TECHNotes

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Microstructure of Ferrous Alloys

Introduction

The microstructure of iron-based alloys is very complicated and diverse, being influenced by composition, homogeneity, processing and section size. Microstructures of castings look different than those of wrought products, even of the same composition and if given the same heat treatment. In general, it is easiest to identify heat-treated structures after transformation and before tempering. For example, if a mixed microstructure of bainite and martensite is formed during quenching, these constituents will become more difficult to identify reliably as the tempering temperature given the product increases towards the lower critical temperature. Further, while ferrous metallographers tend to use nital almost exclusively for etching, nital is not always the best reagent to use to properly reveal all microstructures. It is unfortunate that some companies prohibit use of picral because picric acid can be made to detonate under certain conditions. Picral is an excellent etchant for revealing certain microstructural constituents in steel and accidents have been less common than for nital. Vilella's reagent, which also contains picric acid, is also exceptionally valuable for certain compositions and microstructures. 10% sodium metabisulfite in water (10% SMB) is a very good general-purpose reagent for steels, and safer to use than nital or picral, with a combination of the capabilities of both nital and picral.

Terminology

There is a need to discuss the terminology describing the constituents in ferrous alloys, as there is confusion regarding certain terms and misusage. Certain terms, such as sorbite and troostite, were dropped from the metallographic lexicon in 1937 because they referred to microstructural constituents inaccurately. However, such terms are still occasionally used. The term phase is often used incorrectly in reference to mixtures of two phases, such as pearlite or bainite. A phase is a homogeneous, physically distinct substance. Martensite is a phase when formed by quenching but becomes a constituent after tempering as in decomposes from bct martensite to bcc ferrite and carbides. In the process of describing and illustrating various phases and constituents in ferrous alloys, definitions will be given.

Specimen Preparation

Preparation of steel must be done in such a way to ensure the microstructure is not altered by thermal nor mechanical aspects of the process. Sectioning is most commonly done with abrasive cutters. Sectioning blades employ alumina abrasive and must be relatively soft bonded to ensure the blade bond breaks down efficiently to expose fresh abrasive for cutting throughout the cut. Adequate coolant is essential; good quality coolant prevents thermal damage and enhances free cutting of the blade. Buehler's AbrasiMet line of abrasive cutters are particularly suitable for cutting steel and offer various degrees of automation and sample size capability depending on needs. Mounting is most commonly done using a compression molding press such as the SimpliMet 4000. Cast media can be used in the absence of a mounting press. In which case, good quality epoxy if preferred over acrylic as epoxy exhibits improved edge retention and less shrinkage than acrylic.

Grinding and polishing of ferrous metals is generally straightforward. CarbiMet silicon carbide paper is very effective for grinding, though fixed-abrasive diamond discs, such as the DGD Color, may be used in cases where longer useful life of the grinding surface is desired. Begin grinding with the finest grit that will plane samples within approximately two minutes. For steel, this is perhaps most commonly 320-grit; this will depend on sample size and the number of samples prepared at one time. Coarser grit such as 240 or 180 may be necessary in some cases.

For optically scratch-free surface finish suitable for microscopic examination, three polishing steps are employed after grinding. Wash samples and the specimen holder between steps to ensure cross-contamination of abrasives does not occur. Store polishing cloths in a cabinet away from locations where debris may contaminate the surface. After the fine polishing step, rinse samples under the tap and spray with ethanol or IPA then dry. A suitable preparation procedure is given in figure x.

The AutoMet grinder-polisher is particularly suited for high-volume applications where dozens of samples are prepared daily. For lower volumes, the EcoMet 30 is an excellent option and offers manual and automated preparation.

For more information the preparation of ferrous alloys and other materials, visit our **Metallographic Preparation Solutions by Materials webpage**.

Etchants

If steels are to be examined for inclusions or nitrides, do not etch the specimens. To see the other microstructural constituents, etching is needed. Nital, usually 2%, is most commonly used. It is excellent for revealing the structure of martensite. Nital is also very good for revealing ferrite in a martensite matrix and for revealing ferrite grain boundaries in low-carbon steels. Picral is better for revealing the cementite in ferritic alloys and the structure of ferrite-cementite constituents, pearlite and bainite. Nital and picral both dissolve ferrite but nital's dissolution rate is a function of crystal orientation while picral's rate is uniform. Aqueous sodium metabisulfite reveals ferrite grain boundaries, will color some of the ferrite grains (some stay white), reveals pearlite and bainite much like picral but also etches martensite nicely, as-quenched or tempered. Other reagents have their uses, especially when dealing with higher alloy grades, such as tool steels and stainless steels, or when trying to selectively reveal certain constituents or prior-austenite grain boundaries. Etchants for steels are listed in many standard textbooks and handbooks, and in ASTM E 407.

There are also "tint" etchants that can be used to color specific constituents in steels. These can be quite useful for identifying constituents, for studying grain size, and for detecting segregation and residual deformation.

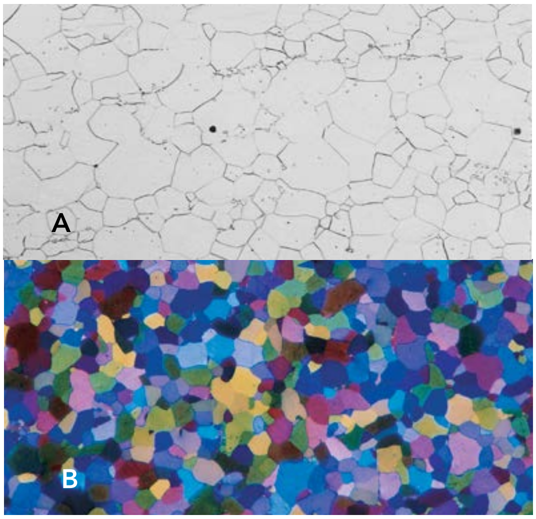

Figure 1. Ferrite grain structure of two low-carbon sheet steels: a) revealed with 2% nital (500x) and b) revealed with Klemm's I color etch (polarized light plus sensitive tint, 100x).

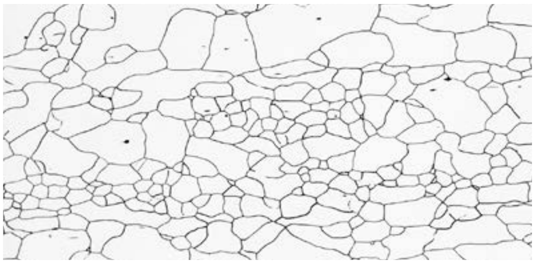

Figure 2. Ferrite grain structure of a ferritic stainless steel (Fe – <0.01% C – 26% Cr – 1.2% Mo – 0.035% Nb – <0.015% N) electrolytically etched with aqueous 60% nitric acid, 1.2 V dc, 15 s (100x).

There are etchants that will color either ferrite or austenite. Unlike standard etchants that reveal only a portion of the grain boundaries, a color etchant colors all grains. If the grains have a random crystallographic orientation, then a wide range of colors, randomly dispersed, is obtained. If texture is present, then a narrow range of colors is observed. Because color etchants are selective, they are very useful for image analysis work where the contrast between what you want to measure and what you do not want to measure must be maximized.

Microstructural Constituents

Alpha Iron and Ferrite

Alpha iron, strictly speaking, refers only to the bodycentered cubic (bcc) form of pure iron that is stable below 912 °C (1674 °F) while ferrite is a solid solution of one or more elements in bcc iron. Often these terms are used as synonyms, which is not correct. Ferrite may precipitate from austenite in acicular form under certain cooling conditions. Strictly speaking, acicular means the shape is needle-like in three dimensions. However, this is not the actual shape of acicular ferrite in three dimensions. Figure 1 illustrates the appearance of ferrite grains in a low-carbon sheet steel. Nital is commonly used to reveal the grain boundaries but it is orientation sensitive and does not bring out all of the ferrite grain boundaries, as shown in Figure 1a. However, if we use a tint etchant that colors ferrite, note that all of the grains can be clearly observed, see Figure 1b.

There are also ferritic stainless steels with high chromium contents and very little carbon. Figure 2 shows the grain structure of 26-1 ferritic stainless steel after electrolytic etching. Ferrite grain structures can be quite difficult to reveal in ferritic stainless steels using standard immersion or swabbing reagents. Ferrite is a very soft, ductile phase, although it looses its toughness below some critical temperature.

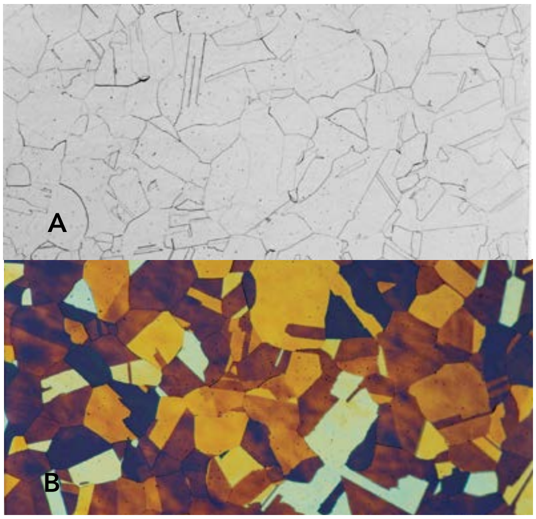

Figure 3. Austenitic grains with annealing twins revealed with different procedures: a) solution annealed 316 swabbed with Kalling's No. 2 etch (100x); b) solution annealed 316 tint etched with 85 mL water-15 mL HCl-1 g $K_2S_2O_5$ (100x).

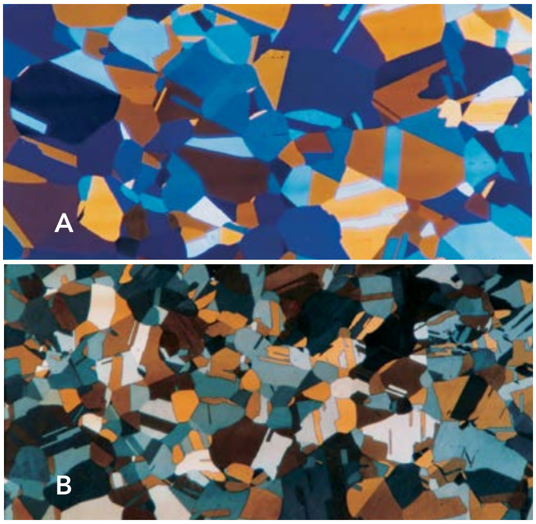

Figure 4. Austenitic grain structure of: a) wrought, solution annealed Hadfield manganese steel (100x); and, b) wrought, solution annealed Fe-39% Ni. Both were tint etched with Beraha's sulfamic acid reagent and examined in polarized light plus sensitive tint (100x).

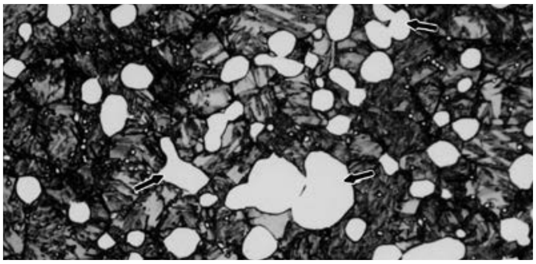

Figure 5. Examples of an "overaustenitized" steel containing excessive amounts of retained austenite, coarse plate martensite (dark) and undissolved primary carbides (arrows) in D3 tool-steel austenitized at 1120 °C and etched with 99 mL water-1 mL HCl and 1 g $K_2S_2O_5$ (1000x).

Gamma Iron and Austenite

Gamma iron, as with alpha iron, pertains to only the facecentered cubic (fcc) form of pure iron that is stable between 912 and 1394°C (1674-2541°F) while austenite is a solid solution of one or more elements in fcc iron. Again, these terms are often used interchangeably, but that is not correct. For heat treatable steels, austenite is the parent phase for all transformation products that make ferrous alloys so versatile and useful commercially. Austenite is not stable at room temperature in ordinary steels. Cr-Ni steels, known as austenitic stainless steels, is a family of very important grades where austenite is stable at room temperature. Figure 3 shows an example of the microstructure of type 316 austenitic stainless steel. In Figure 3a, a 316 specimen was swab etched with Kalling's No. 2 reagent ("waterless" Kalling's) and not all of the boundaries are revealed. Using a tint etch that colors austenite in such grades, as illustrated in Figure 3b, we can bring out all of the grain structure. There are other austenitic iron-based alloys, such as Hadfield manganese steel (Figure 4a) and iron-nickel magnetic grades (see Figure 4b). Austenite is a soft, ductile phase that can be work hardened to high strength levels.

For case-hardened carburized steels and high-carbon, highalloy steels, such as tool steels, use of an excessively high austenitizing temperature will dissolve excessive amounts of carbide which depresses the temperatures where martensite begins and completes its transformation to such an extent that austenite is present (but not necessarily stable) at room temperature (called retained austenite). Figure 5 shows an example of excessive retained austenite (and coarse plate martensite) in a D3 (Fe - 2.1% C - 12% Cr 0.5% Ni - 0.35% Mn) tool steel specimen that was austenitized at 1120 °C, well above the recommended temperature, which dissolved an excessive amount of carbide leading to partial hardening. Note the coarse plate martensite and the massive Cr7C3 carbide that was not dissolved. Excessive retained austenite in tool steels is usually detrimental to die life, as it may transform to fresh martensite and cause cracking, or reduce wear resistance. Retained austenite in a carburized gear tooth is not usually detrimental as the teeth are not normally shock loaded, so that the retained austenite would transform to martensite; and, the toughness of the austenite, when stabilized, may be beneficial. There are grades of stainless steel where the composition is balanced to produce approximately equal amounts of ferrite and austenite at room temperature. Figure 6 shows the microstructure of 2205 duplex stainless steel.

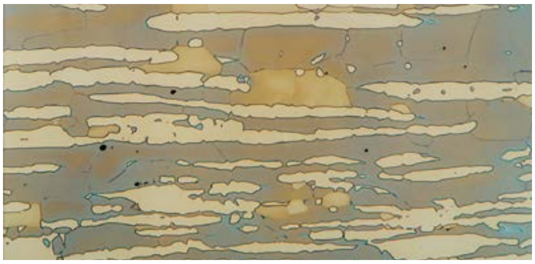

Figure 6. Ferrite (colored) and austenite (white) in 2205 duplex stainless steel electrolyically etched with aqueous 20% NaOH, 3 V dc, 10 s (100x).

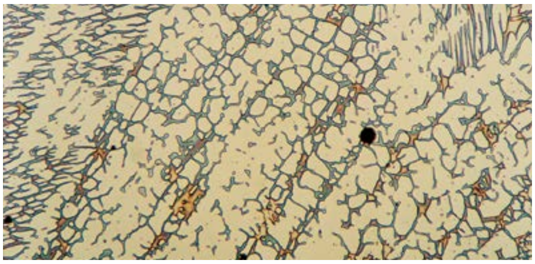

Figure 7. Delta ferrite (colored) in an austenitic matrix in type 312 weld metal (as-welded). The delta ferrite was colored using modified Murakami's reagent (100 °C, 10 s, 500x).

Delta Iron and Delta Ferrite

Delta iron is the bcc form of pure iron that is stable above 1394 °C (2541 °F) to the melting point, 1538 °C (2800 °F) while delta ferrite is the stable high temperature solid solution of one or more elements in bcc iron. Delta ferrite may be observed in as-cast austenitic stainless steels (it will usually be put into solution after hot working and solution annealing), in some precipitation hardened stainless steels, such as 17-4 PH, when the composition is not balanced to avoid it, in some martensitic stainless steels and in some tool steels. Delta ferrite is usually considered detrimental to transverse toughness when it is present in a hardened structure.

Fig. 8

Fig. 9

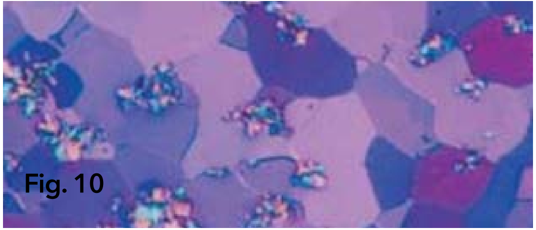

Fig. 10

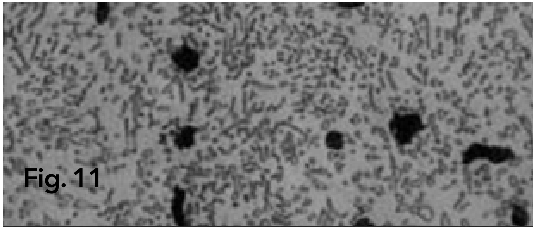

Fig. 11

Figure 8. Coarse flake graphite in a hypereutectic gray iron (as polished, 100x). Figure 9. Nodular graphite in austempered ductile iron (as polished, polarized light plus sensitive tint, 500x). Figure 10. Temper "nodules" in ferritize annealed malleable iron. The ferrite grains were revealed by color etching with Beraha's sulfamic acid reagent and were examined with polarized light plus sensitive tint (500x). Figure 11. Graphite in spheroidize annealed type O6 graphitic tool steel etched with 4% picral (1000x).

Delta ferrite is not always detrimental. When austenitic stainless steels are welded, the weld metal's composition is adjusted to produce a certain level of delta ferrite in the as-cast structure to minimize the risk of hot cracking. Figure 7 shows the structure of type 312 weld metal used to weld 316 stainless steel. The delta ferrite forms in the last regions to solidify and has an interconnected dendritic appearance.

Graphite and Cementite

Carbon in iron exists as either graphite or as cementite. Graphite is the stable form of carbon in iron (mainly observed in cast iron) while cementite is metastable and can transform to graphite under long-term, high-temperature exposure. Graphite in cast iron can take several forms, such as flakes (Figure 8) of various sizes and distributions in gray cast iron and nodules (Figure 9) in ductile cast iron. But, there are other shapes such as temper nodules (Figure 10) in malleable cast iron and short, stubby flakes in compacted cast iron. Graphite is occasionally observed in steels, where it was either deliberately created (as in graphitic tool steels, see Figure 11) or accidentally created by long-term, high-temperature exposure.

Cementite is a compound of iron and carbon with the approximate formula Fe3C and an orthorhombic crystal structure. Some substitution of other carbide forming elements, such as Mn and Cr, is possible. Hence, it is more general to refer to the formula as M3C, where M stands for metal. But, only small amounts of the various carbide forming elements can be substituted before alloy carbides of other crystal structures and formulae are formed. Figure 12 illustrates cementite in white cast iron. Picral is a good etch for revealing carbides as it outlines the massive cementite and also reveals the cementite in the

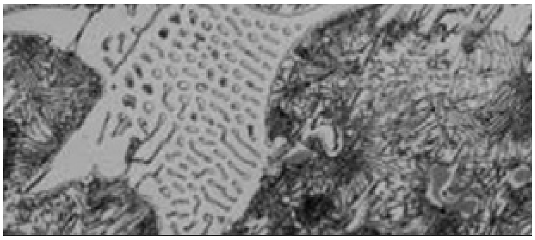

Figure 12. Cementite and pearlite in white case iron etched with 4% picral to outline the primary cementite (white); the very fine cementite in the pearlite looks dark (500x).

pearlite. Several reagents can preferentially color cementite. The carbon content of cementite is 6.67 wt. percent, which is usually the terminus for the Fe-C phase diagram. Cementite is hard (about 800 HV for pure Fe_3C, and up to about 1400 HV for highly alloyed M_3C) but brittle.

Austenite Transformation Products

When carbon or alloy steels are hot worked, they are in the austenitic condition. Subsequent cooling results in the transformation of austenite to other phases or constituents. If a carbon or low alloy steel is air cooled after hot rolling, a diffusion-controlled transformation occurs where ferrite precipitates first, followed by pearlite. Normalizing is a heat treatment process used to refine the grain structure of carbon and low-alloy steels. The steel is austenitized at a somewhat higher temperature than used for quench hardening, followed by air cooling to produce fine ferrite and pearlite.

Pearlite is a metastable lamellar aggregate of ferrite and cementite that forms at temperatures below the lower critical temperature (the temperature where austenite starts forming from ferrite and cementite upon heating). With time and temperature, the cementite in the pearlite will become spheroidized, that is, it changes from a lamellar to a spheroidal shape. Spheroidizing the cementite reduces the strength and hardness of the specimen while increasing its ductility. The degree of change is a function of the carbon content of the alloy. Pearlite forms by the eutectoid reaction. A eutectoid transformation is an isothermal, reversible reaction in which a solid solution (austenite) is converted into two intimately mixed solid phases, ferrite and cementite. All eutectoidal products are lamellar, even in nonferrous systems.

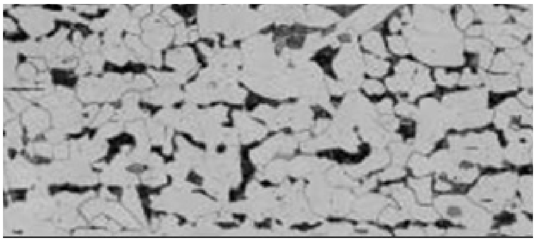

Figure 13. Microstructure of plate steel from the RMS Nomadic containing proeutectoid ferrite (white) and pearlite (dark) revealed by etching with 2% nital (200x).

For steels with carbon contents below the eutectoidal value, ferrite precipitates before the eutectoidal transformation and is called proeutectoid ferrite. Figure 13 shows proeutectoid ferrite and lamellar pearlite in a piece of plate steel from the RMS Nomadic, a tender for the RMS Titanic. The ferrite is white while the pearlite is dark as the lamellae are much too finely spaced to be resolved at this magnification. Figure 14 shows coarse pearlite in a fully annealed specimen of 4140 alloy steel where the lamellae can be resolved. The cementite lamellae appear dark while the ferrite remains white. In steels with carbon contents above the eutectoidal composition, cementite will precipitate in the grain boundaries before the eutectoid reaction occurs and is called proeutectoid cementite, Figure 15. Pearlite increases the strength of carbon steels. Refining the interlamellar spacing also increases the strength and the toughness, as well. In a slowly cooled specimen, the amount of pearlite increases to 100% as the carbon content increases to the eutectoidal carbon content, 0.77%. The hardness of a fully pearlitic eutectoidal steel will vary with the interlamellar spacing from about 250 to 400 HV as the spacing decreases. Pearlite can be cold drawn to exceptionally high tensile strengths, as in piano wire, which also exhibits considerable ductility.

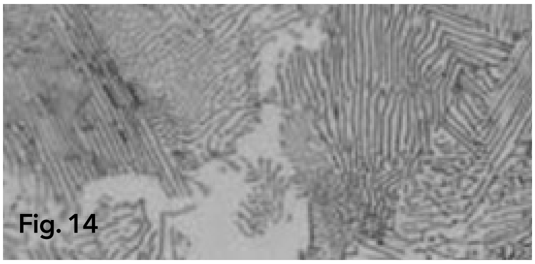

Fig. 14

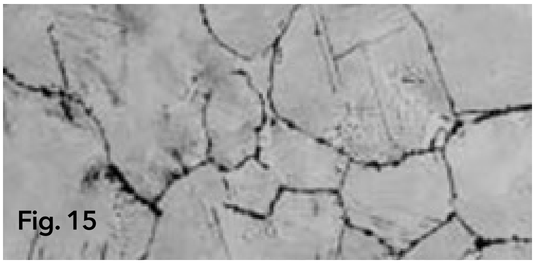

Fig. 15

Figure 14. Coarse pearlite and proeutectoid ferrite in fully annealed 4140 alloy steel revealed by etching with 4% picral, (1000x). Figure 15. Proeutectoid grain boundary cementite (dark) in as-rolled Fe – 1.31% C – 0.35% Mn – 0.25% Si water hardening tool steel revealed by etching in alkaline sodium picrate (90 °C – 2 min., 500x).

If the cooling rate is faster than air, or if alloying elements are added to the steel to increase hardenability, a different two-phase constituent may be observed, called bainite. Bainite is a metastable aggregate of ferrite and cementite that forms from austenite at temperatures below where pearlite forms and above the temperature where martensite starts to form. The appearance of bainite changes with the transformation temperature being called "feathery" in appearance at high temperatures and "acicular" at low transformation temperatures. The feathery appearance of "upper" bainite is also influenced by carbon content and is most appropriate for grades with high carbon contents. The acicular description is not a prefect description of the shape of "lower" bainite. Figures 16 and 17 illustrate the appearance of upper and lower bainite, respectively, in partially transformed 5160 alloy steel specimens.

If the cooling rate from the austenitizing temperature is rapid enough (a function of section size, hardenability and quench medium), martensite will form. Martensite is a generic term for the body-centered tetragonal phase that forms by diffusionless transformation and the parent and product phases have the same composition and a specific crystallographic relationship. Martensite can be formed in alloys where the solute atoms occupy interstitial sites, as for C in Fe, producing substantial hardening and a highly stained, brittle condition. However, in carbon-free alloys with high nickel contents, such as maraging steels, the solute atoms (Ni) can occupy substitutional sites, producing martensites that are soft and ductile. In carbon-containing steels, the appearance of the martensite changes with carbon in the interstitial sites. Low carbon steels produce "lath" martensites while high carbon steels produce "plate" martensite, often incorrectly called "acicular" martensite, when all of the carbon is dissolved into the austenite. Figure 18 illustrates lath martensite. Coarse plate martensite was shown in Figure 5. When quenched from the proper temperature, so that the correct amount of cementite is dissolved (see discussion following) and the grain size is quite fine, martensite will appear virtually featureless by light microscopy, as illustrated in Figure 19 for 52100 bearing steel. Figure 20, for comparison, shows the structure of martensite in nearly carbon-free 18Ni250 maraging steel.

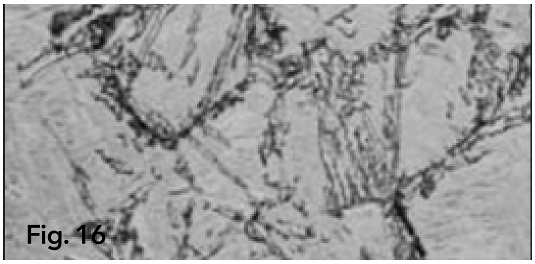
Fig. 16


Fig. 17

Figure 16. Upper bainite (dark) and martensite (light background) in a partially transformed (830 °C – 30 min, 538 ° C for 1 min, water quench) specimen of 5160 alloy steel. The austenite not transformed to upper bainite after 1 minute formed martensite in the quench (2% nital, 1000x). Figure 17. Lower bainite (dark) and martensite (light) in a partially transformed (830 °C – 30 min, 343 °C for 5 min, water quench) specimen of 5160 alloy steel. The austenite not transformed to lower bainite after 5 minute formed martensite in the quench (2% nital, 1000x).

The strength and hardness of martensite varies linearly with carbon in austenite up to about 0.5% C. As the carbon in the austenite increases beyond 0.5%, this curve starts to flatten and then goes downward due to the inability to convert the austenite fully to martensite (retained austenite becomes increasing present). Hence, when high carbon steels are heat treated, the aus-tenitizing temperature is selected to dissolve no more than about 0.6% C into the austenite.

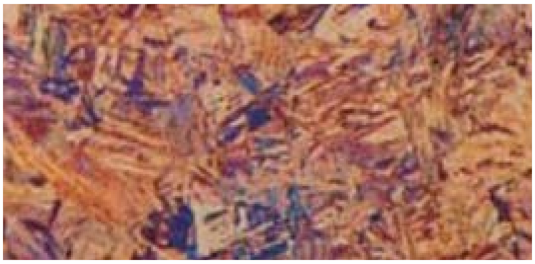

Figure 18. Lath martensite in quenched and tempered 4118 alloy steel revealed by etching with Beraha's sulfuric acid etch, (500x).

Other Constituents

There are other minor constituents in steels, such as nonmetallic inclusions, nitrides, carbonitrides, and intermetallic phases, such as sigma and chi. Nonmetallic inclusions are of two types, those that arise from the restricted solubility of oxygen and sulfur in the solid phase, compared to the liquid, and those that come from outside sources, such as refractories in contact with the melt. The former are called indigenous and the later are called exogenous. Many poor terms are used in reference to inclusions. Nitrides and carbonitrides result when certain nitride forming elements are present in adequate quantities, e.g., Al, Ti, Nb and Zr. A certain amount of nitrogen is always present in the melt and this varies with the melting procedure used. Electric furnace steels usually have around 100 ppm nitrogen while basic-oxygen furnace steels have about 60 ppm nitrogen. Aluminum nitride is extremely fine and can be seen only after careful extraction replica work with the TEM. The other nitrides are often visible in the light microscope, although submicroscopic size nitrides can also be present. Sigma and chi can be produced in certain stainless steels after high temperature exposure. These constituents will not be illustrated.

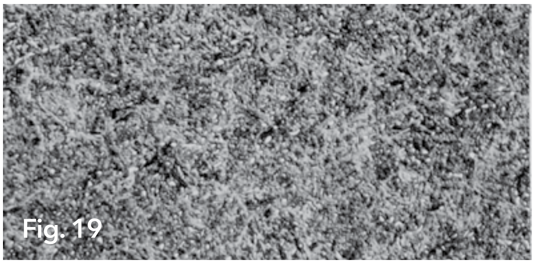
Fig. 19


Fig. 20

Summary

The microstructure of ferrous alloys is very complicated and this review has only touched the surface of knowledge about steel microstructures. It is a basic tenet of physical metallurgy that composition and processing establishes the microstructure and that microstructure influences many properties and service behavior. To maintain control of the quality of steel products and to diagnose problems in processing, testing or service, the microstructure must be identified and, in some cases, quantified. This can only be accomplished when the metallographer can properly distinguish the phases or constituents present. This depends upon proper specimen preparation and etching.

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