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Scanning transmission electron microscopy technique for morphology analysis of anodic oxide film formed on titanium

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ABSTRACT

The application of scanning transmission electron microscopy for morphological observation of anodic oxide films formed on titanium has been successfully explored. Important details of anodic films are readily recorded from high quality images by scanning transmission electron microscopy, which enabled the study of the film morphology, identification of film thickness and the presence of oxygen bubble features. By combining the large field of view with flexible magnification ranges in the scanning transmission electron microscopy, it was possible to study the morphology of the oxide film. A 6-specimen carousel holder would provide an increase in productivity by ~20% compared with a conventional, single-specimen scanning transmission electron microscopy or transmission electron microscopy.

The use of anodized titanium in an increasing range of applications has resulted in a growing demand for detailed information on the morphology of the anodic films in order to derive crystalline structure – property correlations. In the microstructure analysis of anodic oxide films, the structure and occurrence of oxygen evolution are examined to precise a deep understanding of the coating performance. This is also critical for optimization of the titanium surface and processing conditions for specific requirements in the aerospace industries [1–3].

Transmission electron microscopy (TEM) is the most frequently used technique for the study of the morphology of thin film coatings. The TEM technique, however, presents some limitations: the equipment is expensive; the analysis is time-consuming and is somewhat skill-intensive. Recently, some publications have reported the value of the scanning transmission electron microscopy in scanning electron microscopy (STEM-in-SEM) technique in the areas of mineralogy and petrology [4], semiconductors [5], nanomaterials [6,7], polymers and catalysts [8]. The STEM-in-SEM has been shown to be a rapid and easy method for characterization of the morphology and the internal structure of mineral and rock specimens, and it was shown to be particularly useful in microbiology research [9]. In addition, an exhaustive high-resolution STEM-in-SEM study of laser-machined silicon structures was carried out to characterize defects in the crystal lattice, thermal-mechanical damage, internal structure, compositions, and dimensions of the laser-machined structures [10].

However, according to the authors' knowledge, studies of anodic oxide film growth on titanium using an STEM-in-SEM technique have not been reported in any previous research. Thus, in the present work, the application of STEM-in-SEM to anodic oxide films formed on titanium is demonstrated. Some examples of anodic films formed on titanium are presented, with emphasis on the film morphology and oxygen bubble features etc., which are routinely probed by TEM.

A Zeiss Ultra 55 scanning electron microscopy, equipped with a scanning transmission electron microscopy detector was used in the present study. The schematic diagrams of Fig. 1 show a 6-specimen carousel holder and its rotation direction. Within the SEM chamber, the STEM detector unit consists of the detector and an extension arm for the adjustment of the X, Y and Z directions. The extension arm also carries the detector back and forth between a “rest” position and an “active” position when imaging. In the “active” imaging mode, the 6-specimen carousel holder is used and the STEM detector is perfectly aligned. In the “rest” mode, the detector is “parked” away by simply retracting the detector to a safe distance. Also, if the detector is not “parked” away, the joystick function is used to freeze it during the “active” mode in order to protect the STEM detector and, when in the “rest” mode, the

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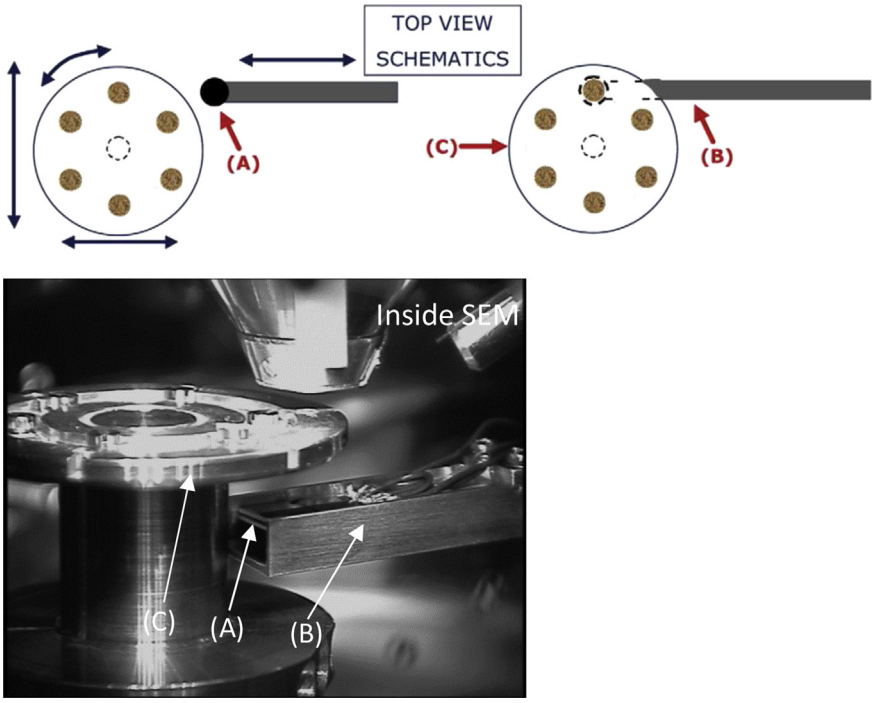

Fig. 1. Photo inside the SEM chamber corresponds to the schematics of the top view of parts (A), (B) and (C), represent for STEM detector, detector extension arm and carousel holder; The 6-specimen carousel is aligned with the electron column; the STEM detector is controlled with the detector arm to back and forth, and the adjustment of X, Y and Z directions; the imagining is ready after the working distance is set for both carousel holder and STEM detector.

joystick is released and controlled to change the position of the grid holder. STEM-in-SEM evaluations were conducted at an operating acceleration voltage of 30 kV in order to improve the electron penetration and the brightness of the source with an optimized working distance of 4 mm.

99.9% pure aluminium foils, of dimensions of 4.0 × 2.0 cm, were electropolished at 20 V for 3 min in a 4 to 1 by vol. mixture of ethanol/perchloric acid at a temperature of 278 K. After electropolishing, the specimens were rinsed in ethanol and deionized water, and dried in a cool air stream. DC magnetron sputtering was carried out on electropolished aluminium substrates using an Oxford Applied Research system, with a 99.6% titanium target of 50 mm diameter. The system was first evacuated to a vacuum condition of 1×10^{-7} Pa, with subsequent deposition from the titanium source at 300 mA in a 99.99% argon atmosphere at 0.5 Pa for 60 min, and a sputter-deposited titanium layer of ~120 nm thickness was obtained. The finished specimens were masked with lacquer 45 to leave an exposed region of dimensions of 1.0 × 1.0 cm for the subsequent anodizing treatment. Individual specimens were anodized at 50 V in 1 M phosphoric acid for 900 s with continuous stirring at ambient temperature. A sheet of pure aluminium, of size 8 × 10 cm, was used as the cathode. The current density − time response was recorded electronically, employing a Labview data acquisition system (National Instruments). After anodizing, the specimen was rinsed with deionized water and dried in a cool air stream. In order to generate thin transparent specimens, a nominally 15 nm thickness of the specimen was prepared using a Leica EM UC7 instrument of ultramicrotomy at a cutting speed of 0.15 mm s^{-1}. The section slices were floated on water behind the diamond knife, and collected on standard TEM mesh copper grids.

Fig. 2 compares images of the ultramicrotomed sections in the SE mode and STEM mode at a very low magnification. The difference in contrast between these selected two modes is evident. It is known that the SE mode detection is operated by secondary electrons emitted by atoms which are excited by the electron beam [11]. Then, by scanning the specimen and detecting the secondary electrons, an image displaying the topography of the surface is

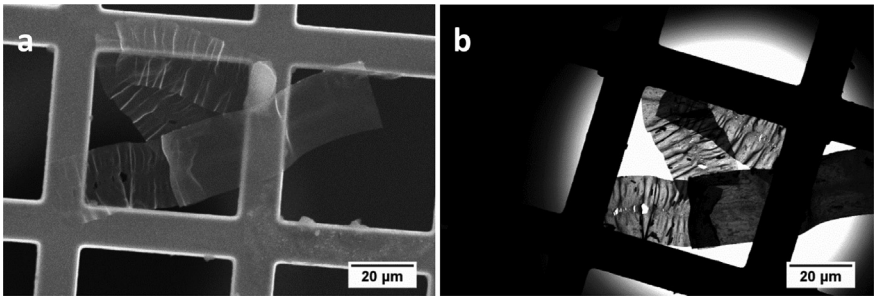

Fig. 2. Scanning electron micrographs in SE mode (a) and STEM mode (b) at very low magnification located at the ultramicrotomed sections on a copper supported grid. SE mode was used to identify the location of the titanium sections on the grid.