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Investigation of the Effect of Over-Etching during Color Etching

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Abstract

During color etching, the examined grain structure undergoes a continuous, cyclic color change. This phenomenon is accompanied by a continuous loss of light intensity reflected from the surface. If the etching process is not stopped in time, the surface will be over etched. As a result, the separability of the individual grains will be greatly damaged, which can lead to a significant loss of information. It was investigated how to determine the moment of over-etching for each grain. During the in-situ observation of the etching, the time at which a particle can be considered over etched was determined by measuring the luminance normalized to the initial state.

Keywords: *color etching, metallography, Beraha I, microscopy, luminance, intensity, in-situ, steel.*

1. Introduction

Etching is a widely applied method for visualization of the microstructure of materials [1, 2]. since right after polishing, different phases and tissue elements cannot be separated. To make these species visible, different chemical and color etchants are needed [3, 4].

According to their mode of action, they can supply information for optical microscopic investigations in several ways. In most cases, the reactivity of the etchant is phase-sensitive, i.e., they can produce a chemical reaction only with certain phases [5]. With the help of this, the ratio of different phases present in the sample can be determined (**Figure 1**).

Within a given phase, the etchant can react with grains and grain boundaries with different velocities. Due to the disorder of the atoms along the grain boundaries, etchants can produce a faster reaction than inside the grains, therefore the grain structure of the material becomes visible. Grains themselves will also be etched during the process, but the speed of the etching is lower [6, 7].

The effect of color etchants is based on this latter phenomenon, since grains having different crystallographic orientations will be etched with different velocities. During the etching process, a precipitation film is formed on their surfaces, which produces thickness-dependent interference with the incoming light. Therefore, the grains of a polycrystalline material will be etched to different colors during a given time [8, 9].

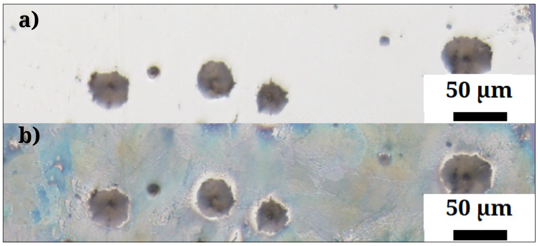

Figure 1. *Selective etching of spheroidal cast iron. Compared to the as-received state (a), Beraha I. etchant reacted only with the ferritic phase and not with the graphite (b).*

As the layer thickness increases, however, the rate of the color development decreases, until the surface will be over-etched. After this point the color change become almost negligible, and the grains can hardly be distinguished.

Since etching is an important part of metallic sample preparation, it is inevitable to adjust its parameters correctly if we want to obtain valuable information about the surface of the material. For this purpose, we performed in-situ observations during the etching process to determine the parameters of the overetching, and what are the connections between overetching and reflected light intensity.

2. Experimental

2.1. Materials and sample preparation

DC01 ferritic steel was investigated. The chemical composition of it was determined by a PMI-Master Sort type optical emission spectrometer. The results are shown in **Table 1**.

Cross section of the sample was then ground and polished. To minimize surface oxidation, etching was performed right after polishing **[10]**.

For etching the ferritic phase of DC01 steel, Beraha I etchant was used, which is a mixture of 3 g $K_2S_2O_5$, 10 g $Na_2S_2O_3$, and 100 ml distilled water **[11]**.

2.2. Microfluidic cell

For recording the color etching process, a closed channel system was created where the controlled laminar flow of the etchant can be ensured. The structure of the cell is shown in **Figure 2.a.** The cell itself was made of poly-dimethyl-siloxane (PDMS), to which a glass sheet was chemically bonded **[12]**. The channel system formed by these two parts is closed by the specimen itself, thus putting the cell below the objective lens of a microscope it becomes possible to follow the complete monitoring of the etching process (**Figure 2.b**).

Microscopic images were taken by an Olympus BX51 optical microscope. Dosing of the etchant during the process was performed by a syringe pump. The flow speed was set to 300 μl/min. Experiments were carried out in an air-conditioned laboratory, where the temperature was 21 °C.

3. Results and discussion

3.1. Color etching

To ensure the reach of the overetched state of the sample, the total etching time was set to 9 minutes. Starting from the arrival of the etchant into the cell, screen savings were made every 5th second from the video recorded during etching. Since the layer formation is relatively slow, this sampling frequency was enough to record the necessary characteristics. The etching process is shown in **Figure 3.**

Table 1. *Chemical composition of DC01 ferritic steel in weight%*

Fe	C	Mn	Cr	Mo
98.9	0.092	0.616	0.081	0.013
Ni	**Al**	**Co**	**Cu**	**Nb**
0.034	0.064	0.017	0.118	0.065

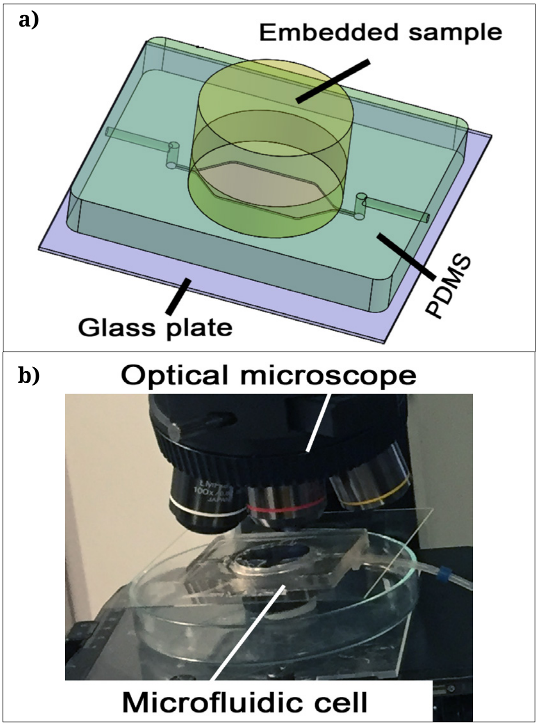

Figure 2. *Structure of the microfluidic cell (a) and the experimental assembly (b*

3.2. Determination of the moment of over-etching

25 grains were selected in the observed area, and the change of their colors was evaluated as the function of time (**Figure 4**).

The evaluation consisted of two parts. First, visual analysis was carried out on the selected grains to determine the exact time of their over-etching. A grain was determined to be over-etched if no color change could be visually detected after 5, 10 or 15 seconds of etching. In the time interval of the experiment (540 sec) most of the selected grains were over-etched (exceptions were Nr. 3 and Nr. 5). Durations that were necessary for over-etching are shown in **Table 2.**

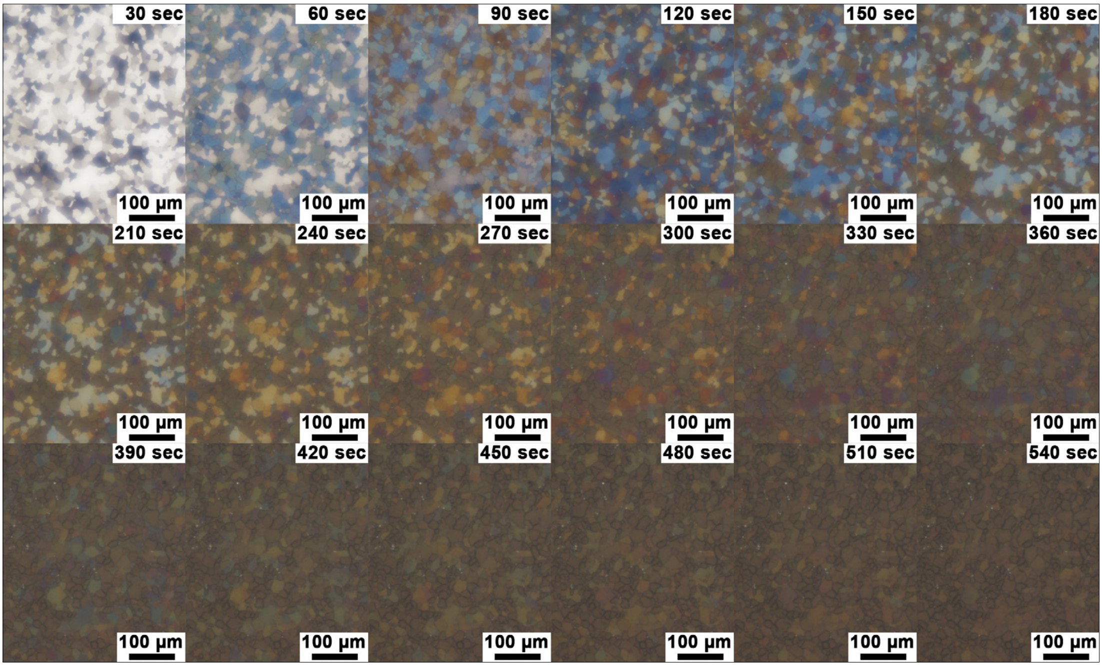

Figure 3. *Color etching of DC01 ferritic steel with Beraha I. etchant. Images were taken in every 30th seconds.*

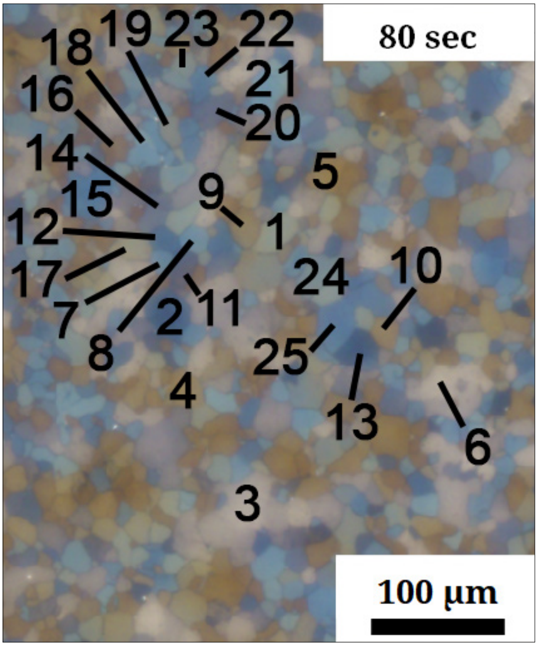

Figure 4. *The selected 25 grains of the examination.*

3.3. Intensity curves

In the second part of investigation, the RGB values of the individual grains were calculated by averaging the colors of the pixels within the grains [9]. Color intensity and luminescence are strongly affected by several factors, thus it was necessary to normalize the light intensities (having different wavelengths) to the initial state. The intensity values of the normalized intensity curves always started from 1 and fell into the range of [0,1].

RGB components (with different wavelengths) of different grains show a cosine-like monotonically decreasing amplitude. This phenomenon is illustrated for grain Nr. 1 in **Figure 5.**

In 2019, Bonyár divided the etching process into 3 parts, which can be observed in **Figure 5.** too [9]. The first is the oxide limited zone, the second is the steady state etching zone and the third is the diffusion limited zone. In the second one, which generally starts approx. from the first local minima, the etching speed of the grain becomes constant, thus the same time expires between the consecutive local minima and maxima of the normalized intensity curves. Before this one can observe the oxide limited part, where the initial oxide layer is being removed from the surface of the specimen. The oxide layer hinders the reaction between the etchant and the etched material, therefore reaching the first maxima requires more time.

Later during the etching process, the reaction speed will decrease again due to the increase of

Table 2. *The necessary time to reach the first minima and the over-etched state for the individual grains using visual observation, and the normalized luminance at these moments.*

#	Time (s)	Norm. lum. at first minima	Time (s)	Norm. lum. at over-etching
1	45	0.257	250	0.088
2	70	0.072	345	0.052
3	120	0,107	Out of range	
4	35	0.289	195	0.122
5	35	0.236	200	0.101
6	130	0.000	Out of range	
7	65	0.294	345	0.070
8	55	0.269	310	0.076
9	35	0.176	200	0.115
10	40	0.320	200	0.101
11	85	0.114	480	0.023
12	65	0.143	350	0.059
13	70	0.055	385	0.047
14	95	0.213	465	0.030
15	70	0.231	385	0.038
16	35	0.33	205	0.134
17	45	0.375	215	0.131
18	55	0.286	320	0.061
19	45	0.232	220	0.113
20	90	0.157	460	0.023
21	55	0.334	315	0.048
22	65	0.257	380	0.040
23	45	0.235	250	0.096
24	45	0.085	270	0.079
25	65	0.230	370	0.060

the layer thickness. The formed layer, similarly to the oxide layer, also hinders direct contact between the etchant and the surface, thus the etchant must diffuse through the layer to react with the surface. As the layer thickness increases, the intensity of the reflected light also decreases, and the intensity differences between the individual grains slowly disappear. From that moment on, the sample is overetched.

In order to understand the process and obtain a more detailed picture, the onset of overetching must be determined using the measured intensity functions. To achieve this, the light intensity components must be investigated simultaneously. According to Eq. 1, a normalized brightness (luminance) was calculated from the individual RGB-components (**Table 2**).

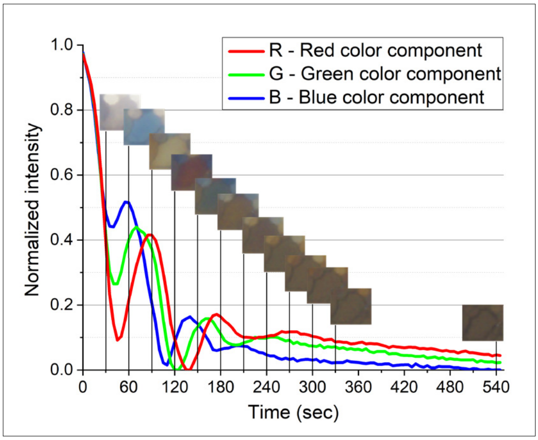

Figure 5. *Normalized color intensity of red (R), green (G) and blue (B) light reflected from grain Nr. 1 as a function of time.*

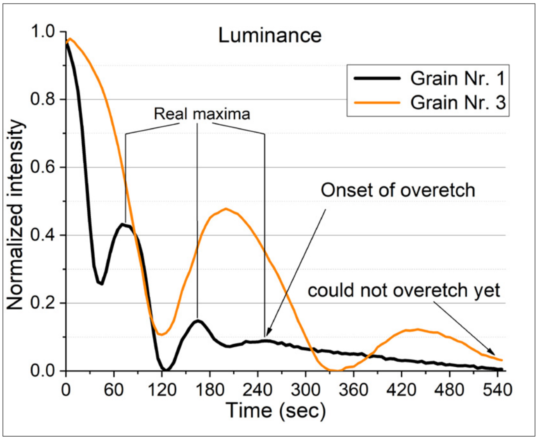

Figure 6. *Luminance curves of grains Nr. 1 and Nr. 3 as a function of time.*

$$L = 0{,}299 \cdot R + 0{,}587 \cdot G + 0{,}114 \cdot B \tag{1}$$

where L is the luminance, R,G and B are the intensity of the red, green, and blue light components [13]. Thus, light intensity curves for the investigated grains were determined (**Figure 6**). Initial maxima of the curves were neglected since the absolute maxima of the curves are irrelevant, only real (local) maxima were considered.

Luminance curves of the grains behave almost identically. Analyzing the curves of the chosen 25 points, they drop below 0.375 while reaching the first minima. This is followed by two and a half sine-like periods with decreasing amplitude. If the curve reaches the third real maxima, its slope becomes straight instead of cosine-like because the amplitude becomes too low.

3.4. Effect of over-etching

An interesting connection can be observed between the luminance curves and the onset of the over-etching: the later the over-etching happens, the smaller the light intensity that can be detected. The maximum value of luminance at the exact moment of over-etching for the examined grains was 0.134, but the average value of these was much smaller, only 0.075.

Besides this, in most cases (except grains Nr. 3 and Nr. 6, where the third maxima were not reached) the start of the overetching was detected right at the third real maxima. In other words, it started at the beginning of the previously introduced straight slope parts of the brightness curves.

The trends of normalized intensity curves of the same wavelength (i.e. red, green or blue) for different grains were similar, but the time necessary for reaching the local maxima was different according to the crystal orientation of the grains. This difference will result the separability of the grains. If we etch them for a certain amount of time, the layer thickness formed on the surfaces of the grains will be different, thus there will be different interference, i.e. different color on them. If, however, the specimen is being over-etched, the layer thickness will be uniform at the beginning of the over-etching, independently of the time needed for reaching the linear decreasing part of the intensity curve.

4. Conclusions

AIn the last period of color etching, the detectable light intensity decreases continuously due to over-etching, and thus the separability of the grains deteriorates. It was shown that over-etching starts at the third real maximum of the time-dependent normalized luminance curves. From this point, the slope of the curves lost its cosine characteristics and became linear. In the case of in-situ etching tests, this point should be avoided by stopping the process before reaching this.

Additionally, the more time needed to reach the onset of over-etching, the smaller will be the measured normalized luminance over the individual grains. Taking advantage of this effect, it could be possible to estimate the crystallographic orientation of these grains.

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