and analyse the structure and composition of the coating system. However, preliminary trials showed that in order to have good compositional data the technique needs to be developed and optimised. This paper presents the experimental work that was carried out in order to achieve this. First the milling area was changed from the centre of sample to the edge of the sample. Second, the mill shape needed to be changed from a rectangle to an isosceles trapezoid to allow better detection of the characteristic X-rays for the detector. Finally the tilt and rotation of the stage were changed for further improvement in X-ray detection.

Focused ion beam/scanning electron microscope (FIB/SEM) was found to be a useful technique to study the cross-sections of pre-painted metal. Information from secondary and backscatter electrons images can reveal the quality of the coating (for example adhesion to substrate, pigment dispersion, interfacial properties etc.) and also the thickness of the coating causing less damage to the sample compared to other mechanical sectioning techniques. Additionally it offers the ability to look at specific areas of interest such as defects, contamination and corroded areas. Energy dispersive X-ray spectroscopy (EDS) analysis allows mapping of the elements which are shown distributed in the coating and also the quantification of those elements. The results obtained from EDS analysis were representative of the components that were formulated into the pre-painted metal product.

1. Introduction

Scanning electron microscopy (SEM) has been in use since 1942, described by Zworykin et al. [1]. It was commercialised in 1965 and tens of thousands of SEMs are in use today [2]. It allows the observation of surfaces of materials by scanning them with a beam of focused electrons. The primary beam interacts with the sample and produces secondary electrons which are low energy electrons that are detected using an Everhart-Thornley detector. This is the most common imaging mode in use and it generates primarily topographical information. For imaging of contrast between areas with different chemical composition, backscattered electron detection is used which can discriminate elements of differing atomic number. High atomic number elements appear brighter than low atomic number elements due to the greater number of backscattered electrons produced. Characteristic X-rays and other photons of various energies can also be detected [1,2]. The images displaying the topography of the surface can range from 2D to 3D-like models at typical lateral resolution of 1–5 nm for a field emission electron source and 10–50 nm for a tungsten electron source [1]. For X-rays, the typical lateral resolution is between 0.2 and 5 μm. The resolution depends on the atomic number of the element, as well as density and accelerating voltage of the SEM [1].

The focused ion beam (FIB) systems have been in use since the 1970′s [3]. They typically use a beam of finely focused gallium (Ga^+) ions at a range of energies which allow the FIB to make a precise cut or cross-section, take an immediate image and deposit conductive or insulating materials onto the sample surfaces [4,5]. However, the destructive nature of ion beam (Ga^+) imaging is a major drawback [5]. The technique is used extensively in the semiconductor

* Corresponding author at: Becker Industrial Coatings Ltd., UK.
E-mail address: sonny.ngo@beckers-group.com (S. Ngo).

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industry for the fabrication of modern semiconductors and other types of electronics by imaging and nano-machining of devices [6–8].

These two techniques have been combined in the last twenty years used to locate and analyse sub-surface defects. It allows samples to be prepared, imaged and analysed resulting in saved time and opening up new application areas. The ion beam is primarily used for precision milling (destructive for imaging) and electron beam for non-destructive, high resolution imaging and monitoring of the cross-section face while the FIB mills [4]. The two beams complement each other in protective depositions, delineation of cross sections, charge reduction and imaging information [5]. Also included is the ability to perform microanalysis of an area of interest using energy dispersive x-ray spectroscopy (EDS), which gives elemental information about the sample [4].

FIB/SEM has the ability to reveal small voids or other fragile features without causing significant surface damage to samples as compared to conventional mechanical sectioning methods. The biggest drawbacks are that only small samples can be machined and the process is very time consuming. Other problems associated with the technique are related to charge damage and artefacts that can be generated due to striations and redeposition [5]. However, steps can be taken to minimise these problems.

Much of the published work related to FIB milling has reported the preparation of samples for transmission electron microscopy (TEM) [9] and also investigating cross-sections of different materials [10]. Typically, the work has been applied to inorganic systems. For polymeric materials, a limited number of investigations have been reported on polymer film thicknesses, the characterisation of aluminium spheres dispersed in a low density polyethylene matrix and the damage caused to polycarbonate by FIB [8,10–12].

Early experience of the combined techniques of FIB/SEM highlighted the problems encountered when trying to analyse the face revealed by cross-sectioning using EDS [4]. The aim of this work, which is part of a larger project investigating organic coil coatings, was to develop an FIB sample preparation method that would allow researchers to fully analyse the face of interest. It also demonstrates the effectiveness of FIB/SEM to study pre-painted metal systems, such as organic coatings deposited over hot dip galvanised (HDG) steel (see Fig. 1).

The ultimate goal was to optimise the technique so that pigment dispersion, interfacial properties and changes occurring after exposure could be studied. Cross-sectional analysis was included in this study to investigate the chemical composition inside the coatings. Only the topcoat side of the pre-painted product was investigated as this is the surface normally exposed to the environment. This investigation constituted part of a larger project assessing corrosion performance of organic primers.

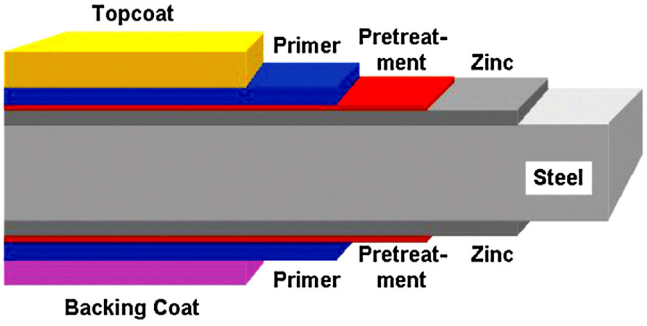

Fig. 1. Schematic diagram of a pre-painted HDG steel [13].

2. Experimental

2.1. Samples

A 0.7 mm thick sample of pre-painted HDG steel (See Fig. 1) was used in this investigation. The paints (topcoat and primer) on top of the treated HDG steel are based on saturated polyester resins thermally cross-linked with melamine. The reaction between the resin and cross-linker is an acid catalysed transetherification [14]. The other components in the paints are solvents, pigments and additives.

The sample was cut to dimensions of 10 mm × 10 mm using an Excel 2BR6 ab guillotine. One edge of the sample was then hand polished with a circular movement on MetPrep silicon carbide abrasive paper discs wetted with tap water. A P120 coarse grit paper was initially used and then fine polished with a P1200 grit paper. Polishing was needed to eliminate the damage to the pre-painted metal caused by the guillotine during cutting. The sample was then mounted onto an SEM stub using carbon cement with the topcoat facing outward and glued with Agar silver paint G3691.

2.2. FIB/SEM analysis

The mounted sample was placed inside an FEI Analytical Quanta 3D FEG dual beam FIB/SEM which uses a field emission gun to produce the electron beam. Observation of the sample was performed by SEM secondary electron imaging with different accelerating voltages while maintaining the same spot size or probe setting. For higher quality imagery 10 kV was used but this had the disadvantage of damaging the coating.

Before using the FIB to remove material, it was necessary to protect the surface of the sample from stray and out of focus Ga^+ ions. This was achieved by depositing a small platinum (Pt) rectangular shape (50 μm × 10 μm) with a thickness of 2 μm onto the surface, through the use of a gas injection system. This was carried out using an accelerating voltage of 16 kV and a beam current of 11 pA. For milling, Ga^+ ions at tilt angle of 52° to the electron beam were employed. A beam current of 42 nA and an accelerating voltage of 16 kV were used. In some cases a high FIB energy (30 kV) was used to remove the material quickly.

The cross-sectioned face was then polished to produce a smooth surface and also to remove any of the Ga^+ ions embedded in the coating during the milling process. A beam current of 7.5 nA and an accelerating voltage of 16 kV at a tilt angle of 53.5° were used. To produce an excellent finish with less curtain effects [2], a low beam current of 1.5 nA was used, however this took a longer time (14.5 h). To remove the material quickly, higher beam currents were used but this tended to produce poorer finishes.

2.3. Elemental analysis

As a result of electron bombardment, emitted X-ray energies are characteristic to individual elements. Energy dispersive X-ray detector (EDS) attached to the FIB/SEM can be used to detect, analyse and plot the characteristic X-ray energies from the sample. The technique can give both qualitative identification and quantitative elemental information from small sample volumes. The lateral resolution is typically between 0.2 and 1 μm for high atomic number elements. While low atomic number elements have a lateral resolution between 1 and 5 μm [1]. Elemental concentrations of 0.1–0.5% represent the limit of element detection [5]. Qualitative analysis of elemental distributions can be obtained by either using line scanning or by mapping of the area of interest. In line scanning, the electron probe is programmed to scan a line across a region of interest on the samples. When mapping, the probe rasters over the full image and records the individual X-ray photon signal as pixels on a