

Color Metallography

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THE USE OF COLOR in metallography has a long history, with color micrographs published over the past eighty-some years. A number of general articles (Ref 1–15) have been published reviewing methods and applications.

Natural color is of use in only a few classic metallographic applications. Prior to the devel-

opment of wavelength-dispersive spectrometers and energy-dispersive spectrometers used on electron microprobe analyzers and scanning electron microscopes, the color of inclusions using different illumination modes was part of the identification schemes used. However, natural color has limited applicability.

Color can be created by optical methods, such as with polarized light and differential interference contrast illumination. Polarized light examination is extremely useful for studying the structure of certain metals, without etching, that have noncubic crystal structures, such as beryllium, hafnium, α -titanium, uranium, and zirconium. In many cases, polarized light can be used with etched specimens, regardless of their crystal structure, to produce color. Differential interference contrast reveals height differences between constituents and the matrix, but in most cases, the color is of esthetic value only.

Color etching methods are widely used, although they are not universal. Color etchants have been developed for a limited number of metals and alloys, and they are not always easy to use, nor are they fully reliable. Color etchants are used by immersion or electrolytically. A complete listing of all color etchants is beyond the scope of this article, but good compilations are available (Ref 7, 10–15). Aside from the immersion tint etchants, there are a number of older

etchants that produced color either by immersion, sometimes in boiling solutions, or electrolytically. Historical information on these etchants can be found in Ref 16.

Tint etchants may color either the anodic (matrix) or cathodic constituents. There are also electrolytic reagents known as anodizing solutions. They have been used most commonly with aluminum and its alloys. These solutions may produce a thin film on the surface, with a degree of roughness. Examination in bright field reveals little, but polarized light reveals the structure clearly.

There are other procedures to create interference films using heat (heat tinting), vapor deposition, or by reactive sputtering. Color can be observed with bright-field illumination but often can be enhanced using polarized light.

Optical Methods for Producing Color

There are few instances where naturally occurring color differences are observed in metallic systems. Specimens plated with copper or gold are a common example. There are two main optical methods for producing coloring: polarized



Fig. 1 Microstructure of a porous high-carbon steel powder metallurgy specimen infiltrated with copper showing the natural color of the copper, which is easier to see when the steel has been tint etched (revealing coarse plate martensite and retained austenite)

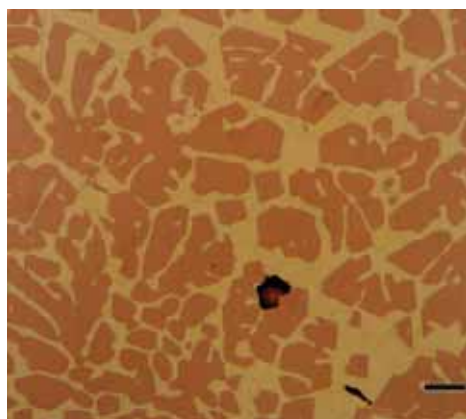


Fig. 2 Microstructure of as-cast Au~22%Al showing the "purple plague," AuAl₂ intermetallic (red-dish), surrounded by the Al-AuAl₂ eutectic after polishing to a 1 μm finish. Magnification bar is 50 μm long.



Fig. 3 Cuprous oxide in tough pitch arsenical copper (hot extruded and cold drawn) viewed in dark field, revealing the classic ruby-red color. Magnification bar is 10 μm long.

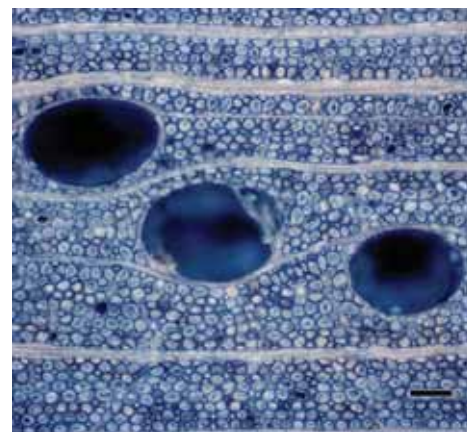


Fig. 4 Microstructure of walnut (plane perpendicular to the trunk axis) showing the cells and pores revealed using dark-field illumination. Magnification bar is 100 μm long.

light and differential interference contrast. In both cases, color per se is of minimal value beyond simple esthetics. The color of inclusion phases in bright field, dark field, and polarized light has been used for identification purposes for many years.

Natural color is not a common occurrence in metallic systems; many metals have a similar white color. When polished, only a few metals exhibit a color other than white; for example, gold and copper appear yellow when polished. Platings of these metals can be easily recognized by their color. A classic example of natural color differences is the detection of liquid metal embrittlement in steels due to copper. In this case,

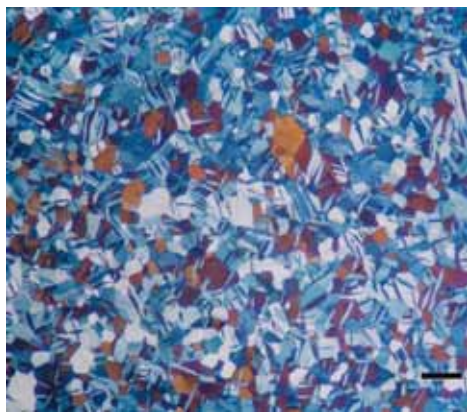


Fig. 5 Extensive mechanical twinning was observed in high-purity, electron-beam-melted zirconium after hot working and cold drawing. Viewed in polarized light. Magnification bar is 100 μm long.

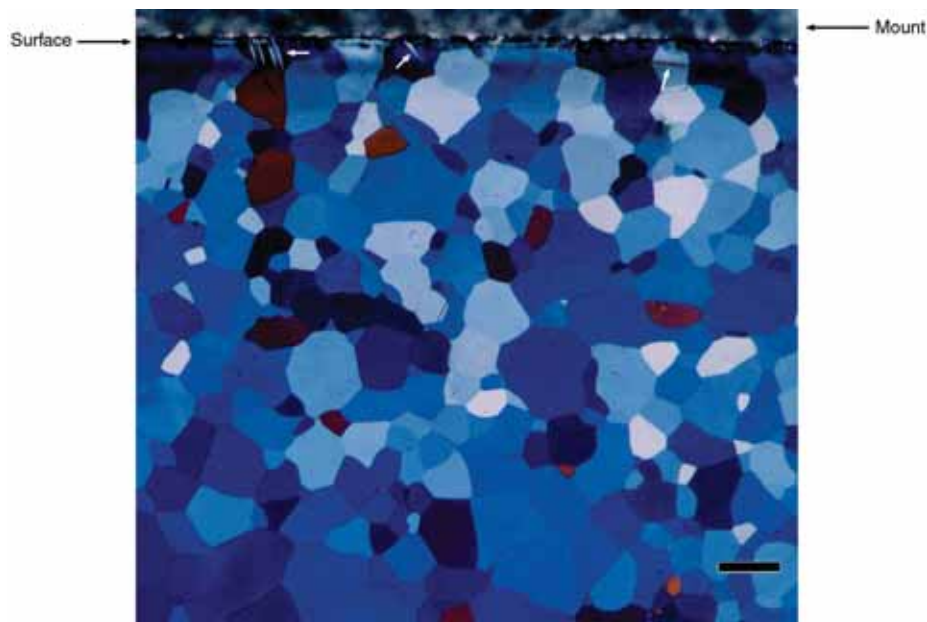


Fig. 6 Microstructure of wrought pure hafnium, with an as-polished specimen viewed in polarized light plus sensitive tint, revealing an equiaxed alpha hexagonal close-packed grain structure. A few mechanical twins can be seen at the surface (arrows). The magnification bar is 100 μm long.

the natural color of copper is clearly seen against the steel matrix. It may be easier to see the copper color when the steel matrix is etched. Figure 1 shows an example of porous high-carbon steel that was partially infiltrated with liquid copper, where the natural color of the copper can be easily observed. There is a substantial difference in the reflectivity of iron and copper. Etching of the high-carbon martensitic/pearlitic matrix increases the image contrast difference, making it easier to see the copper color. The so-called "purple plague," the intermetallic phase Al_2Au that can occur in brazing of integrated circuits, has a natural purple or red-violet color, as illustrated in Fig. 2. Nitrides and some inclusions exhibit specific colors when examined with bright-field illumination, but overall, natural color is uncommon with metals and alloys.

Dark-Field Illumination. Inclusions in metals have been identified using known colors when viewed with bright field, dark field, or polarized light (Ref 17). Cuprous oxide, Cu_2O , in tough pitch copper, for example, is easily recognized because it glows ruby red in dark-field illumination (Fig. 3) but appears bluish-gray in bright field. Cuprous sulfide, Cu_2S , has a similar color in bright field but remains dark and dull in dark field (Ref 18). Wood also exhibits natural color in dark field, as shown in Fig. 4.

Polarized Light. There are purely optical methods for generating color images employing polarized light and differential interference contrast illumination. Polarized light examination is useful with phases or anisotropic metals that have noncubic crystallographic structures (Ref 2), such as antimony, beryllium, cadmium, cobalt, magnesium, scandium, tellurium, tin, tita-

nium, uranium, zinc, and zirconium. Figure 5 shows the grain structure near the surface of an electron-beam-melted crystal bar of high-purity zirconium (not etched) that was hot rolled, annealed, and cold drawn. The deformation process produces mechanical twins that are quite numerous at the surface but nearly absent in the interior. Other examples of color developed with polarized light on as-polished specimens of metals with noncubic crystal structures are shown in Fig. 6, hafnium; Fig. 7, ruthenium; and Fig. 8, Cd-20% Bi.

Unfortunately, not all noncubic phases or metals respond well to polarized light. In some cases, a well-prepared specimen responds to polarized light, revealing the microstructure quite clearly but without appreciable color. The contrast produced, and the color intensity, may be a function of both the degree of anisotropy of the metal or alloy and the quality of specimen

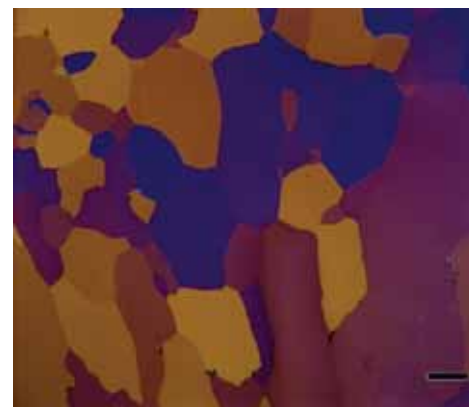


Fig. 7 Microstructure of as-cast pure ruthenium, as-polished and viewed in polarized light plus sensitive tint, revealing a mixture of equiaxed and columnar hexagonal close-packed grains and some small shrinkage cavities (black). The magnification bar is 200 μm long.



Fig. 8 Microstructure of Cd-20%Bi in the as-cast condition, unetched and viewed with polarized light (slightly off the crossed position) plus sensitive tint, revealing cadmium dendrites of various orientation. The interdendritic constituent is a eutectic of cadmium and bismuth but is too fine to resolve at this magnification. Magnification bar is 200 μm long.

preparation. The quality of the surface appears to be the key factor, but the quality of the optical system is also very important. In some cases, the color response in polarized light can be markedly improved after etching specimens having noncubic crystal structures with some specific reagent. Figure 9 shows the grain structure of hot-rolled hexagonal close-packed (hcp) Zn-0.1%Ti-0.1%Cu in the as-polished condition and after etching, which improved polarized light response and color formation. Note that the fine precipitates between the elongated grains are much easier to see in polarized light after etching. Figure 10 shows pure hcp magnesium containing mechanical twins that were brought out vividly in color only after etching with the acetic-picral reagent (other standard

etchants for magnesium did not provide this improvement).

In some cases, isotropic metals and alloys may respond to polarized light after being etched with a particular reagent that either produces an anisotropic film on the surface or roughens the surface. In some cases, anodizing solutions may produce an optically anisotropic film on the surface that produces color by interference. Color tint etchants form a film on the surface of certain metals that produces interference colors. If such a film is formed, color will be observed in bright field. In many cases, color contrast can be further enhanced when viewed with polarized light, due to the birefringence of these films. Anodizing and tint etching are discussed subsequently. The surfaces of many isotropic metals can be etched

with a specific reagent that produces etch pits or furrows within the grains that respond to polarized light. Figure 11 shows an example of an aluminum brass (Cu-22%Zn-2%Al) that was cold worked and annealed at 750 °C (1380 °F). The specimen was etched with the classic potassium dichromate reagent, which produces a black-and-white grain contrast image in bright field that yields excellent color contrast in polarized light. The etch furrows are aligned crystallographically, and this produces grain-orientation coloring in crossed polarized light aided by a sensitive tint plate (also called a lambda plate, a full wave plate, or a first-order red plate). Fine lamellar structures will respond to polarized light regardless of the etchant used, producing strong coloration but often without any benefit except esthetics.

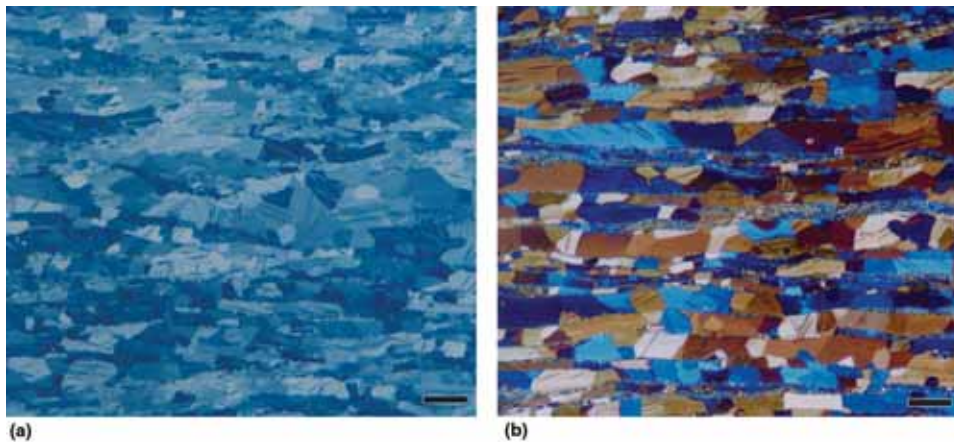


Fig. 9 Microstructure of Zn-0.1%Ti-0.1%Cu hot rolled to 6 mm (0.24 in.) thickness. (a) The as-polished condition, using polarized light, revealed elongated hexagonal close-packed grains containing mechanical twins. Some fine precipitates are present in the grain boundaries but are not clearly revealed. (b) The structure after etching with Palmerton reagent and viewing with polarized light plus sensitive tint better reveals both the precipitates and grain structure. Magnification bars are 50 μm long.

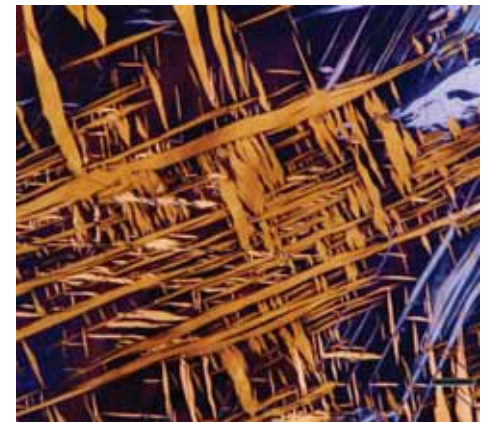


Fig. 10 Microstructure of wrought 99.98% Mg etched with acetic-picral reagent and viewed with crossed polarized light plus a sensitive tint filter. The magnification bar is 200 μm long.

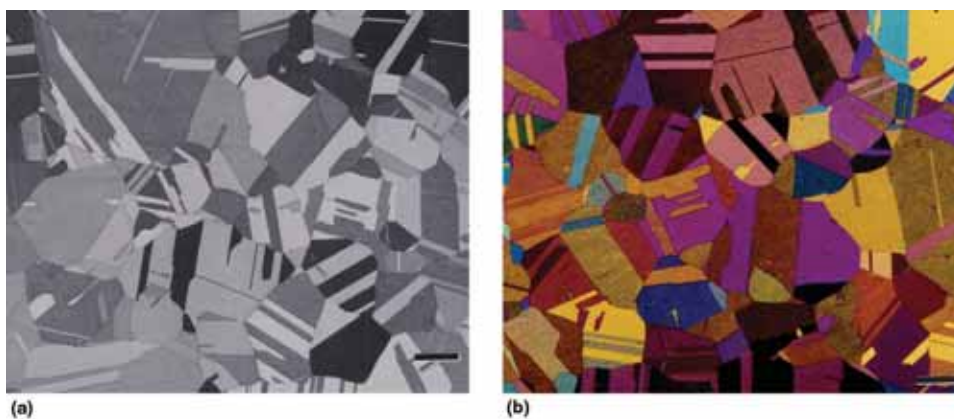


Fig. 11 Wrought aluminum brass (Cu-22%Zn-2%Al) annealed at 750 °C (1380 °F), producing equiaxed alpha grains containing annealing twins, and etched with potassium dichromate. Images in (a) bright field and (b) crossed polarized light plus sensitive tint. The magnification bars are 50 μm long.

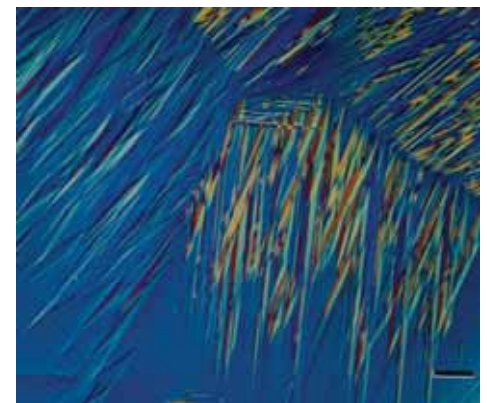


Fig. 12 Microstructure of a shape memory alloy (Cu-26%Zn-5%Al) showing β_1 martensite in a face-centered cubic alpha matrix, using Nomarski differential interference contrast without etching. The magnification bar is 25 μm long.

Differential interference contrast illumination (DIC) (Ref 19) can be used to enhance height differences between constituent and matrix on a prepared surface. Introducing a small, controlled amount of relief in final polishing can enhance these height differences. Color is introduced using a sensitive tint plate. In most cases, the color is of no real value, but in some cases, it has more value. Figure 12 shows an example where Nomarski DIC was highly effective in revealing β_1 martensite in a Cu-26%Zn-5%Al shape memory alloy. A more complex example of a shape memory alloy is given in Fig. 13. This shows the structure of Spangold, a jewelry alloy (Au-19%Cu-5%Al), where some martensite was formed during hot mounting (it could be seen in polarized light). Then, the polished specimen was heated in boiling water and quenched, forming new martensite. The new martensite crosses the original martensite in some places (these are the areas with two crossing sets of parallel colored bands), referred to as antispangle by the alloy inventors.

Figure 14 shows a rather interesting use of DIC. A metallographically prepared specimen of High-Expansion 22-3 alloy (Fe-22%Ni-3%Cr) was cooled to -73°C (-100°F), which caused martensite to form in areas where the austenite stability was low. When martensite forms, it does so by a shear transformation that produces surface movement at a free surface. The specimen was brought back to room temperature, cleaned off, dried, and viewed with Nomarski DIC, producing an excellent rendering of the martensite without etching. In some cases, DIC can be used effectively to study the structure of materials with significant variations in hardness and polishing rates. Figure 15 shows the microstructure of high-density polyethylene containing a filler material, viewed with DIC. In these examples,

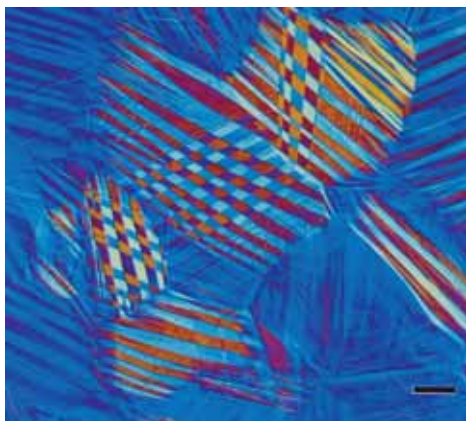


Fig. 13 Microstructure of Spangold (Au-19%Cu-5%Al), a new jewelry alloy, using martensite formation to create ripples ("spangles") on the surface. The specimen was polished, heated to 100°C (212°F) for 2 min, and quenched in water to form martensite, which produces shear at the free surface. This roughness can be seen using Nomarski differential interference contrast without etching. The crisscrossed pattern is produced by forming martensite, polishing, and then forming new martensite. The magnification bar is $50\ \mu\text{m}$ long.

the color was produced by the use of the sensitive tint filter with the Wollaston prism. Without the sensitive tint filter, the images would exhibit gray tones.

Film Formation and Interference Techniques

Color can be produced by a number of techniques that rely on film formation and interference effects. These films can be formed thermally, as in heat tinting, or by chemical deposition, as in tint etching, or by vapor deposition, as in the Pepperhoff interference film method. These methods tend to be selective in nature, in that the films either color a specific phase, but not others, or color all constituents differently. In practice, the color produced is not a reliable means of phase identification compared to what is, or is not, colored.

Anodizing

Anodizing (Ref 20–29) is an electrolytic procedure for depositing an anodic film on aluminum and certain other metals, for example, niobium, tantalum, titanium, uranium, and zirconium. Lacombe and Beaujard (Ref 20) first described the method in 1945. It was initially thought that this film varied in thickness from grain to grain, according to their crystallographic orientation, and that the birefringent properties of the oxide film varied the ellipticity produced by reflection of the beam. However, experiments have shown that a film is not formed on aluminum when anodized by reagents such as Barker's. Instead, the coloration effects in polarized light are due to double reflection from a furrowed surface produced by the anodizing solution, similar to certain chemical etchants discussed previously. Examination of aluminum



Fig. 14 Martensite formed on the free polished surface of High-Expansion 22-3 alloy after refrigeration to -73°C (-100°F) to convert any unstable austenite to martensite. The specimen was brought back to room temperature, cleaned, and viewed with Nomarski differential interference contrast illumination without etching.

specimens after anodizing with Barker's reagent should reveal color in bright-field illumination, if an anodic film is produced, but color is not observed. Instead, the surface looks etch-pitted when examined with the scanning electron microscope at high magnification. Figure 16 shows the surface of 1100 aluminum foil after anodizing with Barker's reagent. The bright-field image (Fig. 16a) simply shows the intermetallic particles that have been slightly attacked by the solution. If Barker's had produced an anodic film, color should be observed. A classic experiment regarding this problem is discussed in the next section. Figure 16(b) shows the specimen viewed in polarized light; note that the grains are revealed in gray-level contrast. Figure 16(c) shows the same area viewed in polarized light with the addition of a sensitive tint filter; this yields the grains in color contrast. Figure 16(d) shows the microstructure of as-continuously cast 1100 aluminum after anodizing with Barker's reagent and viewing with polarized light plus sensitive tint. Dendrites with the same orientation have been colored uniformly. However, Barker's usually does not reveal the segregation within the dendrites. (Compare this result to that using Weck's color tint etch for aluminum, shown in Fig. 52.) Anodizing with Barker's, or other solutions, is the most universal procedure for revealing grain structures in cast and wrought aluminum alloys. Anodizing solutions have been developed for a number of metals and alloys, and some of these do deposit anodic films that produce color by interference effects, but Barker's does not.

Chemical Etching

There are many cases where a chemical etchant, when used on an isotropic metal, results in grain-orientation coloration when viewed with polarized light and sensitive tint. Mott and Haines (Ref 30) and Gifkins (Ref 31) have described suitable preparation and etching proce-

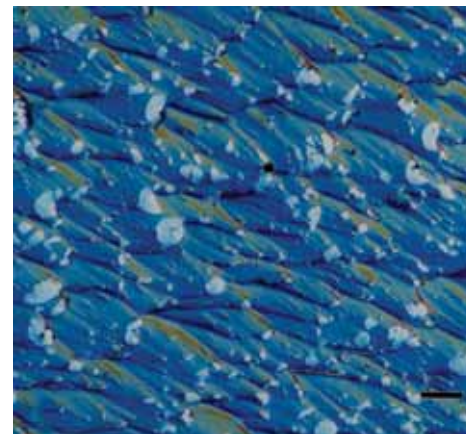


Fig. 15 Microstructure of high-density polyethylene containing a filler revealed using a polished specimen and Nomarski differential interference contrast. The magnification bar is $100\ \mu\text{m}$ long.

dures for a number of isotropic metals and alloys for producing color with polarized light. These procedures have been known and reported since at least the 1920s.

Woodard (Ref 32) studied the deformation of face-centered cubic (fcc) Monel using a grain contrast etchant (3 g chromic acid, 10 mL nitric acid, 5 g ammonium chloride, and 90 mL water) that produced an intensity contrast pattern with polarized light that he attributed to variations in crystal orientation. Woodard proposed that an anisotropic surface film, as in anodizing, produced the grain contrast effect. This is probably not the case, as suggested by the study of Perryman and Lack (Ref 33).

Perryman and Lack (Ref 33) performed a classic study to determine if polarization response was due to surface roughness or to the presence of an anisotropic surface film. The work used four specimens that respond to polarized light. The first two, electrolytically polished zinc and cadmium, are anisotropic metals with hcp crystal structures that respond to polarized light when properly prepared (without need for etching). The second two specimens were isotropic metals with fcc crystal structures that were etched to respond to polarized light. They were electrolytically polished and anodized aluminum and Monel treated using Woodard's method (Ref 32). The surfaces were prepared and examined with

polarized light, and all yielded good colored microstructures. Then, the surfaces were coated by vapor deposition of a thin (80 nm) film of silver. Silver has a fcc crystal structure and is isotropic. Hence, if the polarization effect is due to optical anisotropy, then the coated surface will no longer respond to polarized light. If, however, the polarization response is due to surface roughness, the silver film should not alter polarized light response. After deposition of the silver film, the anisotropic zinc and cadmium specimens did not respond to polarized light, but the anodized aluminum and the etched Monel did respond to polarized light. Thus, surface roughness is responsible for the polarized light response from

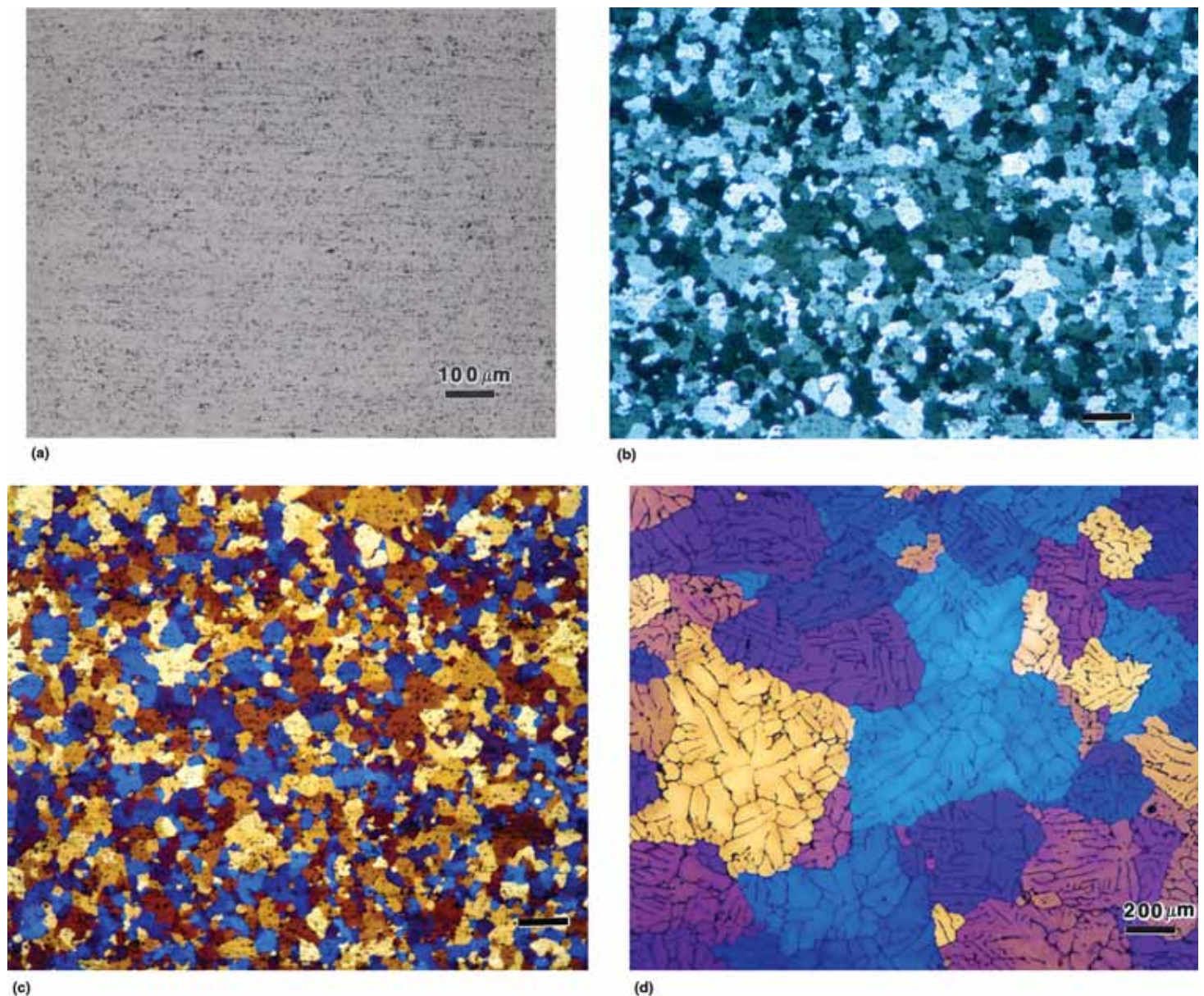


Fig. 16 Grain structure of wrought 1100-grade aluminum foil after electrolytic polishing and anodizing with Barker's reagent (20 V direct current, 2 min). (a) Viewed with bright-field illumination, revealing only the intermetallic precipitates. If anodizing had produced an interference film, colored grains should be visible. (b) Viewed with polarized light and (c) with polarized light plus a sensitive tint filter. The magnification bars in (b) and (c) are 100 μm long. (d) As-cast (concast) 1100 aluminum (>99% Al) anodized with Barker's reagent (30 V direct current, 2 min), revealing a dendritic solidification structure. Viewed with crossed polarized light plus sensitive tint

anodizing or from etching with these specific reagents. This roughness was observed when these surfaces are examined by electron optical methods. Reed-Hill et al. (Ref 34) examined the surfaces of four fcc alloys (Ni 200, Ni 270, Monel 400, and Cu-10 Zn), etched to produce polarized light response, and confirmed the grooved surface roughness responsible for the response.

In general, any fine lamellar structure, etched with any general-purpose reagent, will exhibit color when viewed with polarized light plus sensitive tint. Also, any etchant that yields a grain contrast gray-scale image will exhibit color when viewed with polarized light plus sensitive tint, as shown in Fig. 11. In some cases, precipitation-hardened specimens can exhibit dramatic coloration after a standard etching reagent has been used, but mediocre coloration when a tint etchant is used. Figure 17 shows a classic example of this effect, where beryllium-copper

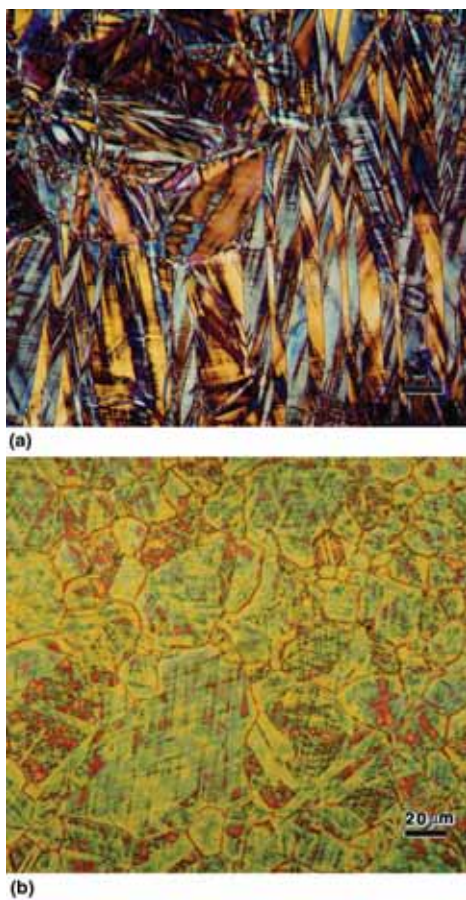


Fig. 17 Wrought, solution-annealed, and aged beryllium-copper (Cu-1.8%Be-0.3%Co) in the heat treated condition: 790 °C (1455 °F), held 1 h, oil quenched, and aged at 315 °C (600 °F) for 2 h (380 HV). (a) Swab etched with equal parts ammonium hydroxide and hydrogen peroxide (3% conc.). Polarized light and sensitive tint bring out the diffuse crisscross markings due to the submicroscopic γ' precipitates and coherency strain fields. The magnification bar is 50 μm long. (b) Tint etching with Klemm's I did not reveal the structure as well, although the grain size is revealed. Tint etchants produce very little etch attack.

that was solution annealed and aged to peak hardness was etched with equal parts ammonium hydroxide and hydrogen peroxide (3% concentration) (Fig. 17a) and with Klemm's I tint etch (Fig. 17b). Results with the standard etch are spectacular and come from the fine surface roughness created by etching a surface containing submicroscopic precipitates and their surrounding coherency strain fields. Klemm's I, like most tint etchants, does not do significant etching of the surface but deposits a film epitaxially with the underlying microstructure. Consequently, only a hint of the strain fields is seen.

Tint Etching

Tint etching, also called stain etching or color etching, can be performed by using simple chemical immersion etchants, by electrolytic etching (such as, but not limited to, anodizing), and by potentiostatic etching. Immersion etching is the simplest; potentiostatic etching is the most complex. Deposition of color films on precipitates or matrix phases has been known for many years, because alkaline sodium picrate (Ref 35, 36), Murakami's reagent (Ref 37, 38), Groesbeck's reagent (Ref 39, 40), and Malette's reagent (Ref 41) have been used for many years. French metallographers (Ref 42–48) were very active in the 1950s developing color etchants based on aqueous solutions containing sodium bichromate, sodium nitrate, sodium nitrite, and sodium bisulfite. Vilella and Kindle (Ref 49) at U.S. Steel tried the sodium bisulfite tint etch and found it useful for steels. However, these etchants are used infrequently today. Electrolytic etching with strong basic solutions also produces color films and is widely used with stainless steels to color delta ferrite or sigma phase (Fig. 18). Alkaline sodium picrate is widely used to color cementite in steels, as shown in Fig. 19.

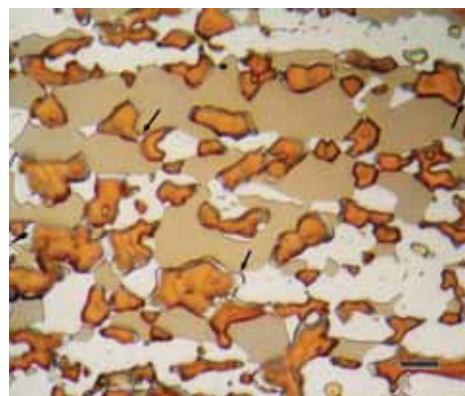


Fig. 18 Microstructure of wrought 7-Mo duplex stainless steel (Fe-<0.1%C-27.5%Cr-4.5%Ni-1.5%Mo) solution annealed and then aged 48 h at 816 °C (1500 °F) to form sigma. Electrolytic etching with aqueous 20% NaOH (3 V direct current, 10 s) revealed the ferrite as tan and the sigma as orange, while the austenite was not colored. The arrows point to austenite that formed during the conversion of ferrite to sigma. Magnification bar is 10 μm in length.

Murakami's reagent has been used to color certain alloy carbides (room-temperature immersion) or delta ferrite and sigma in stainless steels (immersion while boiling). Figure 20 illustrates the use of two modified versions of Murakami's to color delta ferrite and sigma in stainless steel welds. Groesbeck's reagent is used less frequently but is also useful for coloring alloy carbides, as shown in Fig. 21.

Color etching became a more useful and popular tool with the development of reagents by Klemm (Ref 50, 51) and Beraha (Ref 7, 52–64). These works were aided by developments by Benscoter, Kilpatrick, and Marder (Ref 65–68), Lichtenegger and Blöch (Ref 69), Weck (Ref 14), and others. The books by Beraha and Shpi-gler (Ref 7) and by Weck and Leistner (Ref 12–14) have helped metallographers learn these useful techniques.

There are a number of processes, besides metallographic etching, that deposit thin films of various compositions on metals, but not all will reveal the microstructure. Film thickness is important; coloration due to interference effects is a function of film thickness. Passivation treatments, used on aluminum and stainless steels, produce thin, transparent films that do not reveal the microstructure. Oxides produced by high-temperature exposure are usually quite thick and also do not reveal the microstructure. Between these extremes, films of oxides, sulfides, and molybdates produce interference effects, revealing the structure in color as a function of thickness. The classic historical example of a process that yields oxide films of the correct thickness for interference-generated colors is heat tinting. Certain metals, when heated to temperatures that yield thin oxides, produce a visible color on the surface known as temper colors. At some low temperature, the film becomes thick enough to produce a straw-yellow color. As the temperature is increased, the film grows and the color changes to green, then red, violet, and blue. This

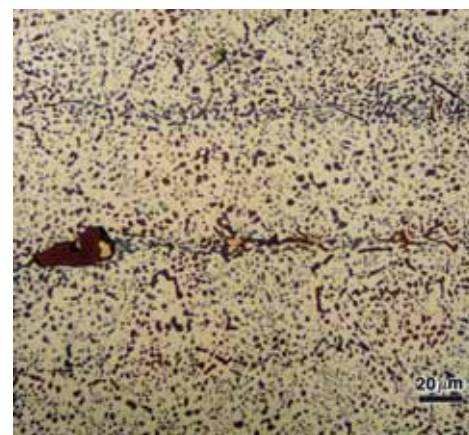


Fig. 19 High-carbon tool steel etched with boiling alkaline sodium picrate to color the cementite. Note the lighter-colored carbides in the segregation streak. These probably contain a small amount of molybdenum, present in this steel.

same sequence is obtained when films are grown on a polished surface during tint etching. It may be difficult to grow a thick enough film to produce good color in bright field for some alloy compositions. In such a case, coloration can usually be improved, sometimes extensively, by viewing the specimen with polarized light plus sensitive tint. Figure 22 demonstrates this, where Monel 400 was color etched with Beraha's selenic acid reagent, producing a weak color image (Fig. 22a). However, polarized light plus sensitive tint yielded a very good color image of the grain structure (Fig. 22b). When a good film can be produced, as illustrated in Fig. 23(a) coloration is excellent in bright field. Using polarized light plus sensitive tint merely changes the color scheme (Fig. 23b) without any improvement in image quality.

There are a great many tint etchants, and it is not possible to list, describe, and illustrate all of

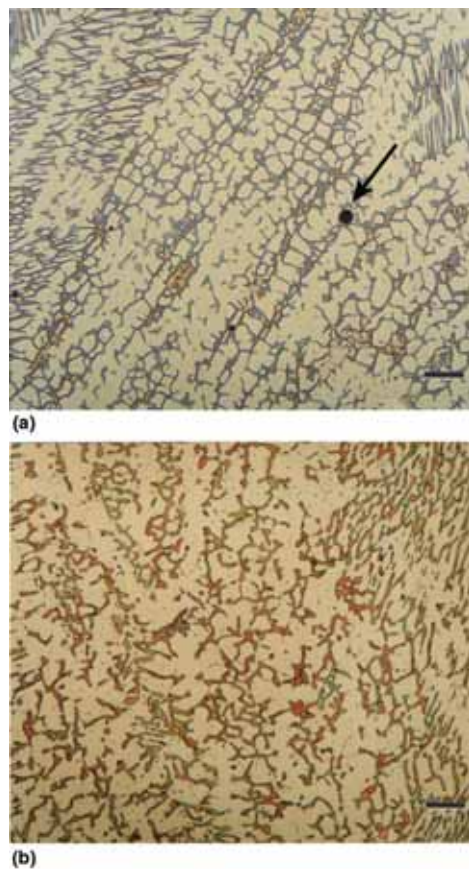


Fig. 20 Use of modified versions of Murakami's reagent to color delta ferrite and sigma phase in stainless steel welds. (a) Delta ferrite colored blue and brown in an austenitic matrix in type 312 stainless steel weld metal (as-welded) using modified Murakami's reagent (30 g sodium hydroxide, 30 g potassium ferricyanide, 100 mL water, at 100 °C, or 212 °F, for 10 s). The arrow points to a slag inclusion in the weld nugget. (b) Sigma phase formed in a type 312 stainless steel weld (from the delta ferrite phase) by aging at 816 °C (1500 °F) for 160 h. Sigma was colored green and orange by etching with Murakami's reagent (10 g sodium hydroxide, 10 g potassium ferricyanide, 100 mL water) for 60 s at 80 °C (175 °F). The magnification bars are 20 μm in length.

them in this article. Instead, some of the more useful and widely used color etchants are discussed. The films are the product of a controlled chemical reaction between the specimen surface and the reagent. The electrochemical potential on the surface of a polished specimen varies. For example, the potential at a grain boundary is different than the grain interior, while the potential of a second-phase particle may be greater than the matrix. In this case, which is quite common, the matrix is anodic while the particles are cathodic, that is, more noble. It is far easier to grow an interference film on the anodic matrix phase than on the cathodic second-phase particles. Anodic tint etchants are quite sensitive to crystallographic orientation, with the film thickness and the color being a function of crystal orientation. This is not the case for cathodic tint etches, which invariably color the noble phase uniformly, regardless of their crystallographic orientation. A few reagents will color both anodic and cathodic constituents and are referred to as complex reagents. In metallographic work, particularly for phase identification or for selective etching before performing quantitative measurements, anodic and cathodic etchants are generally more useful than complex reagents. Reagents that deposit sulfide films are usually anodic, while reagents that deposit selenium or molybdate films are usually cathodic.

Tint etching is always done by immersion, because swabbing would prevent formation of the interference film. Beraha often recommends lightly pre-etching the specimen with a general-purpose reagent before tint etching. This is not always necessary, and the author rarely does it. The author first etches specimens with a general-purpose reagent to see what the structure is. This is also useful because it may help determine what the best tint etchant may be, or at least which to try first. Immerse the specimen in the beaker, and watch the surface for coloration. This may be difficult, because the surface color

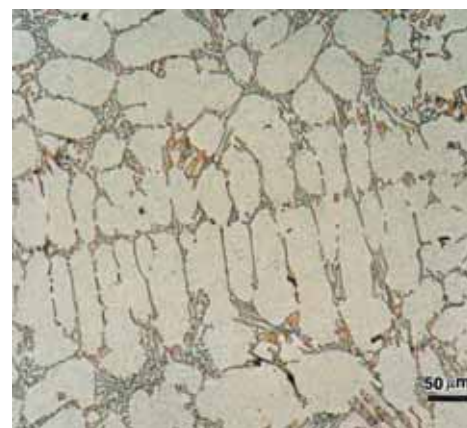


Fig. 21 Alloyed white cast iron (Fe-2.2%C-0.9%Mn-0.5%Si-12.7%Cr-0.4%Mo-0.1%V) with a martensitic matrix and a network of eutectic alloy carbides (colored). Etched with Groesbeck's reagent. (80 °C, or 175 °F, for 30 s) to color the alloy carbides

can look quite different after drying than when immersed. If the solution contains ammonium bifluoride, NH_4FHF , it is best to use a plastic beaker and plastic tongs. Getting the specimen to form a film at the extreme edges can be difficult. This can be improved by wet etching, that is, squirting a small amount of distilled water on the surface before immersing it in the beaker. Then, agitate the specimen strongly for a few seconds. If the surface is not properly cleaned before etching, the results will be poor. Specimen preparation must be performed properly, with all preparation-induced damage removed.

Reagents that Deposit Sulfide Films. These are the best-known tint etches and usually the easiest to use. Klemm (Ref 50, 51) and Beraha (Ref 53, 54, 57, 58) have developed the most

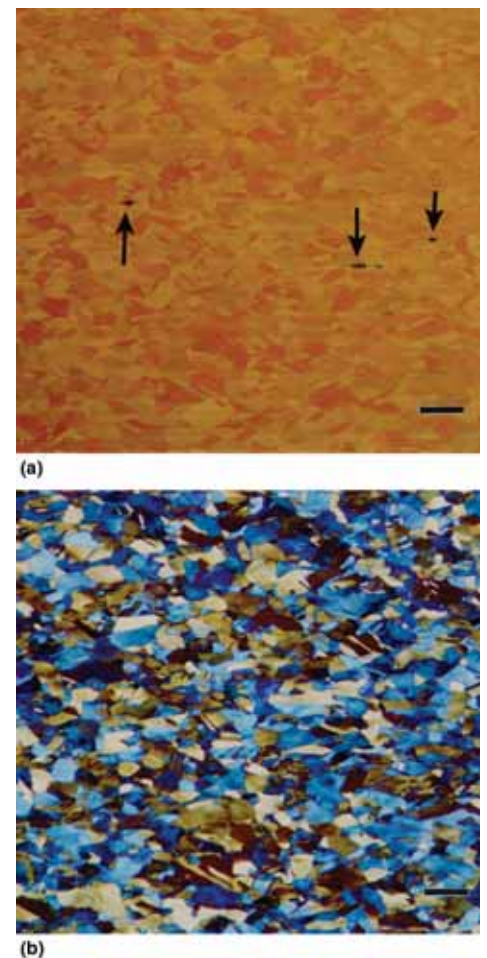


Fig. 22 The microstructure of hot-worked, annealed, and cold-drawn Monel 400 (Ni-32%Cu-<0.3%C-<2%Mn-<0.5%Si) revealed using Beraha's selenic acid etch for copper (longitudinal axis is horizontal). Monel alloys are very difficult to color etch, especially wrought alloys (as-cast alloys are easier). Bright field (a) revealed a weak image, because the interference film produced is thin (inclusions, arrows, can be seen). When this occurs, polarized light (b) will often enhance the image quality dramatically (the sensitive tint filter enhances coloration), as shown. Note the deformed, twinned face-centered cubic alpha grain structure. The magnification bars are 50 μm long.

widely used sulfide-base tint etchants using sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, and potassium metabisulfite, $\text{K}_2\text{S}_2\text{O}_5$. Klemm's I, II, III and one of Beraha's reagents use both ingredients, while Beraha recommends a range of HCl concentrations used with potassium metabisulfite for etching a variety of iron-base alloys. To make Klemm's reagents, prepare a stock solution of cold water saturated with sodium thiosulfate. The compositions of Klemm's three reagents are given in Table 1.

Klemm Color Etchants. To illustrate the use of the Klemm color etchants, Fig. 24(a) shows the microstructure of annealed cartridge brass etched with equal parts ammonium hydroxide and hydrogen peroxide (3%), which produced a weak grain contrast etch. Klemm's I is a bit weak to etch cartridge brass in a reasonable amount of time. After 3 min, weak coloration was obtained in bright field, but results were better in polarized light plus sensitive tint (Fig. 24b). Klemm's II is stronger, and after 2 min immersion, bright field produced a better image (Fig. 24c), while polarized light and sensitive tint yielded a much better image (Fig. 24d). Klemm's II often produces crystallographic line etching within many grains. This can be more easily seen in Fig. 24(c).

Klemm's III is an excellent tint etch for copper alloys and worked best for the cartridge brass (Fig. 24e). Results were very good in bright field (Fig. 24f), although the color range was limited, and even better in polarized light plus sensitive tint (Fig. 24e). Tint etchants produce noticeably different results on specimens that can be age hardened. Figure 25 shows a series of specimens of Kunial brass (Cu-20.34%Zn-5.87%Ni-1.39%Al) that were tint etched with Klemm's III. Figure 25(a) shows the grain structure of the alloy after solution annealing (73 HV hardness), revealing a multitude of colors in the grains and twins. Results were the same with aging at 300 °C (570 °F), which produced only a slight hardness increase (8 HV units). However, aging at 400 °C (750 °F), which increased the hardness to 143 HV, yielded a markedly different color response (Fig. 25b). Aging at the peak temperature, 500 °C (930 °F), increased the hardness to 192 HV, and the coloration within the grains was no longer uniform (Fig. 25c). The grain boundaries also appear to be wide. Overaging at 700 °C (1300 °F) reduced the hardness to 127 HV and produced a mottled-color appearance, precipitate in the grain boundaries, and denuding adjacent to the grain boundaries.

Klemm's I has been used to color ferrite and martensite in carbon and low-alloy steels. Figure 26(a) shows the microstructure of an as-rolled 1.31% C water-hardened tool steel etched with 4% picral. The structure is fine pearlite, and there is a grain-boundary carbide film present, but this cannot be easily seen with nital, even at 500 \times magnification (2% nital was slightly poorer for revealing the cementite films). Figure 26(b) shows the specimen after color etching with Klemm's I and viewed with polarized light plus sensitive tint. Note that the grain-boundary cementite film is clearly visible, because Klemm's

does not color cementite (neither does nital, but the contrast is too weak). Figure 27 shows an example of how Klemm's I colors ferrite in a wrought iron historic artifact. This is a section of a musket barrel that was hammered forged from wrought iron at the Henry gun factory in Nazareth, Pennsylvania, in the 19th century. Across the top is a layer of iron oxide made magenta in color by the sensitive tint filter. At the surface, the grains are coarse and columnar in shape. The central region is fine grained and equiaxed, and uniform colors are seen within the grains. At the bottom of the image, the grains are larger and more irregular in shape, and the grain coloration is not uniform. This difference in the grain structure must be due to differences in the amount of deformation these two regions experienced. The mottled grain color suggests that the composition is more variable in these grains.

Figure 28 shows the microstructure of a powder-made gear that was not fully consolidated (note the dark voids). The structure is tempered martensite, and Klemm's I revealed the structure of the lath martensite. Prior-particle shapes are easily seen.

Figure 29 shows a dramatic example of the value of color etching. Figure 29(a) shows a

montage of the microstructure of a weld in a low-carbon steel after etching with 2% nital. While the structure is visible, the grain boundaries are poorly revealed in the heat-affected zone and the base metal (center and right side). Figure 29(b) shows a montage of the specimen after etching with Klemm's I. It revealed the grain structure with exceptional clarity.

Beraha Color Etching with Sulfide Films. Beraha has a somewhat similar composition (Ref 57) that works much like Klemm's I. It contains 10 g $\text{Na}_2\text{S}_2\text{O}_3$, 3 g $\text{K}_2\text{S}_2\text{O}_5$, and 100 mL water. In these reagents, the metabisulfite ion ($\text{S}_2\text{O}_5^{2-}$) decomposes in an aqueous solution in contact with a metallic surface, yielding SO_2 , H_2S , and H_2 . The SO_2 de-passivates surfaces, particularly stainless steel surfaces, promoting film formation. The H_2S provides S^{2-} ions to form the sulfide film when ions of iron, nickel, or cobalt are present. Figure 46(c) discussed later in the text, shows the microstructure of as-continuously cast low-carbon, high-strength, low-alloy steel grade etched with Beraha's 10/3 version of Klemm's I. In general, this reagent performs much like Klemm's I but with slightly less aggressive coloring of ferrite.

Beraha also developed sulfide-film-forming reagents using a mineral acid (HCl) to permit tinting of stainless steels and nickel- and cobalt-base heat-resisting alloys (Ref 53, 56, 58). Beraha promoted these etches with a wide range of acid content to accommodate variations in corrosion resistance and, with possible additions to the composition, to enhance coloration. These etchants include the BI, BII, and BIII reagents promoted by Weck and Leistner (Ref 13). The basic compositions recommended by Beraha are given in Table 2. The HCl-base reagents are mainly useful for the austenitic stainless steels and nickel- and cobalt-base alloys. The author has not had success with them for ferritic stainless steels, but they can be used to color high-alloy steels, such as tool steels, and martensitic and precipitation-hardenable stainless steels. While they can color duplex stainless steels, they are far more difficult to use than aqueous 20%

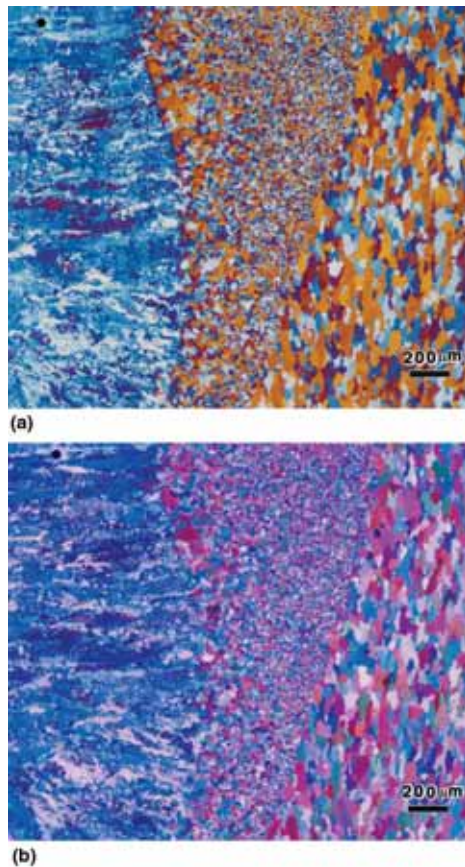


Fig. 23 This carbon steel weld developed an excellent interference film when tint etched with Klemm's I. Consequently, the bright-field image (a) reveals the grain structure very well, and the use of polarized light and sensitive tint (b) merely alters the color scheme without improving the image.

Table 1 Klemm's reagents

Reagent	Composition(a)	Use
Klemm I	50 mL stock solution 1 g $\text{K}_2\text{S}_2\text{O}_5$	Immerse up to 3 min. Colors ferrite and martensite in cast iron, carbon and low-alloy steels; reveals segregation. Colors β -phase in brass (α -phase can be colored, but very slowly). Colors zinc and alloys
Klemm II	50 mL stock solution 5 g $\text{K}_2\text{S}_2\text{O}_5$	Immerse up to 8 min. Colors α -phase in copper brass, tin, and manganese steels
Klemm III	5 mL stock solution 45 mL water 20 g $\text{K}_2\text{S}_2\text{O}_5$	Immerse up to 8 min. Colors bronzes and Monel

(a) Stock solution: aqueous cold-saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution

NaOH electrolytically or Murakami's reagents (Fig. 18, 20, respectively).

Figure 30 shows a portion of a weld made from Nitronic 50 and the heat-affected zone and base metal of 7-Mo PLUS duplex stainless steel color etched with Beraha's BI reagent. Note the coarseness of the heat-affected zone compared to the base metal and the acicular structure of the weld metal. Ferrite was colored, while the austenite was not. Figure 31 shows the austenitic grain structure of Custom Flo 302 HQ stainless steel in the solution-annealed condition. Beraha's BI was used to color the grain structure. Figure 32 shows the austenitic grain structure of 316L stainless steel that was cold reduced 30% in thickness and then solution annealed from 1150 °C (2100 °F). It was color etched with Beraha's BII reagent. The streaks indicate alloy segregation, because they are parallel to the deformation axis. Color etchants are excellent for revealing segregation, and numerous studies have demonstrated that microprobe determinations of compositions can be made on an etched surface without impairment of the chemical analysis results. Figure 33 shows the microstructure of Waspaloy, a nickel-base superalloy, in the so-

lution-annealed and double-aged condition. The specimen was tint etched with Beraha's BIV, with an addition of ferric chloride. Figure 34 shows the microstructure of Elgiloy, a cobalt-base alloy used for watch springs. The strip was hot rolled and then solution annealed at 1040 °C (1900 °F), not high enough for complete recrystallization. The specimen was tint etched with Beraha's BIV plus an addition of ferric chloride.

Beraha's etchants, based on sulfamic acid, a weak organic acid, have not been used much, although they are quite useful, reliable, and easy to employ (Ref 63). The sulfamic-acid-based reagents (Table 3) are applicable to iron, low-carbon and alloy steels, tool steels, and martensitic stainless steels. The author finds them to be highly reliable and simple to use.

The sulfamic acid reagents are very useful for color metallography of iron-base alloys. Furthermore, they are easy to use and quite reliable. However, they do not seem to be used much. Figure 35 shows lath martensite in quenched and tempered 4118 alloy steel (the core of a carburized specimen) tint etched with Beraha's sulfamic reagent 1. Figure 36 shows the microstructure of a Hadfield manganese steel specimen that

was solution annealed and tint etched with Beraha's sulfamic acid reagent 3. Figure 37 shows the fcc grain structure in an Fe-39%Ni magnetic alloy color etched with Beraha's sulfamic reagent 3. Figure 38 shows the decarburized surface of quenched and tempered 420 martensitic stainless steel tint etched with sulfamic reagent 4. Note that ferrite grains are present at the surface.

Beraha has also developed two rather specialized tint etches that deposit cadmium sulfide (CdS) or lead sulfide (PbS) films on the surfaces of steels and copper-base alloys (Ref 61, 62). These two etchants are quite useful. The CdS reagent is useful for carbon and alloy steels, tool steels, and ferritic, martensitic, and precipitation-hardenable stainless steels, while the PbS reagent does an excellent job on copper-base alloys and can be used to color sulfides in steels white (the specimen is pre-etched with nital, and the etch colors the darkened matrix, so that the white sulfides are visible). Table 4 lists these two reagents.

Figure 39 shows the microstructure of quenched and tempered 416 stainless steel, a grade designed for improved machinability. The

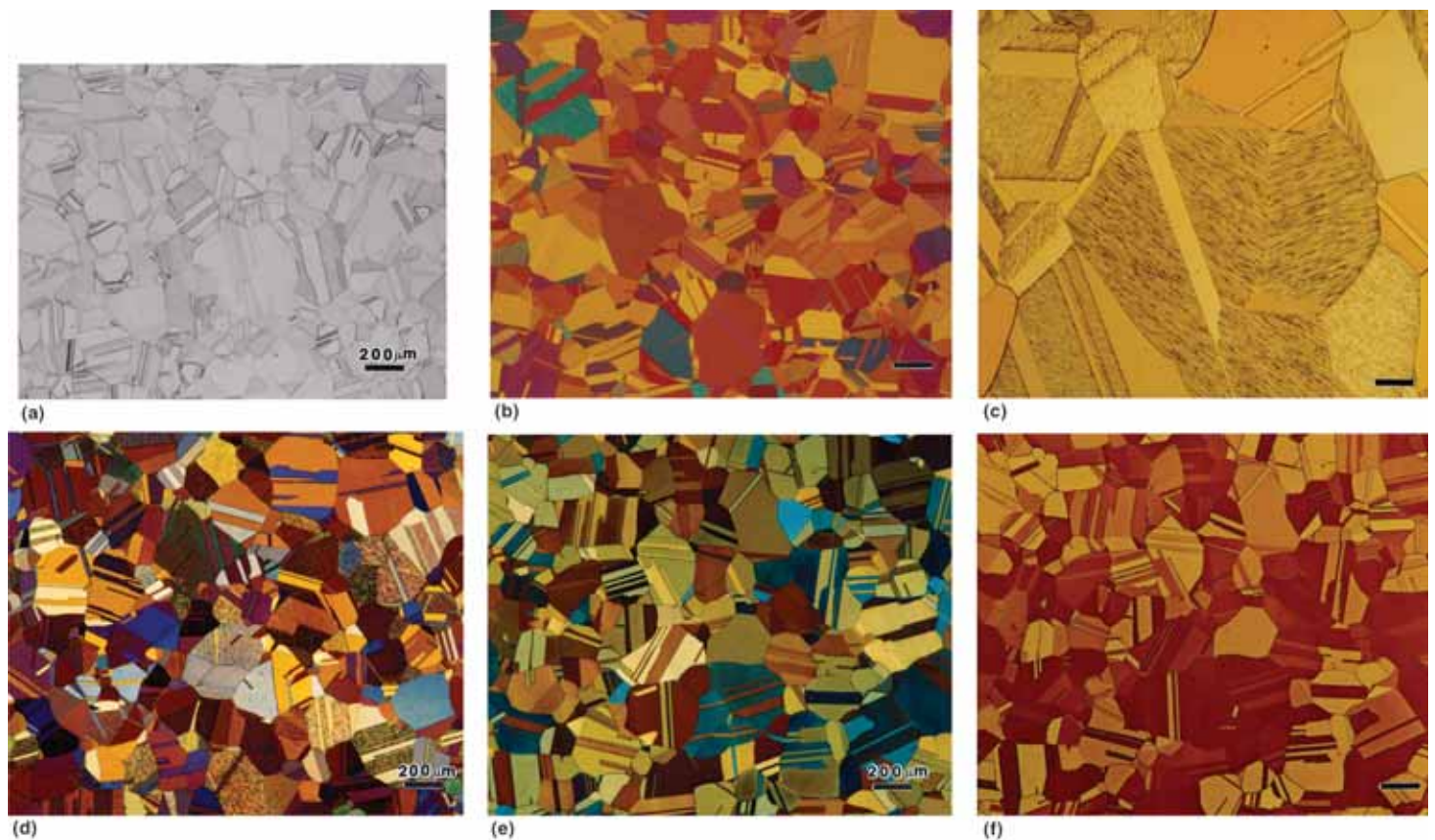


Fig. 24 Wrought cartridge brass (Cu-30%Zn) cold reduced 50% and annealed at 704 °C (1300 °F) for 30 min. Fully recrystallized and grown, equiaxed face-centered cubic grains with annealing twins. (a) Etched with equal parts ammonium hydroxide and hydrogen peroxide (3%). (b) The specimen was tint etched with Klemm's I reagent for 3 min, producing a lightly colored image in bright field. The structure was imaged with polarized light and sensitive tint, which dramatically improved the color contrast. The magnification bar is 200 μm long. (c) Etching with Klemm's II reagent for 2 min produced line etching within certain twins and grains. The lines are parallel to specific crystal planes. The specimen was viewed in bright field. The magnification bar is 50 μm long. (d) Tint etched with Klemm's II reagent and viewed with polarized light plus sensitive tint. This version line-etches many of the alpha grains. (e) Tint etched with Klemm's III reagent and viewed with polarized light and sensitive tint. (f) Viewed with bright-field illumination. Magnification bar is 200 μm long.

CdS reagent has colored the martensitic matrix blue and brown but has not colored the delta ferrite. The sulfide inclusions (gray) were not attacked by this reagent. Figure 40 shows the microstructure of austempered ductile iron after isothermal heat treatment. The CdS reagent colored the ausferrite yellow, brown, and blue, while the retained austenite was not colored (it is tinted slightly by the sensitive tint filter). The nodule structure is visible in color due to the use of polarized light and sensitive tint. Figure 41 shows an as-cast specimen of Ni-Hard alloyed cast iron that was tint etched with Beraha's CdS reagent. Because retained austenite is the dominant matrix phase, the CdS reagent (it often acts as a complex reagent) colored the retained austenite light brown. The massive cementite particles are uncolored by the reagent but are tinted slightly by the sensitive tint filter. The plate martensite is colored light blue, dark blue, and shades of violet.

Figure 42 shows Beraha's PbS reagent used to color the grain structure of the cartridge brass

specimen previously shown in Fig. 24. The coloring is even more dramatic with the PbS reagent than with Klemm's III. Figure 43 shows the microstructure of aluminum brass (Cu-22%Zn-2%Al) that was cold drawn and then annealed at 750 °C (1380 °F). Tint etching with Beraha's PbS reagent gave a good rendering of the grain structure of the alloy.

Sodium metabisulfite (Ref 66, 67, 70) has been used in a number of concentrations, from approximately 1 to 20 g per 100 mL water, as a safe, reliable, and useful color etch for irons and steels. It is not as strong a coloring etch as the others listed previously, and better results are usually obtained by viewing with polarized light and sensitive tint; but, this is not always a problem and sometimes can be an advantage. Figure 44 shows the microstructure of 5160 alloy steel that was austenitized at 830 °C (1525 °F) and then isothermally held at 538 °C (1000 °F) for 60 s (Fig. 44a) and 45 min (Fig. 44b) and then water quenched. The specimens were etched with aqueous 10% sodium metabisulfite and

viewed with bright field (Fig. 44a) for the 60 s hold and with polarized light plus sensitive tint (Fig. 44b) for the 45 min hold. After 60 s, only a small amount of upper bainite (colored white and blue—the blue areas are where the carbide has precipitated) has formed before the remaining austenite was quenched, forming martensite (colored light brown). However, after 45 min, more upper bainite has formed, and the remaining austenite transformed to very fine pearlite (colored violet, green, orange, and dark blue). It is hard to see the bainitic carbide regions, which were colored blue, against the slightly darker blues in the pearlite. Concentrations of 10 to 20% Na₂S₂O₅ have been used to color etch Hadfield manganese steels. Figure 45 shows martensite formed in the decarburized (<0.5% C) surface region of a wrought Hadfield manganese steel specimen etched with 10% sodium metabisulfite and viewed with polarized light plus sensitive tint.

Comparison of Sulfide-Film-Forming Tint Etchants for Steels. As a comparison of these various sulfide-film-forming tint etchants for steels, Fig. 46(a) shows the microstructure of a

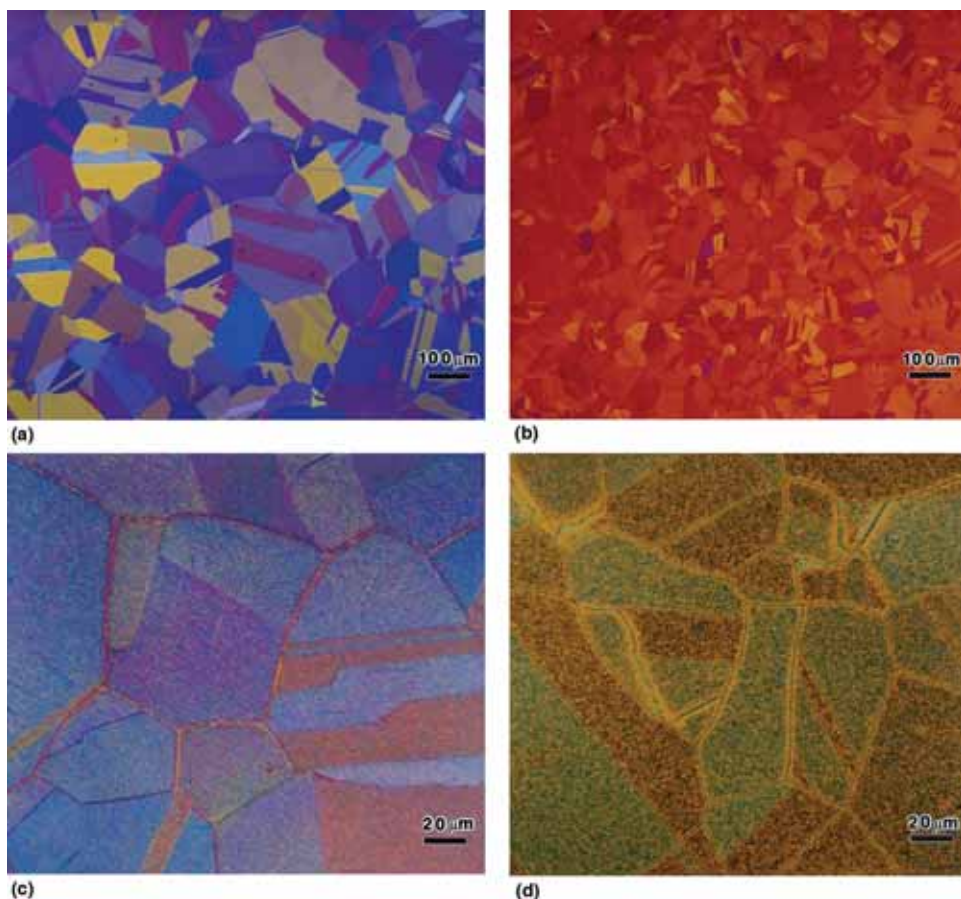


Fig. 25 Microstructure of Kunial brass (Cu-20.3%Zn-5.9%Ni-1.4%Al) that was (a) hot worked and solution annealed at 800 °C (1470 °F) (73 HV) and then tint etched with Klemm's III. (b) Solution annealing and aging at 400 °C (750 °F) (143 HV) and then tint etching with Klemm's III produced less color differences in a specimen with a finer grain size. The color difference may only be due to growth of a thinner interference film. Both specimens were viewed with polarized light plus sensitive tint. (c) The same alloy was hot worked, solution annealed at 800 °C (1470 °F), aged at 500 °C (930 °F) (192 HV, peak aged), and then tint etched with Klemm's III, which produced mottled grain coloring and some elongated features within grains. (d) Solution annealing and aging at 700 °C (1300 °F) (127 HV, overaged) and then tint etching with Klemm's III produced a narrower range of grain colors, and the strengthening precipitates are now visible with the light microscope.

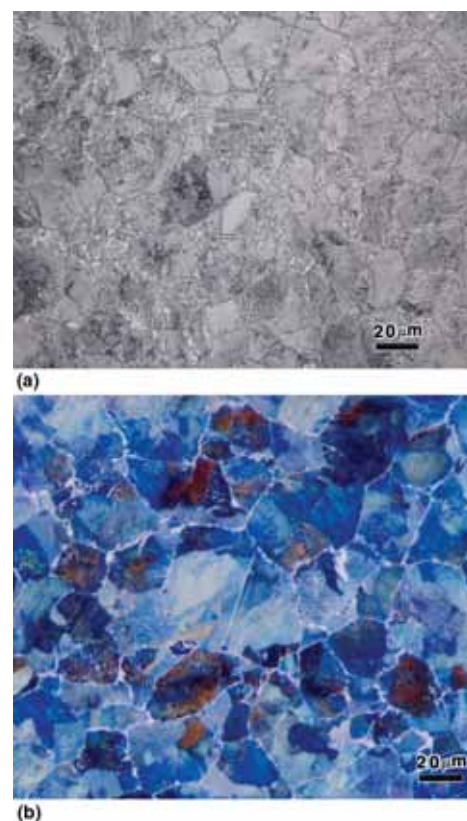


Fig. 26 Microstructure of as-rolled Fe-1.31%C-0.35%Mn-0.25%Si high-carbon water-hardenable tool steel. (a) Etching with picral revealed the Widmanstätten intragranular cementite that precipitated as proeutectoid cementite before the eutectoid reaction, but the intergranular cementite is not visible. Etching with nital was not as good as picral. (b) Color etching of the specimen with Klemm's I clearly revealed the intergranular and intragranular cementite films (viewed with polarized light and sensitive tint).

low-carbon, high-strength, low-alloy steel in the as-rolled condition etched with nital. Segregation streaks were observed in this slab, and some segregated regions contained cracks. Bainite was observed in these streaks (some contained cracks), while the matrix was ferrite and pearlite. Figure 46(b) shows the specimen etched with Klemm's I, where the darkening of the ferrite grains is excessive, and there is poor contrast between the ferrite and the pearlite in the matrix and between the matrix and the segregate streak. Figure 46(c) shows the specimen etched with Beraha's version of Klemm's I. The coloring of the ferrite was less intense, and the structural elements in the matrix and in the streak are easily observed. Figure 46(d) shows the specimen etched with Beraha's sulfamic acid etch number



Fig. 27 Microstructure of a scrapped portion of a musket barrel made in the 19th century at the Henry gun factory near Nazareth, Pennsylvania, etched with Klemm's I and viewed with polarized light plus sensitive tint. The surface layer is scale (iron oxide) from forging the wrought iron. Beneath the scale is a layer of columnar ferrite grains. Below this zone, the grains are smaller and equiaxed. At the bottom of the field, the ferrite grains are larger and show evidence of segregation (the area probably saw less heat and forge work). The fine black spots are slag particles. The magnification bar is 200 μm long.

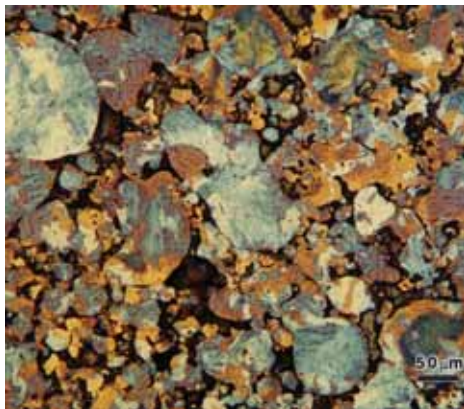


Fig. 28 Lath martensite microstructure of a low-density powder metallurgy alloy steel gear that was tint etched with Klemm's I and viewed with polarized light plus sensitive tint. Note that prior-particle shapes are quite visible due to the low density.

1. The coloring is less intense than with Klemm's I, and the streak is easily seen against the matrix, but the pearlite is hard to distinguish from the ferrite in the matrix. Figure 46(e) shows the specimen etched with 10% sodium metabisulfite, which yielded excellent contrast. The ferrite is not colored, except by the sensitive tint filter. The pearlite in the matrix is easily observed in the matrix, and the segregate streak stands out very well.

Table 2 Beraha's reagents using HCl and potassium metabisulfite

Reagent (Ref)	Stock solution	Additions (per 100 mL stock solution)	Comments
B0 (58)	6 mL HCl 994 mL water	1 g $\text{K}_2\text{S}_2\text{O}_5$	For iron, carbon, alloy and tool steels. Immerse up to 60 s. Shake strongly to start etching, then leave motionless to color.
BI (13, 53, 58)	1000 mL water 200 mL HCl 24 g NH_4FHF	0.1–0.2 g $\text{K}_2\text{S}_2\text{O}_5$ (for martensitic stainless steels) 0.3–0.6 g $\text{K}_2\text{S}_2\text{O}_5$ (for ferritic and austenitic stainless steels)	Immerse up to 90 s. Best to use plastic tongs
BII (13, 53, 58)	800 mL water 400 mL HCl 48 g NH_4FHF	0.3–0.8 g $\text{K}_2\text{S}_2\text{O}_5$ 10–25 mg $\text{Na}_2\text{S(a)}$	For corrosion and heat-resistant alloys. Sodium sulfide can be added to improve color contrast.
BIII (13, 53, 58)	600 mL water 400 mL HCl 50 g NH_4FHF	0.3–0.8 g $\text{K}_2\text{S}_2\text{O}_5$ 1–1.5 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O(a)}$ 1 g $\text{CuCl}_2\text{(a)}$	For corrosion and heat-resistant alloys. The optional additions (to improve coloration) can be made to the stock solution. Immerse up to 180 s.
BIV (58)	500 mL water 500 mL HCl 50 g NH_4FHF	0.3–0.8 g $\text{K}_2\text{S}_2\text{O}_5$ 1–1.5 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O(a)}$ 1 g $\text{CuCl}_2\text{(a)}$	For difficult-to-etch corrosion- and heat-resisting alloys. The optional additions (to improve coloration) can be made to the stock solution.

(a) Optional additions used to improve color response. Note: When water is specified, use distilled water.

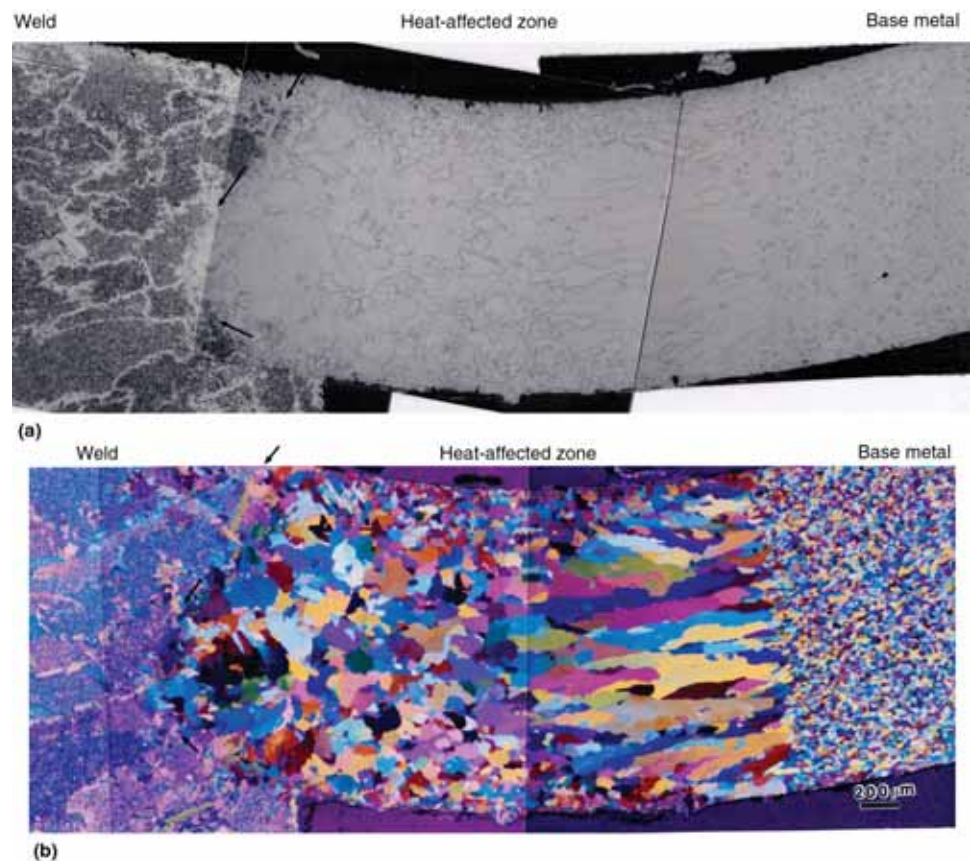


Fig. 29 Color etching to reveal weld microstructure. (a) Montage showing the structure of a large weld in a carbon steel as revealed using 2% nital. Note that the grain size and shape change dramatically from the fusion line (arrows) to the base metal at right. Nital did not fully reveal the grain structure, however. (b) Montage showing the structure of a weld in a carbon steel as revealed by Klemm's I reagent, viewed with polarized light plus sensitive tint. Note that the grain size and shape change dramatically from the fusion line (arrows) to the base metal. The magnification bar is 200 μm long.

Reagents that Deposit Molybdate Films.

Beraha developed two tint etchants that use molybdate ions in nitric acid (Ref 55, 62, 64). The MoO_4^{2-} contains molybdenum at a +6 valence state that can be reduced to a +4 valence state. Reduction can be partial with both the +6 and +4 ion valence levels present. This produces a blue color in the etchant, molyb-

denum blue. Partial reduction occurs at the local microcathodes on the specimen surface, leading to selective coloration. The sodium molybdate tint etchant for steels works well. It will color cementite in steels. Beraha also developed a molybdate-base tint etchant for aluminum alloys, although the author has not found that etchant easy to use. Table 5 lists the

composition of the sodium molybdate reagent for steels.

Figure 47 shows the microstructure of a hot-rolled Fe-1%C binary alloy (not a steel) that was tint etched with Beraha's sodium molybdate reagent. This reagent colors the cementite in carbon and low-alloy steels, as shown in this example. The arrow points to a grain-boundary cementite film. Figure 48 shows the microstructure of a spheroidize-annealed W1 carbon tool steel after etching with Beraha's sodium molybdate reagent. In this case, the ferrite is colored as well as the cementite.



Fig. 30 Microstructure of 7-Mo PLUS duplex stainless steel (Fe-<0.03%C-<2%Mn-27.5%Cr-4.85%Ni-1.75%Mo-0.25%N) welded with Nitronic 50, etched with Beraha's B1 reagent, and viewed with bright-field illumination. Ferrite is colored, and austenite is unaffected. The magnification bar is 200 μm long.



Fig. 32 Austenitic, twinned grain structure of 316L austenitic stainless steel (Fe-<0.03%C-17%Cr-12%Ni-2.5%Mo) that was hot rolled, solution annealed, cold reduced 30% in thickness, and solution annealed (1150 $^{\circ}\text{C}$, or 2100 $^{\circ}\text{F}$, for 1 h, water quenched). The specimen was tint etched with Beraha's B11 reagent and viewed with polarized light plus sensitive tint. The faint lines, slightly off horizontal, are due to alloy segregation and are parallel to the longitudinal axis. The magnification bar is 200 μm long.

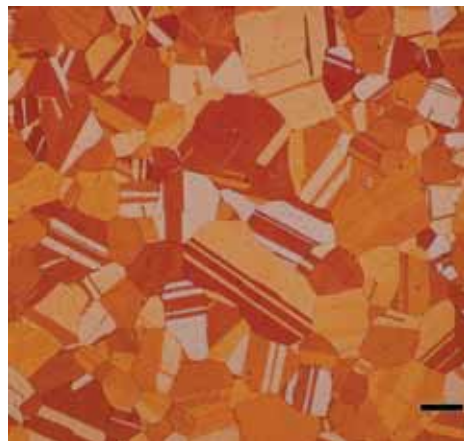


Fig. 33 Microstructure of wrought, solution-annealed, and double-aged (approximately 42 HRC) Waspaloy, a nickel-base superalloy (Ni-0.06%C-19.5%Cr-4.2%Mo-13.5%Co-3%Ti-1.35%Al-0.07%Zr-0.005%B-<2%Fe), tint etched with Beraha's B1V reagent, revealing twinned austenitic grains. Viewed in bright field. The magnification bar is 100 μm long.

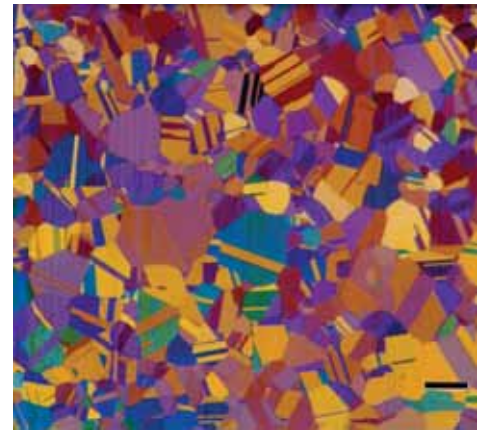


Fig. 31 Microstructure of Custom Flo 302 HQ austenitic stainless steel (Fe-<0.08%C-18%Cr-9%Ni-3.5%Cu) in the hot-rolled and solution-annealed condition after tint etching with Beraha's B1 reagent. The structure is equiaxed, twinned, face-centered cubic austenite. The faint vertical lines are from alloy segregation (longitudinal direction is vertical). Viewed with polarized light plus sensitive tint. The magnification bar is 100 μm long.

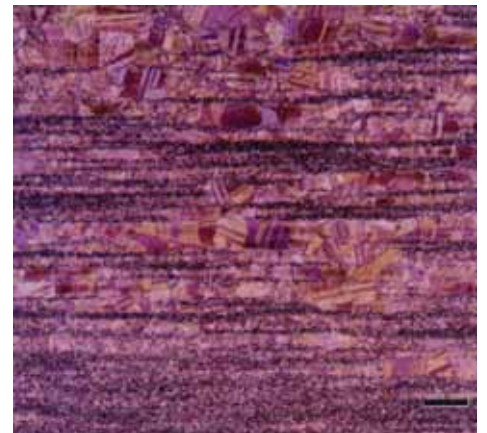


Fig. 34 Microstructure of Elgiloy, a cobalt-base alloy used for watch springs (Co-20%Cr-15%Fe-15%Ni-2%Mn-7%Mo-0.05%B-0.15%C), after hot rolling and solution annealing (1040 $^{\circ}\text{C}$, or 1900 $^{\circ}\text{F}$, for 2 h, water quenched). The specimen is partially recrystallized. The specimen was tint etched with Beraha's B1V plus 1 g FeCl_3 per 100 mL. The specimen was viewed with polarized light plus sensitive tint. The magnification bar is 100 μm long.

Reagents that Deposit Elemental Selenium.

Beraha also developed tint etchants that deposit elemental selenium on the surface of steels and nickel- and copper-base alloys (Ref 59, 60). The selenium ion is reduced at the microcathodes on the surface of the specimens, producing coloration. It is recommended to use plastic tongs with these etchants. Selenic acid is a dangerous acid, and it should be handled with care. These etchants are quite useful. Compositions of seven selenic acid etchants and their characteristics are given in Table 6.

Figure 49 shows the microstructure of a chill-cast gray cast iron etched with Beraha's selenic acid reagent number 1. As it was chill cast, cementite formed in the chill region, along with



Fig. 35 Microstructure of the core of a carburized, heat treated 4118 alloy steel (Fe-0.2%C-0.8%Mn-0.5%Cr-0.12%Mo) tint etched with Beraha's sulfamic acid reagent (No. 1) and viewed with polarized light plus sensitive tint, revealing a lath martensite structure. The magnification bar is 20 μ m long.

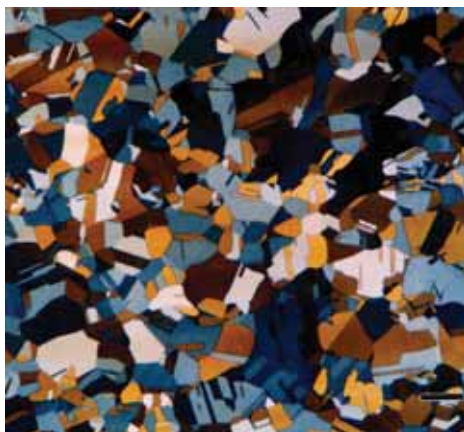


Fig. 37 Twinned austenitic grain structure of wrought, annealed Fe-39%Ni tint etched with Beraha's sulfamic acid solution (No. 3) and viewed with polarized light plus sensitive tint. The magnification bar is 100 μ m long.

regions containing small graphite flakes. The selenic acid etch colored the cementite reddish-orange, while the ferrite was not colored. Note the ferrite dendrites in the specimen. Beraha's selenic acid reagent will also color cohenite, (Fe, Ni, Co)₃C, a carbide found in certain meteorites (Ref

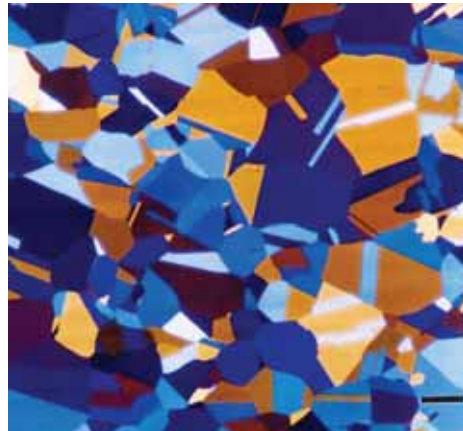


Fig. 36 Twinned austenitic grain structure of solution-annealed, wrought Hadfield manganese steel (Fe-1.12%C-12.7%Mn-0.31%Si) tint etched with Beraha's sulfamic acid reagent (No. 3) (100 mL water, 3 g potassium metabisulfite, and 2 g sulfamic acid) and viewed with polarized light plus sensitive tint. The magnification bar is 100 μ m long.

71). Figure 50 illustrates the use of Beraha's selenic acid reagent number 7 for copper-base alloys. The specimen is alpha-beta brass, Cu-40%Zn, that was hot extruded and cold drawn. The selenic acid reagent colors the twinned alpha phase nicely and produces a mottled-colored appearance in the beta phase. Thus, it acts as a complex tint etchant.

Other Tint Etchants. There are many more tint etchants, but only a few that the author has tried and found to be useful are discussed. Lichtenegger and Blösch (Ref 69) developed an unusual reagent that will color austenite in duplex stainless steels, rather than ferrite (as nearly all

Table 3 Beraha's sulfamic acid etchants

Reagent	Composition	Comments
1	100 mL water 3 g K ₂ S ₂ O ₅ 1 g NH ₂ SO ₃ H	For cast iron, iron, carbon and alloy steels, manganese steels. Immerse up to 4 min. Good for 2-4 h. Discard when solution is yellow.
2	100 mL water 6 g K ₂ S ₂ O ₅ 2 g NH ₂ SO ₃ H	Use as reagent 1, but faster acting
3	100 mL water 3 g K ₂ S ₂ O ₅ 2 g NH ₂ SO ₃ H	Use as reagent 1, but faster acting. Immerse up to 90 s.
4	100 mL water 3 g K ₂ S ₂ O ₅ 1 g NH ₂ SO ₃ H 0.5-1 g NH ₄ FHF	Use for martensitic stainless steels, tool steels, manganese steels. Immerse up to 3 min.

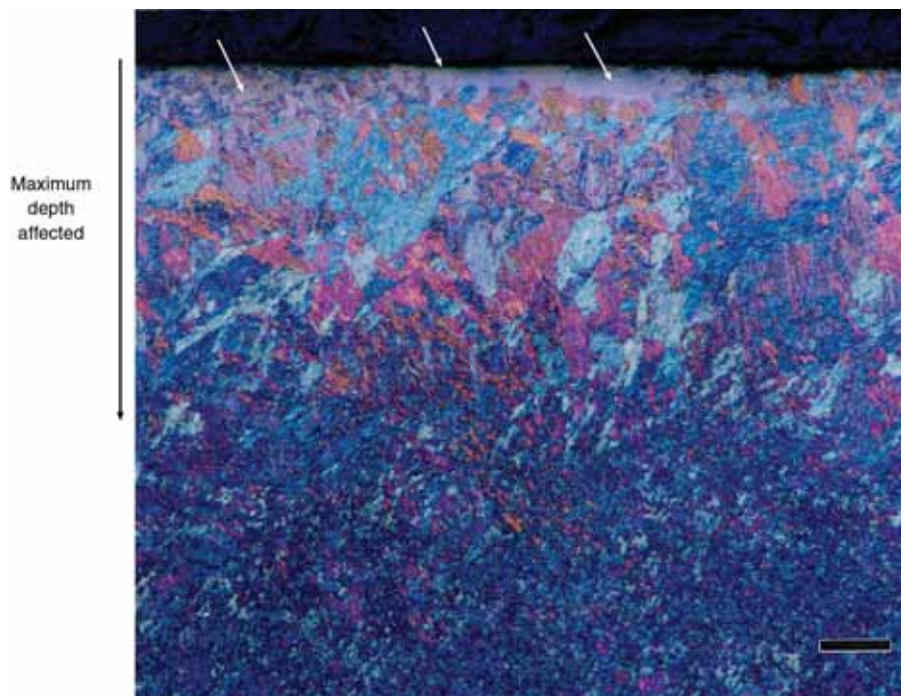


Fig. 38 Microstructure at the surface of a decarburized, hardened specimen of type 420 martensitic stainless steel (Fe-0.35%C-13%Cr) tint etched with Beraha's sulfamic acid reagent (No. 4) and viewed with polarized light plus sensitive tint. Note the free ferrite (arrows) at the surface (complete loss of carbon) and the change in the appearance of the martensite in the partial decarburized zone. The magnification bar is 100 μ m long.

others do). It consists of 20 g of ammonium bifluoride (NH_4FHF) and 0.5 g potassium metabisulfite ($\text{K}_2\text{S}_2\text{O}_5$) dissolved in 100 mL water. Although most chemicals, when dissolved in water, generate heat, that is, produce an exothermic reaction, ammonium bifluoride absorbs heat; that is, the reaction is endothermic. So, if the distilled water is at room temperature, the solution gets colder, and the ammonium bifluoride will not dissolve. Consequently, one must heat the water before dissolving the ammonium bifluoride. The etchant is generally used at approximately 25 to 30 °C (77 to 86 °F), rather than at room temperature. Weck (Ref 14) made several modifications of this etchant. Figure 51 shows the microstructure of an as-cast duplex stainless steel, ASTM A 890, grade 5A, etched with the LB1 reagent, as it is generally called. It colored the austenite phase (no twins are observed, because this is an as-cast structure).

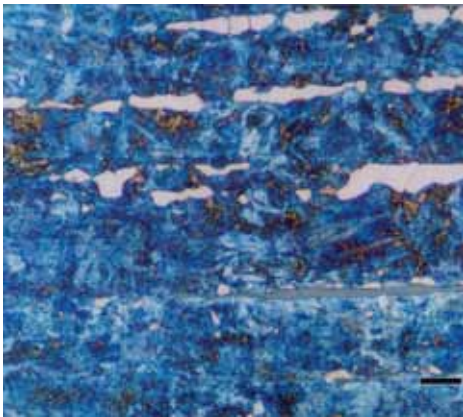


Fig. 39 Martensitic microstructure of Project 70 416 stainless steel ($\text{Fe} > 0.15\% \text{C} > 0.15\% \text{S} - 13\% \text{Cr}$) in the wrought heat treated condition (approximately 98 HRB) tint etched with Beraha's CdS reagent. The white grains are delta ferrite, and the elongated gray particles are manganese sulfides. The longitudinal direction is horizontal. The magnification bar is 200 μm long.

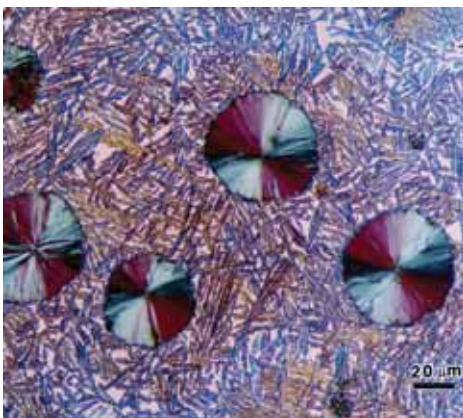


Fig. 40 Microstructure of austempered ductile iron tint etched with Beraha's CdS reagent. The microstructure shows large graphite nodules, ausferrite (blue and brown), and retained austenite (white) when viewed with polarized light plus sensitive tint.

Weck (Ref 12–14) developed a number of tint etchants, while using many of those shown in her research. While several have been developed for coloring aluminum, the most useful consists of 100 mL water, 4 g KMnO_4 , and 1 g NaOH (similar to Groesbeck's carbide reagent, but 1 g instead of 4 g of NaOH). This tint etch is easier to use with cast aluminum alloys than with wrought alloys, but when successful, it will reveal the grain structure of many wrought aluminum alloys. Figure 52 shows the microstructure of the as-cast 1100 aluminum specimen shown in Fig. 16(d) after anodizing. Note that Weck's reagent reveals the segregation (coring) in the dendrites, while anodizing did not. Another example is shown in Fig. 53, where a cast 206 aluminum alloy was tint etched with Weck's reagent for aluminum. The intermetallic precipitates in the interdendritic regions can be easily seen, and the segregation within the dendrites is vividly revealed. Figure 54 shows the microstructure of wrought aluminum alloy 6061-T651 after etching with Weck's. It was successful in bringing up the grain structure, while other standard reagents failed. As a final example of the

use of Weck's, Fig. 55 shows the interface between the base metal and the weld in a friction stir weld in alloy 2519.

Weck also developed several color etchants for titanium. Of them, one works better than the others, but it must be modified slightly. This reagent consists of 100 mL water, 50 mL ethanol, and 2 g ammonium bifluoride. When the author has used this composition, small, white butterfly-shaped artifacts could be observed in the structure. Reducing the ethanol content to 25 mL (Ref 72) eliminates this problem, and good etch results are obtained. The solution colors the alpha phase in titanium and its alloys. Figure 56 shows commercial-purity titanium, ASTM F 67, grade 2, color etched with modified Weck's for titanium. Figure 57 shows the structure of as-cast Ti-6Al-4V color etched with Weck's reagent.

Two etchants have been found useful for coloring theta phase, AlCu_2 , in aluminum-copper alloys. The first was developed by Liénard (Ref 73, 74) and consists of 200 mL water, 1 g ammonium molybdate, and 6 g ammonium chloride. The specimen is immersed for up to 2 min, which colors the theta phase violet, as shown in

Table 4 Beraha's CdS and PbS reagents

Reagent	Composition	Comments
CdS	1000 mL water 240 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 30 g citric acid 20–25 g cadmium chloride Note: Cadmium sulfate or cadmium acetate can be substituted for cadmium chloride.	For iron, steel, ferritic and martensitic stainless steel: Dissolve chemicals in the order shown. Age 24 h in a dark bottle in darkness at 20 °C (70 °F). Before use, filter 100 mL of the solution. Immerse 20–90 s. For steels, after 20–40 s, ferrite is colored red or violet; with longer times, ferrite is yellow or light blue, phosphide is brown, and carbides are violet or blue. For stainless steel: Immerse 60–90 s to color carbides red or violet-blue, matrix yellow; ferrite colors vary. Immersion >90 s colors the sulfides red-brown.
PbS	1000 mL water 240 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 30 g citric acid 24 g lead acetate	For copper and copper alloys: Dissolve in order given, and age as above. Do not filter stock solution. Immersion colors face-centered cubic matrix. For cast iron and steel: Pre-etch with nital. Add 0.2 g NaNO_2 to 100 mL of solution with vigorous stirring. Immerse until surface is colored as follows: ferrite, violet to blue; cementite, pale violet or blue; phosphide, yellow; and sulfides, white.

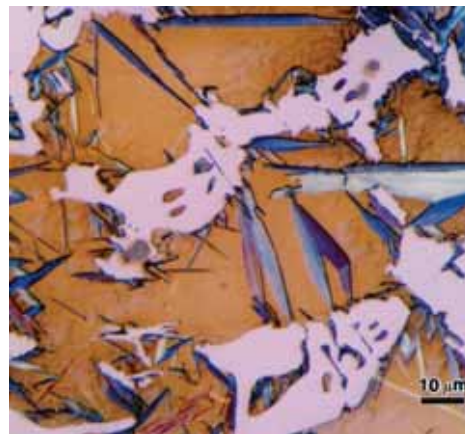


Fig. 41 As-cast Ni-Hard cast iron ($\text{Fe} - 2.98\% \text{C} - 0.64\% \text{Mn} - 0.85\% \text{Si} - 4.4\% \text{Ni} - 2.34\% \text{Cr}$) containing cementite (white), retained austenite (light brown), manganese sulfides (gray particles), and plate martensite needles (light blue and medium blue) after tint etching with Beraha's CdS reagent and viewing with polarized light plus sensitive tint.



Fig. 42 Wrought cartridge brass (Cu-30%Zn) cold reduced 50% and annealed at 704 °C (1300 °F) for 30 min to produce a fully recrystallized, coarse-grained, equiaxed, face-centered cubic grain structure with annealing twins. Tint etched with Beraha's PbS. Viewed with polarized light and sensitive tint. The magnification bar is 200 μm long.

Fig. 58. The second etchant, of unknown origin, consists of a solution containing 20 mL water, 20 mL nitric acid, and 3 g ammonium molybdate. To use, add from 20 to 80 mL ethanol to this solution, and immerse until the surface is colored. This colors the theta blue, as shown in Fig. 59. Other solutions also exist for coloring theta or other constituents in aluminum alloys.

Several color etchants have been developed for molybdenum (Ref 10, 75, 76) and for tungsten (Ref 77). The author, however, has used an etchant for molybdenum that was developed at Oak Ridge National Laboratory (Ref 78) and consists of 70 mL water, 10 mL sulfuric acid, and 20 mL hydrogen peroxide (30% concentration). The specimen is immersed for 2 min. If the specimen is swabbed with the reagent, a color film will not form, but a grain-boundary flat etch will result. Figure 60 illustrates results with this reagent for pure molybdenum.

Thermal Methods to Produce Color

Although many textbooks state that heat tinting is not reproducible, the author's experience has been otherwise. Heat tinting is an almost universal method that can be applied to many metals and alloys. There are some restrictions. First, one must work with an unmounted specimen; otherwise, the polymeric mounting material will burn. Low-melting-point metals and alloys are unsuitable. If the heat tinting temperature will alter the microstructure, then the method should not be used. However, many metals and alloys can be successfully colored by heating them in air until a light oxide film forms on the surface. As the film grows, it will become thick enough to produce interference colors. When the surface reaches a visible color—generally, a red-violet color works well, but thinner films are often useful—remove the specimen from the furnace, and cool it back to room temperature. As with tint

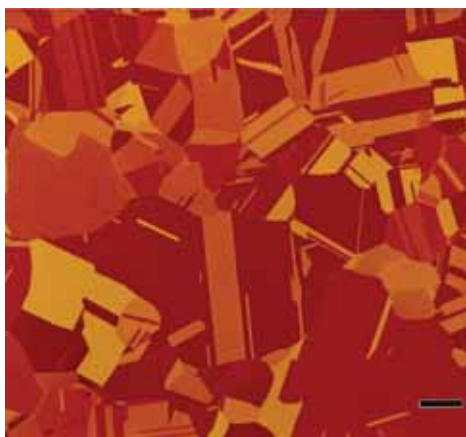


Fig. 43 Microstructure of aluminum brass (Cu-22%Zn-2% Al) that was cold drawn and annealed at 750 °C (1380 °F) after etching with Beraha's PbS reagent, revealing a coarse alpha face-centered cubic grain structure with annealing twins. The grain size is ASTM 0.8, and the hardness is 61 HV. The magnification bar is 200 μ m long.

etching, polarized light and sensitive tint can improve the results. Heat tinting can also be quite selective, but the temperature must be kept low so as to not color everything. However, with practice, the best temperature can be determined for a particular alloy. Table 7 shows a listing of temperatures published in the literature for different metals and alloys. Figure 61 shows the structure of commercially pure titanium, ASTM F 67, grade 4, in the annealed condition after heat tinting, while Fig. 62 shows the structure of as-cast Ti-6Al-4V after heat tinting.

Vapor Deposition Methods to Produce Color

In 1960, Pepperhoff showed that microstructures could be revealed without etching but by

vacuum deposition of a suitable material onto the prepared surface. The deposition produced a thin, low-absorption, dielectric film with a high refractive index. Small differences in reflectivity usually exist between microstructural constituents, and therefore, they are invisible or barely visible in the as-polished condition. In such cases, Nomarski DIC may reveal the structure well but not always. The Pepperhoff method produces a thin interference layer in a different manner than by chemical etching or heat tinting, but the end results are similar. Contrast between two constituents is maximized when a film is produced using a material with a high refractive index. Suitable materials include ZnTe, ZnSe, TiO₂, and ZnS. The method is described in depth by Bühler and Hougardy (Ref 79). Reactive sputtering is a similar technique and equally useful.

Conclusions

Color can be an extremely useful tool for examining the microstructure of many metals and alloys as well as other materials. Natural color is very limited but useful when it is present. Optical methods can introduce color with good results. Dark-field illumination has some limited applications. Polarized light, perhaps aided with a sensitive tint filter (always examine the structure with and without the sensitive tint filter, and a variable sensitive tint filter is very useful), is useful with metals and alloys that have noncubic crystal structures. However, some of these metals respond weakly to polarized light, and certain etchants may aid the response. Also, some cubic metals and alloys may respond to polarized light and sensitive tint after being etched.

This article has listed compositions of tint etchants that produce good results, and illustrations of these results were given. It is important to remember that the specimen must be properly prepared before using a tint etchant. Any residual

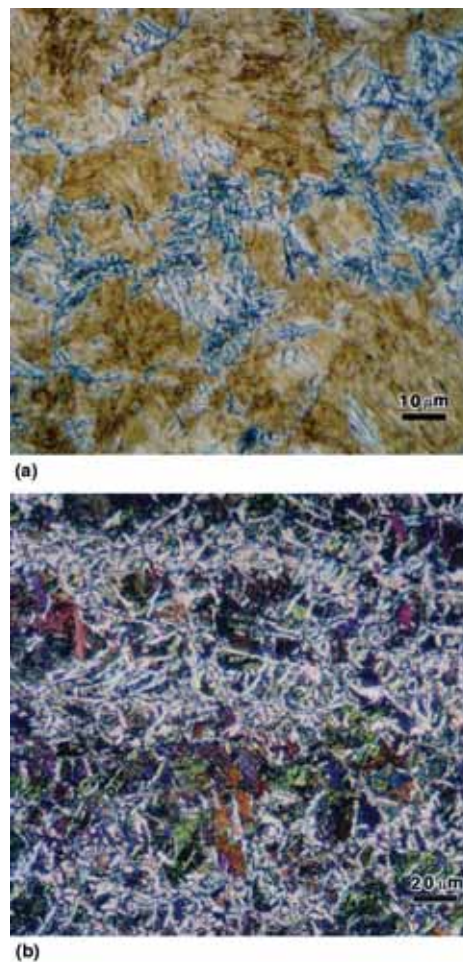


Fig. 44 Use of sodium metabisulfite to reveal structure in 5160 alloy steel (Fe-0.6%C-0.85%Mn-0.25%Si-0.8%Cr). (a) Upper bainite and as-quenched martensite in a specimen that was austenitized at 830 °C (1525 °F) for 30 min, isothermally held at 538 °C (1000 °F) for 60 s to partially transform the austenite, and then water quenched (untransformed austenite forms martensite). (b) Upper bainite and pearlite in a specimen held 45 min at 538 °C (1000 °F) to produce complete transformation. Both specimens etched with aqueous 10% Na₂S₂O₅, which colored the martensite light brown, the upper bainite blue, and the pearlite various shades of orange, green, blue, and red.

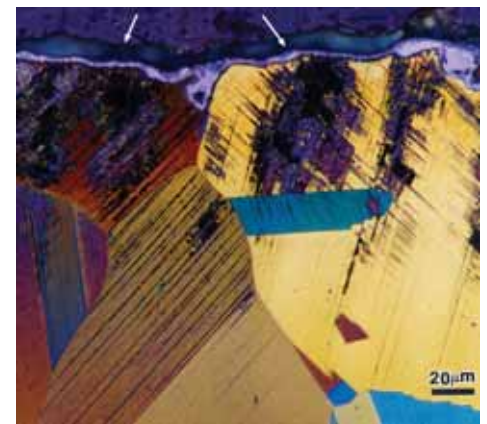


Fig. 45 Etching with 10% sodium metabisulfite revealed epsilon martensite at the surface of this hot-worked and solution-annealed specimen of Hadfield manganese steel. The arrows point to a substantial shrinkage gap between the phenolic mount and the specimen. The light-blue layer at the surface is iron oxide.

preparation damage that is present and may be virtually invisible with a normal etch will be highly visible after color etching, and this will impair results. However, color etchants do reveal information that cannot be obtained with standard black-and-white etchants. First, they usually reveal grain structures much more fully than

traditional etchants. Second, in single-phase structures, the degree of preferred crystallographic orientation can be gaged by looking at the range of colors produced. If a wide range of colors is observed, then there is a random orientation of the grains. If a narrow range of colors is obtained, then there may be a preferred texture

present. Color etching cannot tell one the nature of the preferred orientation. That can be determined by x-ray diffraction methods. Color etchants reveal segregation and residual deformation quite well. Further, microprobe analyses can be conducted on a tint-etched surface, because the film will not interfere with the chemical analysis.

Table 5 Beraha's sodium molybdate reagent

Composition	Comments
Stock solution: 1000 mL water 10 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	To color phosphide and cementite yellow-orange (ferrite unaffected): For cast iron: Add HNO_3 to the stock solution to bring the pH to 2.5–3.0. Immerse 45–60s. For low-carbon steel: Adjust pH and add 0.1 g NH_4FHF per 100 mL of stock solution. Immerse 45–60 s to color as above. For medium- and high-carbon steel: As above but add 0.3 g NH_4FHF per 100 mL of stock solution and immerse 30–45 s.
	To color carbides red-violet and ferrite yellow: For all steels: Add 0.5 g NH_4FHF and adjust the pH to 3–3.5. For low-carbon steels, immerse 20–30 s. For medium- and high-carbon steels, immerse 45–90 s. Beraha recommends pre-etching specimens with nital, but this is not absolutely necessary.

REFERENCES

1. A. Portevin, Colored Films in Micrography, *Met. Prog.*, Vol 36, Dec 1939, p 761
2. R.P. Loveland, Metallography in Color, *ASTM Bull.*, May 1944, p 19
3. W.D. Forgeng, Color Metallography, *Iron Age*, Vol 162 (No. 16), 14 Oct 1948, p 130
4. *Symposium on Metallography in Color*, STP 86, ASTM, 1949
5. H. Yakowitz, Some Uses of Color in Metallography, *Applications of Modern Metal-*

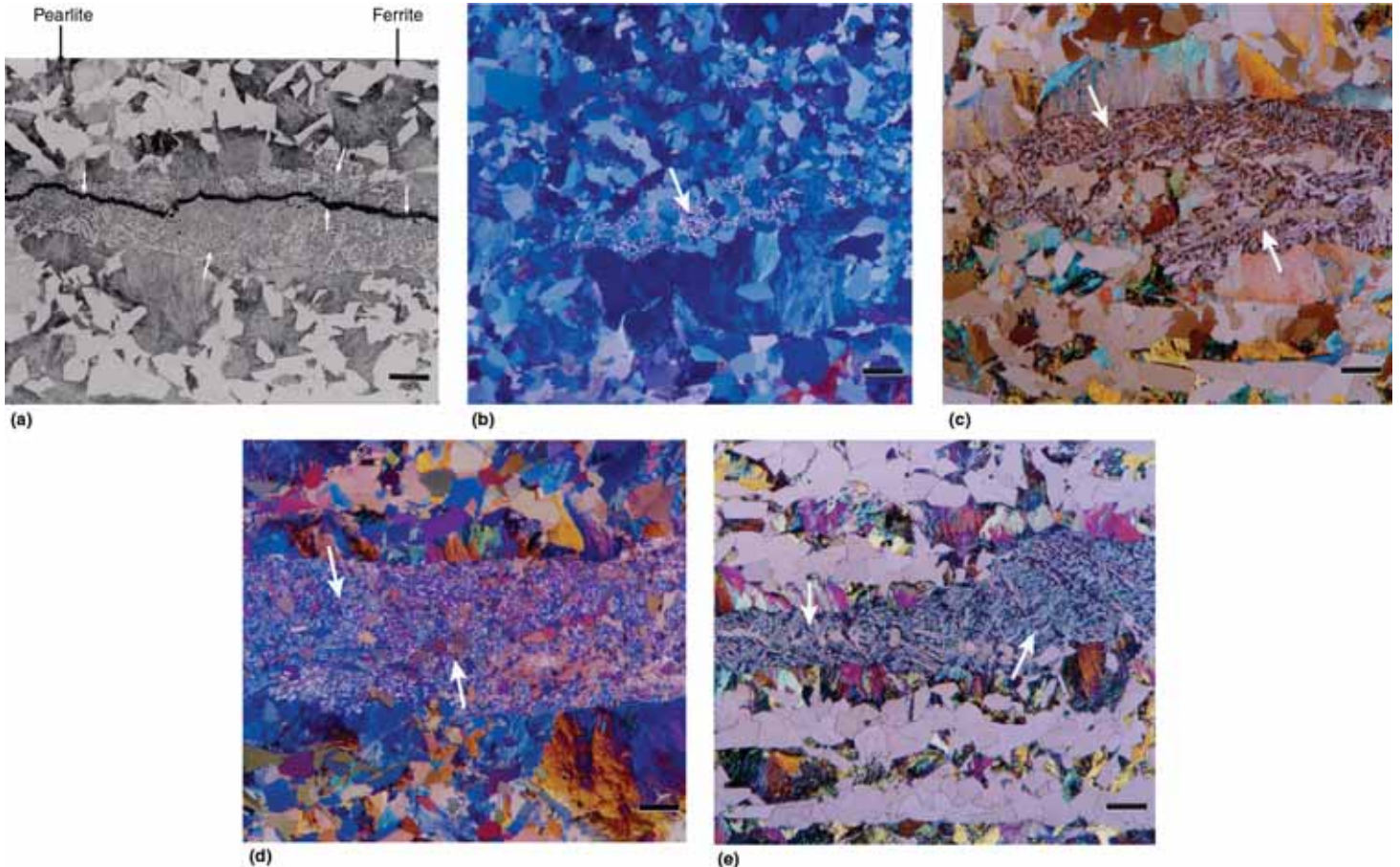


Fig. 46 Microstructures of as-rolled, continuously cast high-strength, low-alloy steel (Fe-0.19%C-1.24%Mn-0.37%Si-0.08%V). (a) Specimen containing segregation and some cracks (arrows) etched with 2% nital. The normal structure is ferrite and pearlite, but bainite was observed in the segregated regions (greater hardenability). Average hardness values were 180, 260, and 325 HV for the ferrite, pearlite, and bainitic segregation streaks, respectively. The magnification bar is 50 μm . (b) Specimen containing segregation etched with Klemm's I and viewed in polarized light plus sensitive tint. The normal structure is ferrite and pearlite, but bainite (arrow) is observed in the segregated regions. The segregated regions are hard to detect using Klemm's I, because it darkens the ferrite in the bainite as heavily as the matrix ferrite. The magnification bar is 50 μm long. (c) Specimen containing segregation etched with Beraha's 10/3 etch (10% $\text{Na}_2\text{S}_2\text{O}_3$ + 3% $\text{K}_2\text{S}_2\text{O}_5$) and viewed in polarized light plus sensitive tint. The normal structure is ferrite and pearlite, but bainite (arrows) is observed in the segregated regions. The magnification bar is 50 μm long. (d) Specimen containing segregation etched with Beraha's sulfamic acid etch (No. 1) (aqueous 3% $\text{K}_2\text{S}_2\text{O}_5$ + 1% $\text{H}_2\text{NSO}_3\text{H}$) and viewed with polarized light plus sensitive tint. The normal structure is ferrite and pearlite, but bainite (arrows) is observed in the segregated regions. The segregated regions are easier to detect with this etch than using Klemm's I, but 10% sodium metabisulfite and Beraha's 10/3 reagents were better, in this case. The magnification bar is 50 μm long. (e) Specimen containing segregation and some cracks (arrows) etched with aqueous 10% $\text{Na}_2\text{S}_2\text{O}_5$ (in polarized light plus sensitive tint). The magnification bar is 50 μm .

- lographic Techniques, STP 480, ASTM, 1970, p 49
- R.S. Crouse, R.J. Gray, and B.C. Leslie, Applications of Color in Metallography and Photography, *Interpretive Techniques for Microstructural Analysis*, Plenum Press, 1977, p 43
 - E. Beraha and B. Shpigler, *Color Metallography*, American Society for Metals, 1977
 - H. Gahm and F. Jeglitsch, Color Methods and Their Application in Metallography, *Met. Prog.*, Aug 1981, p 48
 - H. Gahm and F. Jeglitsch, *Microstructural Science*, Vol 9, Elsevier North Holland, Inc., 1981, p 65

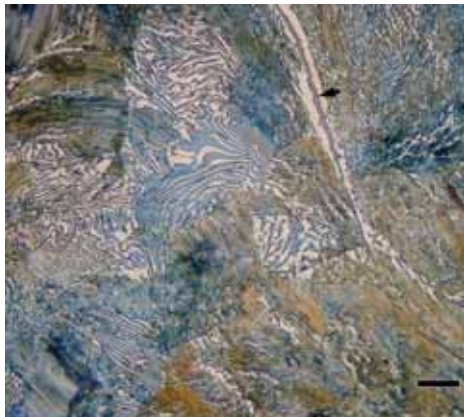


Fig. 47 Cementite in an as-hot-rolled Fe-1%C binary alloy revealed by tint etching with Beraha's sodium molybdate tint etch. The arrow points to proeutectoid cementite that precipitated in a prior-austenite grain boundary. The etch also colored the cementite in the pearlite. The specimen was viewed in bright-field illumination. The magnification bar is 20 μ m long.

- G.F. Vander Voort, *Metallography: Principles and Practice*, McGraw-Hill Book Co., 1984; reprinted by ASM International, 1999
- G.F. Vander Voort, Tint Etching, *Met. Prog.*, Vol 127, (No. 4), March 1985, p 31
- E. Weck and E. Leistner, *Metallographic Instructions for Colour Etching by Immersion, Part I: Klemm Colour Etching*, Vol 77, D.V.S. Verlag GmbH, Düsseldorf, 1982
- E. Weck and E. Leistner, *Metallographic Instructions for Colour Etchants by Immersion, Part II: Beraha Colour Etchants and Their Different Variants*, Vol 77/II, D.V.S. Verlag GmbH, Düsseldorf, 1983

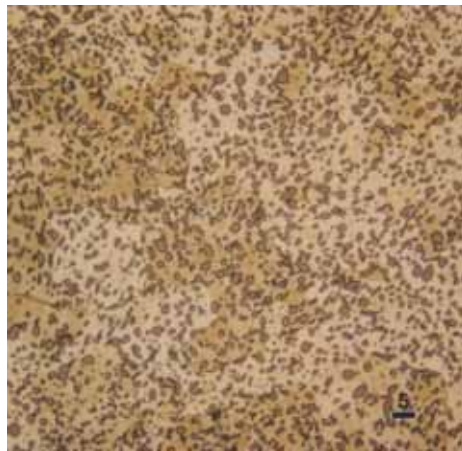


Fig. 48 Spheroidize-annealed microstructure of type W1 carbon tool steel (Fe-1.05%C-0.25%Mn-0.2%Si) etched with Beraha's sodium molybdate reagent, which colored both the cementite particles (brownish-red) and the ferrite matrix. The magnification bar is 5 μ m long.

- E. Weck and E. Leistner, *Metallographic Instructions for Colour Etching by Immersion, Part III: Non-Ferrous Metals, Cemented Carbides and Ferrous Metals, Nickel-Base and Cobalt-Base Alloys*, Vol 77/III, D.V.S. Verlag GmbH, Düsseldorf, 1986
- P. Skočovský, Colour Contrast in Metallographic Microscopy, *Slovmetal*, 1993
- T. Berglund, *Metallographers' Handbook of Etching*, Sir Isaac Pitman & Sons, Ltd., London, 1931
- T.R. Allmand, *Microscopic Identification of Inclusions in Steel*, British Iron and Steel Research Association, London, 1962
- L.V. Foster and J.E. Wilson, The Examination of Metals in Polarized Light, *Proc. Am. Soc. Test. Mater.*, Vol 38 (Part II), 1938, p 315

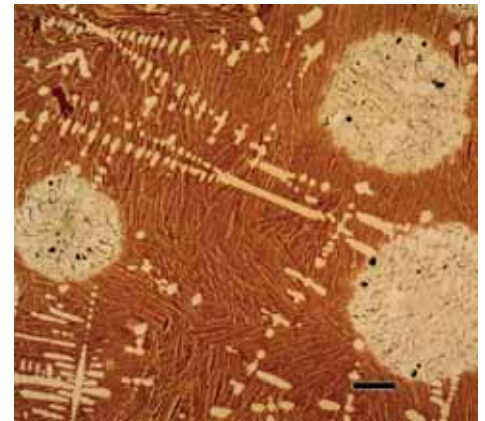


Fig. 49 Cementite colored in chill-cast hypoeutectic gray iron using Beraha's selenic acid reagent (No. 1) (bright field). The magnification bar is 100 μ m long.

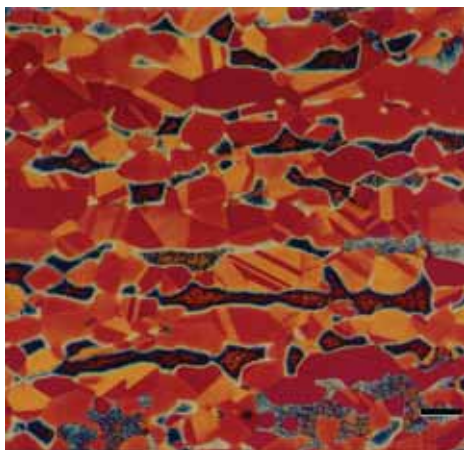


Fig. 50 Microstructure of hot-extruded and cold-drawn Muntz metal (Cu-40%Zn) tint etched with Beraha's selenic acid reagent (No. 7) for copper, which colored the twinned face-centered cubic alpha grain structure shades of yellow and red and nonuniformly colored the beta phase (note the light-blue border around the beta phase). Viewed in bright field. The magnification bar is 20 μ m long.

Table 6 Beraha's selenic acid reagents

Reagent	Composition	Comments
1	100 mL ethanol 2 mL HCl 1 mL selenic acid	For cast iron: Immerse 15–30 s. Colors phosphides red-brown or violet. Pre-etching is useful.
2	100 mL ethanol 1–2 mL HCl 0.5 mL selenic acid	For cast iron: (Use 2 mL HCl) Immerse 5–10 min to color phosphides blue or green and cementite red or violet (blue or green in white cast iron). For tool steels, martensitic or precipitation-hardenable stainless steels: Immerse 3–10 min if pre-etched and 5–15 min if as-polished to color carbides and nitrides orange, red-violet, or blue; ferrite, yellow or brown. Pre-etching is useful.
3	100 mL ethanol 10 mL HCl 3 mL selenic acid	For cast iron: Immerse up to 2 min to color phosphide red-brown or violet, while cementite and ferrite are unaffected. Pre-etching is useful.
4	100 mL ethanol 5–20 mL HCl 1 mL selenic acid	For austenitic stainless steel: Use 20–30 mL HCl for higher alloyed grades; do not pre-etch. Immerse 1–10 min (depending on HCl content), until the surface is colored yellow or light brown to detect carbides and nitrides or longer (until the surface is colored orange-red). Delta ferrite is brighter than the matrix. Also good for maraging steels. Do not pre-etch.
5	100 mL ethanol 10–30 mL HCl 3 mL selenic acid	For nitrogen-base superalloys: Use 20 mL HCl to detect gamma prime, which is revealed after 1–3 min immersion (carbides colored red or violet). Immerse 3–15 min, until the surface is colored yellow to light brown to color carbides and nitrides red, violet, or blue.
6	100 mL ethanol 30–50 mL HCl 3 mL selenic acid	For higher alloy high-temperature alloys. Addition of 10–40 mL water may help increase etch rate. Use in same manner as number 5.
7	300 mL ethanol 2 mL HCl 0.5–1 mL selenic acid	For brass and copper-beryllium alloys: Store in a dark bottle. Pre-etch specimen for best results. Immerse until the surface is violet-blue to blue. Pre-etching is useful.

19. H.E. Rosenberger, Differential Interference Contrast Microscopy, *Interpretive Techniques for Microstructural Analysis*, Plenum Press, 1977, p 79
20. P. Lacombe and L. Beaujard, Anodic Oxidation Regarded as a Means for the Study of Surface Conditions of Aluminum and its Alloys, *Journées des Etats de Surface [Comptes Rendus]*, 23–26 Oct 1945 (Paris), 1946, p 44
21. A. Hone and E.C. Pearson, Grain Orientation in Aluminum Revealed by Anodic Film, *Met. Prog.*, Vol 53, March 1948, p 363
22. L.J. Barker, Revealing the Grain Structure of Common Aluminum Alloy Metallographic Specimens, *Trans. ASM*, Vol 42, 1950, p 347
23. A. Hone and E.C. Pearson, A New Anodic-Film Method for Studying Orientation in Aluminum, *Met. Prog.*, Vol 58, Nov 1950, p 713
24. H.G. Cole and W.J.D. Brooks, A Simple Anodizing Process for Revealing the Grain Structure of Aluminum Alloys, *Metallurgia*, Vol 50, Aug 1954, p 97
25. H.S. Yang, An Electrolytic Etching/Anodizing Method for Revealing the Microstructures of Common Aluminum Alloys, *Pr. Metallogr.*, Vol 27, 1990, p 539
26. E. Ence and H. Margolin, Phases in Titanium Identified by Cumulative Etching, *J. Met.*, March 1954, p 346
27. R.H. Hiltz, Jr., “Metallographic Methods: Color Staining of Titanium and Its Alloys,” Watertown Arsenal Laboratory Report WAL 132/24, 20 April 1956
28. R.S. Crouse, “Identification of Carbides, Nitrides and Oxides of Niobium and Niobium Alloys by Anodic Staining,” Oak Ridge National Laboratory Report ORNL-3821, July 1965
29. M.L. Picklesimer, Anodizing for Controlled Microstructural Contrast by Color, *Microscope*, Vol 15, Oct 1967, p 472
30. B.W. Mott and H.R. Haines, Examination of Metals Under Polarized Light, Part II: Applications, *Research*, Vol 4, 1951, p 63

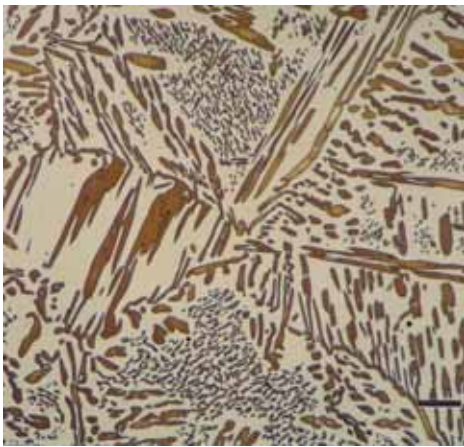


Fig. 51 Microstructure of as-cast ASTM A 890-5A duplex stainless steel (Fe-<0.03%C-<1.5%Mn-<1%Si-25%Cr-7%Ni-4.5%Mo-0.2%N) in the solution-annealed condition. Etched with LB1 (100 mL water, 20 g NH₄FHF, and 0.5 g K₂S₂O₅). Austenite is colored, and ferrite is unaffected. Because it is as-cast, there are no annealing twins in the austenite. The magnification bar is 100 μm long.

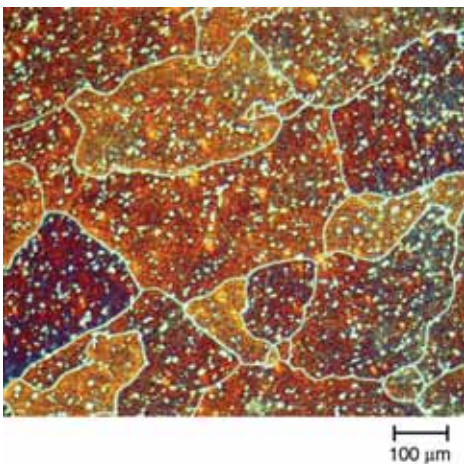


Fig. 54 Grain structure of 6061-T651 revealed by tint etching with Weck's reagent and viewing with polarized light plus sensitive tint. 200×

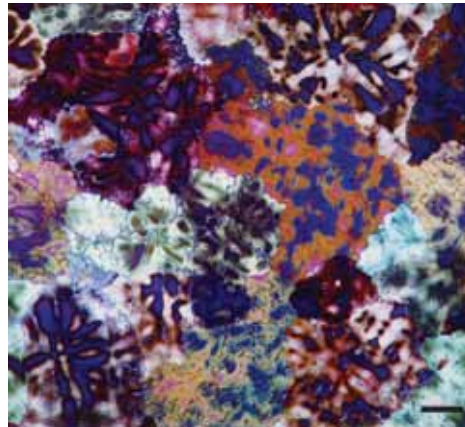


Fig. 52 As-cast (concast) 1100 aluminum (>99% Al) tint etched with Weck's reagent, revealing a dendritic solidification structure. Viewed with crossed polarized light plus sensitive tint. Magnification bar is 200 μm long.

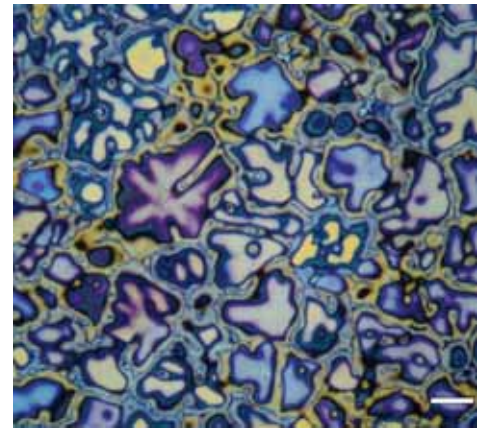


Fig. 53 As-cast 206 aluminum (Al-4.4%Cu-0.3%Mg-0.3%Mn) tint etched with Weck's reagent and viewed with crossed polarized light plus sensitive tint. See text. Magnification bar is 50 μm long.

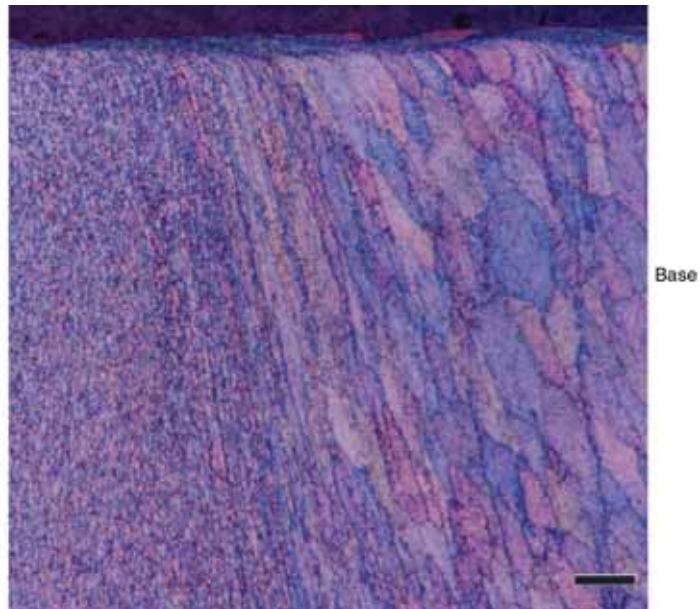


Fig. 55 Microstructure of a friction stir weld in 2519 aluminum (Al-5.8%Cu-0.3%Mn-0.3%Mg-0.06%Ti-0.1%V-0.15%Zr) etched with Weck's reagent and viewed with polarized light plus sensitive tint. Original at 100×. The magnification bar is 100 μm long.

31. R.C. Gikfins, *Optical Microscopy of Metals*, American Elsevier Publishing Co., Inc., 1970, p 122
32. D.H. Woodard, Stages in the Deformation of Monel Metal as Shown by Polarized Light, *Trans. AIME*, Vol 185, 1949, p 722
33. E.C.W. Perryman and J.M. Lack, Examination of Metals by Polarized Light, *Nature*, Vol 167 (No. 4247), 1951, p 479
34. R.E. Reed-Hill, C.R. Smeal, and L. Lee, The Examination of fcc Metals with Polarized Light, *Trans. AIME*, Vol 230, Aug 1964, p 1019
35. W. Ischewsky, New Micrographic Structures on the Surface of Heat Treated Steels, *Stahl Eisen*, Vol 23, 1903, p 120
36. L. Loskiewicz, A Study of the Time Factor in the Etching of Iron-Carbon Alloys, *Rev. Metall.*, Vol 19, 1922, p 681
37. T. Murakami, The Structure of Iron-Carbon-Chromium Alloys, *Sci. Rep. Tohoku Imperial Univ.*, Vol 7 (Part I), 1918, p 217
38. T. Murakami, Note on the Structure of Iron-Carbon-Chromium Alloys, *J. Iron Steel Inst. Jpn.*, Vol 100 (No. 2), 1919, p 445
39. E.C. Groesbeck, Solutions for Carbides, etc., in Alloy Steels, appendix to report of Committee E-4 on Metallography, *Proc. ASTM*, Vol 26 (Part I), 1926, p 569
40. E.C. Groesbeck, Metallographic Etching Reagents, Part III: For Alloy Steels, *U.S. Bureau of Standards Scientific Papers*, S518, 1925, p 527
41. J. Malette, Color-Producing Reactions for Microscopic Examination of Carbon Steels, *Comptes Rendus*, Vol 201, 1935, p 1385
42. L. Beaujard, New Reagents for Revealing the Micrographic Structure of Steels by the Formation of Colored Films, *Comptes Rendus*, Vol 233, 1951, p 653
43. L. Beaujard and J. Tordeux, The Use of Sodium Bisulfite as an Etching Solution for Ferritic Steels, *Comptes Rendus*, Vol 235, 1952, p 1304
44. L. Beaujard, Micrographic Coloring Reagents for Iron and Steels, *Rev. Metall.*, Vol 49, July 1952, p 531
45. L. Beaujard, Color Etching of Iron and Steel, *Met. Treat. Drop Forg.*, Nov 1952, p 499
46. P Lacombe and M. Mouflard, The Application of Color Metallography by Formation of Very Thin Epitaxial Layers with Interference Colors for the Study of Aluminium, Iron and Copper, *Métaux-Corros.-Ind.*, No. 340, Dec 1953, p 471
47. L. Beaujard and J. Tordeux, A New Sodium Bisulfite Reagent for the Micrographic In-



Fig. 56 Microstructure of commercially pure titanium (ASTM F 67, grade 2) (longitudinal plane) etched with modified Weck's reagent and viewed with crossed polarized light plus sensitive tint to reveal the grain structure. Magnification bar is 100 μm long.

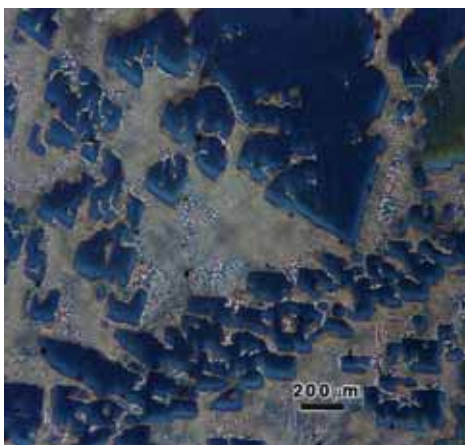


Fig. 59 Theta phase, AlCu_2 , colored blue by an etchant consisting of water, nitric acid, and ammonium molybdate, diluted with ethanol (bright-field illumination) in a hypereutectic Al-45%Cu cast alloy

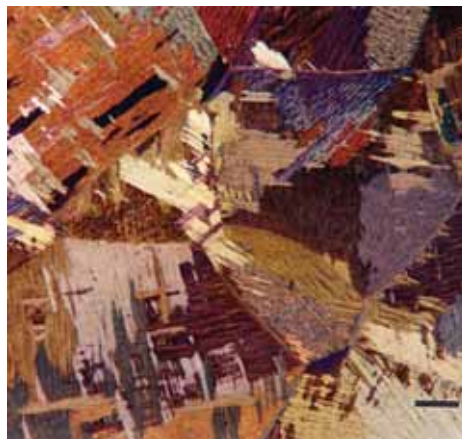


Fig. 57 Microstructure of as-cast Ti-6Al-4V etched with modified Weck's reagent, and viewed with polarized light to reveal a coarse basketweave alpha/beta matrix structure. The boundaries of several former beta grains can be seen. Magnification bar is 200 μm long.

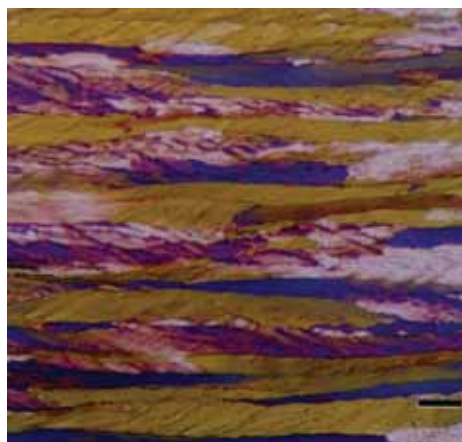


Fig. 60 Microstructure of wrought, nonrecrystallized pure molybdenum (longitudinal direction horizontal) tint etched with the Oak Ridge National Laboratory solution (90 mL water, 20 mL hydrogen peroxide [30% conc.], and 10 mL H_2SO_4) and viewed with polarized light plus sensitive tint, revealing highly elongated body-centered cubic alpha grains containing substantial deformation. The magnification bar is 20 μm long.

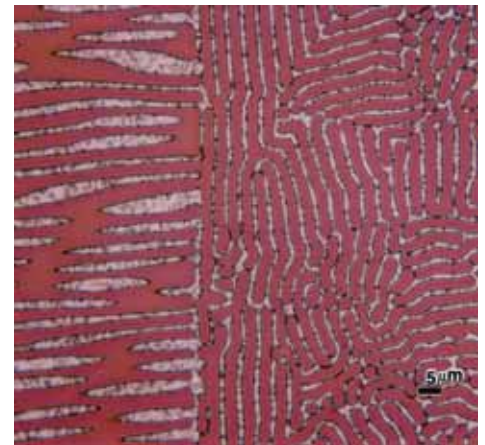


Fig. 58 Theta phase, AlCu_2 , colored violet by Liénard's reagent in an as-cast Al-33%Cu eutectic alloy

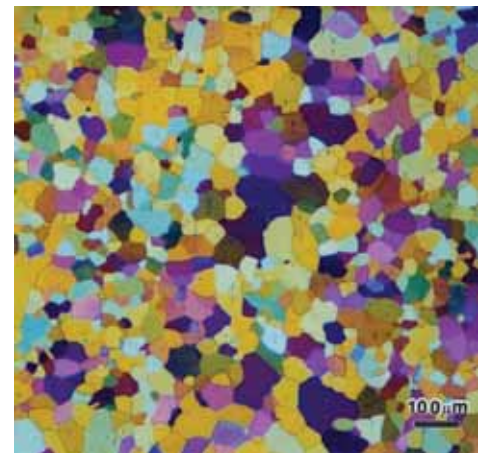


Fig. 61 Microstructure of commercially pure titanium (ASTM F 67, grade 4) (transverse plane, specimen was annealed) heat tinted on a laboratory hot plate, and viewed with polarized light plus sensitive tint to reveal the grain structure.

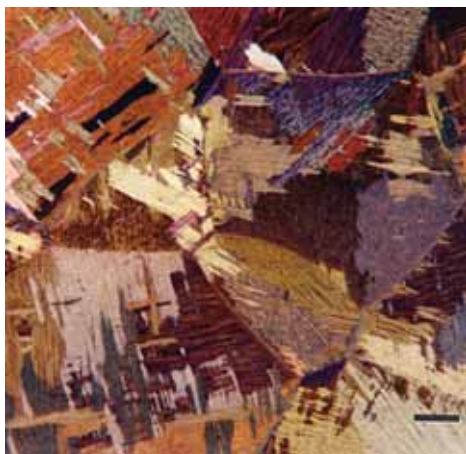


Fig. 62 Microstructure of as-cast Ti-6Al-4V heat tinted on a laboratory hot plate, and viewed with polarized light plus sensitive tint to reveal the coarse alpha-beta basketweave matrix structure. Magnification bar is 100 μm long.

- vestigation of Steels, *Rev. Métall.*, Vol 52, Sept 1955, p 750
48. B.V. Guellard, A New Etching Reagent for Steel and Cast Iron, *Metallurgia*, Vol 54, Aug 1956, p 93
 49. J.R. Vilella and W.F. Kindle, Sodium Bisulfite as an Etchant for Steel, *Met. Prog.*, Vol 76, Dec 1959, p 99
 50. H. Klemm, Color Etching of the Fine Structure of Metals with Sodium Thiosulfate, *Metallkundliche*, Vol 45, Verlag Technik Berlin, 1952
 51. H. Klemm, Uses of Sodium Thiosulfate (Klemm's Reagent) as an Etchant, *Pr. Metallogr.*, Vol 5, April 1968, p 163
 52. E. Beraha, Metallographic Reagent for the Identification of Cementite in Iron and Steel, *J. Iron Steel Inst. Jpn.*, Vol 203, May 1965, p 454
 53. E. Beraha, New Metallographic Reagents for Stainless Steel and Heat-Resisting Alloys, *J. Iron Steel Inst. Jpn.*, Vol 204, March 1966, p 248
 54. E. Beraha, Two New Metallographic Reagents, *Met. Prog.*, Vol 90, Sept 1966, p 135
 55. E. Beraha, Etching Cast Iron, *Met. Prog.*, Vol 90, Oct 1966, p 13
 56. E. Beraha, New Metallographic Reagent for Iron, Carbon-Alloy, and Tool Steels, *J. Iron Steel Inst. Jpn.*, Vol 205, Aug 1967, p 866
 57. E. Beraha, Metallographic Reagents for the Determination of Chemical and Physical

Table 7 Temperatures for heat tinting

Metal	Temperature and time in air	Comments
Beryllium	900 °C (1650 °F) for 30 min	Grain boundaries are revealed at a slightly higher temperature.
Cast iron	400 °C (750 °F) for 20 min	Fe ₃ C, blue; Fe ₃ P, cream
Stainless steel	500–700 °C (930–1290 °F) for \leq 20 min	Gamma colored before sigma and sigma before carbides. 650 °C (1200 °F) for 20 min gave: γ , blue-green; α , light cream; σ , orange; and carbides, not colored
Nickel	600 °C (1110 °F) for 5–10 min	...
Rare earth metals	200 °C (390 °F) for minutes to hours	...
Titanium	400–700 °C (750–1290 °F) for up to 30 min	...
Zirconium	400 °C (750 °F) for 5 min	...
Sintered carbides	300–600 °C (570–1110 °F) for 5 min	Cobalt binder colored brown at low temperatures, up to approximately 400 °C (750 °F); WC starts to color at approximately 540 °C (1000 °F). Time affects colors.

- Heterogeneity in the Microstructure of Iron and Steels, *Pr. Metallogr.*, Vol 4, Aug 1967, p 416
58. E. Beraha, Staining Metallographic Reagent for Stainless Steels, Corrosion and Heat-Resisting Alloys, *Pr. Metallogr.*, Vol 5, Aug 1968, p 443
 59. E. Beraha, Staining Metallographic Reagent for Detection of Phosphides, Carbides and Nitrides in Iron, Steel, Tool Steels, Stainless Steel and Heat-Resisting Alloys, *Pr. Metallogr.*, Vol 5, Sept 1968, p 501
 60. E. Beraha, Staining Metallographic Reagent for Copper-Base Alloys, *Pr. Metallogr.*, Vol 7, March 1970, p 131
 61. E. Beraha, Metallographic Reagents Based on Sulfide Films, *Pr. Metallogr.*, Vol 7, May 1970, p 242
 62. E. Beraha, Staining Metallographic Reagents for Cast Iron, *Microstructures*, Vol 2, June/July 1970, p 23
 63. E. Beraha, Staining Metallographic Reagents for Cast Iron, Steels, Tool Steels, Manganese Steels, and Ferritic and Martensitic Stainless Steel, *Pr. Metallogr.*, Vol 8, Sept 1971, p 547
 64. E. Beraha, Metallographic Reagents Based on Molybdate Solutions, *Pr. Metallogr.*, Vol 11, May 1974, p 271
 65. A.O. Bencotter, J.R. Kilpatrick, and A.R. Marder, An Etching Technique for Fe-Ni Massive Martensite, *Pr. Metallogr.*, Vol 15, Dec 1968, p 694
 66. A.O. Bencotter, J.R. Kilpatrick, and A.R. Marder, Sulfate and Sulfite Compounds as Etchants for Low-Carbon Iron Martensite, *IMS Proceedings*, 1969, p 37
 67. J.R. Kilpatrick, A.O. Bencotter, and A.R. Marder, Tint Etching Improves Resolution and Contrast of Microstructures, *Met. Prog.*, Dec 1971, p 79
 68. J.R. Kilpatrick, A New Etching Technique for Galvanneal and Hot Dipped Galvanized Coatings, *Pr. Metallogr.*, Vol 28, Dec 1991, p 649
 69. P. Lichtenegger and R. Blösch, Colour Etching of High Alloy Steels, *Pr. Metallogr.*, Vol 12, 1975, p 567
 70. G.F. Vander Voort, Etching Isothermally Treated Steels, *Heat Treat. Prog.*, Vol 1, April/May 2001, p 25–32
 71. G.F. Vander Voort, Metallography of Iron Meteorites, *Adv. Mater. Process.*, Vol 159, Feb 2001, p 37, 40, 41
 72. J.M. Radzikowska, The Foundry Research Institute, Kraków, Poland, personal communication, 2000
 73. P. Liénard and C. Pacqué, Analysis of the Selective Coloring Mechanism for Identification of Different Phases in Al-Si-Cu Foundry Alloys, *Hommes Fonderie*, No. 126, June/July 1982, p 27–35
 74. P. Liénard, Etching of Aluminium Alloys, *Structure*, Vol 8, June 1984, p 17–20
 75. R. Hasson, Metallography of Molybdenum in Color, *Microscope*, Vol 16, 1968, p 329–334
 76. R. Hasson, An Improved Orientation-Dependent Chemical Anodizing Color Reagent for Molybdenum, *Microscope*, Vol 22, 1974, p 317–322
 77. S. Lehwald et al., An Orientation-Sensitive Colour-Etching Method for Polycrystalline Tungsten, *Pr. Metallogr.*, Vol 9, Sept 1972, p 510–515
 78. R.S. Crouse, Oak Ridge National Laboratory, personal communication, 1982
 79. H.E. Bühler and H.O. Hougardy, *Atlas of Interference Layer Metallography*, Deutsche Gesellschaft für Metallkunde, Oberursel, Germany, 1980