

# **Understanding the mechanism of Beraha-I type color etching: determination of the orientation dependent etch rate, layer refractive index and a method for quantifying grain orientation**

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## **Abstract**

A grey cast iron specimen was investigated by Beraha-I type color etching for the purpose of developing a functional model for the etching kinetics and subsequently a method which would enable the determination of ferrite grain orientations solely based on optical microscopy. For this, the etching process was observed real-time in a microfluidic cell and a custom image processing software was developed to interpret the color information. Scanning electron microscopy with electron backscatter diffraction (SEM-EBSD) and atomic force microscopy (AFM) were used to determine the grain orientation and the relative thickness of the developed interference layer respectively, which were used for further calculations. It was proved, that a time independent cycle etch rate can be defined between the first interference minimum and maximum, which is also independent from preparation and experimental conditions, and which shows correlation with both the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  orientations. The exact value and orientation dependence of this cycle etch rate was experimentally determined along with the refractive index of the developed film. Our method was demonstrated to be applicable for the estimation of ferrite grain orientations with respect to the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions with an average absolute error of  $3^\circ$ , by using optical microscopy only. The method is implemented and was made available in the form of a Matlab program.

## **Keywords**

color etching, cast iron, ferrite, EBSD, AFM, grain orientation

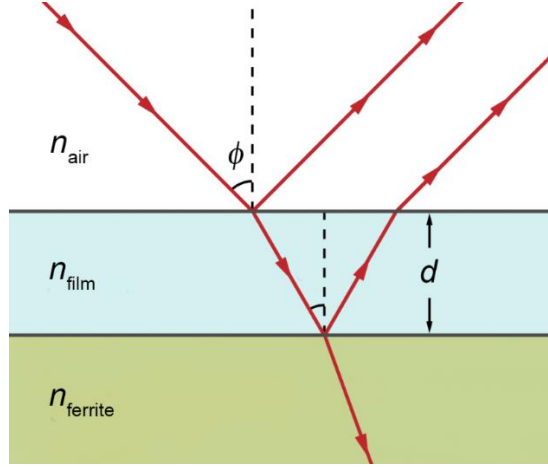
# 1. Introduction

Color etching is an increasingly popular type of metallographic sample preparation, where the fine microstructure of a metal can be made visible after polishing [1]. The generally phase and orientation specific coloring is much easier to be evaluated by optical microscopy and accompanying image processing, than by using expensive instrumentation, e.g. scanning electron microscopy (SEM) for the same purpose. Originally the method was used only to identify the different phases and tissue element in cast iron [2] and steel [3] to correlate and describe macroscopic mechanical properties, such as tensile strength vs. spheroidal graphite grain size, or tensile strength vs. amount of pearlite. More recently efforts were made to correlate the shade of the color of the developed layer above the ferrite grains with their crystallographic orientation. First Szabó and Kardos [4] showed in 2010 that the measured luminescence and RGB color intensities show a correlation with the angle between the specimen normal and the  $\langle 100 \rangle$  direction, for a sequential chemical etching with nital and Beraha-I type [5,6] color etching. This paper initiated a series of works aiming to describe the mechanism of Beraha-I type color etching, all in the hope of providing a method which would enable the estimation of ferrite grain orientation based on color etching and optical microscopy only, without using expensive and limitedly available methods based on electron scattering, such as electron backscatter diffraction (SEM-EBSD). Our group showed, that the sequential use of nital chemical etching and Beraha-I color etching is not beneficial, since the orientation dependence of the two etchings are plainly opposite, considering the  $\langle 100 \rangle$  direction [7, 8]. We also showed that the developed interference layer above the ferrite grains does not have an even surface, the layer thickness varies above the grains (therefore shows the different colors), which can be observed through the surface features [8].

A couple of years ago D. Britz et. al introduced a novel approach, to investigate the color etching real-time, by using a microfluidic cell. They successfully distinguished the sequential cycles (orders) or layer interference, and gave an estimation to assess the general orientation of the grains based on the resulting color of the layer after a specific amount of elapsed time [9,10]. Their method still has weaknesses which prevent the precise determination of grain orientation. As will be extensively demonstrated later, the etching/layer development speed is not constant in time and several material and experimental properties (e.g. sample preparation) influence both the initiation phase and the later, diffusion limited stage of the etching. These make the grain color vs. elapsed time relationship unreliable. Also, the observed color of the grain would depend on the illumination conditions and instrumentation, which renders the method hard to generalize and independently applicable by others with sufficient precision. Even more recently Reisinger et.al found similar correlation between the developed color and luminescence of the grain, after nital and Klemm etching, and the  $\langle 100 \rangle$  direction in granular bainitic steel [11], however, their proposed method suffers from the same above mentioned disadvantages.

To reach our common goal, and devise a method which would enable the determination of ferrite grain orientation based on only the color information with the desired precision (a couple of degrees) and independently from experimental and sample preparation conditions we need to understand the etching process in more detail.

Fig. 1 illustrates the principle of thin film interference, which occurs above the color etched ferrite grains. Since in this case  $n_{ferrite} > n_{film} > n_{air}$  (where  $n$  refers to the refractory index of the different materials) Equations (1) and (2) describe the conditions of destructive and constructive layer interference in the developed film, respectively.



**Fig. 1:** Illustration of thin film interference above the color etched ferrite grains.

$$2n_f(\lambda)d \cos(\phi) = \left(m - \frac{1}{2}\right) \lambda \quad (1)$$

$$2n_f(\lambda)d \cos(\phi) = m\lambda \quad (2)$$

The parameter  $m$  refers to the order of interference, and considering normal incidence  $\cos(\phi)$  reduces to 1. The refractive index of the developed film ( $n_f(\lambda)$ ) is expected to have a Cauchy-dispersion in function of the wavelength of illumination and since this film is composed of a variety of compounds, mostly sulfates with unknown composition, its exact value have not been determined or estimated before. The thickness of the developed layer ( $d$ ) is calculated as (3) for a given etching time ( $t_e$ ).

$$d = \int_0^{t_e} v(t, \theta, T, c) dt \quad (3)$$

The etching or layer development rate ( $v$ ) is depending on several factors. First of all, it is not expected to be constant during the whole duration of etching, thus time dependence ( $t$ ) is a factor to be considered. It was previously shown that the development of the film is depending on the crystallographic orientation of the ferrite grains ( $\theta$ ). The effect of temperature ( $T$ ) and material composition ( $c$ , e.g. alloying compounds in the iron or steel) also expected to have significant influence, but these two factors will not be investigated in the current work.

The aims of our work is to create a functional model of Beraha-I type color etching and determine – for the first time ever – the orientation dependent etch rate, and also the refractive index of the developed layer. For this a cast iron specimen and extensive instrumentation (optical microscopy, SEM-EBSD and AFM) will be used. Our ultimate goal, to develop a method for the estimation of

ferrite grain orientation by only the color information in a reliable and precise way will also be successfully demonstrated.

## 2. Experimental

### 2.1. Materials and sample preparation

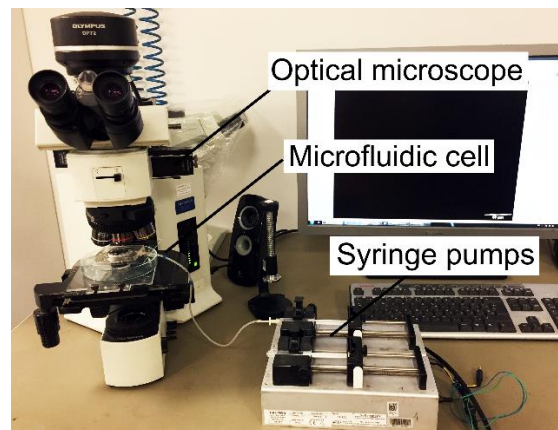
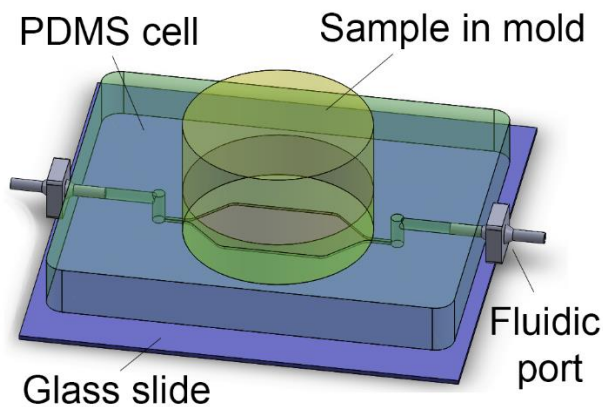
A spheroidal cast iron specimen was used for the experiments. Its chemical composition and mechanical properties are collected in Table 1. Before the experiments a traditional metallographic sample preparation was done (grinding and polishing). For SEM-EBSD measurements, the final polishing step was performed with a 0.05  $\mu\text{m}$  colloid silica gel for 30 minutes, to produce a proper surface. Color etching was done with fresh Beraha-I type solution, prepared by dissolving 3 g  $\text{K}_2\text{S}_2\text{O}_5$  and 10 g  $\text{Na}_2\text{S}_2\text{O}_3$  in 100 mL distilled water. All experiments were performed in an air-conditioned laboratory at 22°C.

**Table 1.** Chemical composition and mechanical properties of the cast iron specimen.  $R_m$  corresponds to the ultimate tensile strength,  $A$  to the total elongation at failure, while HB is the Brinell hardness.

| Chemical composition [wt%] |      |      |       |       |       | Mechanical properties      |           |     |
|----------------------------|------|------|-------|-------|-------|----------------------------|-----------|-----|
| C                          | Si   | Mn   | Mg    | S     | P     | $R_m$ [N/mm <sup>2</sup> ] | $A_5$ [%] | HB  |
| 3.59                       | 2.43 | 0.36 | 0.063 | 0.012 | 0.046 | 580                        | 9.2       | 198 |

### 2.2. Microfluidic cell preparation

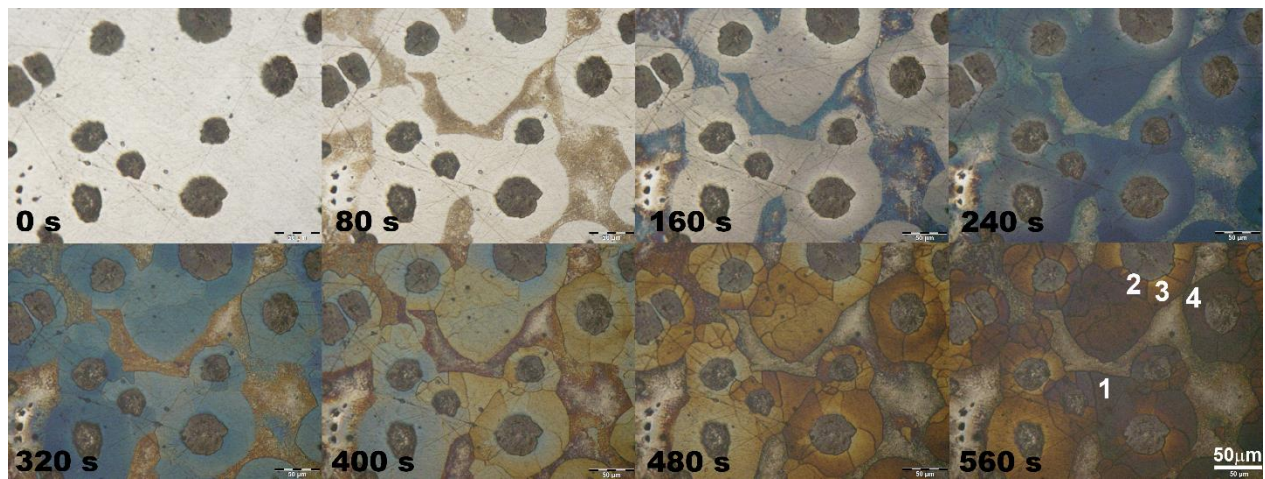
For the real-time observation of the color etching process we developed a microfluidic cell, as presented in Fig. 2 left. The cell is made of PDMS (poly-dimethyl-siloxane), a transparent, flexible and chemically inert material, frequently used in the field of microfluidics. The silicone pre-polymer and the curing agent of a Sylgard 184 elastomer kit from Dow Corning [12] were thoroughly mixed in the recommended ratio of 10:1. The molding form for the cell was fabricated by an Objet Eden 250 3D printer. Curing of the polymer was done in a pre-heated oven at 100 °C for 60 min. As a last step, the PDMS cell was bonded to a glass sheet (thickness 1 mm), by treating both the glass and the cell with corona discharge for 1 min. The technology of cell fabrication is described in more detail elsewhere [13].



**Fig. 2: Left:** 3D design of the PDMS based microfluidic cell with the introduced sample. **Right:** The measurement setup for the optical microscopy (note: the cell is upside-down).

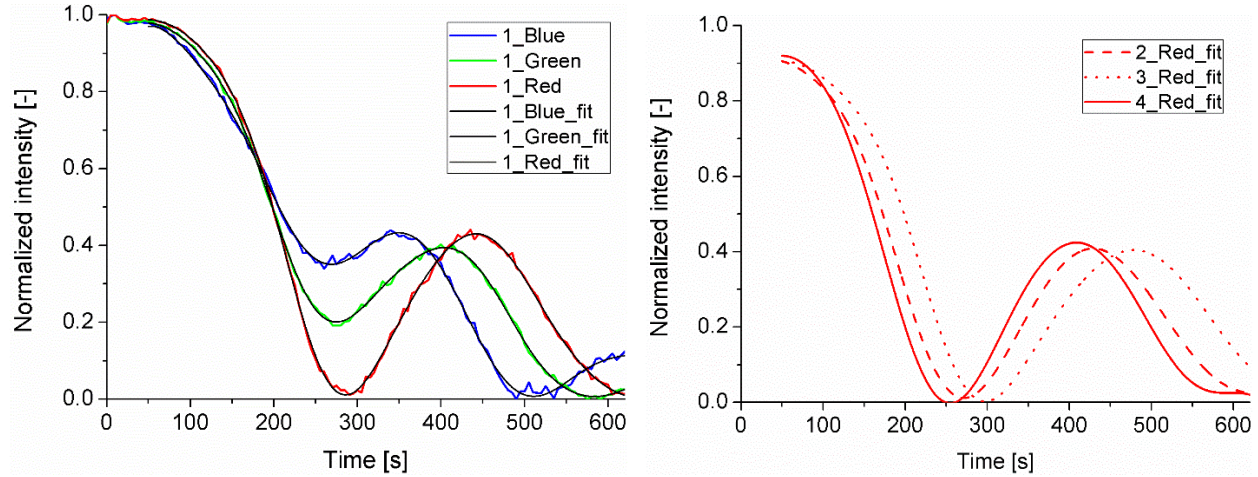
### 2.3. Optical microscopy and image processing

The experimental setup for the real-time monitoring of the color etching can be seen in Fig. 2/right. An Olympus BX51 optical microscope with DP72 digital camera and LMPlanFI 50x /0.50 long working distance lens were used. For the controlled introduction of the Beraha-I type etchant a syringe pump was used at a flow rate of 110  $\mu\text{l}/\text{min}$ . To stop the etching distilled water was introduced into the channel at a flow rate of 1100  $\mu\text{l}/\text{min}$  to quickly flush out the etchant. Both the starting time and the end time of the experiment is clearly visible in the recorded video, which can be seen in the supplementary materials section. Fig. 3 presents screenshot images from one of the experiments after every 80 s.



**Fig. 3:** Optical microscopy images from the investigated area of the specimen after 80 s periods, during color etching. Scalebar: 50  $\mu\text{m}$ . The whole video of the etching can be seen in the supplementary materials.

To evaluate the color change of the grains a custom MATLAB script was written. The whole script, which is able to assess the crystallographic orientation of the selected grains with respect to the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  orientations is also available in the supplementary materials, with extensive comments. The main steps of calculations are the following. The frames of the video is exported at a given time step (e.g. in every 5 s). The user first need to define an area (e.g. a  $10 \mu\text{m} \times 10 \mu\text{m}$  area in the center of a grain), by using cursors. The software then imports the pixels of the selected area from all of the images and calculates the average RGB (red, green blue color space) values for the pixels. The RGB intensities are normalized for the whole duration of the etching (considering  $t = 0 \text{ s}$  as reference), which results in the curves presented in Fig. 4/left. The last step is to fit a suitable function to make the determination of the local maxima and minima more convenient. For this purpose we used a 5-term sum of sine function, which gives a reasonably good fit, as can be seen in Fig. 4.



**Fig. 4: Left:** Normalized intensity of the RGB color components in function of time, evaluated for grain #1 in Fig. 3. **Right:** Normalized intensity in function of time for only the red component, evaluated for three random grains (#2, #3, #4) from Fig. 3.

It is very important to emphasize that our model, which will be introduced in Section 3, only uses the time values associated with the minima and maxima of the curves, which are corresponding to given layer thicknesses fulfilling the destructive and constructive interference conditions defined by Equations (1) and (2). The amount of RGB intensities or their variation are not used by our model. Thus the experimental conditions such as spectral composition of the illumination, CCD sensitivity or exposure time will not be affecting our results, the local minima and maxima of the normalized curves always characterize the time required for a given layer thicknesses to develop.

## 2.4. Other instrumentation

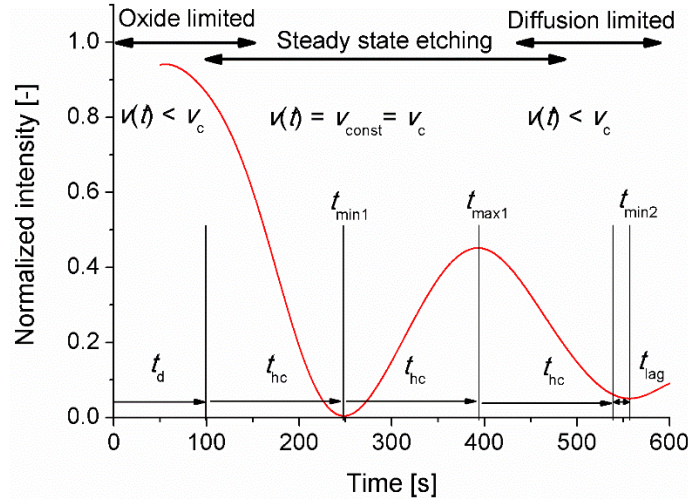
A FEI QUANTA 3D scanning electron microscope with a TSL OIM electron back scattering diffraction (EBSD) system was used for the determination of the individual grain orientations.

A Veeco (lately Bruker) diInnova atomic force microscope (AFM) was used with an ART D160 diamond probe (spring constant 5 N/m) in contact-mode to measure the height difference of the grains. The images were obtained in  $100\ \mu\text{m} \times 100\ \mu\text{m}$  scan size, with a sampling resolution of  $512 \times 512$  and 1 Hz scan rate. The obtained images were post-processed with the Gwyddion 2.36 software [14].

### 3. Results and Discussions

#### 3.1. Etching kinetics model

In order to reach our goal – to determine the speed of interference layer development, layer refractive index and to develop a method for grain orientation estimation based on only the color data – we first need to understand the mechanism and kinetics (time dependence) of color etching in more detail. In Fig. 4 we presented examples, which demonstrated how the RGB color components change during the development of the layer (Fig. 4/left) and for random grains with different orientation how the color vs. time curves vary (Fig. 4/right). In order to be able to characterize the process we need to set up a functional model of the etching process.



**Fig. 5:** The proposed functional kinetics model with different regions for etching, based on the normalized intensity curve (red component) measured on a ferrite grain of the cast iron specimen, presented in Fig. 3.

In Fig. 5 we can see, that three partially overlapping domains can be identified and separated in the kinetics of the etching. Thus, for our functional model, let us define an intermediate domain, where we will assume that the etching rate (layer buildup rate) is steady and can be characterized by the constant cycle etch rate ( $v_c$ ) and half-cycle time ( $t_{hc}$ ). The latter can be obtained by measuring the time difference between the first interference minimum and maximum, as in Eq. (4).

$$t_{hc} = t_{max1} - t_{min1} \quad (4)$$

It is clear that in the first phase of etching ( $0 < t < t_{min1}$ ) the etch rate is smaller, the process is delayed. It can also be seen, that the third half-cycle ( $t_{max1} < t < t_{min2}$ ) also takes a longer time to complete, here the etching also experiences a delay compared to the second half-cycle. Thus in our model let us define the time dependent etch rate as Eq. (5).

$$v(t) = \begin{cases} v_c * g(t), & 0 < t < t_{min1} \\ v_c, & t_{min1} \leq t \leq t_{max1} \\ v_c * w(t), & t_{max1} < t \end{cases} \quad (5)$$

Here  $g(t)$  and  $w(t)$  are weight functions (between 0 and 1) and characterize the change in the etch rate compared to the constant cycle velocity ( $v_c$ ). The physical meaning of these functions and the observed delays are the following. The reason for the delay observed in the third half-cycle ( $t_{max1} < t$ ) is that the kinetics of etching is limited by the diffusion through the developing film. This diffusion limited region is characterized by  $v_c * w(t)$  and a lagging time ( $t_{lag}$ ), defined as Eq. (6).

$$t_{lag} = t_{min2} - t_{max1} - t_{hc} \quad (6)$$

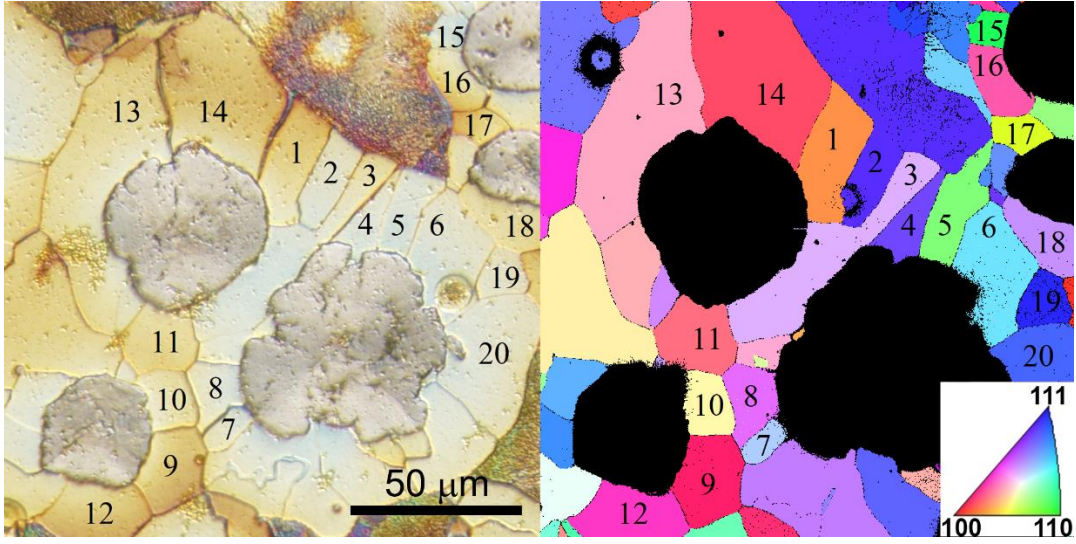
In our experiments this lag was around 0.1-0.2 ( $t_{lag}/t_{hc}$ ) in the third half-cycle. The amount of this delay is depending on the thickness of the developed layer, which in turn on the orientation dependent etch rate. For the same reason the green and red components are more sensitive for this delay than the blue component. This delay makes the evaluation of the resulting color, and its correlation with the orientation more complicated, thus it is not beneficial to prolong to etching into this region, it is better to stop the process around the first interference maximum ( $t_{max1}$ ), considering all grains.

The other delay observed at the start of the etching is both more significant and a bit harder to explain. This effect can be associated with breaking an oxide barrier above the ferrite grains at the start of the etching. This statement will be proved later. Here  $v_c * g(t)$  from Eq. (5) characterize the oxide limited kinetics. We can also introduce a delay time ( $t_d$ ), defined in Eq. (7) for this region.

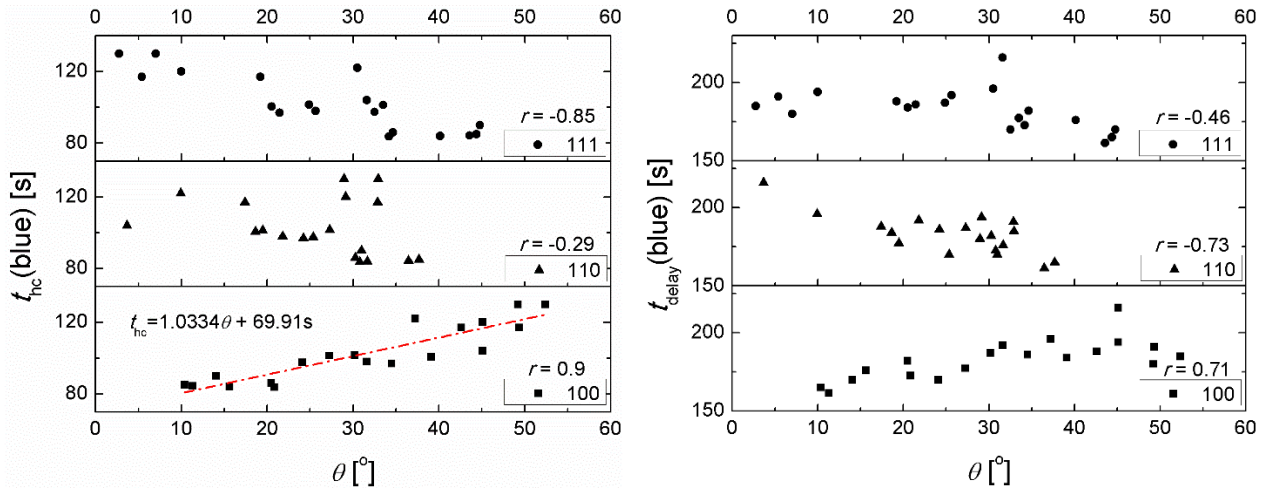
$$t_d = t_{min1} - t_{hc} \quad (7)$$

To investigate the correlation between these two introduced characteristic time intervals ( $t_{hc}$ ,  $t_d$ ) and the crystallographic orientation of the grains, we performed an experiment with the cast iron specimen. As can be seen in Fig. 6, an EBSD inverse pole figure map was obtained from an area, which same area was later color etched, and the defined parameters describing the etching kinetics were evaluated based on the RGB data. The total etching time ( $t_e$ ) was selected to be 445 s, since based on the previous experiments (see Figs 4 and 5) it stops the etching before the diffusion limited region for the blue component, even for the faster grains. Thus we can neglect the effect of the diffusion limited region for the further calculations for the blue component.

Fig. 7 presents the correlation maps for the 20 grains numbered in Fig. 6. The correlations of  $t_{hc}$  and  $t_d$  with the three main crystallographic orientations ( $\langle 100 \rangle$ ,  $\langle 110 \rangle$ ,  $\langle 111 \rangle$ ) are presented, where  $\theta$  refers to the angle between the surface normal and the given direction. It can be seen, that  $t_{hc}$  correlates best with  $\langle 100 \rangle$  ( $r = 0.9$ ), which is in good accordance with the correlation data found in previous studies [8, 10, 11]. It also negatively correlates – a slightly worse ( $r = -0.85$ ), – with  $\langle 111 \rangle$ . However, it is interesting to see, that  $t_d$  shows a not too strong, but definite negative correlation with  $\langle 110 \rangle$ , which was not a dominant orientation for  $t_{hc}$ . As it was shown by Chen et. al, in BCC ferrite, the oxidation processes are faster for grains close to the  $\langle 110 \rangle$  direction [15]. The observation that these grains have the highest delay times can prove our previous proposition that the delay times in the first phase of the etching can be connected to surface oxidation.



**Fig. 6: Left:** Optical microscopy image of the investigated area after  $t_e = 445$  s color etching. **Right:** EBSD image of the same area.



**Fig. 7: Left:** Correlation between the half-cycle time ( $t_{hc}$ ) and the tree main crystallographic orientations. **Right:** Correlation between the delay time ( $t_d$ ) and the same main orientations.  $\theta$  refers to the angle between the surface normal and the given direction

This statement can also be indirectly proved in the following way. It was observed, that by waiting for a longer time after sample preparation (polishing) and before initiating the color etching, the average delay times will increase. It will be shown and proven in Section 3.3 that only the delay times are modulated by these idle periods in sample preparation, the half cycle times are not affected. The average of delay times (blue component) for the 20 grains measured in the experiment presented in this chapter was 183 s (see Fig. 7, right). In the experiment presented in Section 3.3 the average of delay times was 101 s, for 10 grains. The difference was caused by a much faster sample preparation in the latter experiment. Considering all of our experience with the cast iron specimen, it was not possible to reduce the average delay time below 80 sec, even with the fastest possible sample preparation, which means only around 2 min idle time between the polishing and the start of experiment, which is needed for the setup of the cell.

Conclusively it can be seen, that surface oxidation and thus sample preparation are critical factors, which should be considered when trying to interpret the kinetics of color etching. If one only wants to relate the developed color with the total elapsed time – as previous studies did – the effect of sample preparation will always influence the results and prevent us from the reliable quantification of grain orientation.

In the other hand, if the half-cycle time does not depend on the sample preparation or oxidation we can use its strong correlation with the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions to quantify grain orientation. To do this, we have to determine the constant cycle etch rate, and layer refractive index experimentally.

### 3.2. Determination of the constant cycle etch rate and layer refractive index

To determine the constant cycle etch rate ( $v_c$ ) based on the data gained from optical microscopy and EBSD (Fig. 6) first we need to simplify our model and Eq. (5).

Based on Equations (1) and (2) we can state that for a fixed wavelength the developed film thickness, or precisely,  $n_f(\lambda)d$  is the same between  $0 < t < t_{min1}$  and  $t_{min1} \leq t \leq t_{max1}$ . In other words Eq. (8) must be true based on the interference model.

$$\int_0^{t_{min1}} v(t)dt = \int_{t_{min1}}^{t_{max1}} v(t)dt \quad (8)$$

By using Eq. (5) this leads to Eq. (9).

$$v_c \int_0^{t_{min1}} g(t)dt = v_c t_{hc} \quad (9)$$

This means that for the determination of  $v_c$  we can approximate  $g(t)$  with any weight function as long as we fulfill Eq. (9). For the sake of simplicity, let us use a simple step function, defined by Eq. (10).

$$g(t) = \begin{cases} 0, & t < t_d \\ 1, & t \geq t_d \end{cases} \quad (10)$$

By using this simplification we can modify Eq. (5) to Eq. (11) as long as we stop the etching before the diffusion limited region, which is true for the blue component of our previous experiment ( $t_e = 445$  s).

$$v(t) = \begin{cases} 0, & t < t_d \\ v_c, & t \geq t_d \end{cases} \quad (11)$$

With this simplified model it is finally possible to estimate the constant cycle etch rate. For this we would still need the metric layer thickness ( $d$ ) which was developed during the total time of etching, which (based on Eq. (11)) is the time of experiment minus the delay time ( $t_e - t_d$ ). To incorporate the dependency on the crystallographic orientation we introduce the  $S(\theta)$  parameter, which is defined as the ratio between the cycle etch rates (or half-cycle times), defined in Eq. (12), considering the  $\langle 100 \rangle$  orientation as a reference.

$$S(\theta) = \frac{t_{hc|\theta}}{t_{hc|\langle 100 \rangle}} = \frac{v_c|\langle 100 \rangle}{v_c|\theta} \quad (12)$$

The correlation diagram of Fig. 6/left can be used to obtain  $t_{hc}|_{\langle 100 \rangle}$  by fitting a linear regression on the dataset. From this  $t_{hc}|_{\langle 100 \rangle} = 69.91$  s, and the  $S(\theta)$  values for every grain orientation can also be calculated. Unfortunately measuring the thickness of the developed layer individually for every grain is not directly possible. This would require the removal of only a small part of the layer, to measure the thickness of the intact part with atomic force microscopy (AFM).

However, a method was developed to circumvent this problem, and calculate the cycle etch rate ( $v_c$ ) based on the differences in the layer thicknesses above the individual grains with AFM. Let us consider two grains, A and B with different crystallographic orientation and thus cycle etch rates ( $v_{cA}, v_{cB}$ ), and delay times ( $t_{dA}, t_{dB}$ ). Let us also fix that the etching is faster for grain A (depending on the  $\langle 100 \rangle$  direction), thus  $v_{cA} > v_{cB}$  and at the end of the etching  $d_A > d_B$ . The relationship between  $t_{dA}$  and  $t_{dB}$  is not important at this point, since the layer development time is calculated as  $t_e - t_d$  separately for each grain. Thus, by using Eq. (11) the difference of the layer thicknesses ( $\Delta d$ ) at the end of the experiment can be written as (13).

$$\Delta d = d_A - d_B = v_{cA}(t_e - t_{dA}) - v_{cB}(t_e - t_{dB}) \quad (13)$$

By using the  $S(\theta)$  parameters from Eq. (12) we can write Eq. (14) for the two grains.

$$v_{cA} = \frac{S_B}{S_A} v_{cB} \quad (14)$$

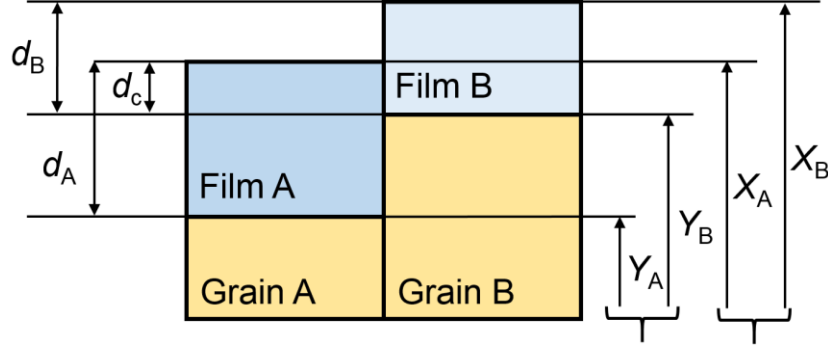
Placing Eq. (14) into Eq. (13) and rearranging, we can finally have the constant etch rate for grain B as Eq. (15).

$$v_{cB} = \frac{\Delta d}{\frac{S_B}{S_A}(t_e - t_{dA}) - (t_e - t_{dB})} \quad (15)$$

To determine  $\Delta d$  with AFM we will use a method we reported in our previous work [8]. It is possible to remove the developed interference layer without damaging the underlying ferrite grains, by immersing the sample into a mild, 0.5 %  $H_2SO_4$  aqueous solution for only 1-2 s. Fig. 8 illustrate the layer structure before and after the removal of the interference layer for the two grains. AFM can be used to determine the heights, but it is important to note, that the pairs ( $X_A, X_B$  after color etching, and  $Y_A, Y_B$  after layer removal) are measured on separate AFM images, with no common reference point, thus the layer thicknesses cannot be directly determined as  $X_A - Y_A$  or  $X_B - Y_B$ . Instead let us use the approach given in Eq. (16) where  $d_c$  marks the eliminated common part of the thickness, as illustrated in Fig. 8, and the height pairs in the brackets are measured on the same AFM images.

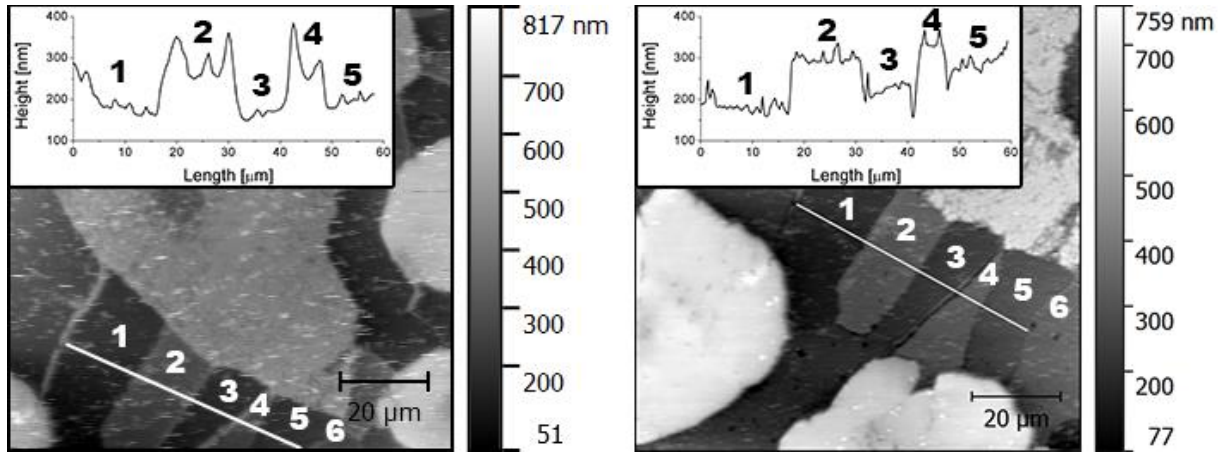
$$\Delta d = d_A - d_B = (Y_B - Y_A) + d_c - (X_B - X_A) - d_c \quad (16)$$

Fig. 9 shows two AFM images from the same area which was presented in Fig. 6. Fig. 9 left was measured after 445 s color etching, Fig. 9 right was after interference layer removal with mild sulfuric acid. This area was selected for the AFM measurements because small grains were needed close to each other with diverse orientations (see Fig. 6). At larger scan sizes the AFM image is sensitive to artifacts which would make the precise determination of the relative heights harder.



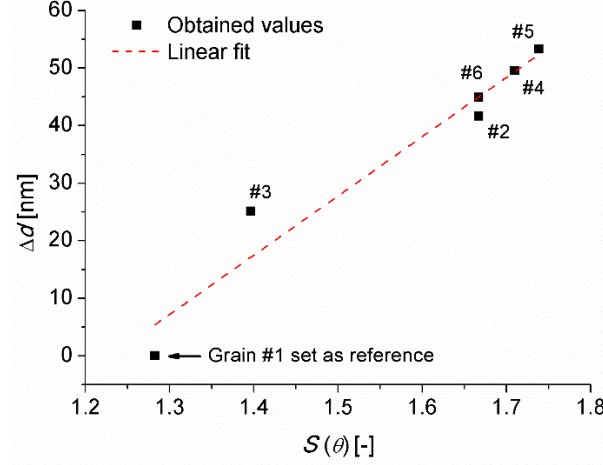
**Fig. 8:** Illustration of the interference layer structure for two grains. The relative heights can be measured after color etching ( $X_A$ ,  $X_B$ ), and after layer removal with mild sulfuric acid ( $Y_A$ ,  $Y_B$ ).

Grain #1 was selected as a reference, since it was the closest to the  $\langle 100 \rangle$  orientation based on the EBSD data. The quantitative results are presented in the supplementary materials (Table 2). As can be seen in the cross-sectional profiles, the surface of the grains are not even. This observable tilt of the grains after etching was investigated in previous works [7, 8]. To compensate this effect, the grain height was determined at the geometrical center of each grain and averaged for an area of approx.  $10 \mu\text{m} \times 10 \mu\text{m}$ .



**Fig. 9: Left:**  $100 \mu\text{m} \times 100 \mu\text{m}$  contact-mode AFM image after  $t_e = 445 \text{ s}$  color etching the same area which was presented in Fig. 3. **Right:** AFM image after removing the interference layer with 0.5% sulfuric acid.

In Fig. 10 left we plotted the resulting  $\Delta d$  values in function of the  $S(\theta)$  parameters for these six grains, considering grain #1 as the reference. It can be seen that  $\Delta d$  correlates with  $S(\theta)$ , which support the previous observations regarding the dominance of the  $\langle 100 \rangle$  orientation. However, this correlation is not perfect, since the total etching/layer development time is modulated by the different  $t_d$  values (Eq. 11).



**Fig. 10:** Relative layer thickness ( $\Delta d$ ) of the six grains in Fig. 9, measured with AFM, in function of their  $S(\theta)$  values determined based on the image processing and EBSD results (Eq. (12)). Grain #1 is considered as a reference.

Now that we have all parameters, by using Eq. (15) the calculation of the constant cycle etch rates for these five grains is possible (except for the reference). With this we can also estimate the refractive index of the interference film for the grains. By using Eq. (2) – Eq. (1) we can write the refractive index at a given wavelength as Eq. (17).

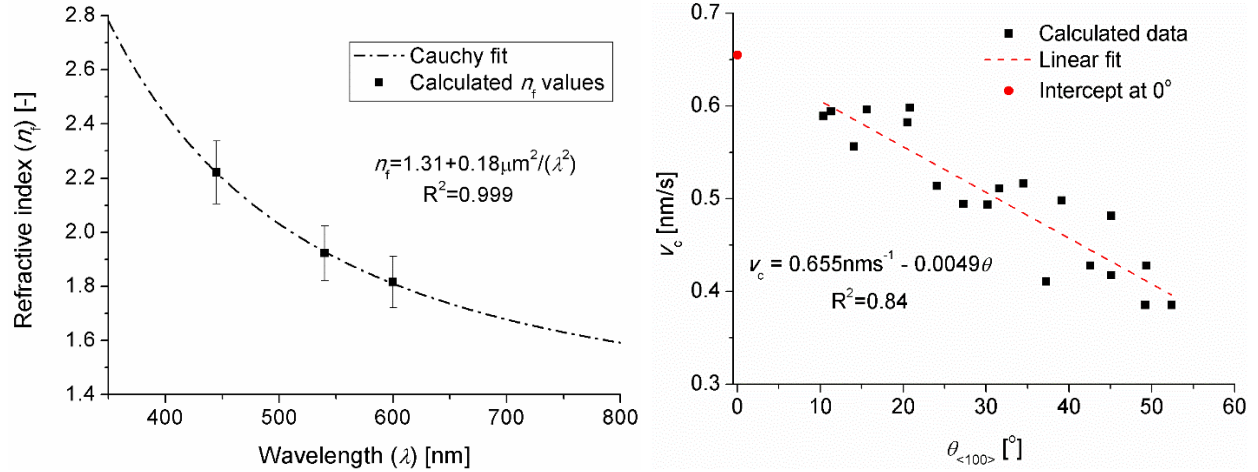
$$n_f(\lambda) = \frac{\lambda}{4(d|t_{max1} - d|t_{min1})} = \frac{\lambda}{4t_{hc}v_c} \quad (17)$$

To use Eq. (17) we need to consider how the RGB values are calculated based on the optical microscopy images. For this we decided to use the CIE standard observer reference functions [15]. It is true, that the calculated RGB components does not correspond to only one wavelength, and that the reconstruction of the spectral information is not possible from the RGB values. However, as discussed in Section 2.3 we are not interested in the spectral composition or their relative intensities, we only care about the location of the intensity minima and maxima. They are related to given layer thicknesses, which in turn correspond to the most intensive wavelength component of the CIE standard observer color spectra. In other words, at the local minima and maxima of the curves presented in Fig. 4, where the interference criteria (Eq. (1) and (2)) are fulfilled, we can approximate the wavelength with the peak positions of the CIE standard observer reference spectra for the three color component: 445 nm for blue, 540 nm for green and 600 nm for red, respectively.

In Fig. 10 right, we plotted the calculated refractive indexes for these three characteristic wavelengths. The error bars represent the standard deviation for the six measured grains, and it can be considered realistic, given that it incorporates the relative errors of all the measurements (determination of the characteristic times based on the optical data, angles and  $S(\theta)$  parameters from EBSD and height values from AFM). We also extrapolated the data with the two-term Cauchy dispersion, defined in Eq. (18), which resulted in a quite good fit ( $A = 1.31, B = 0.18 \mu m^2$ ).

$$n_f = A + \frac{B}{\lambda^2} \quad (18)$$

Now the respective cycle etch rates ( $v_c$ ) for all the 20 grains in Fig. 6 can be calculated either by using their  $S(\theta)$  parameters and the AFM data (Eq. (15)) or by using the now known refractive indexes and their half-cycle times ( $t_{hc}$ ) with Eq. (17). The two approaches result in a relative difference between 0.2 % (data not shown). The cycle etch rates calculated by the latter approach are given in Fig. 11 right, for all of the grains in the experiment. The cycle etch rate of the grain ideally close to the  $\langle 100 \rangle$  orientation results in 0.655 nm/s. The linear regression in function of the angle with the  $\langle 100 \rangle$  direction is given in the figure.



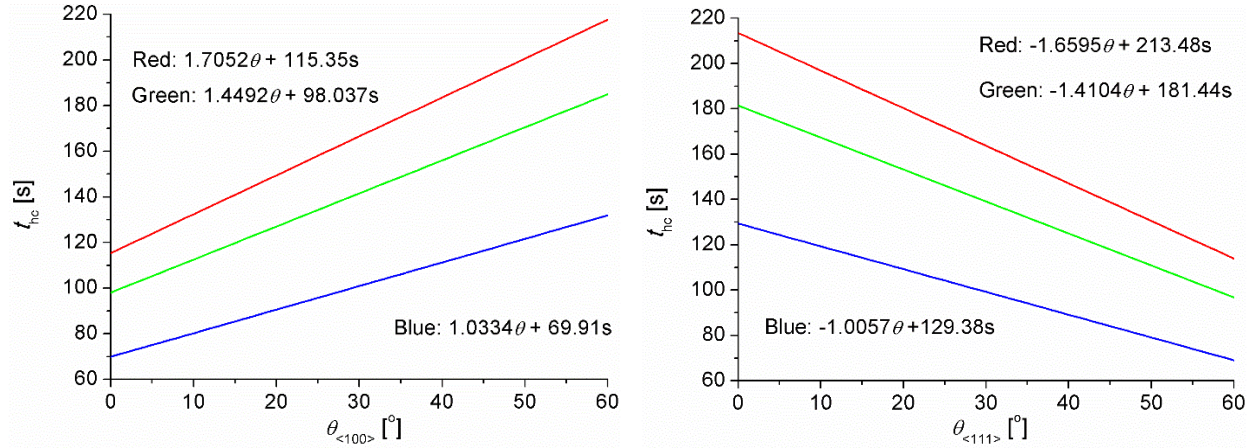
**Fig. 11: Left:** The calculated refractive indexes of the developed film at the characteristic peaks of the CIE standard observer spectra (based on Eq. (17)). **Right:** The obtained constant cycle etch rates ( $v_c$ ) for the 20 grains presented in Fig. 6.

Conclusively, with our functional model and the combined use of image processing, EBSD and AFM we were able to estimate the orientation dependent cycle etch rate and the refractive index of the developed film. Now it is time to test the results as a method to determine the grain orientation based on optical data only.

### 3.3. Quantification of grain orientation

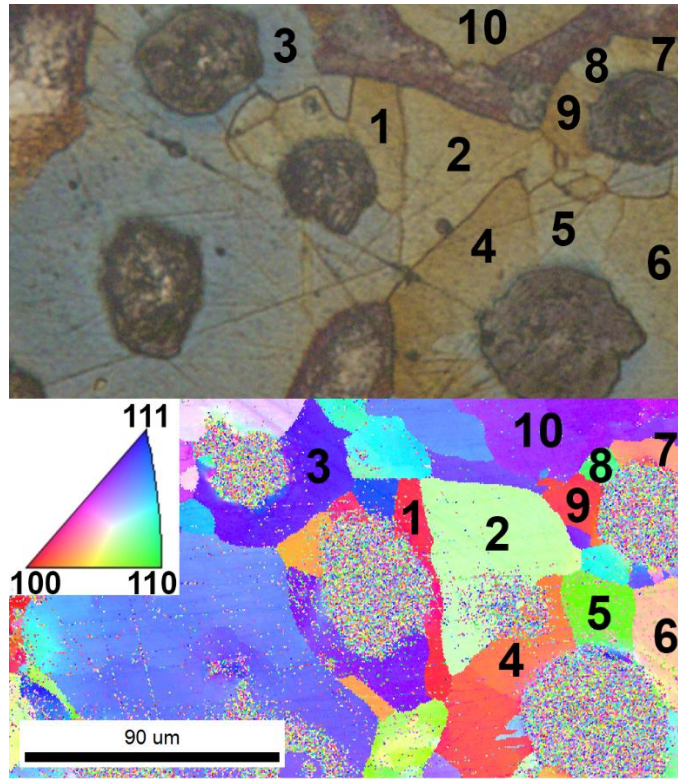
We have previously seen, that due to the variation of the delay times ( $t_d$ ) at the start of our experiments, which can be related to surface oxidation and differences in sample preparation, the use of total elapsed time of etching ( $t_e$ ), or even the location of interference maxima and minima ( $t_{max}, t_{min}$ ) are not suitable for the quantification of grain orientation. We postulated however, that the introduced half-cycle times ( $t_{hc}$ ) are independent from  $t_d$  and are characteristic for each grain.

To prove this we made another experiment, aiming to test the applicability of the half-cycle times ( $t_{hc}$ ) to measure the orientation of the grains based on only the optical data. First we used the data from the previous experiment in section 3.2 (refractive index and the linear regression of cycle velocities presented in Fig. 11 and EBSD data for the grains), to calculate the  $t_{hc}$  vs.  $\theta$  characteristics by using a rearranged form of Eq. (17) both for the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions. These two characteristic charts for the three color component are given in Fig. 12 left and right.



**Fig. 12:** Half-cycle times ( $t_{hc}$ ) in function of the angle difference ( $\theta$ ) with the  $\langle 100 \rangle$  direction (left) and  $\langle 111 \rangle$  direction (right) for the three RGB color components.

The linear equations given in Fig. 12 can be used to calculate the orientation of a random grain based on the measured  $t_{hc}$  values, for each color component. To test the method an experiment was performed on the same specimen at another area, including 10 random grains, presented in Fig. 13. The total etching time was 600 s, and the characteristic times ( $t_{max1}$ ,  $t_{min1}$ ,  $t_{hc}$ ) were calculated based on the image processing data. The results are given in Table 3 of the supplementary materials section.



**Fig. 13: Top:** Optical microscopy image of the investigated area after 400 s color etching (exported from the video, the total etch time was 600 s). **Bottom:** The SEM-EBSD image of the same area.

By using the half-cycle times and the equations given in Fig. 12, the grain orientations were calculated for the grains. The angles with the <100> and <111> directions are given in Tables 2 and 3, respectively. The absolute errors compared to the EBSD data measured for the same grains are also presented. Based on the results we can make the following conclusions:

- 1) The absolute error of the estimated orientation is higher for a single color component compared to the average of the three channels. The reason for this is that the raw color information of a single channel is noisy, as can be seen in Fig. 4, and even after fitting, the determination of the local minima and maxima has some deviation. These added errors can be reduced by averaging the results of the three channels.
- 2) The error for the averaged signal is in the  $\pm 5.5^\circ$  range (average absolute error:  $2.9^\circ$ ) for the <100> direction while in the  $\pm 9^\circ$  range (average absolute error:  $3.2^\circ$ ) for the <111> direction. These are quite impressive figures of merit for a purely optical method.
- 3) It is very important to emphasize, that the establishment of the model and the determination of the etch rate and refractive index were done in a completely separate experiment compared to this one, where we tested the established method and the derived parameters. As a result of faster sample preparation (less idle time before the start of etching) the average of delay times ( $t_d$ ) were 101 s for these 10 grains, compared to the 183 s average for the 20 grains in the previous experiment.
- 4) Moreover, the fact that our method works for an independent experiment directly proves, that the cycle etch rates ( $v_c$ ) and half-cycle times ( $t_{hc}$ ) are not depending on the experimental conditions or delay ( $t_d$ ), and that are characteristic for a given grain orientation.

**Table 2.** The calculated grain orientation of the grains in Fig. 13, considering the angle between the surface normal and the <100> direction. The color data is derived from image processing, by the determination of  $t_{hc}$  and using the characteristics given in Fig. 12.

| Grain No. | EBSD      | Blue      |            | Green     |            | Red       |            | Average   |            |
|-----------|-----------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
|           | Angle [°] | Angle [°] | ±Error [°] | Angle [°] | ±Error [°] | Angle [°] | ±Error [°] | Angle [°] | ±Error [°] |
| 1         | 7.61      | 10.73     | 3.13       | 14.47     | 6.86       | 13.87     | 6.26       | 13.02     | 5.42       |
| 2         | 32.90     | 35.89     | 2.99       | 27.58     | -5.32      | 26.18     | -6.71      | 29.88     | -3.01      |
| 3         | 46.69     | 56.21     | 9.53       | 55.18     | 8.49       | 43.78     | -2.91      | 51.72     | 5.04       |
| 4         | 11.90     | 10.73     | -1.17      | 15.16     | 3.25       | 16.22     | 4.31       | 14.03     | 2.13       |
| 5         | 36.52     | 36.86     | 0.34       | 32.41     | -4.11      | 29.70     | -6.81      | 32.99     | -3.53      |
| 6         | 24.31     | 29.12     | 4.81       | 23.44     | -0.88      | 22.08     | -2.23      | 24.88     | 0.57       |
| 7         | 20.05     | 20.41     | 0.36       | 15.16     | -4.89      | 16.80     | -3.24      | 17.46     | -2.59      |
| 8         | 42.49     | 42.66     | 0.18       | 35.86     | -6.63      | 34.39     | -8.09      | 37.64     | -4.85      |
| 9         | 8.48      | 11.70     | 3.22       | 9.63      | 1.16       | 8.59      | 0.11       | 9.98      | 1.50       |
| 10        | 38.16     | 46.28     | 8.13       | 37.24     | -0.92      | 32.64     | -5.52      | 38.72     | 0.56       |

**Table 3.** The calculated grain orientation of the grains in Fig. 13, considering the angle between the surface normal and the <111> direction. The color data is derived from image processing, by the determination of  $t_{hc}$  and using the characteristics given in Fig. 12.

| Grain No. | EBSD      | Blue      |            | Green     |            | Red       |            | Average   |            |
|-----------|-----------|-----------|------------|-----------|------------|-----------|------------|-----------|------------|
|           | Angle [°] | Angle [°] | ±Error [°] | Angle [°] | ±Error [°] | Angle [°] | ±Error [°] | Angle [°] | ±Error [°] |
| 1         | 47.29     | 48.70     | 1.41       | 44.27     | -3.02      | 44.88     | -2.41      | 45.95     | -1.34      |
| 2         | 29.71     | 22.85     | -6.86      | 30.80     | 1.09       | 32.23     | 2.52       | 28.63     | -1.08      |
| 3         | 8.05      | 1.97      | -6.08      | 2.44      | -5.61      | 14.15     | 6.10       | 6.19      | -1.86      |
| 4         | 44.31     | 48.70     | 4.39       | 43.56     | -0.75      | 42.47     | -1.84      | 44.91     | 0.60       |
| 5         | 34.19     | 21.86     | -12.34     | 25.84     | -8.36      | 28.61     | -5.58      | 25.43     | -8.76      |
| 6         | 34.23     | 29.81     | -4.42      | 35.05     | 0.83       | 36.44     | 2.22       | 33.77     | -0.46      |
| 7         | 37.56     | 38.76     | 1.20       | 43.56     | 6.00       | 41.87     | 4.31       | 41.40     | 3.83       |
| 8         | 29.34     | 15.89     | -13.45     | 22.29     | -7.04      | 23.79     | -5.55      | 20.66     | -8.68      |
| 9         | 46.74     | 47.71     | 0.96       | 49.23     | 2.49       | 50.30     | 3.56       | 49.08     | 2.34       |
| 10        | 16.58     | 11.91     | -4.67      | 20.87     | 4.29       | 25.60     | 9.02       | 19.46     | 2.88       |

In the Supplementary Materials section we provided the Matlab script to determine the orientation of a ferrite grain based on our proposed method. The script is extended with comments, to help the users adapt the code to their needs. The most important advice is that the noise of the resulting normalized RGB intensity curves is depending on the amount of averaged pixels, thus the size of the evaluated area. The larger the area, the smaller the noise. However, as can be seen in the optical microscopy images, the surface of the layer and the grains are usually inclined after the etching (investigated previously in [7, 8]), which results in a color gradient along the grain. Thus, to match the color with the corresponding orientation one must select an area in the geometric center of the grain to compensate this effect. Selecting an area at the edge of a grain can result in false obtained orientation.

#### 4. Conclusions

It was proved that our proposed functional model for the color etching of ferrite grains in a cast iron specimen with Beraha-I type etchant can be used to determine the crystallographic orientation of the ferrite grains based on only optical microscopy and subsequent image processing. It was shown that the etching process experiences a delay, which can be connected to braking an oxide barrier and is influenced by idle times during sample preparation. It was proved that a time independent cycle etch rate exists and the corresponding half-cycle times (between first interference minimum and maximum) are characteristic to the grain orientation and can be used for its determination. For the first time, the exact value of this cycle etch rate, its dependence on the angle with the <100> direction and also the refractive index of the developed film (in function of the wavelength) were experimentally determined. Our proposed method – implemented and distributed via a Matlab program – was demonstrated to be applicable for the quantification of

grain orientation with respect to the  $\langle 100 \rangle$  and  $\langle 111 \rangle$  directions, with an average absolute error of around  $3^\circ$ .

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## Supplementary materials

**Table 1.** The EBSD and characteristic time results for the experiments presented in Section 3.1 and 3.2.

| Grain No. | Angle [°] |       |       | Characteristic times         |                                |                               |                               |                           |                        |
|-----------|-----------|-------|-------|------------------------------|--------------------------------|-------------------------------|-------------------------------|---------------------------|------------------------|
|           | <100>     | <110> | <111> | $t_{\min 1}$<br>(red)<br>[s] | $t_{\min 1}$<br>(green)<br>[s] | $t_{\min 1}$<br>(blue)<br>[s] | $t_{\max 1}$<br>(blue)<br>[s] | $t_{hc}$<br>(blue)<br>[s] | $t_d$<br>(blue)<br>[s] |
| 1         | 14.07     | 30.98 | 44.76 | 285.5                        | 281.8                          | 260                           | 350                           | 90                        | 170                    |
| 2         | 49.35     | 32.86 | 5.39  | 328                          | 320                            | 308                           | 425                           | 117                       | 191                    |
| 3         | 31.60     | 21.80 | 25.64 | 310                          | 302                            | 295                           | 393                           | 98                        | 197                    |
| 4         | 45.10     | 29.13 | 9.97  | 332.4                        | 324.6                          | 314                           | 434                           | 120                       | 194                    |
| 5         | 37.25     | 9.92  | 30.49 | 335.1                        | 326.1                          | 318.1                         | 440.1                         | 122                       | 196.1                  |
| 6         | 42.60     | 17.40 | 19.20 | 330                          | 323                            | 305                           | 422                           | 117                       | 188                    |
| 7         | 39.12     | 18.62 | 20.51 | 313                          | 296.8                          | 284.5                         | 385                           | 100.5                     | 184                    |
| 8         | 30.20     | 27.27 | 24.88 | 314.4                        | 300.2                          | 288.5                         | 390                           | 101.5                     | 187                    |
| 9         | 10.39     | 37.67 | 44.38 | 274                          | 264.2                          | 250                           | 335                           | 85                        | 165                    |
| 10        | 27.27     | 19.47 | 33.49 | 296.3                        | 288.8                          | 278.7                         | 380                           | 101.3                     | 177.4                  |
| 11        | 15.62     | 31.65 | 40.13 | 278.8                        | 270.1                          | 260                           | 344                           | 84                        | 176                    |
| 12        | 20.81     | 30.77 | 34.16 | 285.1                        | 271.1                          | 256.3                         | 340                           | 83.7                      | 172.6                  |
| 13        | 24.10     | 25.35 | 32.51 | 282.7                        | 275.4                          | 267.5                         | 365                           | 97.5                      | 170                    |
| 14        | 11.31     | 36.46 | 43.56 | 258.9                        | 252.5                          | 245.7                         | 330                           | 84.3                      | 161.4                  |
| 15        | 45.12     | 3.67  | 31.59 | 348                          | 338.3                          | 320                           | 424                           | 104                       | 216                    |
| 16        | 20.51     | 30.25 | 34.62 | 291.7                        | 278                            | 268                           | 354                           | 86                        | 182                    |
| 17        | 26.57     | 18.43 | 39.23 | 279.4                        | 276.1                          | 270                           | n.a.                          | n.a.                      | n.a.                   |
| 18        | 34.51     | 24.21 | 21.43 | 300                          | 290                            | 283                           | 380                           | 97                        | 186                    |
| 19        | 52.37     | 32.91 | 2.75  | 335.9                        | 330.1                          | 315                           | 445                           | 130                       | 185                    |
| 20        | 49.20     | 28.93 | 7.03  | 343                          | 333.8                          | 310                           | 440                           | 130                       | 180                    |

**Table 2.** The result of the AFM measurements presented in Section 3.2, along with the calculated etch rate and refractive index parameters.

| Grain No. | AFM      |          |                 |                 |                 | Image processing    |             |                  |                        | Calculated parameters |                |                |                |
|-----------|----------|----------|-----------------|-----------------|-----------------|---------------------|-------------|------------------|------------------------|-----------------------|----------------|----------------|----------------|
|           | $X$ [nm] | $Y$ [nm] | $\Delta X$ [nm] | $\Delta Y$ [nm] | $\Delta d$ [nm] | $t_{hc}$ (blue) [s] | $S(\theta)$ | $t_d$ (blue) [s] | $t_e - t_d$ (blue) [s] | $v_c$ [nm/s]          | $n_f$ (445 nm) | $n_f$ (540 nm) | $n_f$ (600 nm) |
| 1         | 128.30   | 180.90   | 0.00            | 0.00            | 0.00            | 90.00               | 1.29        | 170.00           | 275.00                 | n.a.                  | n.a.           | n.a.           | n.a.           |
| 2         | 221.00   | 315.20   | 92.70           | 134.30          | 41.60           | 117.00              | 1.67        | 191.00           | 254.00                 | 0.40                  | 2.37           | 2.05           | 1.93           |
| 3         | 168.00   | 245.70   | 39.70           | 64.80           | 25.10           | 98.00               | 1.40        | 197.00           | 248.00                 | 0.49                  | 2.33           | 2.01           | 1.90           |
| 4         | 229.70   | 331.80   | 101.40          | 150.90          | 49.50           | 120.00              | 1.72        | 194.00           | 251.00                 | 0.43                  | 2.17           | 1.87           | 1.77           |
| 5         | 200.00   | 305.90   | 71.70           | 125.00          | 53.30           | 122.00              | 1.75        | 196.10           | 248.90                 | 0.43                  | 2.12           | 1.83           | 1.73           |
| 6         | 262.50   | 360.00   | 134.20          | 179.10          | 44.90           | 117.00              | 1.67        | 188.00           | 257.00                 | 0.45                  | 2.13           | 1.84           | 1.74           |

**Table 3.** The characteristic times determined for the 10 grains of the experiment presented in Section 3.3.

| Grain No. | Blue           |                |              | Green          |                |              | Red            |                |              |
|-----------|----------------|----------------|--------------|----------------|----------------|--------------|----------------|----------------|--------------|
|           | $t_{\min}$ [s] | $t_{\max}$ [s] | $t_{hc}$ [s] | $t_{\min}$ [s] | $t_{\max}$ [s] | $t_{hc}$ [s] | $t_{\min}$ [s] | $t_{\max}$ [s] | $t_{hc}$ [s] |
| 1         | 225            | 306            | 81           | 236            | 355            | 119          | 251            | 390            | 139          |
| 2         | 218            | 325            | 107          | 236            | 374            | 138          | 246            | 406            | 160          |
| 3         | 266            | 394            | 128          | 278            | 456            | 178          | 300            | 490            | 190          |
| 4         | 233            | 314            | 81           | 238            | 358            | 120          | 251            | 394            | 143          |
| 5         | 234            | 342            | 108          | 250            | 395            | 145          | 264            | 430            | 166          |
| 6         | 220            | 320            | 100          | 242            | 374            | 132          | 253            | 406            | 153          |
| 7         | 220            | 311            | 91           | 235            | 355            | 120          | 246            | 390            | 144          |
| 8         | 228            | 342            | 114          | 245            | 395            | 150          | 256            | 430            | 174          |
| 9         | 214            | 296            | 82           | 226            | 338            | 112          | 240            | 370            | 130          |
| 10        | 228            | 346            | 118          | 243            | 395            | 152          | 254            | 425            | 171          |