Effect of Beracha-I type color etchant on the ferrite phase in different type Fe-C alloys

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Abstract. In material science, and particularly in metallography, various etching processes are frequently used to visualize grain structure. For some etching processes, it is sufficient to immerse the specimen into the etchant only for a few seconds, but for color etching, samples must be kept in the etchant for several minutes to achieve a colored surface layer. In our research, a measurement environment was created, in which the process of color etching can be observed in real-time. A closed microfluidic system ensured the controlled laminar flow of the etchant. The surface of the observed spherical graphite cast iron and DC01 low carbon steel was monitored from the beginning to the end of etching. Comparing the etching of the spherical graphite cast iron and the low carbon steel samples give a more comprehensive picture of the effect of Beraha-I type color etchant on the ferritic structure. Though the etchant reacts with the same ferritic phase in both cases, the etching process develops in different ways. The layer formation was much faster in the ferritic phase of DC01 steel, compared to ferrite in cast iron specimens.

1. Introduction

Etching is an essential step in the sample preparation of metallic materials. The purpose of this process is to reveal the microstructure of the materials for further microscopic examination. The advantage of etching compared to other methods is that it is cheaper and requires less preparation, such as other technologies, like electron microscopy [1-2].

One of the typical etching processes is color etching [3]. The test sample is immersed in a container filled with the etchant. The etching agent reacts with the surface. As a result, a thin, plastic layer begins to form on the surface of the sample. This layer is a chemical mixture (usually compound) of the examined metal and the etchant. Depending on the type of etchant, the film may also be oxide, sulfide, selenium, chromate, or complex molybdate [4]. The formed layer is transparent, and its thickness increases with the etching time. In practice, a layer can reach a thickness of 40-500 nm during a measurement. Depending on its thickness, the film interferes with light waves reflected from the metal surface, which causes colors specified by the interference criterion [5]. If the thickness of the layer satisfies the conditions of destructive interference, then the wavelength components will fall out of the reflected light, causing the observed color. Therefore:

\[ d = m \frac{\lambda}{4n} \]
In Eq. (1), \( m \) is an odd integer, \( \lambda \) is the incident light wavelength, and \( n \) is the refractive index of the film. If a given light component falls out of the visible light range due to interference, the surface below the layer will appear as a complement to the light that is lost [6]. As a result, the layer absorbs light of different wavelengths periodically, depending on the thickness of the layer. Thus, the color of the layer and the grain beneath it changes cyclically. It is also proved that the layer thickness depends on the etching time and the etching speed of the grain [7-8].

Depending on the investigated materials, different types of etchants are used [9-14]. Since our tests were carried out with Beraha-I type etchant, the specimens used were chosen accordingly. Beraha-I is an anisotropic etchant for ferritic materials, so the etching rate is highly dependent on the orientation of the individual grains. As a result, particles with different orientations are etched at different speeds, which causes a definite difference in their color after a given etching time. Although the ferrite grains differ in color due to the different etching speed, the process allows the individual particles to be separated.

Our current work aims to investigate how the Beraha-I type etchant reacts with different ferritic phases under the same conditions. By using the recorded etching processes of the investigated spherical graphite cast iron and low carbon steel samples, it was possible to compare the reaction of materials with different chemical compositions.

2. Experimental

2.1. Instrumentation

To carry out the planned investigations, it was necessary to create a measurement setup capable of keeping the etching under controlled conditions. Besides, the surface of the sample must be monitored by microscopy throughout the whole process. Thus, a microfluidic cell was designed and created to follow the etching of the samples. In order to design a microfluidics cell, however, the geometric dimensions and setup of the tools available must be known. For optical microscopy, an Olympus BX51 type LMPlan FI 50 \( \times \) / 0.50 long-range objective microscope was used. The microscope was connected to a DP72 type digital camera, so microscopic images were recorded directly. The continuous laminar flow of the etchant was provided by a syringe pump.

2.2. Design and fabrication of the microfluidic cell

To create the microfluidic cell, the technical specifications of the instruments already available had to be considered, such as the focal length of the microscope objective and the orientation of the surface to be examined (Fig. 1). The focal length of the used objective was 2 mm; therefore, the microfluidic cell must be designed so that the surface of the sample should be accessible to 2 mm. In the designed system, this is accomplished with a 0.4 mm thick flow channel and a 0.7 mm thick, cell sealing glass sheet. This leaves an additional 0.9 mm for the objective to approach the microfluidic cell.

![Figure 1](design consideration for microfluidic cell.png)

**Figure 1.** Design considerations for the microfluidic cell. The flow channel is 0.4 mm thick, while the glass sheet is 0.7 mm. Thus, the objective has an additional 0.9 mm to approach the examined surface.
Since the etchant would also react with the equipment, materials inert to the etchants must be used. The microfluidic system had to be adequately sealed in order to isolate the etchant from other equipment. Besides, it must provide laminar flow within the whole cell.

The designed microfluidic cell is presented in Fig. 2. The base of the cell is poly-dimethyl-siloxane, which is a chemically inert, flexible material. It is frequently used in the field of microfluidics [15]. The curing agent and the silicon pre-polymer were mixed in the prescribed ratio of 1:10. The mixture was filled into a molding form, created by an Objet Eden 250 type 3D printer. The filled molding form was set into a pre-heated oven at 100°C for 60 min to cure the polymer. After polymerization, the cell was bonded to a 1 mm thick glass sheet with corona discharge for 1 min. Further details of the technology were described elsewhere [15]. The upper, still open part of the cell is closed by the sample itself. The volume of the flow channel in the closed cell is 205 mm³.

Figure 2. 3D CAD model of the microfluidic cell and microfluidic cell with an embedded sample

2.3. Materials and preparations
Spherical graphite cast iron and DC01 low carbon steel were used for the tests. The chemical composition of the examined samples is shown in Table 1.

| Chemical composition (wt%) | Spherical cast iron | DC01 Low carbon steel |
|---------------------------|--------------------|-----------------------|
| C            | 3.59  | 0.05   |
| Si           | 2.43  | 0.524  |
| Mn           | 0.36  | 0.082  |
| Mg           | 0.063 | 0.025  |
| S            | 0.012 | 0.062  |
| P            | 0.046 | 0.013  |

After 4% nital pre-etching, it was assessed that the grain structure of the low carbon steel was too fine. At the intended magnification, the grains could not be distinguished. Therefore, the DC01 steel samples were heat-treated before testing [16]. After heating up to 850 °C for 3 hours, the samples were annealed at a cooling rate of 1 °C / min. After the approx. 14 hours of annealing, the steel samples were embedded, then ground and polished. After polishing, the resulting particle diameter was checked by a repeated 4% nital etching.

The Beraha-I etchant used for the tests was freshly mixed by dissolving 3g K₂S₂O₇ and 10g Na₂S₂O₃ in 100 ml distilled water. In all cases, etching was performed in an air-conditioned laboratory at 22 °C.

2.4. Measurement setup
After the sample and microfluidic cell preparations, the measurement setup was prepared, as shown in Fig. 3. The figure shows how the syringe pump is connected to the microfluidic cell. Changes of the sample surface were tracked through the Olympus BX51 microscope's large focal length lens. During the etching of both samples, the flow rate was set on the syringe pump at 110 µl / min.
3. Results and discussion

Screenshots were made from the video recorded during etchings. Fig. 4. shows the surface of the spherical graphite cast iron sample and Fig. 5. shows the surface of the DC01 low carbon steel sample.

The observed area in cast iron could be easily identified several times due to the constant visibility of the graphite particles. During the etching of the cast iron sample, ferritic phases were attacked by Beraha-I. In the first 30 seconds, there were no visible changes. As we have shown in our previous article, the etchant was supposed to take so long to break the oxide layer on the surface [17]. From 30 seconds on, the perlite in cast iron sample darkens, as the etchant attacked the ferritic phase of the less corrosion-resistant fabric element. After approximately 180 seconds, the etching of the pure ferritic phases also begins. From this point on, the cyclic color change of the ferrite can be observed. The ferrite phase in the perlite is over etched after approximately 300 seconds, from which time no significant color change occurs in the perlite phase. The ferritic phases around the graphite particles changed color much longer. They needed approximately 580 seconds to reach the same state as perlite.
The DC01 low carbon steel shows a significant difference compared to the cast iron specimen, though it has a similar ferritic structure. After 95 seconds, the particles became visible on the surface of the steel sample. It means that breaking through the surface oxide layer was much easier compared to cast iron’s ferritic phases. All this suggests that the whole etching process took place at a much faster rate. While in the cast iron sample, the grains were over etched at approximately 580 seconds and darkened completely, the same condition of the steel sample was reached approx. 240 seconds earlier.

4. Conclusions
The ferrite phase of perlite in the cast iron sample was similar to the etching of low carbon steel’s ferritic phase. In both of the cases breaking through the oxide layer took approximately 90 seconds, followed by a cyclic color change of approximately 270 seconds. The purely ferritic grains of cast iron were much more resistant to Beraha-I, requiring approximately 160 sec to begin layering. The etching and deposition rates were significantly slower here. The periodic color change was observed almost twice as long time, approximately 420 seconds long. As the test conditions were the same, the difference in etching can only be attributed to the difference in the chemical composition of the examined samples.

In order to gain a deeper understanding of the etching processes, the experiment should be extended later by a quantitative approach, such as the one presented in our previous work [17]. Comparing the results obtained would make it possible to quantify the visual difference.

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