Armenian Journal of Physics, vol. 1, 2008, pp. 183-187 COLOR IRIDIZATION AND BACKSCATTERING ELECTRON IMAGING IN THE STUDY OF METAL ALLOY MICROSTRUCTURES

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1. Introduction

We have studied microstructure of clean or anodically oxidized Ti surfaces after special chemical, electrochemical and physical treatment by quantitative metallography [1]. The motivation behind this study originates from the wide use of TiO₂ as a photocatalyst and catalytic support. TiO₂ is used as a heterogeneous catalyst, and in solar cells, gas sensors, pigments, and various other items and devices [1]. The oxidized thin films are forming during chemical and electrochemical treatment which characterized by defined density, thickness and color iridization (interference color). Dielectric thickness and grains dimensions can be determined depending on path-lenghts difference [3]. Research laboratories typically and physical use backscattered (BS) electron imaging of as-polished surfaces [4], while industrial laboratories favor optical images of etched surfaces [5], primarily due to time and cost considerations. It can be challenging to try to compare the results from the two techniques. Hence, the question arises as to whether the two measurement techniques yield statistically equivalent results. It is well-known that some etchants preferentially attack grain and inter-phase boundaries and others preferentially coat or tink various phases [6]. In addition, etchants may affect one phase in a two-phase microstructure; for example, the α phase of α - β titanium is preferentially attached by special reagent.

A quantitative analysis of the primary - α volume fraction in the same region of several samples of commercially pure titanium and BT-1-0 was performed with both optical and SEM approaches in order to determine if there is a systematic difference between the two measurement techniques.

The assessment of imaging technique is critical to ensure proper measurement of microstructural features. BS electron imaging of polished BT-1-0 samples and optical imaging of the same samples appropriately etched with special reagent (distilled water, nitric acid, and hydrofluoric acid) showed equivalent measurements. BS shows the challenge of shading primary

both light and dark depending on crystal orientation as well as phase edge blurring as a function of voltage. Optical imaging of etched samples will show similar challenges.

2. Materials and methods

A major issue with measurement of percent primary α in $\alpha - \beta$ titanium alloys is the area of sample that must be measured to determine the correct average value. Assessed the affect of magnification and quantity of images on measured volume fraction of primary α phase. It was determined that while BS electron imaging is often conducted at relatively high magnifications, it is more appropriate to image $\alpha - \beta$ titanium alloys at ~200× and perform measurements on a minimum of three adjacent locations to determine an accurate primary α volume fraction. Slight variations in primary α can be seen in $\alpha - \beta$ titanium alloys due to segregation.

Three samples of $\alpha - \beta$ forged BT-1-0 were prepared using standard metallographic techniques: with final polish to yield an as-polished surface suitable for SEM. Fiducially marks comprising microhardness indents were placed on each specimen to locate specific regions of interest. BS images were then taken from the interesting regions using a Tesla BS 300. Following SEM imaging, each sample was lightly etched three times (for 5s, 10s and 15s) to successively deeper depths using special reagent, and optical images were taken using MIM-8 microscope in the same regions as the SEM BS electron photomicrographs. The volume fraction of primary α in each set of backscatter and optical images was measured. The results from the two imaging techniques were then compared.

For the optical images the contrast and darkness of micro structural features changed substantially as the material was etched for increasing periods of time. As expected, the etchant attacked the phase boundaries first, revealing the general microstructure. Once all the boundaries were revealed, the etchant attacked regions within the boundaries resulting in artefacts that did not correspond to microstructural features per se and hence may have skewed quantitative metallographic measurements. For this reason, there was an optimum time that the material should be exposed to the etchant, but this time was dependent on the microstructural features and properties of each specific sample, making it difficult to know the etching time a priori. Thus, the measured volume fraction of a given micro structural feature in an optical image for an $\alpha - \beta$ titanium alloy varied depending on the etching time. Typically, the volume fraction of primary α was underestimated for short etching times because all of the boundaries were not revealed and primary α particles were mistaken for difficult-to-resolve, fine transformed β phase. In particular, 16% primary α was measured for the first succession of light etching and optical

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microscopy. Following two cycles of light etching and optical microscopy, all grain boundaries were revealed, and a clear measurement of percent primary α could be measured. With the appropriate etching time, the measured percent of primary α in an optical image, specifically ~ 25% primary α , was indeed the percent of primary α on the etched surface. For long etching times, the volume fraction was overestimated because etching artefacts unrelated to microstructure appeared as primary α globules, thus increasing the apparent volume fraction of primary α . Specifically, 25% primary α was measured after three cycles of etching and optical microscopy.

It is expected that any further etching will increase the ambiguity in micro structural features in this particular region. Additionally, the percent of primary α increased with increasing exposure time. As the exposure time increases, the rate of growth decreases. This decline in rate of percent α growth can be explained by the kinetics of the etchant with the metal. The surface will only appear burnt after long etching times, as the etchant begins to attack the α phase rather than the grain boundaries. These observations agree with measurements for each etching time. BS electron images are considered to measure the area fraction exactly, as the penetration depth is typically of the order of nanometers and the particle sizes of the order of micrometers. However, due to the finite penetration depth of the electron beam, BS electron measurements of the volume fraction of primary α were affected by the voltage of the beam.

When imaging was done with a high voltage of 15 kV, a blurring affect accrued at the edges of particles due to averaging over the penetration depth, loading to an overestimation of the area fraction of primary α . This error is small and accounts for less than 1% error of the final measurement. In particular, if the sectioned surface of spherical α particle lies above its diametric plane, the area of the sectioned surface will be less than the area just below the surface when using low-to-moderate voltage. On the other hand, when the sectioned surface of a spherical particle was below the diametric plane, the sectioned area on the surface was greater than the sub-surface and no blurring occurred. Overall, the area fraction of primary α was slightly overestimated under BS electron techniques when a high voltage was used.

In particular, 25% primary α was measured for the as-polished and BS electron-imaged case. By reducing the voltage to 10 kV, the penetration depth was reduced and the tendency for overestimating the volume fraction was reduced. By comparing the measured percent of primary α for the optical micrographs of three etching conditions and the BS electron micrograph of the as-polished condition, the affect of etching-reagent exposure time on quantitative metallographic measurements could be assessed, and the most appropriately etched micrograph could then be compared to the BS electron micrograph of the same location on the sample. The measured

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percent of primary α was essentially equivalent for the appropriately etched micrograph and the BS electron micrograph. This comparison validated that an appropriately etched optical micrograph yields equivalent quantitative results as an as-polished BS electron micrograph.

3. Conclusions

We have determined that optical microscopy of a properly etched surface yields a statistically equivalent quantitative measurement of primary α volume fraction compared with measurements on as-polished surfaces using backscattered electron imaging in scanning electron microscope. However, care must be taken with optical techniques because the etchant can attack different regions of the surface at different rates. Therefore, a quantitative measurement performed optically is valid if the region is a representative region of the entire specimen and does not contain any suspect etching artefacts. Additionally, it is critical to understand the appropriate procedure for volume fraction measurement. These findings show that the two different techniques to collect a micrograph yield equivalent results, not that a single micrograph is sufficient to measure the volume fraction of a sample. Thus, an appropriate number of representative micrographs are still necessary to yield statistically relevant measurements. Formed thin film removed from left part of titanium surface.



Fig.1. Optical micrograph of electrochemical etched surface of a $\alpha - \beta$ titanium alloy.

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