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Advantages of colour etching in quality control of graphitic cast irons

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Abstract

Graphitic cast irons are the most important and most widely used materials for the production of castings. Increasing requirements for the quality of these castings lead to increased demands on the control of foundry production from raw materials through technological operations to the finished product. An integral part of this control process is structural analysis, because the properties of graphitic cast irons depend mainly on their structure (on the shape, size and number of graphitic particles and on the character of a metal matrix in which graphite occurs).

The paper deals with the structural analysis of graphitic cast irons using the classical black and white contrast, as well as the use of colour metallography, which enables to obtain additional information about the structure of cast iron. The article contains photographs of microstructures of graphitic cast irons, obtained using black and white etching, as well as colour etching. It deals with the advantages of colour etching compared to the use of classical black and white methods.

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1. Introduction

Cast iron is a cast alloy of iron, carbon and accompanying elements, eventually alloying elements, which is made by remelting pig iron, steel scrap and other additives. For differentiation from steel, cast iron is defined as an alloy in which the carbon content exceeds the limit value of carbon solubility in austenite and thus ensures the solidification of the final phase with eutectic transformation. Eutectic crystallization is crucial for the basic division of cast irons according to structure into white and graphitic. In white cast iron, eutectic crystallization takes place under conditions of metastable equilibrium (according to the iron – cementite diagram) and its product is ledeburite. However, the practical use of white cast irons is very limited; graphitic cast irons are more important. In graphitic cast irons, eutectic transformation takes place under conditions of stable equilibrium (according to the iron – carbon diagram) and one of its products is graphite. Graphite can occure in a flake shape (lamellar cast iron), worm shape (vermicular cast iron) or spheroidal shape (nodular cast iron) (Skočovský, 2005).

The microstructure of graphitic cast irons consists of graphite and a metal matrix, which is most often formed by different content of ferrite and pearlite, but (depending on the chemical composition and heat treatment) it may also contain bainite (ausferrite), martensite or austenite. Moreover, other phases may be present in the microstructure, e.g. carbide of iron (cementite) or other types of carbides and phosphidic eutectic (steadite). All these structural components can be observed and evaluated by light metallographic microscopy.

Light metallographic microscopy is a basic method of studying the structure of metals, which allows the observation of structural components on the planar cut of a specimen with a size of one to hundreds of μm. This interval includes all crucial structural components in graphitic cast irons, therefore light metallographic microscopy is essential for the study and evaluation of the microstructure of these materials. The properties of graphitic cast irons depend mainly on their microstructure (on the shape, size and count of graphitic particles and on the character of the metal matrix), therefore the microstructural analysis of cast irons is an integral part of the quality control of castings (Skočovský, 2007).

The condition for distinguishability of individual structural formations is the optical contrast between them. The most commonly used method of structure visibility (contrast enhancement) is etching. The classical black and white etching creates a microrelief on the surface of the cut, which gives a different representation of the phases and interfaces between them in the reflected light (Fig. 1a) (Skočovský, 2007).

The information obtained by black and white contrast can in some cases be significantly extended by using the colour contrast of structural components, which can be achieved in several ways. The most important way for developing colour contrast in metallographic microscopy is colour etching. The reaction between the surface of the metallographic cut and the colour etchant leads to the formation of a transparent film which has the function of an interference coating. If the observed specimen is covered with a transparent film, interference of light arises due to the division of the reflected light into components reflected at the air – coating interface and at the metal – coating interface.

The thickness of the transparent interference coating, resulting from the effect of the colour etchant, will change depending on the chemical composition of the microlocality, and consequently, the colour of the individual microlocalities will also change (Fig. 1b) (Skočovský, 2001).

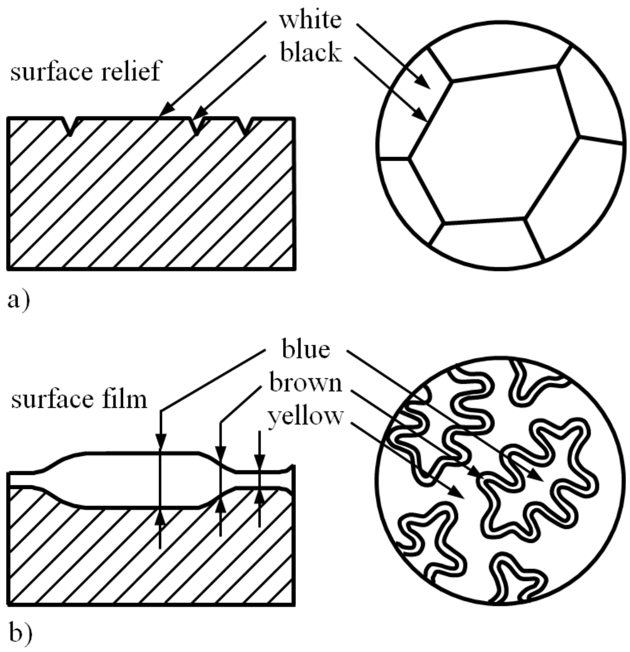


Fig. 1. Principles of etching;
a) black and white etching, b) colour etching

Chemical composition of the etchant and etching time are chosen so that it is possible to create (in a reproducible manner) coatings with a varying thickness in the range of approximately 100 to 150 nm, using the dependence of the coating thickness on the chemical composition of the investigated structural components. During etching, chemical reactions occur between the specimen and the etchant, and their time course can only be checked visually (according to the colour of the specimen).

2. Experimental material and methods

Structural analysis was performed on specimens of different types of graphitic cast irons. The observed specimens of cast irons differ in the shape of graphite and the character of matrix. Graphite in the specimens occures in a flake shape (lamellar cast iron), worm shape (vermicular cast iron) or spheroidal shape (nodular cast iron). Matrix is composed of ferrite and/or pearlite, bainite (ausferrite) or austenite. In some specimens, other phases such as carbides and phosphidic eutectic are also present.

Mechanical properties of the cast irons used for these experiments are not presented in the paper because they do not have a direct effect on used etchants. The etchant is not chosen according to the properties of the cast iron but according to the character of structure and the purpose of the investigation.

Specimens for metallographic analysis were prepared by a conventional metallographic procedure consisting of cutting the specimen, preparation, grinding, polishing and etching. The procedure for preparing metallographic specimens is described in detail in the literature (Geels, 2007; Konečná, 2014; Radzikowska, 2015; Weidmann, 2019).

The contrast between the individual structural components was achieved using classical black and white etching, as well as colour etching. Metallographic analysis of the specimens was carried out on the light metallographic microscope Neophot 32 with a digital camera Nikon DS-Fi3 and an image analyzer NIS-Elements AR 5.20.

For etching graphitic cast irons, there are many etchants with different possibilities of use in structural analysis (Petzow, 1999; Radzikowska, 2000; Radzikowska, 2004; Vander Voort, 2004; Vander Voort, 2005; Vander Voort, 2010; Zhou, 1993; Zhou, 2009 a,b,c; Zhou, 2010 a,b,c,d). Selected etchants suitable for etching graphitic cast irons are listed in Tab. 1. The particular etchant is chosen according to the type of examined cast iron and according to the purpose of the examination (Skočovský, 2007).

The most common etchant for cast irons is Nital. It is used for etching of microstructure in general; it is suitable for microstructures containing ferrite and/or pearlite, cementite or phosphidic eutectic. For heat-treated cast irons, picric acid is used. To distinguish bainite from martensite, it is convenient to use a mixture of Nital and picric acid. In some cases, it is quite difficult to distinguish phosphidic eutectic from cementite, for which Murakami etchant can be used. Stead etchant is suitable for making the boundaries of eutectic cells visible in cast irons containing a higher phosphorus content. In cast irons with higher purity, colour etching with sodium picrate or sodium chromate is used for the same purpose. These etchants enable to etch the macrostructure and to make visible the segregation of main elements. Klemm I etchant is also used to visualise the segregation of main elements (e.g. silicon and manganese) dissolved in a solid solution. Beraha-Martensite etchant is suitable for distinguishing between bainite and martensite in heat-treated cast irons (Skočovský, 2007; Kardos, 2013; Vazehrad, 2015; Weilnhammer, 2017; Varman, 2018; Renkó, 2020; Schaberger, 2000).

Table 1. Selected etchants for graphitic cast irons

Etchant/ Composition	Use
1% Nital 1.6 ml nitric acid 99.4 ml ethanol	microstructure in general, ferritic and ferrite-pearlitic matrix
4% Nital 6.4 ml nitric acid 93.6 ml ethanol	microstructure in general, pearlite-ferritic matrix, phosphidic eutectic
Picric acid 4 g picric acid 100 ml ethanol	microstructure in general, pearlitic and bainitic matrix
Picric acid + Nital 1 g picric acid 95 ml ethanol 2 to 5 drops of 4% Nital	distinction between bainite and martensite
Stead 10 g copper chloride 40 g magnesium chloride 20 ml hydrochloric acid the rest up to 100 ml ethanol	eutectic cell boundaries
Murakami 5 g potassium ferrocyanide 25 g potassium hydroxide 70 ml distilled water	phosphidic eutectic
Sodium picrate 25 g sodium hydroxide 5 g picric acid 75 ml distilled water	macrostructure of lamellar cast irons, phosphidic eutectic (colour)
Sodium chromate 35 g sodium hydroxide 5 g chromium oxide 100 ml distilled water	macrostructure of quality types of cast irons (colour)
Klemm I 100 ml of basic solution Klemm (saturated aqueous solution of sodium thiosulphate) 2 g potassium pyrosulphite	segregation of main elements, e.g. silicon and manganese (colour)
Beraha-Martensite 2 g potassium pyrosulphite 2 g ammonium hydrogen-difluoride 100 ml of basic solution BWI (5 parts distilled water + 1 part hydrochloric acid)	distinction between bainite and martensite (colour)

3. Experimental results and discussion

For structural analysis of the specimens of graphitic cast irons, the black and white etchants and colour etchants listed in Tab. 1 were used. The following photographs show those etchants that best achieved the desired effect. The other etchants did not bring anything new compared to these etchants or brought a worse result. However, these etchants may give the desired result for other types of cast irons or for a different purpose of observation.

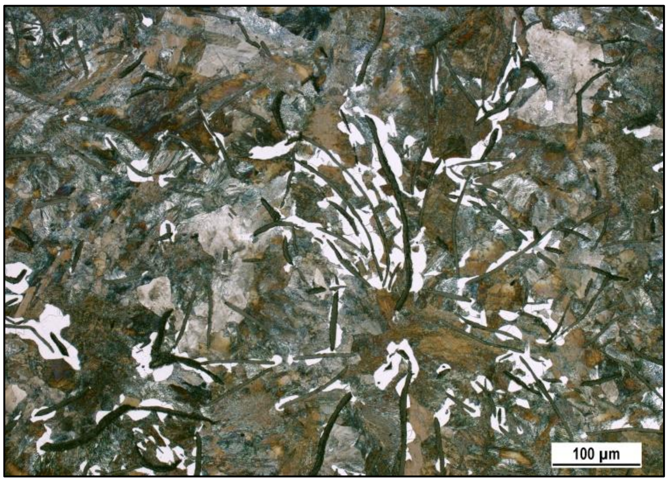
The microstructures of graphitic cast irons etched by conventional etchants for black and white contrast are shown in Fig. 2. The microstructures of graphitic cast irons etched by colour etchants are given in Fig. 3 and 4.

The basic etchant for black and white etching is Nital, which is used to distinguish ferrite and pearlite in the matrix. In the case of heat-treated cast irons, picric acid or a combination of picric acid with Nital are used, which allows to distinguish bainite and martensite. Etchant Beraha-Martenzit is suitable for the same purpose (distinguishing bainite from martensite), and it is also used for colour etching.

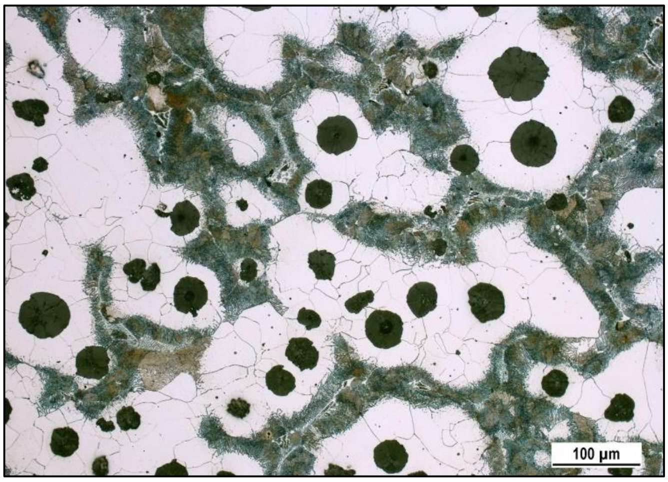
The microstructure of lamellar cast iron etched by 3% Nital (Fig. 2a) consists of a small ratio of ferrite (white colour), a large ratio of pearlite (gray colour) and flake graphite (black colour) with a uniform distribution. The microstructure of nodular cast iron etched by 1% Nital (Fig. 2b) has a higher ratio of ferrite (white colour), a smaller ratio of perlite (gray colour) and spheroidal graphite (black colour). The use of picric acid did not provide any new information about the microstructure of these specimens. Etchant Beraha-Martenzit was used for isothermally heat-treated nodular cast iron (referred to ADI) (Fig. 2c). The microstructure contains bainite (ausferrite) (gray-blue colour), retained austenite (white colour) and spheroidal graphite (gray colour), without the presence of martensite.

The use of colour etching (Fig. 3) can provide new information about the microstructure of graphitic cast irons. Sodium picrate and sodium chromate are used to etch the macrostructure; both etchants are suitable for all types of cast iron. Sodium picrate is a classical etchant for developing the primary structure of cast iron based on the segregation of phosphorus and other elements. It is also used to distinguish cementite from phosphidic eutectic. Sodium chromate is sensitive to the segregation of major elements and thus emphasizes the boundaries of eutectic cells. Etchant Klemm I shows the segregation of main elements (silicon and manganese) dissolved in a solid solution.

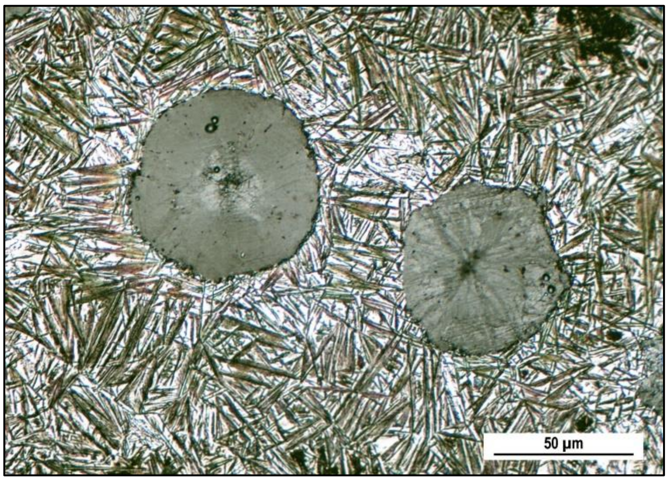
Lamellar cast iron etched by sodium chromate (Fig. 3a) has a colour contrast formed by a spectrum of colours from light yellow through red to brown. The pearlitic matrix is yellow-red, with the red colour indicating the boundaries of the eutectic cells. In nodular cast iron etched by sodium chromate (Fig. 3b), a spectrum of colours from white through light blue and dark blue to brown-red was observed. There is a light blue ferrite around the graphitic particles, the pearlitic part of the matrix is brown. In both cases, it is possible to observe the segregation of main elements. After etching by Klemm I (Fig. 3c), the colour of the matrix changes from white through light brown and dark brown to blue, which is caused by the segragation of main elements dissolved in ferrite. Silicon content is highest near the graphitic particles (white colour) and lowest in the spaces between these particles (blue colour). The segregation of manganese is inverse (the lowest content near the graphitic particles).



a) pearlite-ferritic lamellar cast iron, etched by 3% Nital

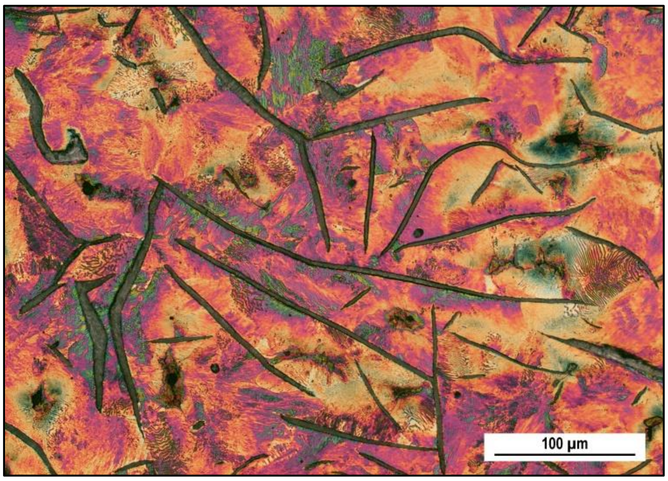


b) ferrite-pearlitic nodular cast iron, etched by 1% Nital

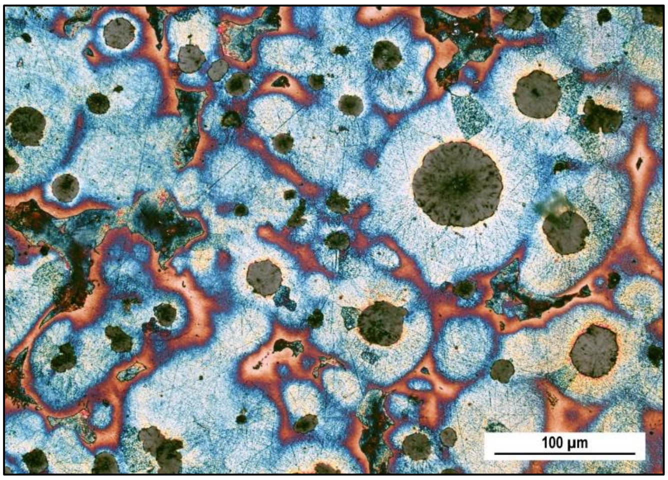


c) ausferritic nodular cast iron (ADI), etched by Beraha-Martensite

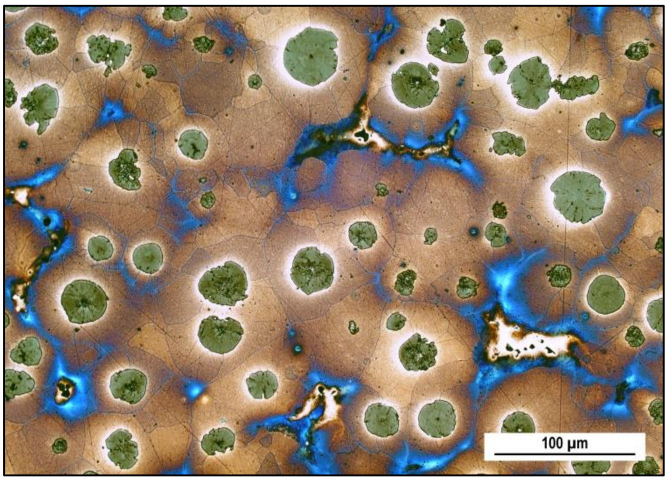
Fig. 2. Microstructure of graphitic cast irons in black and white contrast



a) pearlitic lamellar cast iron, etched by sodium chromate



b) ferrite-pearlitic nodular cast iron, etched by sodium chromate

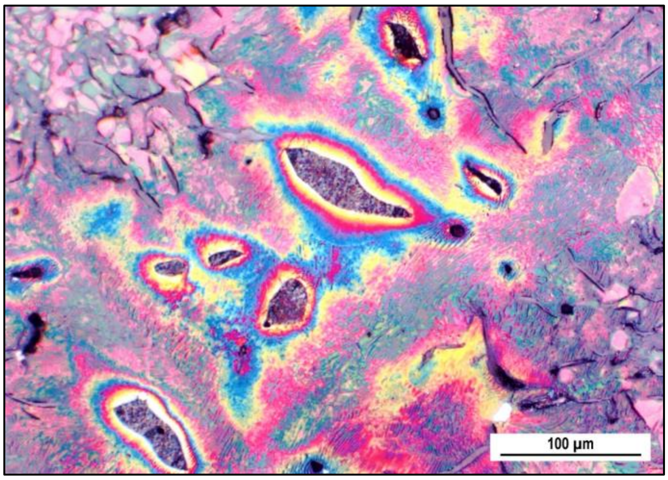


c) ferrite-pearlitic nodular cast iron, etched by Klemm I

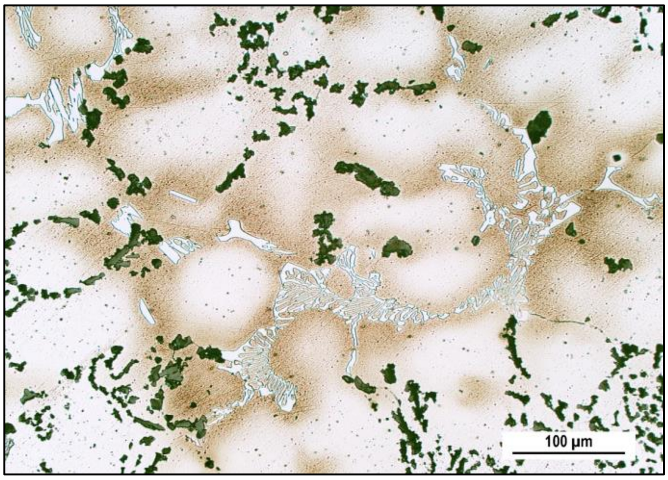
Fig. 3. Microstructure of graphitic cast irons in colour contrast

Colour etching can also be used to differentiate phosphidic eutectic, cementite or other carbides. The microstructure of lamellar cast iron etched by sodium picrate (Fig. 4a) consists of flake graphite (black colour) and pearlitic matrix (purple colour) in which phosphidic eutectic (bordered in yellow) occurs. To distinguish between phosphidic eutectic and cementite, sodium picrate can be used as a selective etchant that colours the phosphidic eutectic and leaves the cementite particles white.

In some cases, it is also possible to use such etchants which are not directly intended for etching cast irons. For example, Kalling´s 2 etchant (5g copper dichloride, 100 ml hydrochloric acid and 100 ml ethanol) is primarily intended for etching stainless steels and nickel alloys. However, it can also be used for etching austenitic nodular cast iron alloyed by nickel and chromium (Fig. 4b). This etchant enables to distinguish carbides (white colour) from Chunky graphite (black colour) and austenitic matrix (beige colour).



a) pearlitic lamellar cast iron, etched by sodium picrate



b) austenitic nodular cast iron (with Chunky graphite), etched by Kaling´s 2

Fig. 4. Microstructure of graphitic cast irons in colour contrast

The specific etchant should be chosen according to the type of examined cast iron (i.e. according to its microstructure) and according to the purpose of the examination, e.g. whether it is necessary to distinguish structural components in the matrix (ferrite and pearlite, bainite and martensite, carbides and phosphidic eutectic etc.), to emphasize the boundaries of eutectic cells, or to make visible the segregation of main elements (silicon, manganese, phosphorus etc.) in solid solutions. When choosing an etchant, it is recommended to follow the information given in Tab. 1 (column Use). In some cases, it is necessary to try several types of etchants before the desired effect is achieved.

4. Conclusion

The information about the microstructure of graphitic cast irons obtained by the classical black and white contrast can in many cases be significantly extended by using the colour contrast of structural components, which can be obtained, for example, by colour etching.

Colour contrast in the structural analysis of graphitic cast irons is relatively little used, despite the fact that the basic methods of its developing and enhancing are known and summarily described in the technical literature. The basic structural components can also be distinguished using classical black and white metallography, but the colour contrast between microlocalities allows, for example, to distinguish phases (eventually the significant segregation in a solid solution) which are difficult to distinguish when using black and white contrast, or cannot be distinguished at all.

The colour etching of metallographic specimens enables mainly to enhance the differences in the chemical composition of microlocalities, therefore it is suitable for the study of segregation phenomena, heat-affected zones, diffusion layers and for distinguishing phases with significantly different chemical composition.

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彩色蚀刻在石墨铸铁质量控制中的优势

關鍵詞
铸铁
微观结构
黑白蚀刻
彩色蚀刻
蚀刻剂

摘要
石墨铸铁是生产铸件的最重要和最广泛使用的材料。对这些铸件质量的要求越来越高，导致对从原材料到技术操作再到成品的铸造生产控制的要求越来越高。该控制过程的一个组成部分是结构分析，因为石墨铸铁的性能主要取决于它们的结构（取决于石墨颗粒的形状、大小和数量以及石墨所在的金属基体的特性）。 本文使用经典的黑白对比，以及使用彩色金相法来处理石墨铸铁的结构分析，从而获得有关铸铁结构的更多信息。该文章包含使用黑白蚀刻和彩色蚀刻获得的石墨铸铁微观结构照片。与使用经典的黑白方法相比，它处理了彩色蚀刻的优点。