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Color metallography; a suitable method for characterization of martensite and bainite in multiphase steels

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Abstract
Color metallography is a useful method for characterizing microstructures of steels with multiple phases. In this paper, application of three different color etching techniques for a bainitic-martensitic steel is reported. Comparisons between the results showed that 10% $Na_2S_2O_5$ aqueous solution was the best etchant for distinguishing martensite, bainite and ferrite phases. The obtained micrographs were clear and sharp. Nanoindentation test was also carried out in order to approve the results of color metallography.

Keywords: Color metallography, Multiphase steel, Microstructure

1- Introduction
Identification and characterization of type and morphology of phases in metals and alloys is very important. The type of each phase can be predicted from chemical composition, and history of heat treatment or phase diagrams, but the appropriate qualitative and quantitative method is the experimental method [1,2]. Optical microscopy, scanning and transmission electron microscopy and X-ray diffraction are usually used for microstructural investigations. Classical etchants such as nital and picral are very popular for microstructural investigation of steels. However, these etchants can only be used for simultaneous investigation of a restricted number of phases. For example, due to the similarity between bainitic and martensitic microstructures, usual metallographic techniques are not suitable to distinguish these phases from one another. Electron microscopy is a very good way to distinguish martensite and bainite, but it is expensive and also may not be trustable for small regions of the specimen. Therefore, better etchants are required for multiphase microstructures to distinguish each of microstructural components reliably and to produce a good contrast between phases [3].
Color etching is widely used for visualizing different phases in metals and alloys. This method can produce different colors for different phases. Color metallography is the best way to recognize phases such as martensite and bainite and can be used for image analyzing and determining the volume fraction of each phase [4]. Many solutions are prepared based on thiosulfate and metablsulfite salts [1-5]. These solutions produce chemical thin films on the surface of specimens that appear in different colors under polarized light.
In this study, three techniques of color metallography were used to produce a good contrast between phases in a bainitic-martensitic steel and the best etchant was determined for characterizing martensite and bainite phases.

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2- Experimental procedure
A low alloy carbon steel with designation of DIN 1.6526 standard was used in this work. The chemical composition is given in table 1. Fig1 shows the CCT diagram of such steel. Specimens with 10 mm thickness were cut from the hot-rolled plates and were austenitized at 830 ˚C for 45minutes and then quenched in oil. Phase identification analysis was carried out using X-ray diffraction (XRD Philips X'pert) with Cu-K_α radiation.

Table 1. Chemical composition of the steel used in this work (wt%)

C	Si	Mn	P	S	Mo	Cr	Ni	Fe
0.2	0.2	0.8	0.02	0.02	0.2	0.5	0.5	balance

Three techniques of color metallography were used based on thiosulfate and metabisulfite salt solutions. These techniques are explained below.
(1) The etchant was a mixture of 1% aqueous solution of sodium metabisulfite (1 g $Na_2S_2O_5$ in 100 ml distilled water) and 4% picral (4 g dry picric acid in 100 ml ethanol) that were mixed in a 1:1 ratio just before using. The polished surface of the specimen was immersed in tint etchant for about 10 to 15 s and the specimen was oscillated strongly in the whole etching time.
(2) After polishing, the specimen surface was prepared by pre-etching with 4% picral. A continuous oscillation was performed during the

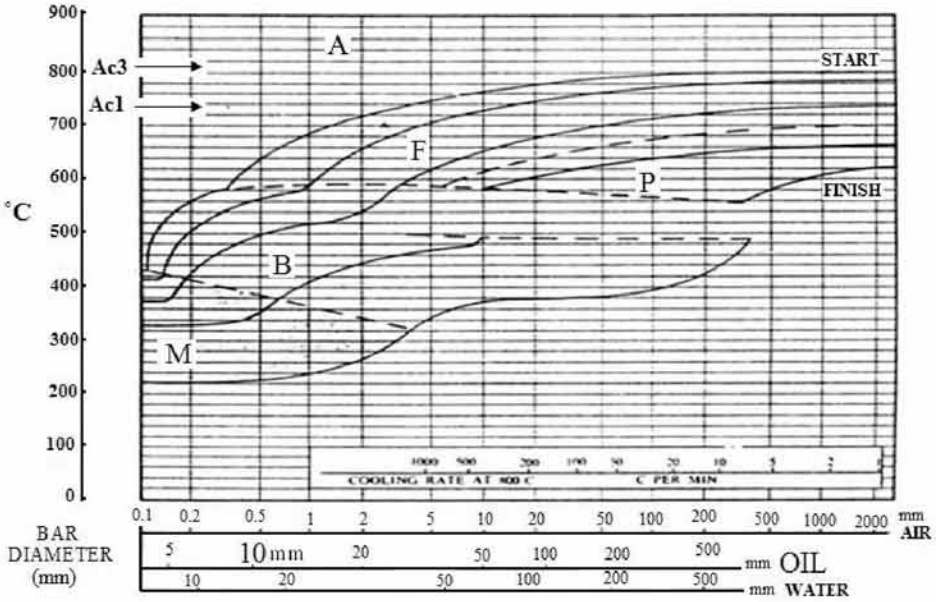

Fig. 1. The CCT diagram of DIN 1.6526 steel [6].

whole pre-etching lasting about 60 s. After pre-etching, the specimen was etched with a mixture of 10 g sodium thiosulfate anhydrous ($Na_2S_2O_3$), 3 g potassium metabisulfite ($K_2S_2O_5$) and 100 ml distilled water. The etching time was about 30 s with permanent oscillation.

(3) The specimen surface was polished and then was pre-etched similar to technique (2). The color etchant for this technique was 10% aqueous solution of sodium metabisulfite (10 g $Na_2S_2O_5$ in 100 ml distilled water). The etching time was about 15 s and oscillation was performed strongly during the whole etching time.

In all the above techniques, after pre-etching or etching stage, the specimen surface was washed with water followed by ethanol and was blown dry in warm air. The etched specimens were finally observed with a microscope equipped with high brightness halogen lamp. The volume fraction of each phase was calculated by the Clemex vision image analysis software. Nanoindentation measurements were carried out on each individual constituent using CSM NHTX instrument with a load of 30 mN in order to validate the color metallography results.

3- Results and dissections

3-1- XRD measurements

Fig. 2 shows XRD pattern of the quenched specimen. All five picks in this pattern are for phases with the bcc lattice. It reveals neither austenite nor ε martensite. Due to quenching of specimen in oil from austenite temperature, it is probable that the final microstructure mainly consists of martensite phase. Therefore, the measured picks are for ferrite and ά martensite. In these steels, because of low carbon content, the volume fraction of octahedral spaces that are occupied with carbon atoms is very small and tetragonality of martensite (c/a) descends to nearly one. Therefore, in low carbon steels, the pick angles of martensite and ferrite are similar in XRD pattern. This shows that the XRD technique could not be a suitable method to identify the phases in the as-quenched specimen [7, 8].

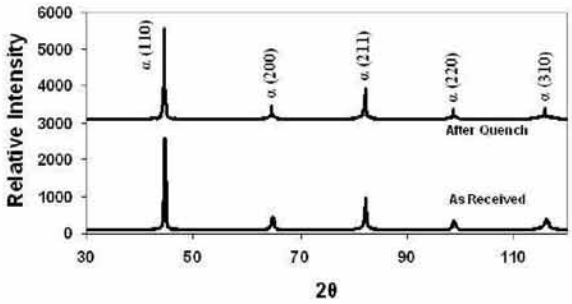

Fig. 2. The XRD patterns of the as received and as-quenched specimens.

3-2- Color metallography

The color micrograph from technique (1) is shown in Fig. 3. As can be seen in this figure, almost three phases are shown with blue, white and brown colors. This technique is named Lepera [9]. If steel is etched with Lepera solution, ferrite appears as blue or dark blue, bainite is brown and both martensite and austenite are white. The alloying element especially carbon and silicon have a strong influence on the ferrite color. The color of ferrite turns gradually from blue to brown when the content of carbon or silicon elements is decreased. Practically, color differentiation between ferrite and bainite is easier when the silicon content is higher than 1 wt% [3]. Microstructure of the quenched steel consists of ferrite, bainite and martensite. The white color can

depend an martensite and can retain austenite. As the XRD pattern did not show any picks of austenite, therefore the white color is only related to martensite. Lepera etchant produces very good contrast in steels with ferritic matrix that have martensite and bainite islands dispersed in the matrix. As can be seen in Fig 3, the contrast between phases especially bainite and martensite is very low in this steel and using image analysis software is difficult to determine the volume fraction of each phase. If the percentage of bainite is more than 5 wt%, this technique gives inconsistent results [10].

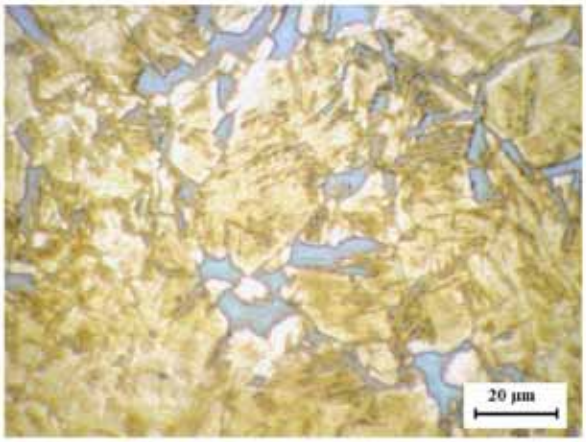

Fig. 3. Microstructure of specimen resulted from etching with technique (1).

Fig 4 shows microstructure of steel that was pre-etched with 4% picral to prepare for color metallography using techniques (2) and (3). As can be seen, it is impossible to determine the type and volume fraction of phases correctly. The bright area can be related to ferrite but the determination of other phases is difficult.

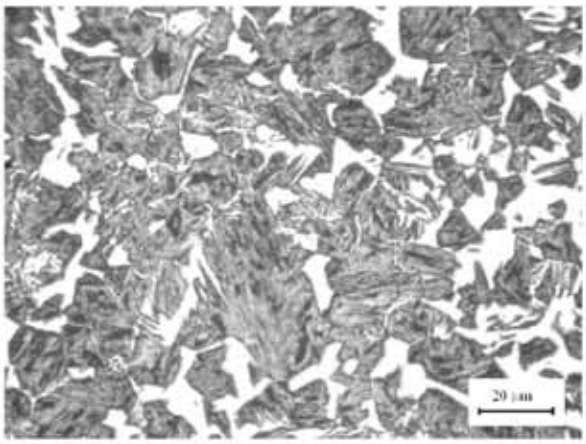

Fig.4. Microstructure of steel pre-etched with 4% picral.

The pre-etching stage has a very important role in techniques (2) and (3). For martensite and bainite, picral is the best solution that provides the required surface property for better influence of tint etchant. Picral makes the carbides and bainites better delineated. Picral attacks interphases between ferrite and carbide. Therefore, carbides and bainite are revealed much better. If a few drops of concentrated hydrochloric acid (about 1 ml per 100 ml picral) are added for pre-etching, grain boundaries and iron carbides appear better [5]. Nital is another solution that can be used for pre-etching. However, nital attacks ferrite grains and grain boundaries. In fact, picral is better for the microstructures consisting of bainite phase, but pre-etching by nital could produce a rather good contrast between phases, especially between ferrite and martensite after color etching [4].

The results of color metallography using technique (2) are shown in Figs. 5a and 5b. These two images are prepared from the same position of specimen using this technique with similar conditions. As can be seen, different colors appear after tint etching. The blue color illustrates the martensite phase [11]. This color can be distinguished from other phase because of its very good contrast. It would then be easy to determine the volume fraction of martensite by image analysis software. The problem of this technique is that it can only be used for martensite and is not suitable for other phases because of its low repeatability. As can be seen, the volume fractions of other colors are changed in each image. The volume fraction of the blue phase is only rather constant. Based on the Clemex image analysis calculations, the volume fractions of martensite for Figs. 5a and 5b are about 45 and 42%, respectively. This shows good repeatability of this technique for the martensite phase.

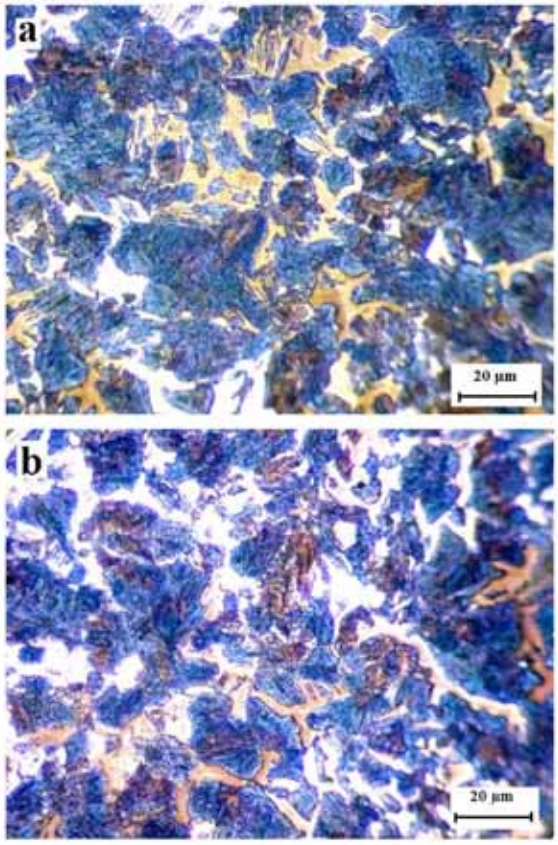

Fig. 5. Micrographs of the specimen resulted from technique (2)

Figs. 6a and b show microstructure of the as-quenched specimen after pre-etching by 4% picral followed by tint etching with 10% $Na_2S_2O_5$ aqueous solution (technique 3). As can be seen, three colors appear in the microstructures. By etching of steel with this tint etchant, bainite appears in blue, martensite in brown, ferrite in white and austenite in tin white [5,12]. Therefore, microstructure of the as-quenched steel consists of bainite, martensite and ferrite. The contrast between phases, especially martensite and bainite, is very important because of their similar shape. This technique can produce appropriate contrast between these phases. On the other hand, it has a good repeatability for all phases. The only problem of this etchant is that in the microstructure consisting of retained austenite, it is difficult to distinguish between ferrite and austenite. This problem can be solved by semi quantitative calculations of volume fraction of retained austenite using XRD pattern of specimen [13,14]. Calculations of Clemex image analysis software for Fig. 6a showed that the volume fraction of martensite, bainite and ferrite was about 44, 30 and 26%, respectively. The volume fraction of martensite resulting from this technique was similar to that in technique (2). The small difference between the volume fraction of phases predicted by this technique and CCT diagram may be due to the practical errors of austenitizing temperature and quenching operation.

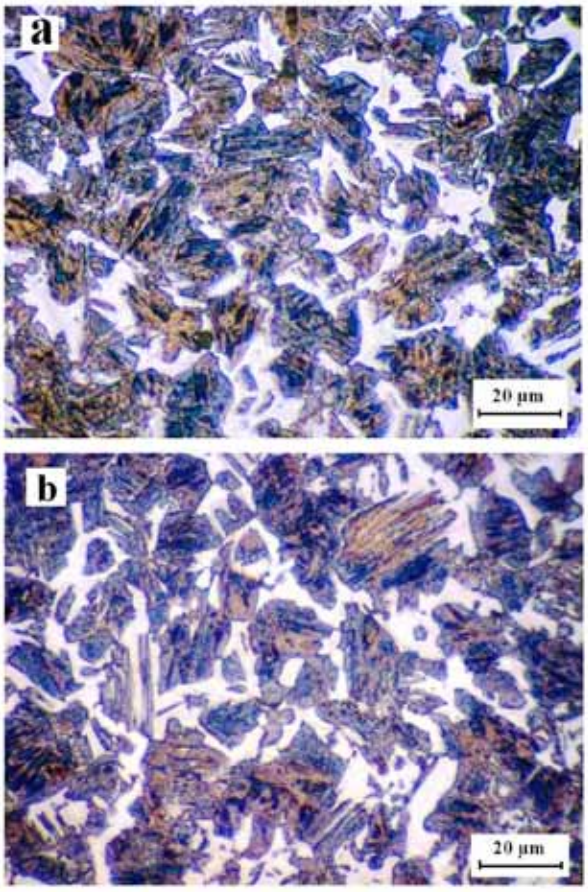

Fig. 6. Micrographs of the specimen resulted from technique (3).

The solutions used for color metallography by the above techniques work based on chemical deposition on metallic surfaces. For the balanced reagent, the corrosion products remain on the metallic surfaces and stable thin films are obtained. Depending upon the chemical composition of the color etchants, oxide, sulfide or complex molybdate films are produced on the specimen surface. Metabisulfite salt decomposes in water and produces H_2S, SO_2 and H_2 in the presence of metals. H_2S supplies S^{2-} that reacts with metallic ions causing precipitation of thin sulfide films on the surface of metallographic specimens. These sulfide films grow as a function of crystallographic orientations. The colors seen in the microscope under polarized light are due to the interference effect and different thicknesses of the sulfide films [2,11].

3-3- Nanoindentation results

Fig. 7 shows results of the nanoindentation tests carried out on individual constituents. The specimen was color etched with technique (3). The Vickers hardness values of different phases were computed from the force-penetration depth data as shown in Table 2. As can be seen, hardness of the white, blue and brown phases is about 165, 321 and 456 Vickers, respectively. A reasonable agreement can be seen between the measured hardness values with the data from literature [5]. This confirms that the white, blue and brown phases are ferrite, bainite and martensite, respectively.

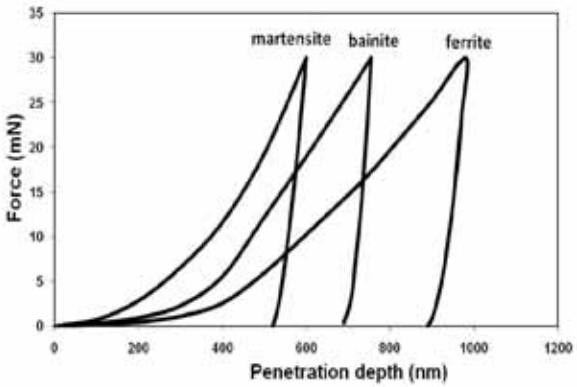

Fig. 7. The force versus penetration depth for different phases in the nanoindentation test.

Table 2. The Vickers hardness values of ferrite, bainite and martensite phases

Phase	Ferrite	Bainite	Martensite
Nanoindentation test	165	321	456
Reference [5]	< 200	305	440

4- Conclusion

In this work, three color etchants based on thiosulfate and metabisulfite salts were used for characterization of bainite and martensite in steels. The best solution for simultaneous investigation of martensite, bainite and ferrite, was found to be the 10% $Na_2S_2O_5$ aqueous solution. The specimen is first pre-etched with 4% picral and then immersed in this solution for about 15 s. The martensite, bainite and ferrite phases appear as brown, blue and colored white, respectively. Due to the good contrast between phases, the volume fraction of phases can be easily computed. The nanoindentation results of individual phases confirmed the color metallography predictions.

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