

A New Look At Cast Iron Microstructure

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Cast irons belong to a family of iron-carbon (Fe - C) alloys with free carbon in the form of graphite, a very soft constituent of iron microstructures, that improves machinability and damping properties of castings, or combined carbon, in the form of cementite, that improves wear resistance. Graphitic cast irons include grey iron, compacted iron, malleable iron, and ductile iron. Cementite irons include white cast iron and alloy cast irons. Solidification of graphite directly from molten metal takes place between 1145 °C (2093 °F) and 1152 °C (2105 °F), according to the Fe - C equilibrium diagram. The above considerations regard only pure Fe - C alloys. In cast iron, a multicomponent alloy, these temperatures are affected by

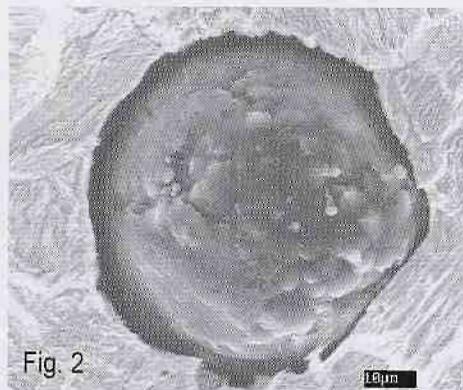
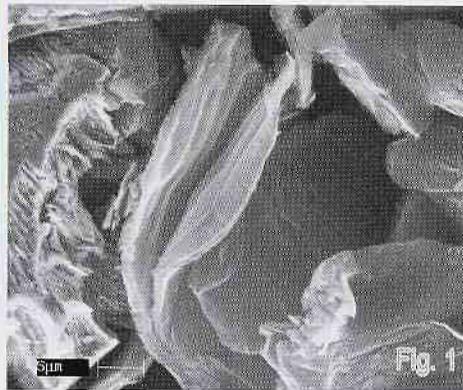
Specimen preparation

Metallographic specimens must be properly prepared for the examination of microstructure. After cutting pieces from a casting or tensile test bar, they are embedded in the proper polymeric resin, automatically or manually ground on water-cooled SiC grit papers, and polished using different cloths. Several sizes of diamond paste with progressively finer particle sizes are followed by final polishing using an aqueous alumina slurry with a very fine (~0.05µm particle size).

Microexamination methods

Examination of cast iron microstructures with the light optical microscope is always the first step for phase identification and morphological studies. One should always begin microstructural investigations by examining the as-polished specimen. This is a necessity, of course, for cast iron specimens, if we are to properly examine the graphite phase.

The shape of graphite is a characteristic property of each type of cast iron, e.g., flake graphite in gray cast iron and spheroidal graphite in ductile cast iron. The names for white and gray iron come from the color of the fractured casting. Contrary to graphite flakes that solidify as aggregates, and each such agglomeration is bounded by one eutectic cell, spheroidal graphite solidifies as separate precipitates with a nearly perfect spherical form in 3D. The "ductile" name for cast iron with nodular graphite particles comes from its better mechanical properties compared to



different factors, e.g., chemical composition and the cooling rate during solidification of the casting. Components such as silicon and carbon promote graphitization as do low cooling rate, which is characteristic for thick wall castings. Depending on chemical specifications, cast irons may be non-alloyed or alloyed. The composition range for alloyed irons is much wider and they contain either higher amounts of common components, like silicon and manganese, or special additions, such as nickel, chromium, molybdenum, tungsten, vanadium, copper, titanium, plus others.

gray cast iron.

Eutectic cells are the elementary units for graphite solidification. Graphite within a eutectic cell has a continuous skeleton, but on the 2D surface of a metallographic specimen this is not always obvious. Figures 1 and 2 show, respectively, three-dimensional graphite flakes in gray cast iron and a graphite nodule in ductile iron; both examples were examined with the scanning electron microscope. The specimens were deeply etched with a 50% aqueous solution of hydrochloric acid (HCl) to chemically dissolve the matrix surround-

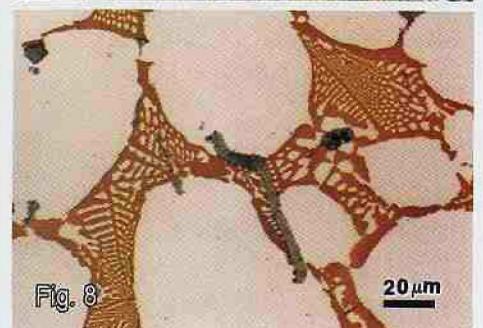
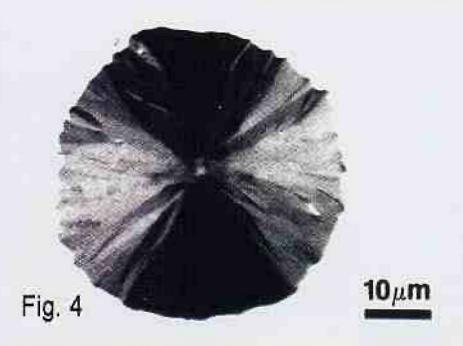
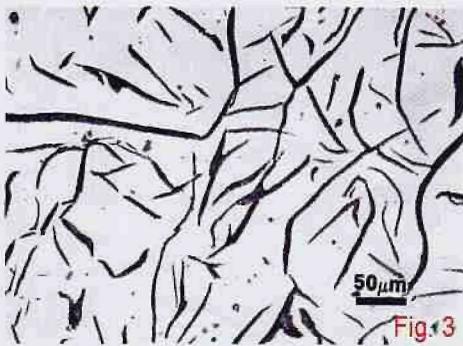




Fig. 9

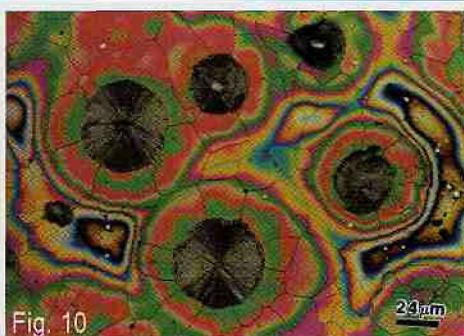


Fig. 10



Fig. 11

ing the graphite precipitates to reveal its 3D shape. Figures 3 and 4 show as-polished, flat cross sections through these two types of graphite structures, as observed with the light optical microscope.

After graphite crystallization, the rest of the metal solidifies during cooling to form the matrix. The most typical constituents of the matrix microstructure in non-alloyed and low alloyed cast irons are: pearlite and ferrite; the amounts can vary from fully ferrite to nearly all pearlite. In cases where, the cooling rate during solidification is too high, as in thin wall castings, free cementite or Ledeburite can form instead of graphite. Cementite is a very hard phase that reduces machinability but, on the other hand, imparts wear resistance, which sometimes can be a desired property of cast iron. A phosphorous eutectic known as "Steadite" is a characteristic constituent of gray cast iron microstructures. It solidifies at the cell boundaries, in the last liquid metal, when the phosphorus content exceeds 0.06%. It is hard and brittle and can be a ternary eutectic, consisting of ferrite, cementite and iron phosphide, or a binary eu-

ing shape and size of carbides. They are hard and fragile phases and protrude slightly from the softer matrix that is observed at the surface of metallographic specimens. The matrix of high chromium cast irons, containing over 15% Cr, can be ferritic, austenitic or a mixture of these two phases with the austenite having a dendritic form. During cooling, eutectic carbides solidify in hypoeutectic alloys in the interdendritic spaces, forming a complex interconnected space lattice. Figure 12 shows the microstructure of such a cast iron, containing 1.6% C, 18.64% Cr and 2.86% Mn, after etching with glyceric acid. The higher content of Cr and C promotes solidification of carbides in the shape of long hexagonal rods. They are called "primary" and can occur in a cast iron containing, e.g., 3.0% C and 35% Cr, with a ferritic matrix. Glyceric acid is a mixture of glycerine, hydrochloric acid (HCl) and nitric acid (HNO₃) and is recommended for revealing the microstructure of high-chromium white irons. During etching, the boundaries of carbides are revealed, while the matrix remains colorless.

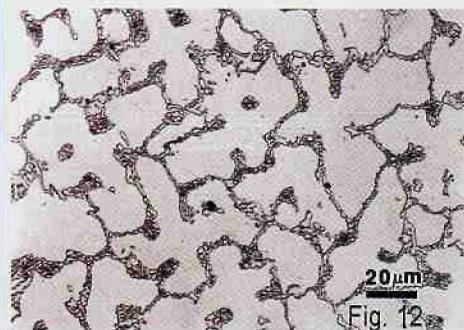


Fig. 12

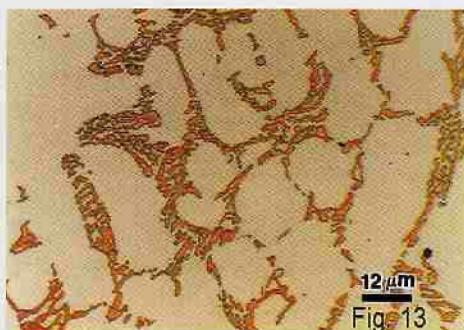


Fig. 13

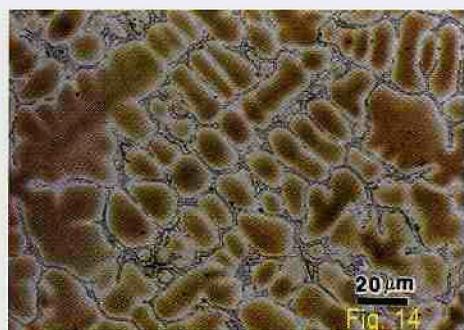


Fig. 14

tectic with ferrite and iron phosphide, depending on the amount of phosphorus and silicon.

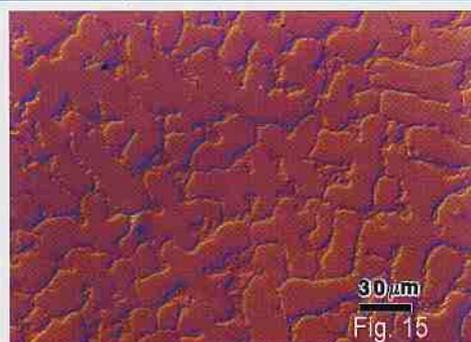
Chemical etching

Specimens must be etched to see the microstructure of the cast iron matrix. The standard "black and white" etching method is based on a chemical corrosion process and has been used by metallographers for many years. Nital, a 2 - 4% alcoholic solution of nitric acid (HNO₃), is commonly used for revealing the microstructural constituents mentioned above. Figure 5 shows the microstructure of ductile iron with "colored" pearlite, while the precipitations of cementite and Ledeburite remain white. Pearlite is a mixture of cementite and ferrite, which solidifies in a lamellar form. The corrosion resistance of ferrite is weaker than cementite, so nital produces dissolution of the ferrite lamellae with the cementite lamellae in relief. If the interlamellar spacing is small, light scattering from the etched structure will make pearlite dark and look like a single phase (*i.e.* the lamellae are not resolved). The colors of pearlite are the result of the chemical reaction between the etchant and metal (ferrite).

To achieve a friction wear resistant cast iron, chromium (Cr) is added to Fe-C alloys and carbon is combined in chromium carbides. These carbides have different chemical formulas with vary-

Selective color etching

More information about the details of cast iron microstructures is obtained by use of the selective color etching method. The reagents, generally referred to as "tint" etchants, are usually acidic solutions with either water or alcohol as the solvent. They are chemically balanced to deposit a thin (40 to 500 nanometers) transparent film of oxide, sulfide, complex molybdate, elemental selenium, or chromate, on the sample surface. Coloration is developed by interference between light rays reflected at the inner and outer film surfaces. Crystallographic orientation, local chemical composition, and etching time effect film thickness and control color production. Figure 6 shows the microstructure of gray cast iron after etching with 4% nital: the white areas look like the binary phosphorous eutectic, while the rest of the matrix is pearlite with small white patches of ferrite at the graphite precipitates. The use of hot, alkaline sodium picrate reveals the small amount of cementite in the ternary phosphorous eutectic, tinting this phase into dark blue and brown colors, Fig. 7. This is obtained from the application of an aqueous solution of sodium hydroxide (KOH) and picric acid; note that it does not color ferrite or iron phosphide. Figure 8 shows that hot Murakami's reagent (potassium hydroxide (KOH), potassium ferricyanide [K₃Fe(CN)₆]



and distilled water) tints only iron phosphide, Fe_3P ; the rest of the phases in the iron microstructure remain colorless. This dual etching technique enables us to estimate the amount of each constituent in Steadite.

To reveal the very strong silicon segregation in ductile iron that occurs during solidification, different selective color etchants can be used. One is Beraha's CdS etchant, which is an aqueous solution of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), citric acid ($C_6H_8O_7 \cdot H_2O$) and cadmium chloride ($CdCl_2 \cdot 2.5H_2O$). Figure 9 shows the microstructure of austempered ductile iron (ADI): a ductile iron given an "austempering" heat treatment to produce a matrix of acicular ferrite and austenite. The regions outlining the cell boundaries (low in silicon content) are tinted into a blue color, while the thin "halos" around the graphite nodules (where the silicon content is highest) remain colorless. Acicular ferrite is orange and austenite is not tinted.

Use of a hot aqueous solution of sodium hydroxide (NaOH), picric acid and potassium pyrosulfite ($K_2S_2O_5$) reveals information about silicon segregation inside the eutectic cells of non-alloyed ductile iron. Figure 10 shows the different colors of microstructure that change from green through red, yellow, blue, and dark brown to light brown as the silicon content changes going from the graphite nodule to the cell boundaries. The regions with lowest silicon content at the cell boundaries remain colorless. The as-cast microstructure was pearlitic, but before selective etching, the specimen was given a heat treatment, called "ferritisation," that enhanced the visibility of the microstructural colors that arise as a result of silicon segregation.

When a casting is heated to temperatures around 900 - 1000 °C (1652 - 1832 °F) and then rapidly cooled in water (or in oil or air for certain chemical compositions), the microstructure transforms to martensite, with an "acicular" form. The non-transformed microstructure is residual austenite. That type of heat treatment is called "quenching" and makes the casting hard and brittle, but also wear resistant. Estimation of the amount of residual austenite, which is softer than martensite, is very important. Good results in differentiation of these two constituents are achieved by selective color etching. Figure 11 shows a martensitic-austenitic matrix microstructure after etching with a 10% aqueous solution of sodium metabisulfite ($K_2S_2O_5$). The martensite "needles" are tinted, while the residual austenite remains colorless and is clearly visible.

When estimation of the amount and morphology of carbides by a quantitative method is desired, better results are achieved when the carbides are tinted. Figure 12 shows the microstructure of a chromium white cast iron after etching with glyceric acid, while Fig. 13 shows the same microstructure with carbides that are tinted orange with Murakami's reagent (used by immersion at the room temperature).

When white chromium cast iron contains substantial nickel (Ni), microsegregation of chemical elements occurs inside the austenitic dendrites and can be revealed with the LB I reagent, an aqueous solution of ammonium difluoride ($NH_4F \cdot HF$) and potassium metabisulfite ($K_2S_2O_5$). In chromium-nickel alloys, LB I tints

austenite, while carbides and ferrite (if present) remain unaffected (white). Figure 14 shows dendritic segregation in the microstructure of Fe-Cr-Ni cast iron: the white areas at the edges of dendrites, enriched with silicon and chromium, may be ferrite, as they both promote solidification of this phase. The rest of the dendrite areas, tinted brown, are austenite.

Differential interference contrast and polarized light

Optical techniques other than bright field illumination (BFI) can be used with the optical metallographic microscope to produce color. One such technique is differential interference contrast (DIC). When crossed polarized light is employed along with a double quartz prism (Wollaston prism), placed between the objective and the vertical illuminator, two light beams are produced that exhibit coherent interference in the image plane. This leads to two slightly displaced (laterally) images differing in phase ($\lambda/2$) that produces higher contrast for non-planar detail. This is called differential interference contrast. The difference in hardness, if appreciable, can be used to reveal phases by introducing relief on the surface of the metallographic specimen during final polishing. Although this relief may be too small to be observed in BFI, it can be enhanced and revealed using DIC. Figure 15 shows the microstructure of the same alloyed white cast iron specimen, as in Fig. 12, but as-polished and examined with DIC. The much harder chromium carbides protrude from the matrix and can be seen very well without etching.

In the polarized light technique, polarizer and analyzer filters are placed in the crossed position, and a sensitive tint plate (lambda plate) may be inserted to further enhance coloration that may be adjustable. This method improves the contrast of certain microstructures, providing more structural details. Figure 16 shows the microstructure of as-polished ductile iron. The radial structure of a graphite nodule that grows from a central "nucleus," is clearly visible. Also, the "crosses" inside graphite precipitates, which are characteristic of perfectly formed nodules, are visible only in polarized light. Figure 17 shows in polarized light the microstructure of austempered ductile iron after etching with 4% nital. The patches of acicular microstructure have different colors due to different crystal lattice orientations, which is not visible with traditional bright field illumination.

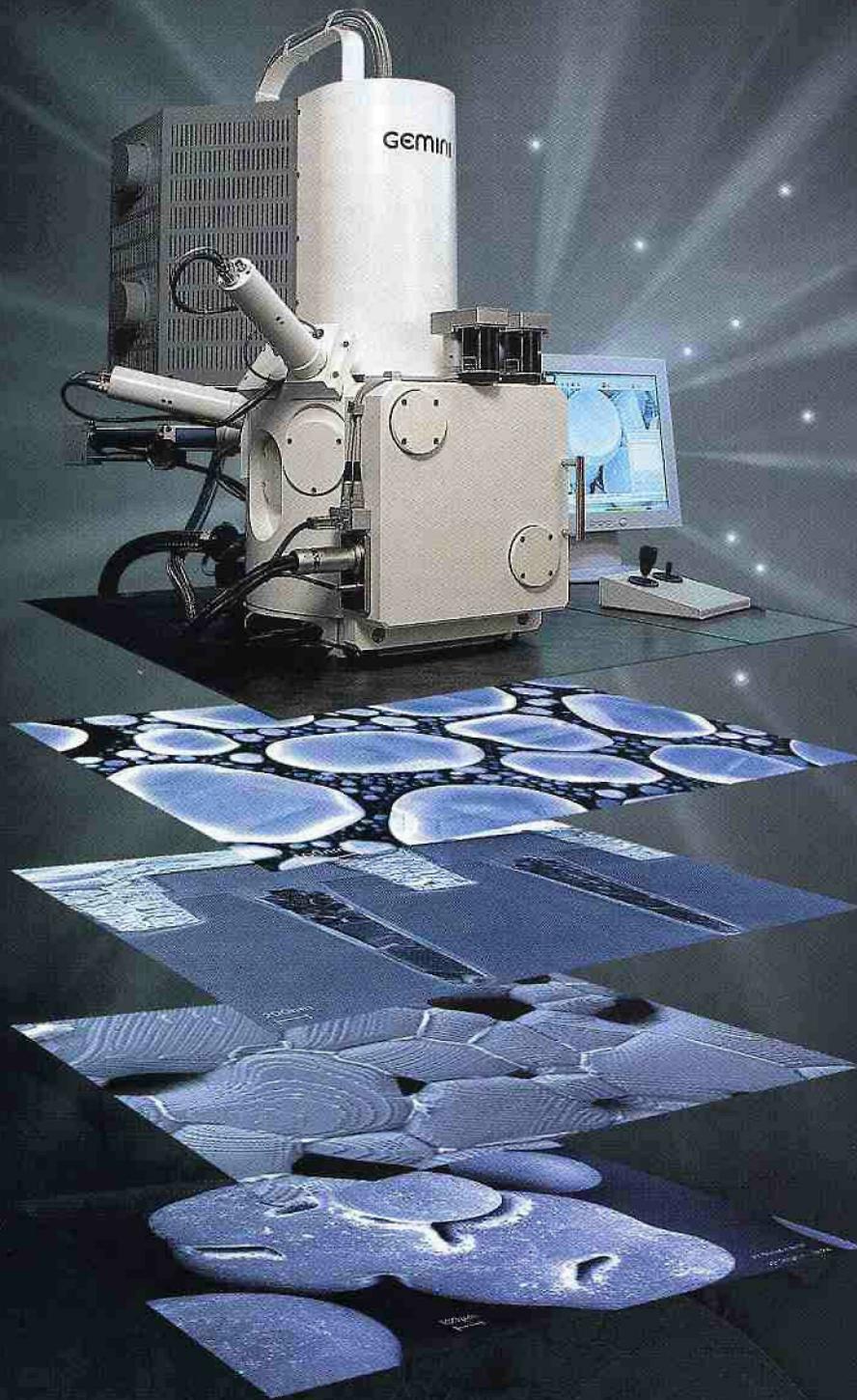
This article has shown how the use of different "color" techniques for light optical microscopic examination of cast iron microstructures revealed more details than the traditional B&W etching methods. The beauty of cast iron microstructures, which can be very colorful, may be revealed, bringing joy to metallographers who decide to extend the range of their investigation methods. ■

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