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PHASE IDENTIFICATION BY SELECTIVE ETCHING

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The identification of phases or constituents in metals and alloys is a common metallographic problem. Metallographers can often predict which phases are likely to be present in a given alloy from a knowledge of its sample chemical composition, processing history, previously published information on its characteristics, or by reference to phase diagrams. Guided by such information, the metallographer examines the microstructure to identify the phases present. Even when one is possessed of such information, however, the task is often far from trivial, even for well-documented alloy systems. Only after the phases have been identified should a quantification of the amount and morphological characteristics of the phases be attempted.

Many techniques can be used to obtain a qualitative description of the microstructure of materials. Some methods require expensive X-ray or electron metallographic devices, but light microscopy remains the cornerstone of the analytical procedure. Conventional general-purpose etchants that outline the phases are often adequate, but errors are possible. Etchants selective to a particular phase provide positive, unambiguous phase identification and are ideal for image-analysis measurements that depend on gray-level image differences for phase detection. These etchants are also valuable for manual measurements. This chapter will present information on selective etching solutions and their implementation for a variety of commercial materials.

PHASE IDENTIFICATION METHODS

Phases are identified by means of known differences in composition, crystal structure, optical reflectance, morphology, or corrosion behavior. This information can be obtained for most systems in the literature. When one is dealing with unfamiliar systems, compilations of phase diagrams make a good starting point. Basic aids to phase identification will be described in the following sections.

Quantity or Morphology

In some instances, phase identification may be aided by differences in quantity of constituents or morphology. In simple two-phase systems with essentially equilibrium microstructures, the matrix (major) phase can usually be distinguished from isolated, dispersed, second-phase constituents of lower volume fraction. When approximately equal amounts of two phases are present with no obvious continuous-matrix phase, however, identification becomes more difficult.

Reflectance

Some phases of alloys in the as-polished condition, can be detected reliably by means of reflectance differences. Well-known examples include graphite in cast iron, inclu-



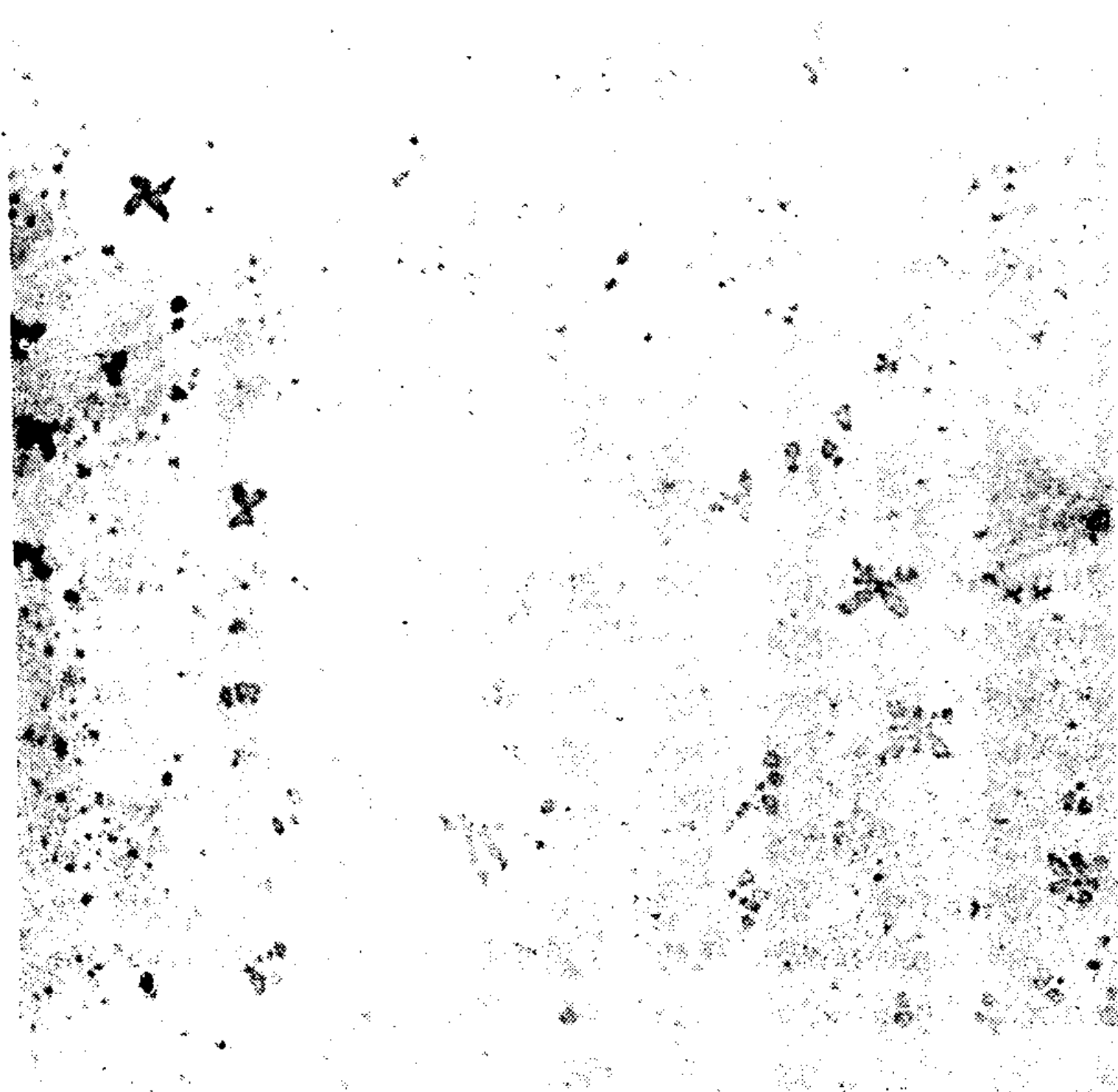
Fig. 1-1. Cu_2Sb in as-cast Sb-10%Cu revealed in the as-polished condition by reflectivity differences (at 100 \times).

2 APPLIED METALLOGRAPHY

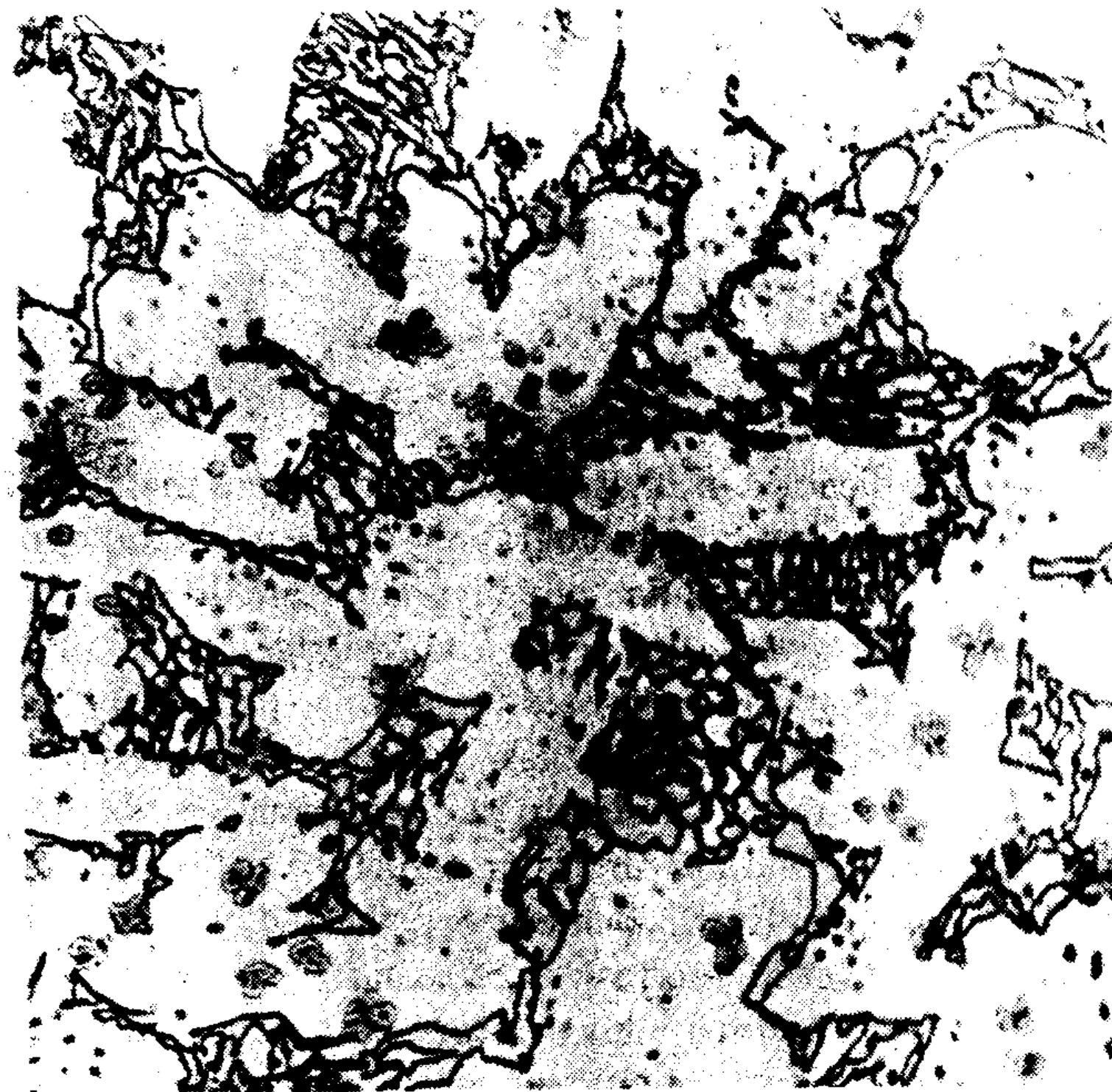
sions, and certain nitrides and intermetallic phases. Figure 1-1 presents a less common example: η phase (Cu_2Sb) in as-cast Sb-10%Cu in the as-polished condition revealed solely by reflectance differences. Beta phase in alpha-beta brass can be detected in the as-polished condition because it appears as a dark yellow compared to the light yellow of the alpha phase. Reflectance differences are important because they are the basis of phase detection by image analyzers.¹

Polarized Light Response

Phases with noncubic crystallographic structure can be detected by their positive response to crossed polarized light. Alpha phase in titanium alloys responds to polarized light, whereas beta phase does not. Sigma phase in stainless steels also responds to polarized light. Cu_2O in tough-pitch copper can be discriminated from copper sulfide in the as-polished condition by the use of polarized light;



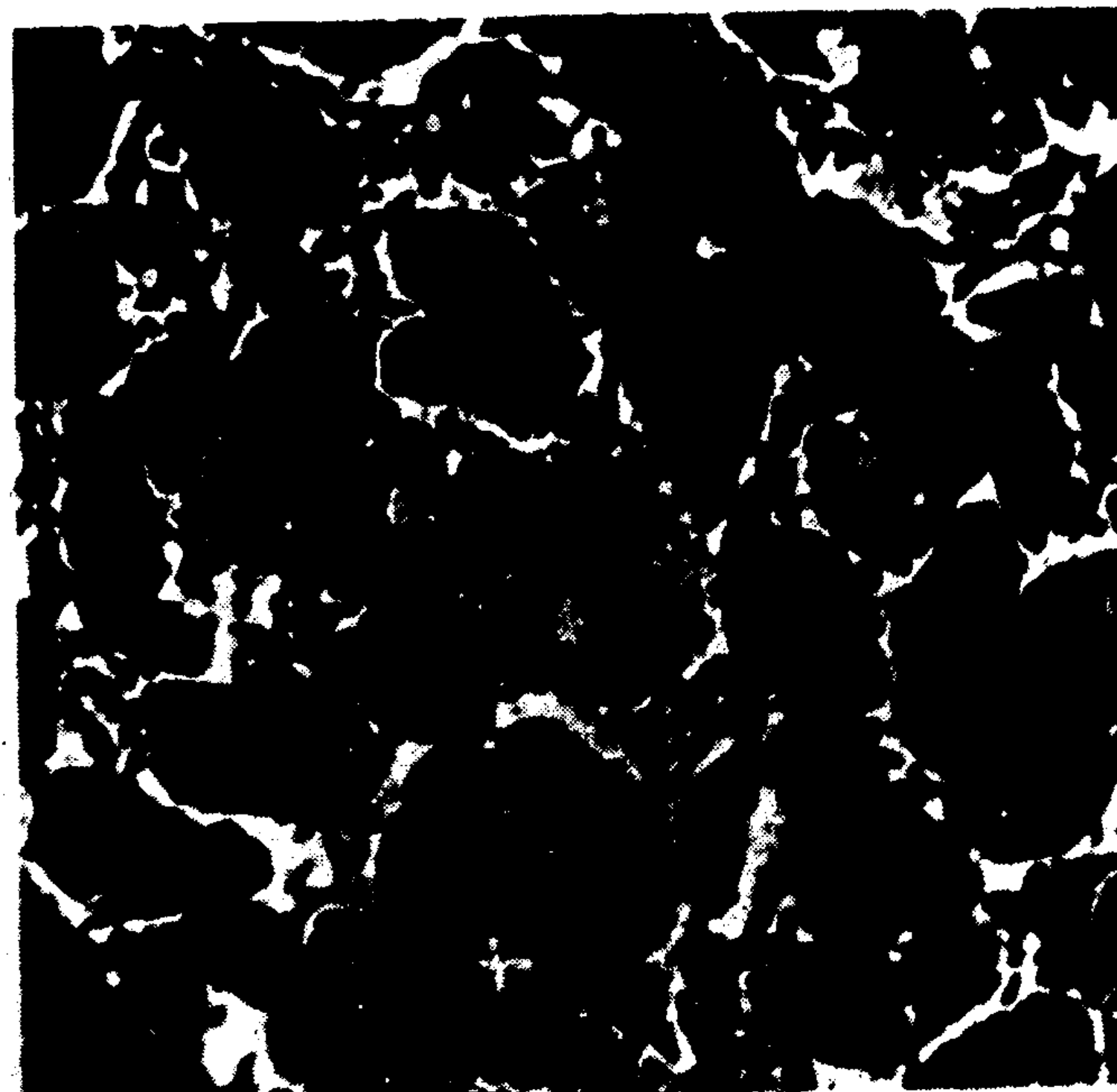
As-Polished



10% Ammonium Persulfate



10% Sodium Thiosulfate
(etch 2a)



Beraha's Lead Sulfide Tint
Etch (etch 3h, no NaNO_2)

Fig. 1-2 In the as-polished condition, the γ_2 phase in aluminum bronze is faintly visible, whereas the iron particles are somewhat darker. Relief cannot be developed between these phases and the matrix because of inadequate hardness differences and etching must be employed. (All at 500 \times .)

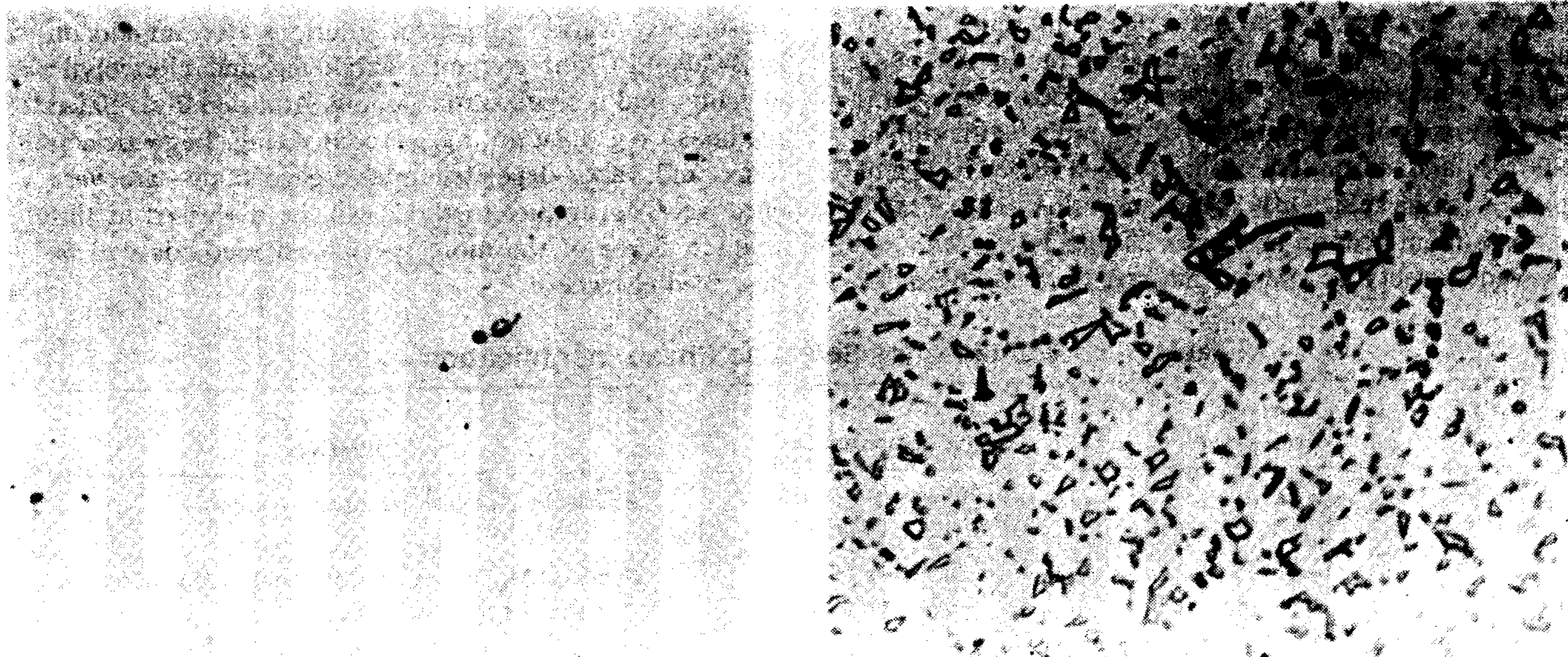


Fig. 1-3. In the as-polished condition, porosity and graphite can be observed on WC-Co samples (left). Relief polishing outlines the cobalt binder phase (right). (Both at 1000 \times .)

it appears ruby red under such illumination whereas the sulfide is dark.

Relief

In some systems, a minor phase may exhibit little or no difference in reflectivity from the matrix, but the difference in hardness, if appreciable, can be used to reveal the phase by introducing relief during final polishing. Although the relief effect can be observed with bright-field illumination, it can be enhanced by using oblique lighting or differential-interference contrast illumination.

The following two figures illustrate the use of reflectance and relief effects for phase discrimination. Figure 1-2 shows the microstructure of aluminum bronze (Cu-10.5%Al-3.8%Fe-0.3%Ni) heat-treated to produce γ_2 (Al_4Cu_9) in an alpha matrix with insoluble iron particles. In the as-polished condition, the iron particles appear light blue whereas the γ_2 particles are only faintly visible. Relief cannot be developed between these particles, and the matrix and etching must be utilized as shown to reveal them clearly. Figure 1-3 shows an as-polished WC-Co sintered-carbide cutting tool. In this condition, its porosity and graphite can be detected. After relief polishing, the cobalt binder phase appears to be outlined as a result of the very high difference in hardness between Co and WC.

ANALYTICAL METHODS

If these simple methods are inadequate for positive identification, other procedures must be utilized. In general, the preceding methods have limited, if important, applicability. The availability of more sophisticated tools simpli-

fies phase identification for the metallographer. For example, X-ray diffraction can be employed to identify phases that are present in amounts greater than 1 to 2 percent. Although this technique tells the metallographer what phases are present, each must be identified on a polished cross section of the sample.

Because phases usually exhibit compositional differences, energy-dispersive or wavelength-dispersive detectors in scanning electron microscopes (SEM) or in electron microprobe analyzers (EMPA) can provide means for phase identification. Since energy-dispersive detectors cannot detect lightweight elements such as carbon, oxygen, and nitrogen, their value is somewhat limited. Neither instrument is suitable for identification of particles smaller than about 2 μ in diameter. For such particles, it is necessary to use electron diffraction of extracted particles or other advanced techniques. Identification procedures for fine particles exceed the scope of this chapter (but see Chap. 11).

Selective Etching

Many metallographers who do not have access to X-ray and electron metallographic instruments for routine work can utilize the etching response to specifically chosen reagents for phase identification, except in the case of very fine particles. Prior to the development of the SEM and the EMPA, the response to selected etchants was widely used to identify inclusions in steels and intermetallic constituents in aluminum alloys, but such procedures are rarely employed for these purposes today.

The use of selective etchants is invaluable for quantitative metallography, a field of growing importance. To detect features by image analysis, the desired phase must

be darker or lighter than all other phases present.¹ Unfortunately, etchant selection is empirical in nature and often requires considerable trial-and-error. Selection of potential etchants is aided by referring to published compilations of standard and specialized etchants.²⁻⁴ A list of typical etchants sufficiently specific in action to be suitable for phase identification appears in Table 1-1.

A wide variety of etching methods may be used for

phase identification: chemical solutions (for immersion or swabbing), tint etchants, anodizing and electrolytic etchants, and potentiostatic etching. Additionally, related methods—e.g., heat tinting, gas contrasting, magnetic colloids, and vapor-deposited interference films—are very effective. The simpler methods will be discussed in this chapter. Some of the more specialized methods will be described elsewhere.

Table 1-1. Etchants for Selective Phase Identification.

METAL	PHASE DETECTED	ETCH COMPOSITION	COMMENTS
1. Aluminum alloys	(a) FeAl ₃	0.1–10 ml HF 90–100 ml water*	Attacks FeAl ₃ ; other constituents outlined.
	(b) Al ₃ Mg ₂	1–2 ml HNO ₃ 98–99 ml ethanol	Colors Al ₃ Mg ₂ brown (Al–Mg alloys). Immerse for 15 min for 1-percent solution.
	(c) CuAl ₂	20 ml water 20 ml HNO ₃ 3 g ammonium molybdate	Mix one part of reagent with four parts ethanol. Immerse until surface is colored. CuAl ₂ blue.
	(d) CuAl ₂	200 ml water 1 g ammonium molybdate 6 g NH ₄ Cl	Immerse for 2 min. CuAl ₂ violet. (Lienard and Pacque.)
2. Copper	(a) γ ₂	100 ml water 10 g sodium thiosulfate	Colors γ ₂ in aluminum bronze. Immerse 90 to 150 sec. (Aldridge.)
	(b) Alpha	One part water One part H ₂ O ₂ (3%) One part NH ₄ OH	Swab etch. Colors alpha in alpha-beta brass.
	(c) Beta	50 ml saturated aq. sodium thiosulfate 1 g potassium metabisulfite	Colors beta in alpha-beta brass. Immerse about 3 min. (Klemm's I reagent.)
	(d) Beta	10 g cupric ammonium chloride 100 ml water	Add NH ₄ OH until solution is neutral or slightly alkaline. Colors beta in alpha-beta brass.
3. Iron and Steel	(a) Ferrite	50 ml saturated aq. sodium thiosulfate 1 g potassium metabisulfite	Colors ferrite (blue and red), martensite (brown), austenite and carbide (not affected). Immerse 60 to 120 sec after light pre-etch with nital or picral. (Klemm's I reagent.)
	(b) Martensite	8–15 g sodium metabisulfite 100 ml water	Pre-etch lightly with nital. Immerse for about 20 sec. Darkens as-quenched martensite; carbides unaffected.
	(c) Ferrite	(1) 8 g sodium thiosulfate 6 g ammonium nitrate 100 ml water (2) 1 ml HNO ₃ 2.5 ml H ₃ PO ₄	To 100 ml of (1) heated to 70°–75°C, add 0.5 ml of (2). Pre-etch lightly with picral. Immerse in solution for about 1 min. Etch only good for 15 min. Colors ferrite; cementite unaffected. (Beraha.)
	(d) Fe ₃ C	100 ml water 1 g sodium molybdate 0.1–0.5 g ammonium bifluoride	Add HNO ₃ to decrease the pH to 2.5–3.5. Pre-etch lightly with picral. Immerse in solution about 15 sec. Colors Fe ₃ C yellow-orange; ferrite unaffected. (Beraha.)
	(e) Fe ₃ C Ferrite Fe ₃ P	1000 ml Water 240 g sodium thiosulfate 20–25 g cadmium chloride 30 g citric acid	Dissolve in order given. Allow each to dissolve before adding next. Age 24 hr at 20°C in dark bottle. Filter 100 ml of solution; good for 4 hr. Pre-etch with picral. Immerse 20 to 40 sec; colors ferrite. After 60 to 90 sec, ferrite is yellow or light blue, Fe ₃ P brown, carbides violet or blue. (Beraha.)

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Table 1-1 (continued)

METAL	PHASE DETECTED	ETCH COMPOSITION	COMMENTS
	(f) Ferrite	1 g potassium metabisulfite 1 ml HCl 100 ml water	Pre-etch lightly with picral. Immerse in solution until surface is colored. Colors ferrite. (Beraha.)
	(g) M_3C M_6C	2 g picric acid 25 g NaOH 100 ml water	Immerse in boiling solution 1 to 15 min, or use electrolytically at 6 V dc, 20°C, 0.5–2 A/in ² , 30 to 120 sec. Colors M_3C and M_6C brown to black.
	(h) Ferrite Fe_3C MnS	1000 ml water 240 g sodium thiosulfate 24 g lead acetate 30 g citric acid	Mix and age in same manner as etch No. 3e. Add 0.2 g sodium nitrite to 100 ml of solution; good for 30 minutes only. Pre-etch with picral. Immerse in solution until surface is colored. Cementite will be darker than ferrite; MnS white. (Beraha.)
	(i) Oxygen	145 ml water 16 g CrO_3 50 g NaOH	Alkaline chromate etch to detect oxygen enrichment during or before hot working. Heat to 118° to 120°C; immerse for 7 to 20 min. Enriched areas are white. (Fine.)
	(j) Fe_3P Fe_3C Alloy carbides Sigma Delta ferrite	100 ml water 10 g $K_3Fe(CN)_6$ 10 g KOH	Immerse at 20°C; M_7C_3 is attacked; M_6C turns brown to black; Fe_3C is unaffected. Bring to boil. Fe_3P darkens in 10 sec; Fe_3C is lightly colored after 2 min. For stainless steels, immerse at 20°C to reveal carbides, sigma after 3 min. At 80°C to boiling for 2 to 60 min, carbides turn dark; sigma, blue; delta, yellow to brown; austenite is unaffected. (Murakami's reagent.)
	(k) Sigma Carbides Delta ferrite	100 ml water 20 g $K_3Fe(CN)_6$ 20 g KOH	For stainless steels, use cold to boiling; carbides turn dark; delta, yellow; sigma, blue; austenite is unaffected. (LeMay and White.)
	(l) Sigma Carbides Delta ferrite	100 ml water 30 g $K_3Fe(CN)_6$ 30 g KOH	For stainless steels, use at 95°C for 15 sec; sigma turns reddish brown; delta, dark gray; carbide, black; austenite is unaffected. (Kegley.)
	(m) Austenite	Heat tint in air at 500 to 700°C, up to 20 min.	For stainless steels; austenite colors before delta ferrite.
	(n) Sigma Delta ferrite	10 N KOH (56 g KOH in 100 ml water)	For stainless steels, use electrolytically at 2.5 V dc, 20°C for 10 sec to color sigma orange and delta light blue and brown; austenite is unaffected.
	(o) Sigma Delta ferrite	100 ml water 20 g NaOH	For stainless steels, use electrolytically at 5 V dc, 20°C for 20 sec to color sigma orange and delta tan; austenite is unaffected.
	(p) Carbide	NH_4OH (Conc)	For stainless steels, use electrolytically at 1.5 V dc; carbide completely revealed in 40 sec and sigma unaffected after 180 sec. At 6 V dc, sigma is etched after 40 sec.
4. Magnesium alloys	(a) $Mg_{17}Al_{12}$	90 ml water 10 ml HF	Immerse for 3 to 30 sec. Darkens $Mg_{17}Al_{12}$; $Mg_2Al_3Zn_3$ unetched. (George.)
	(b) MgZn	1000 ml water 50 g CrO_3 4 g Na_2SO_4	For Mg–Zn alloys, a 2-sec immersion severely attacks MgZn; Mg_7Zn_3 is slightly attacked. (Clarke and Rhines.)
5. Nickel alloys	(a) γ'	50 ml HCl 1 to 2 ml H_2O_2 (30%)	For superalloys, immerse 10 to 15 sec to attack gamma prime.
	(b) γ' Carbides	100 ml ethanol 1 to 3 ml selenic acid 20 to 30 ml HCl	Tint etch for superalloys. Immerse 1 to 4 min at 20°C. Colors carbides and gamma prime, matrix unaffected. (Beraha.)
6. Titanium alloys	(a) Retained beta	10 ml 40% Aq. KOH 5 ml H_2O_2 (30%) 20 ml water	Swab up to 20 sec or immerse for 30 to 60 sec at 70° to 80°C. Stains alpha and transformed beta; retained beta remains white.

Table 1-1 (continued)

METAL	PHASE DETECTED	ETCH COMPOSITION	COMMENTS
	(b) Retained beta Alpha Martensite Carbides	Heat tint in air at 400° to 700°C	Tint until surface is colored red-violet. After 60 sec at 600°C, retained beta turns deep violet to bright blue; alpha, dull to golden yellow; martensite, yellow with violet coloring from fine retained beta; carbides, brilliant bright blue or yellow.
7. Sintered carbide	(a) Cobalt binder	HCl saturated with FeCl ₂	Immerse 1 to 5 min at 20°C to blacken the cobalt binder phase. (Chaporova.)
	(b) Eta	100 ml water 10 g K ₃ Fe(CN) ₆ 10 g KOH	Immerse 2 to 10 sec at 20°C to darken eta; longer times attack eta. TiC attacked; WC unaffected (outlined). (Murakami's reagent.)
	(c) Cobalt binder	Heat tint at 316° to 593°C in air	Tint in air at 316°C for 5 min to color cobalt brown; carbides are unaffected. At higher temperatures, carbides are colored, TiC before WC.

* Use distilled water in all reagents where water is required.

CHEMICAL ETCHANTS

Successful use of etching solutions requires development of controlled corrosive action between areas of different electrochemical potential. Etching is a result of electrolytic action at structural constituents caused by chemical or physical differences on the sample surface. Under the imposed conditions, these variations cause certain areas to be anodic and others cathodic.

Contrast between similar constituents may be developed as a result of variations in etch rate produced by differences in crystallographic orientation. Such etchants produce reflectivity differences and, hence, grain contrast. When more than one phase is present, an etch may attack one phase preferentially, thereby producing elevation differences between the constituents. If this attack is uniform, little reflectance difference will be noted between the constituents, but the phase boundaries will be visible. Such behavior is encountered when annealed steels containing ferrite and carbide are etched with either picral or nital. Both these etchants attack the ferrite phase, leaving the carbide in relief.

In some instances, the phase being attacked is roughened during etching, and this roughness produces reflectance differences. Figure 1-4, for example, shows an as-cast Zn-15%Sn sample whose zinc-rich proeutectic phase has been preferentially attacked by etching with a solution containing 82 ml water, 1 ml HF, and 15 ml H₂SO₄ at about 38°C for 30 sec. At low magnifications, the zinc-rich primary dendrites appear dark and vividly revealed in contrast to the tin-rich, unetched continuous-eutectic constituent. High magnification reveals the roughening of the zinc-rich phase. Such an etching response is unsuitable for high magnification work.

Examples

Two examples of two-phase alloys in which either phase can be selectively attacked by simple chemical etchants

will be given here. The first, an unfamiliar example, is an as-cast Cd-37%Cu alloy that consists of two intermetallic compounds, δ (Cd₈Cu₅) and γ (Cd₃Cu₄). Figure 1-5 shows the microstructure of this alloy—primary δ containing precipitated excess γ in a matrix of eutectic δ plus γ . Etching with a solution consisting of equal parts of 10-percent aqueous FeCl₃ and HCl attacked and darkened the γ phase, whereas etching with 10-percent aqueous ammonium persulfate attacked and darkened the δ phase.

A more common example of such dual etching behavior is shown in Fig. 1-6 where α/β brass (Cu-40%Zn) (β phase is ordered) has been etched with four different reagents. Etching with 10-percent aqueous ammonium persulfate attacked the β phase, but it was not roughened, and only the phase boundary is visible, producing an outlining of each β grain. Kehl and Metlay⁵ have shown that nearly all chemical etchants are specific to the β phase. Only one etchant—equal parts of water, H₂O₂ (3 percent), and NH₄OH (swab)—will attack the α phase preferentially. This etch produces vivid grain contrast.

Several etchants have been commonly employed to darken the β phase preferentially. A commonly used etchant is 10-percent aqueous cupric ammonium chloride made neutral or slightly alkaline by adding NH₄OH (the solution has a pH of 2.5; addition of 6 ml NH₄OH to 100 ml of etch increased the pH to 7.25). This etch (No. 2d in Table 1-1) roughens the β phase. Tint etchants, such as Klemm's I reagent (No. 2c in Table 1-1), will color the β phase after a short immersion. After about an hour in this solution, the alpha matrix is slightly revealed.

For pure metals and single-phase alloys, etching response is due to potential differences between differently oriented grains or between grain boundaries and grain interiors or is due to concentration gradients within solid-solution phases. For two-phase and multi-phase alloys, there are also potential differences between phases of dif-

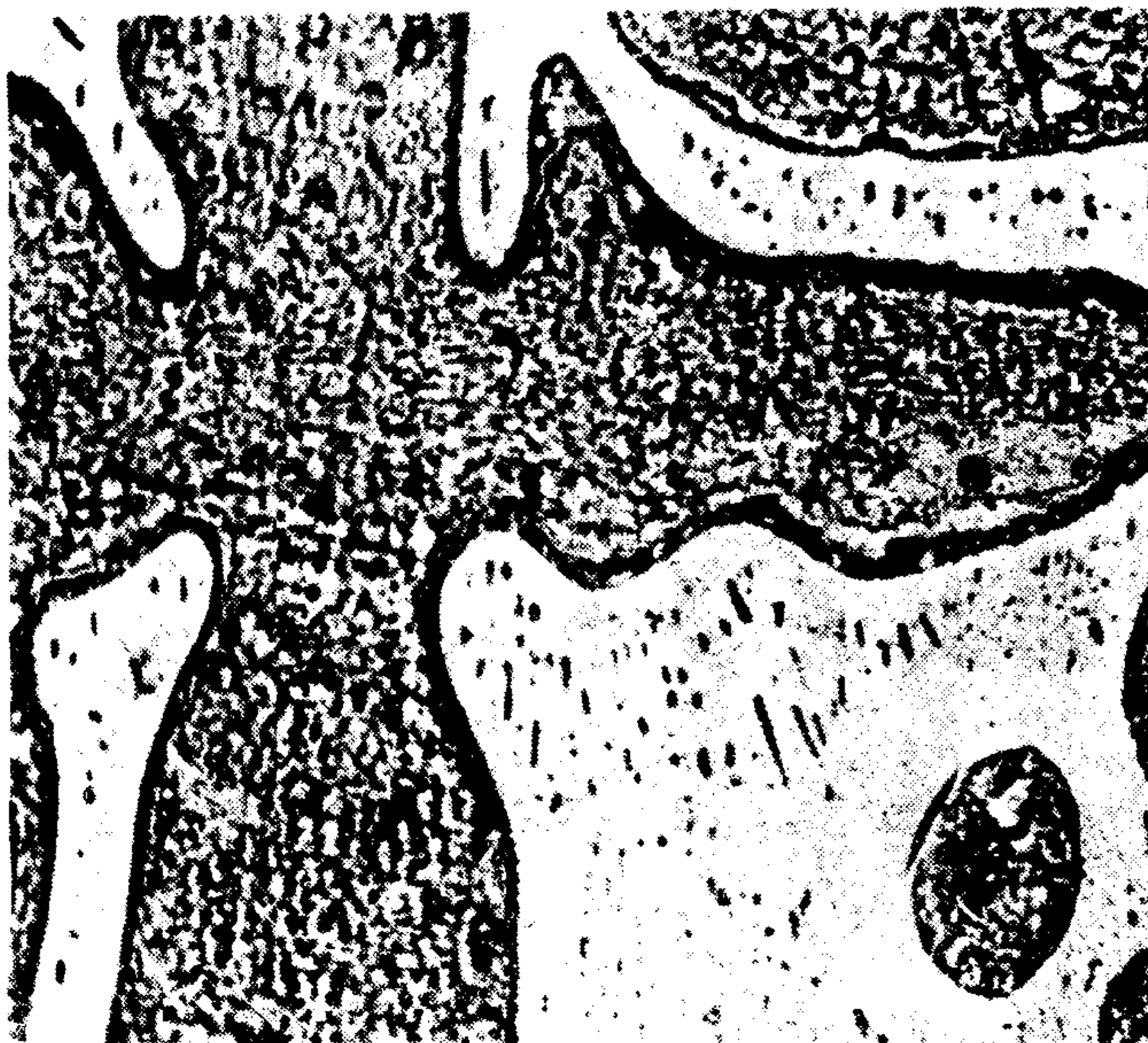
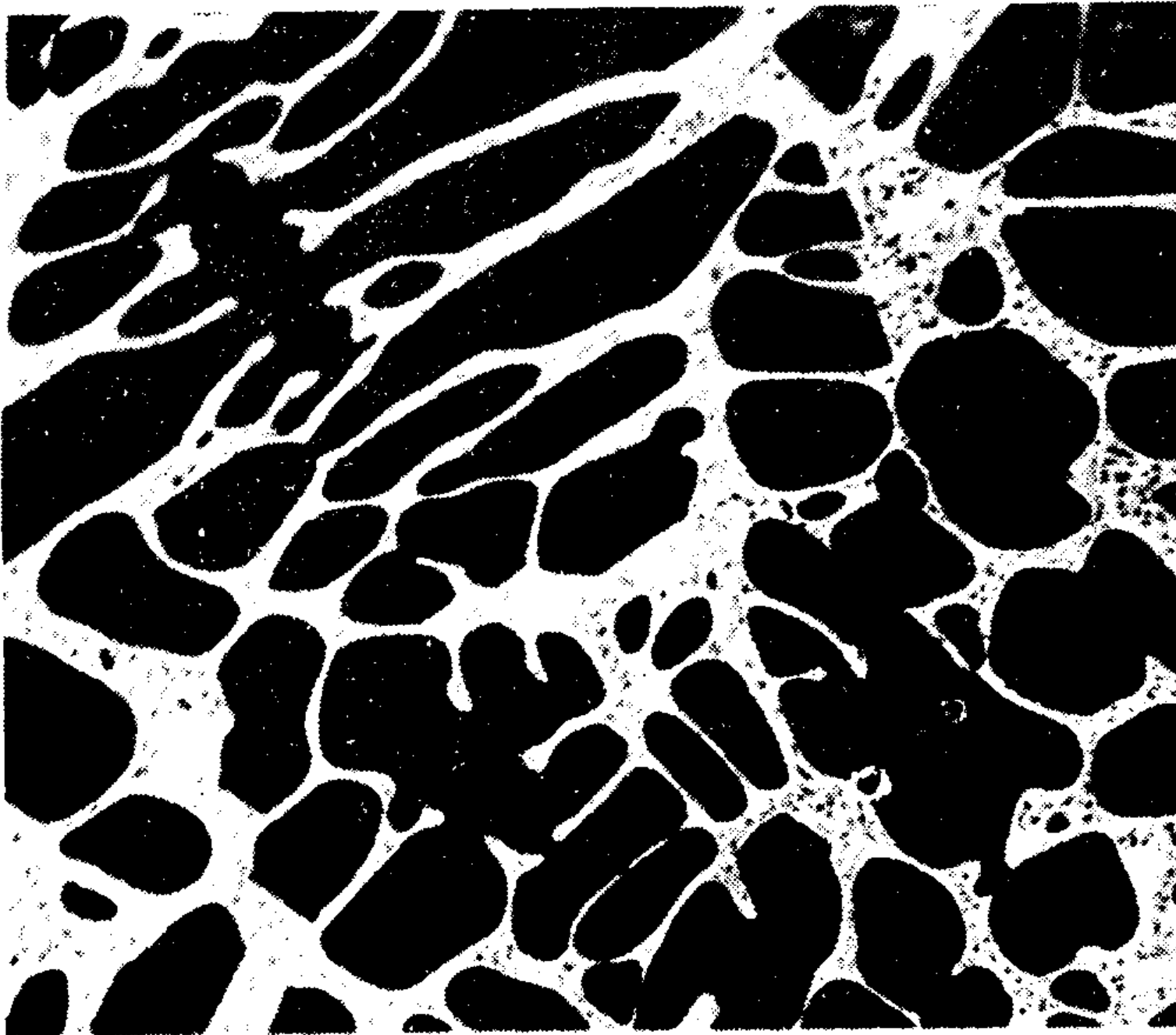


Fig. 1-4. Bottom: the primary zinc-rich dendrites in an as-cast Zn-15%Sn alloy and the zinc-rich portion of the Zn-Sn continuous eutectic were attacked and roughened by etching in a solution containing 82 ml water, 1 ml HF, and 15 ml H₂SO₄ (at 500X). Top: this attack produced good contrast for low magnification examination (at 100X).

ferent composition. Impurity segregation to grain boundaries also promotes selective grain-boundary etching. Such potential differences control the nature of etch dissolution, thus producing differences in the rate of attack that reveal the microstructure.

In a two-phase alloy, one phase will be higher in potential than the other phase; i.e., it is anodic to the other (cathodic) phase in a particular etchant. The more electro-positive (anodic) phase is attacked, whereas the electro-negative (cathodic) phase is attacked superficially or not at all. Duplex alloys etch more readily than pure metals or single-phase alloys because of the greater potential difference between the two phases.

The unetched cathodic phase will stand in relief and

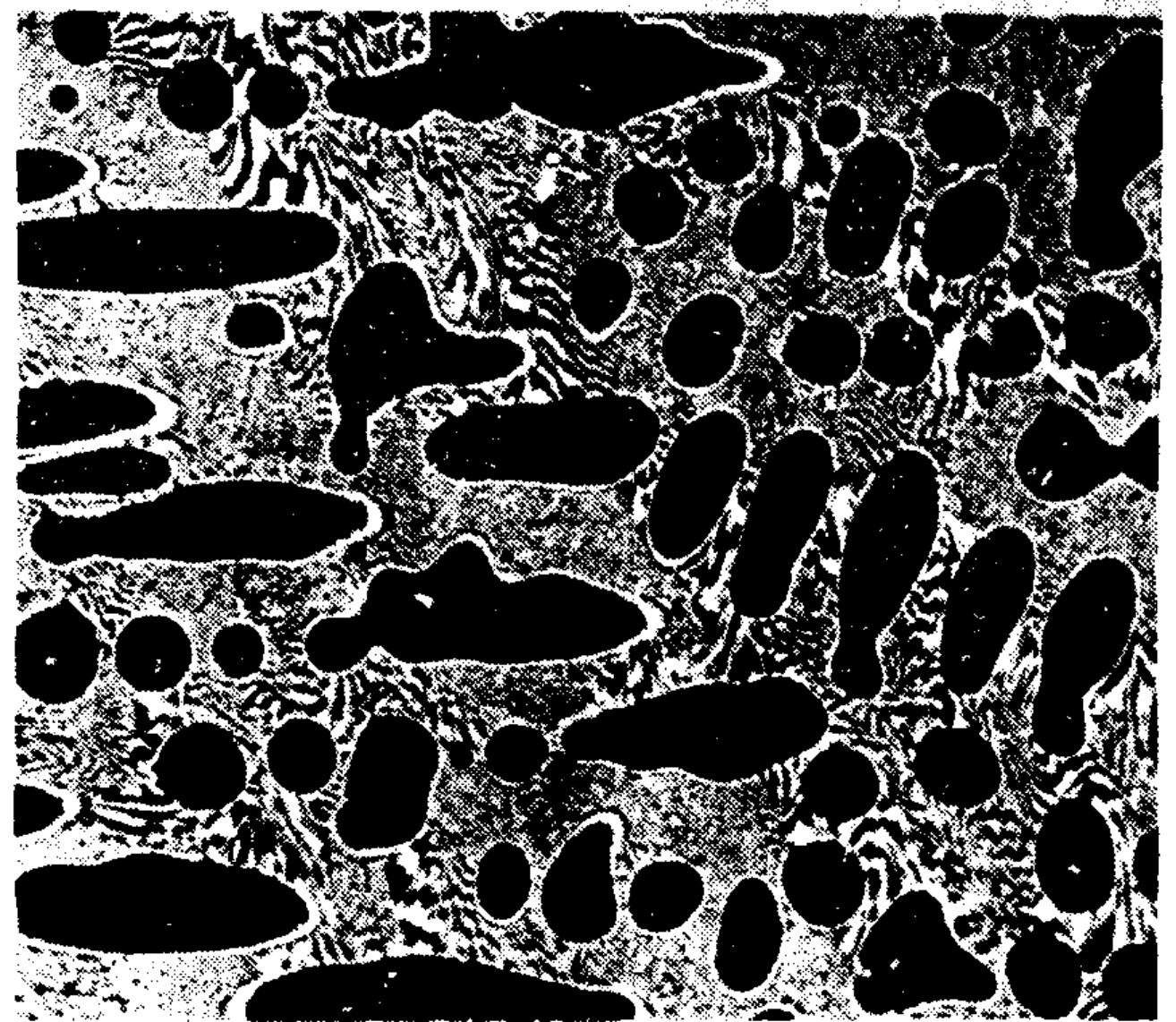
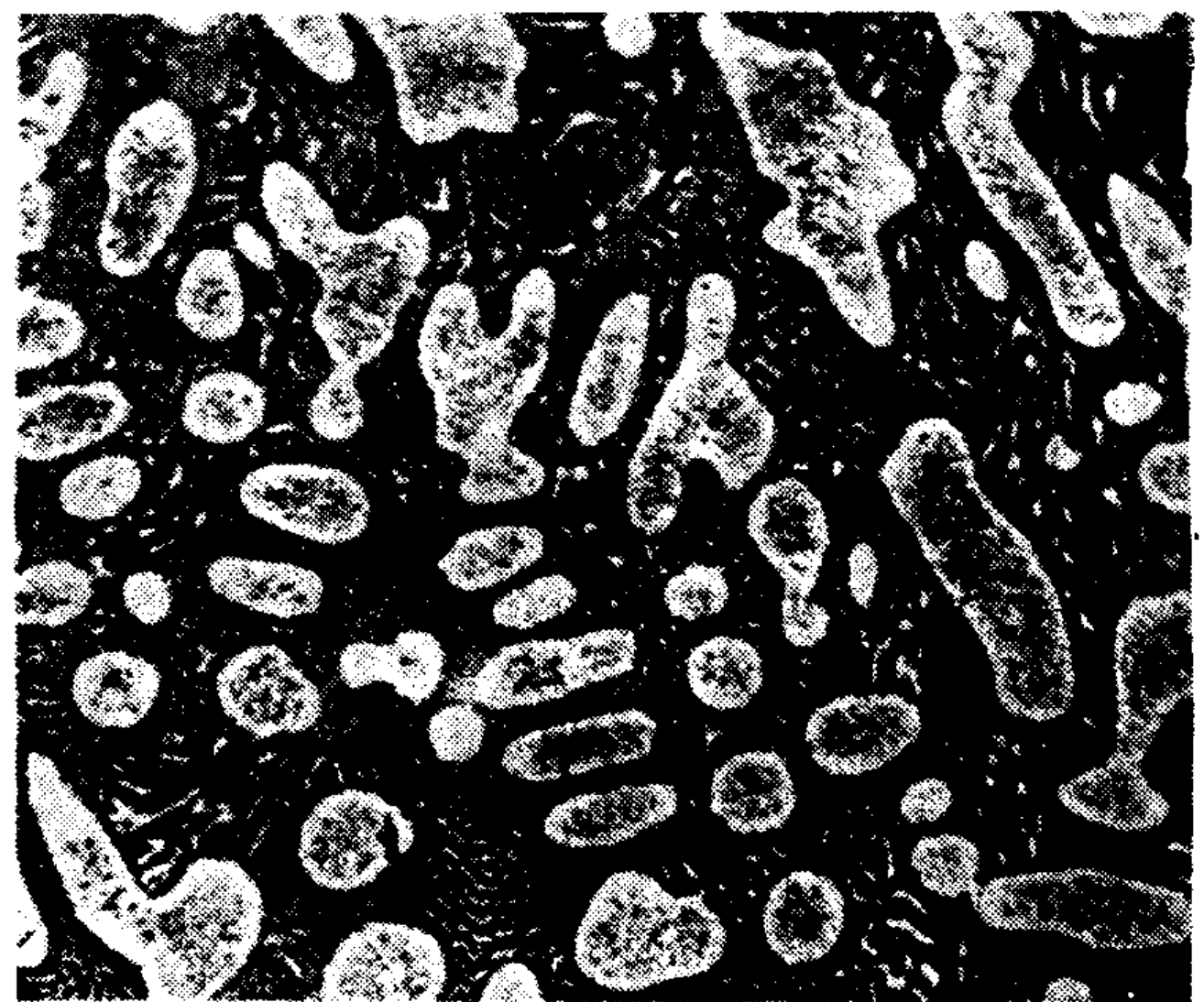


Fig. 1-5. Simple immersion etchants can reveal either phase in as-cast Cd-37%Cu. Top: etching with equal parts 10-percent aqueous FeCl₃ and HCl colors the γ phase (Cd₃Cu₄). Bottom: etching with 10-percent aqueous ammonium persulfate colors the δ phase (Cd₈Cu₅). (Both at 200X.)

appear bright, whereas the anodic phase is recessed below the plane-of-polish and will appear either light or dark depending on whether or not its surface was roughened. Simple chemical etchants work in this manner. For most two-phase alloys, nearly all etchants will attack one phase—the anodic phase—producing either phase-boundary etching only or darkening of the anodic constituent. For most two-phase alloys, it is rather difficult to find a simple etchant that will attack the other phase; i.e., for most chemical immersion etchants, the same phase will be anodic.

TINT ETCHANTS

Considerable progress has been made in the development of simple immersion solutions that produce selective color contrast by film formation, substantially because of the work of Beraha.⁶ Such reagents, generally referred to as tint etchants, are usually acidic solutions with either water or alcohol as solvents. They are chemically balanced to

deposit a thin (40 to 500 nm) film of oxide, sulfide, complex molybdate, elemental selenium, or chromate, on the sample surface. Coloration is developed by interference between light rays reflected at the inner and outer film surfaces. Recombination of two light waves with a phase difference of 180 degrees causes light of a certain wavelength to disappear so that the reflected light is of a complementary color. Crystallographic orientation, film thickness, and refractive index of the film control the colors produced.

Tint etchants are either anodic reagents that precipitate

a thin film on the anodic constituents to color only these areas, cathodic reagents that precipitate a thin film on the cathodic constituents to color only these areas, or complex reagents where the film is precipitated from a complex reaction.⁶

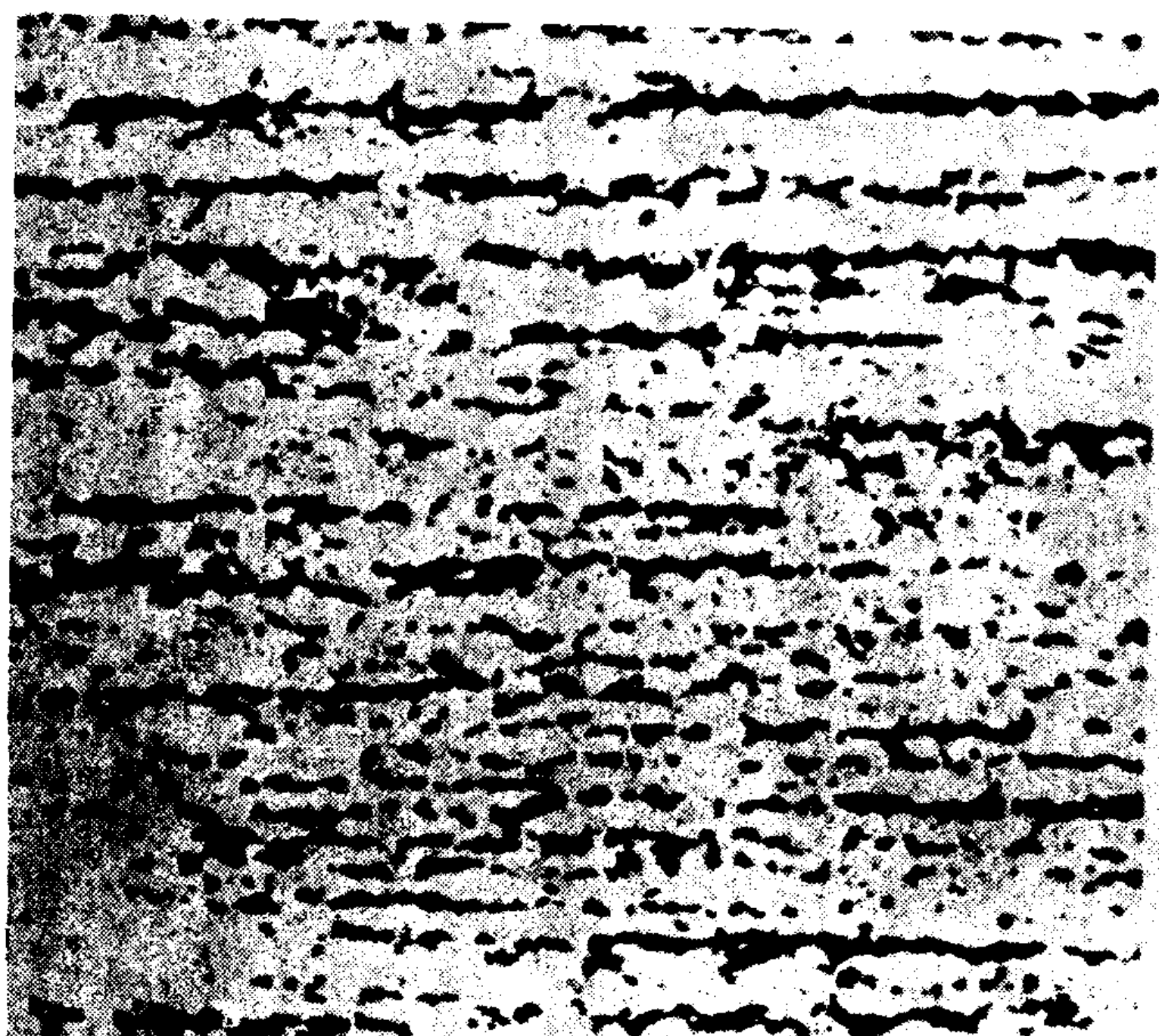
Some of the most common ingredients of tint etchants are sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), potassium metabisulfite ($\text{K}_2\text{S}_2\text{O}_5$), and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). When dissolved in water, the metabisulfite salt decomposes during etching, producing SO_2 , H_2S , and H_2 (producing a characteristic odor). When etching passivated



10% aqueous ammonium persulfate



$\text{NH}_4\text{OH}/\text{H}_2\text{O}_2(3\%)/\text{H}_2\text{O}$ (swab, etch 3b)



10% Aqueous Cupric Ammonium Chloride (NH_4OH to 7.25 pH)



Klemm's I Reagent (etch 2c)

Fig. 1-6. Influence of different etchants on the microstructure of alpha-beta brass (Cu-40%Zn). Top left: beta phase outlined but not roughened. Top right: alpha phase contrast etched; beta not affected. Bottom left: beta phase attacked and darkened. Bottom right: beta phase colored by tint etch. (All at 100 \times)

surfaces—e.g., stainless steel— SO_2 depassivates the surface, and the H_2S provides sulfur ions that combine with metallic ions from the sample to produce the sulfide staining film. The addition of HCl to tint etchants extends their use to the corrosion-resistant alloys.

In tint etchants based on these compounds, anodic constituents—e.g., ferrite, martensite, and austenite—are colored, whereas the cathodic constituents—e.g., carbides and nitrides—are unaffected and appear bright. A variety of hues are produced in the anodic constituents as a result of differences in crystallographic orientation. In most cases, coloration can be further enhanced by observation with polarized light.

Tint etchants based on selenic acid (a dangerous chemical) produce film deposition on cathodic areas by reduction of the acid to elemental selenium, which deposits on the cathodic features. Tint etchants containing sodium molybdate also color cathodic constituents by precipitation of a complex molybdate film on these features.

Beraha⁶ also developed a complex thiosulfate tint etchant containing lead acetate and citric acid. This etchant (No. 3h in Table 1-1) is useful for tint etching copper-based alloys (see Fig. 1-2) and for staining cementite or phosphide in cast-iron or sulfide inclusions in steels. The film produced is due to the deposition of lead sulfide.

Mixing of these etchants should be done strictly according to the instructions provided by the developer (see References 4 and 6 and also Table 1-1). Some of these reagents must be aged in a dark bottle before use. Although selenic acid is highly corrosive and toxic and should be handled with extreme care, most of them are relatively safe to use and some can be stored as stock solutions. In most work, a light pre-etch with a general-purpose etch that produces uniform attack without roughening of the constituents improves image sharpness after tinting.

The sample is immersed in a suitable quantity of the tint etchant for the recommended time (not necessarily correct for all samples), usually long enough to produce a red-violet macroscopic color. After tinting, do not touch the sample surface. Polishing must be of a very high quality to obtain best results since tint etchants will reveal vividly even the most superficial surface scratches, even when none appear to be present before tinting. Final polishing with colloidal silica—aided in some cases by attack-polishing solutions⁴—is usually very effective for such work. When successfully performed, tint-etch results can be remarkably beautiful as well as technically valuable.

Examples: Nonferrous Alloys

Figure 1-6 illustrated the use of Klemm's I tint etch (etch 2c in Table 1-1), a very versatile reagent. Klemm's I will tint etch all-alpha, copper-based alloys, but the rate of film formation varies with sample composition and processing. For example, single-phased cartridge

brass ($\text{Cu}-30\%\text{Zn}$) may require up to an hour or more to tint etch, whereas single-phase phosphor bronze ($\text{Cu}-5\%\text{Sn}-0.2\%\text{P}$) etches in a few minutes. Cold-rolled cartridge brass etches much more quickly than annealed cartridge brass.

Figure 1-7 shows the microstructure of an annealed (790°C ; cool $25^\circ\text{C}/\text{hr}$ to 590°C ; air cool), as-cast $\text{Cu}-10\%\text{Sn}-10\%\text{Ni}$ alloy. Etching with aqueous 3-percent ammonium persulfate, 1-percent ammonium hydroxide outlined and slightly colored the γ phase $(\text{Cu}, \text{Ni})_3\text{Sn}$ in the α plus γ lamellar structure. Tinting with Klemm's I reagent colored the α phase. Figure 1-8 shows the microstructure of an as-cast $\text{Ag}-28\%\text{Cu}$ eutectic alloy, a mixture of essentially pure copper and pure silver. Etching



Fig. 1-7. Microstructure of annealed, as-cast $\text{Cu}-10\%\text{Sn}-10\%\text{Ni}$ revealed by two etchants. Top: γ phase $(\text{Cu}, \text{Ni})_3\text{Sn}$ outlined with aqueous 3-percent ammonium persulfate, 1-percent NH_4OH . Bottom: alpha matrix phase colored by Klemm's I reagent. (Both at $500\times$.)

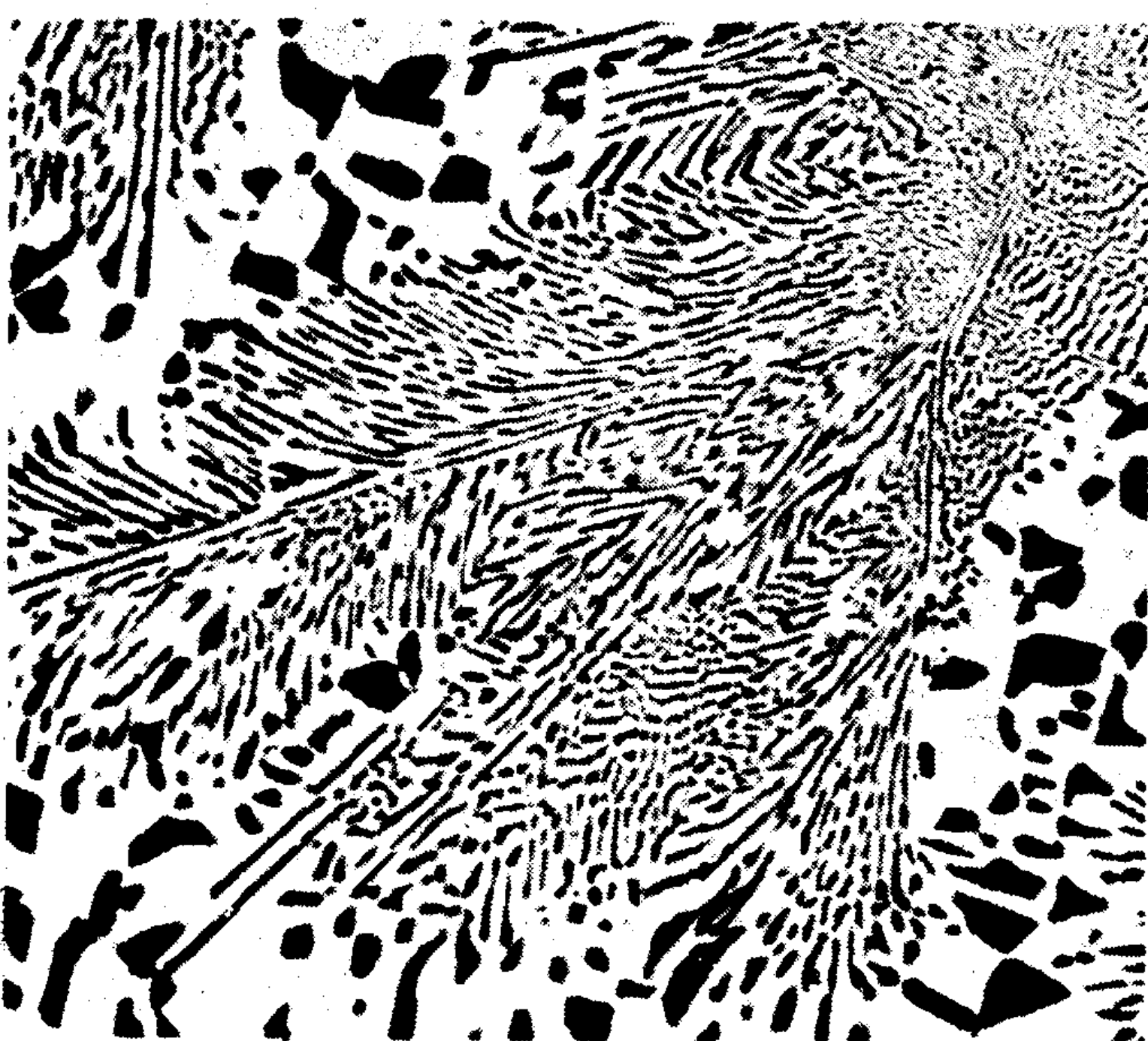
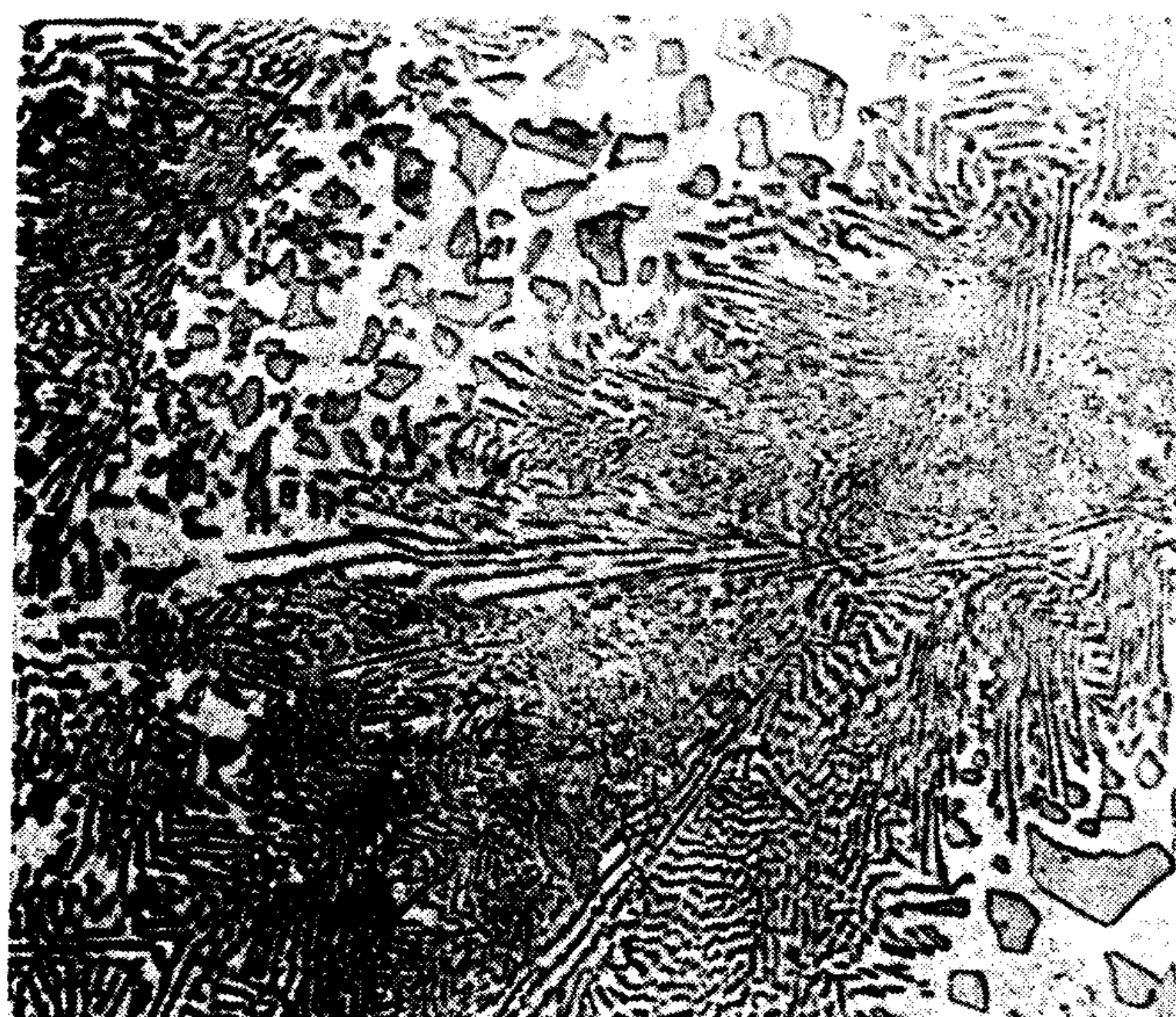


Fig. 1-8. Eutectic microstructure of Ag-28%Cu revealed by two etchants. Top: copper phase outlined with 500 ml H_2O , 7.5 g CrO_3 , 4 ml H_2SO_4 . Bottom: copper phase colored with Klemm's I reagent. (Both at 500 \times .)

with a solution containing 500 ml water, 7.5 g CrO_3 , and 4 ml H_2SO_4 outlined the copper phase, which is visible because of the reflectance difference between copper and silver. Tint etching with Klemm's I reagent darkened the copper grains producing strong color contrast.

Several etchants will selectively color θ phase (CuAl_2) in Al-Cu alloys. Figure 1-9 illustrates the use of etchants to outline or color CuAl_2 in an as-cast eutectic Al-33%Cu alloy. Keller's reagent (95 ml water, 1.5 ml HCl , 1 ml HF , 2.5 ml HNO_3) outlines the CuAl_2 phase, which appears darker than the matrix as a result of reflectance differences. Two reagents (etchants Ncs. 1c and 1d in Table 1-1)—both based on ammonium molybdate—were used. Etch No. 1c, from Anderson's compilation,² colored

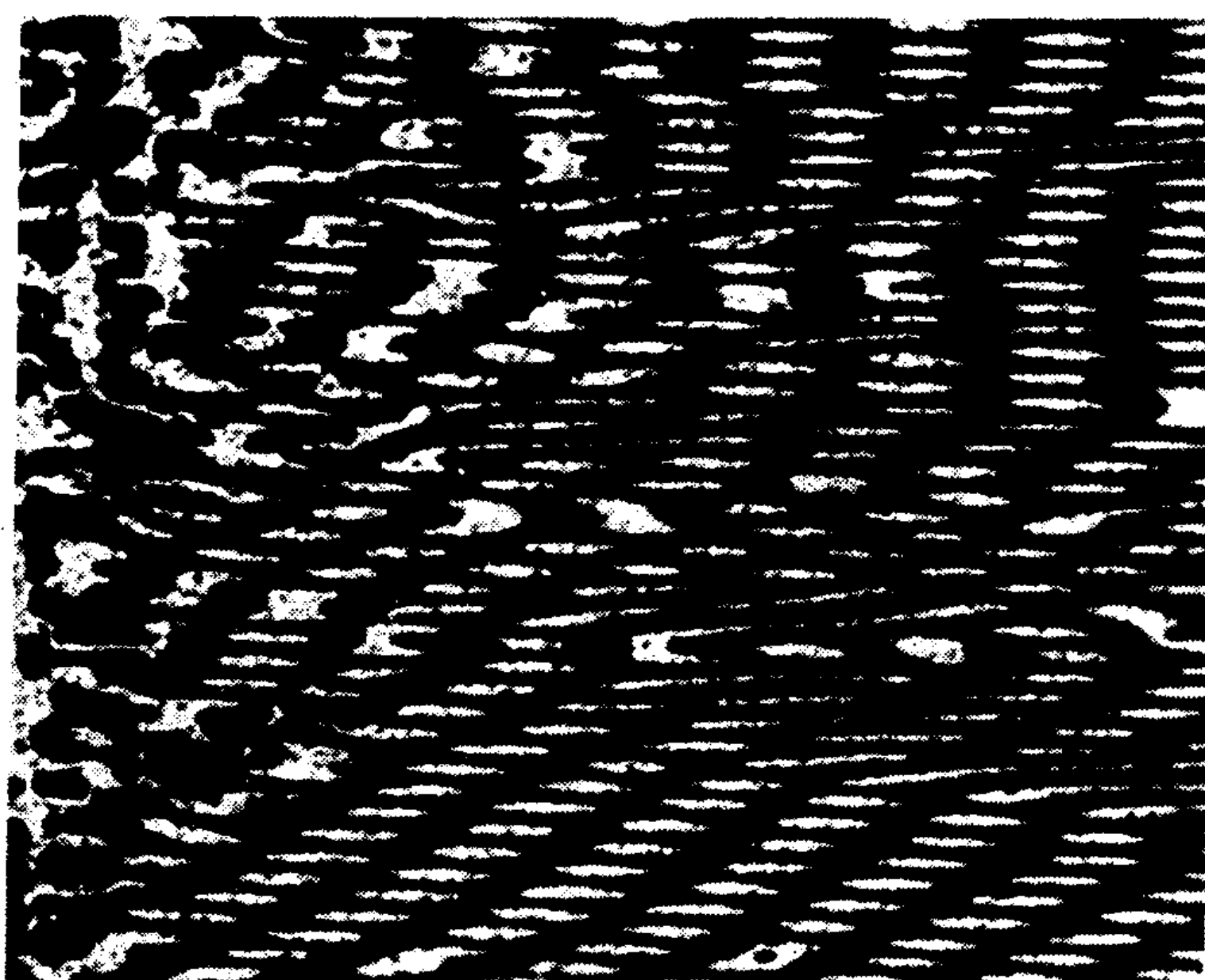
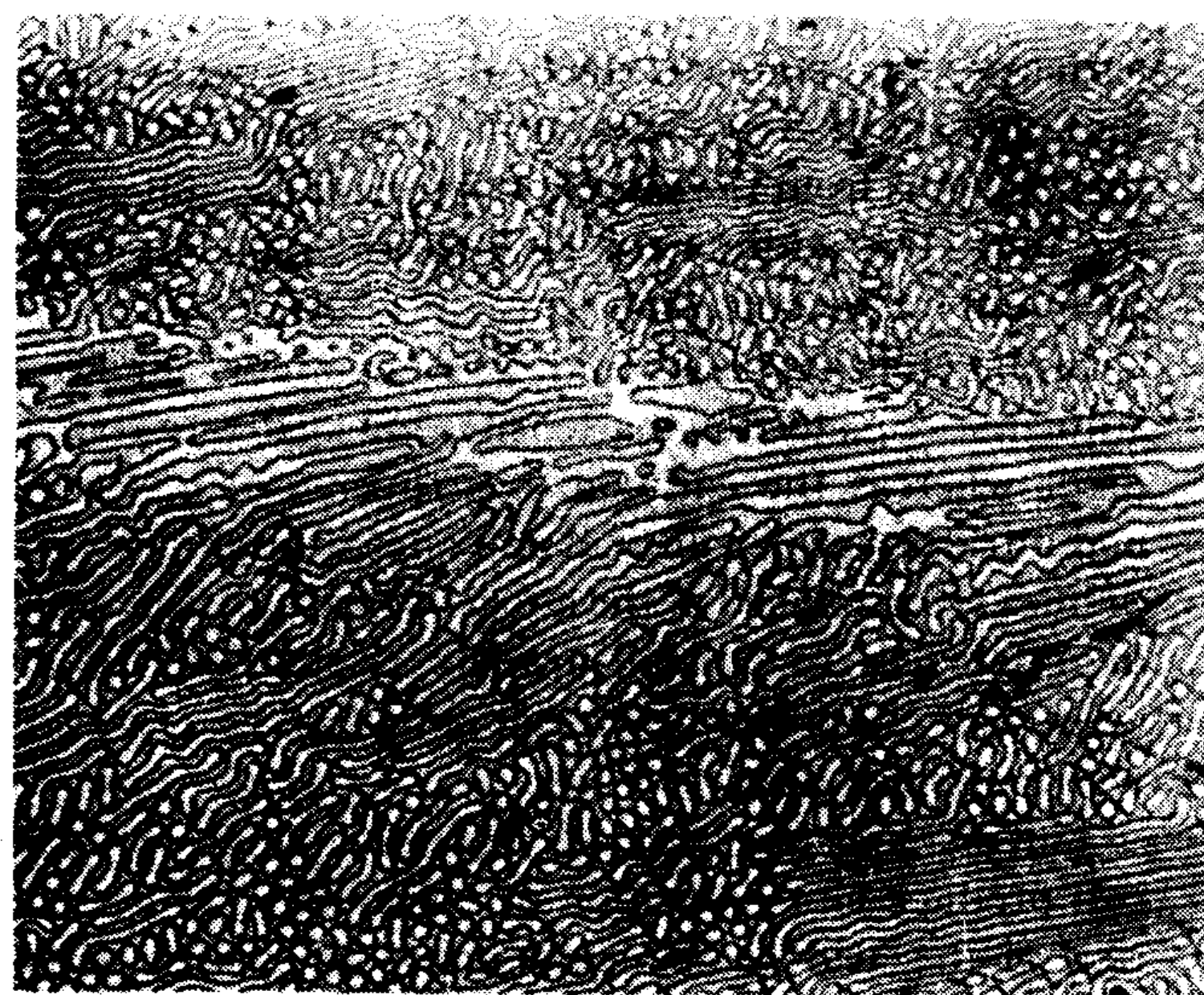


Fig. 1-9. Eutectic structure in as-cast Al-33%Cu revealed using three reagents. Top: Keller's reagent outlines CuAl_2 . Middle: CuAl_2 colored blue with etch No. 1c. Bottom: CuAl_2 colored violet with etch No. 1d. (All at 500 \times .)

CuAl_2 blue, whereas etch No. 1d⁷ colored CuAl_2 violet.

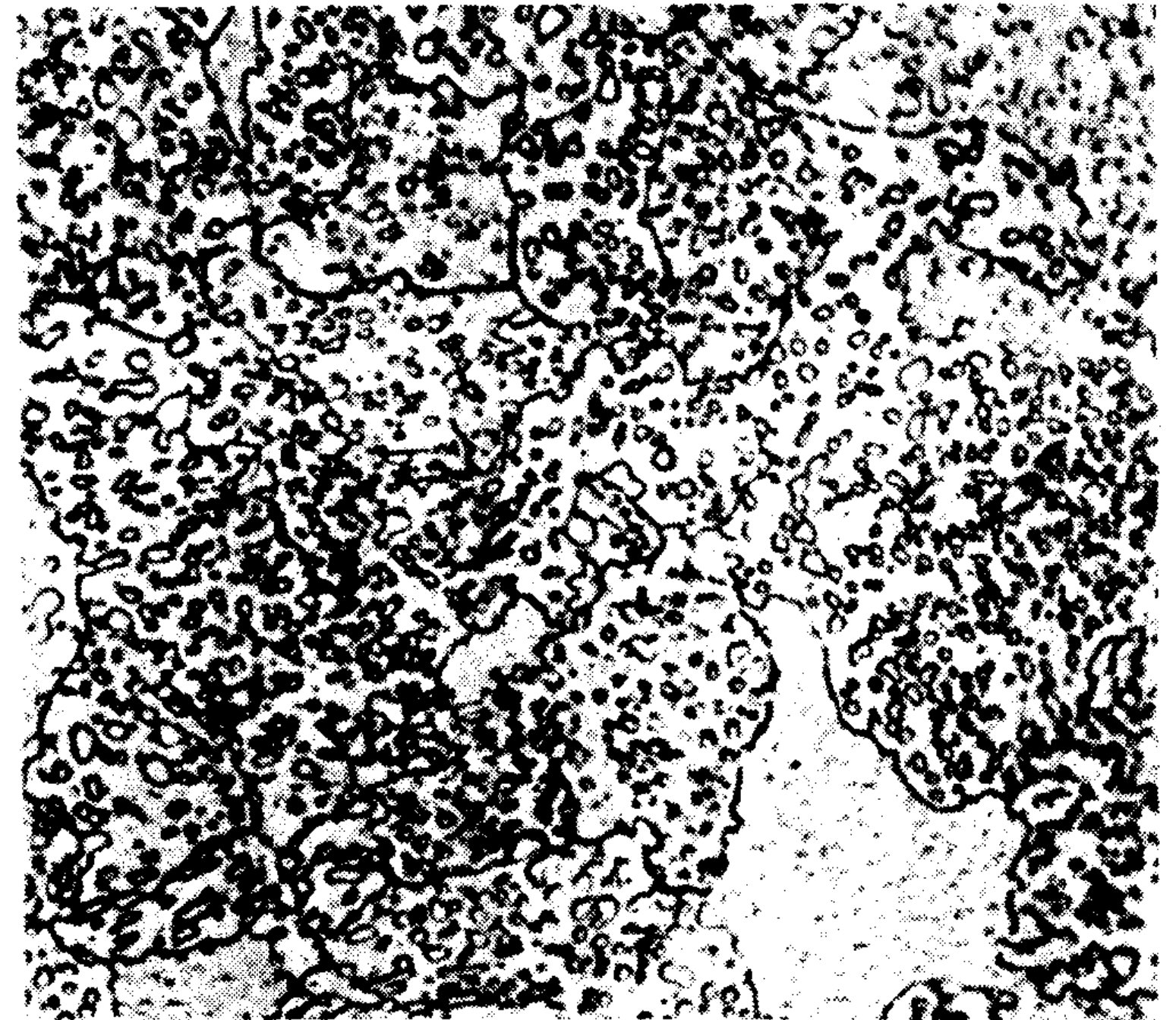
Examples: Ferrous Alloys

Figure 1-10 shows eight examples of how spheroidized cementite in a ferritic matrix (AISI W2 tool steel, Fe-1%C-0.3%Mn-0.1%V) can be revealed. Nital or picral are commonly used to etch such a structure. Both attack the anodic ferrite phase, leaving the carbide standing in relief. Nital, however, is sensitive to crystallographic orientation, and the carbides within some grains are poorly delineated. Nital also reveals the ferrite grain boundaries,

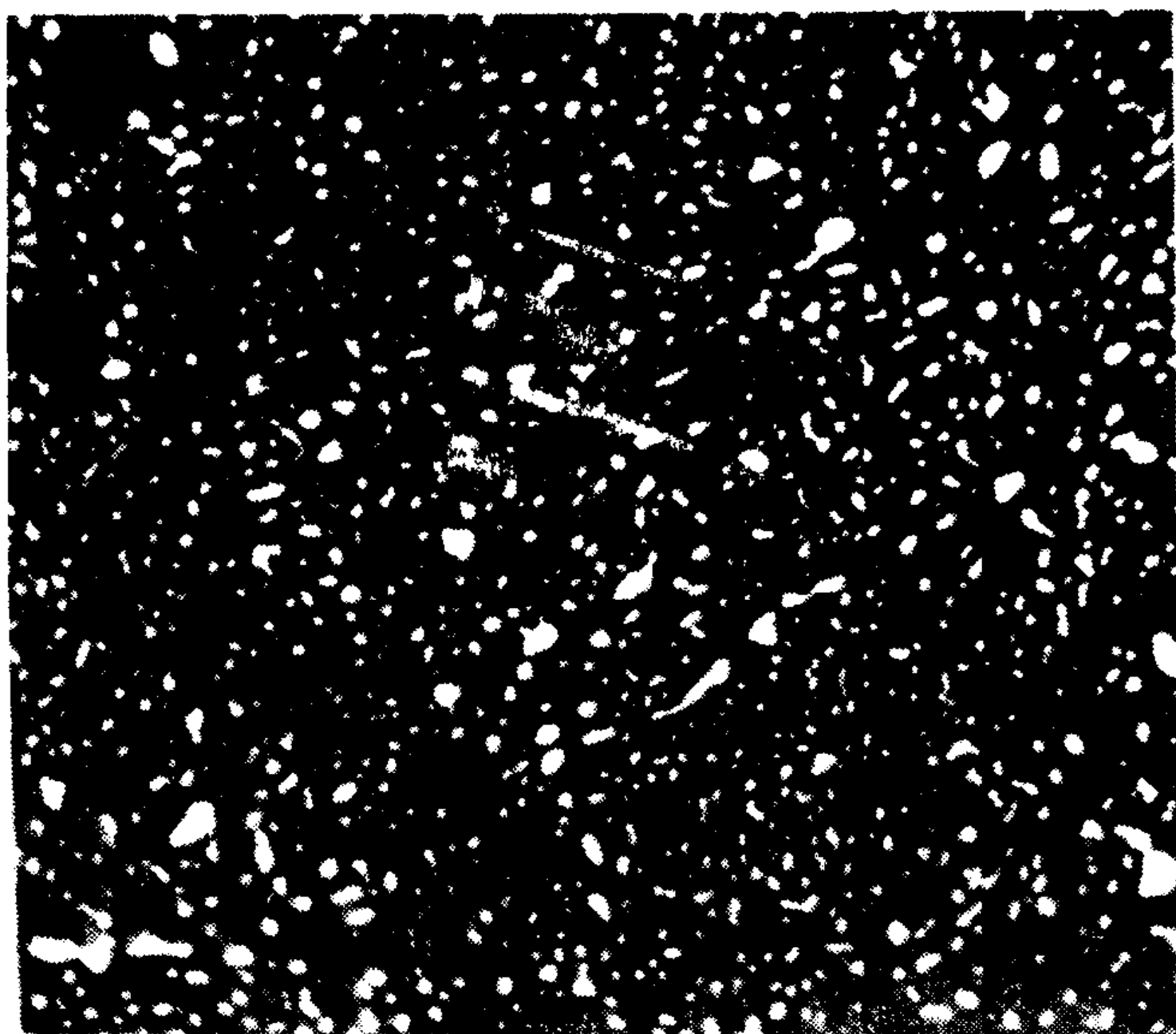
an undesirable result if the amount of cementite is to be measured by image analysis. Strong contrast between these phases can be obtained by using selective etchants. Klemm's I reagent (etch No. 3a) colors the ferrite red and blue, leaving the cementite white. Boiling or electrolytic alkaline sodium picrate (etch No. 3g) colors cementite preferentially. Several of Beraha's tint etchants can be used to color either ferrite or cementite. Beraha's sodium thiosulfate-ammonium nitrate solution (etch No. 3c) and his potassium metabisulfite-HCl reagent (etch No. 3f) both color the ferrite, although the former produced pitting. Beraha's sodium-molybdate reagent (etch No. 3d) and his cadmium sulfide-reagent (etch No. 3e)



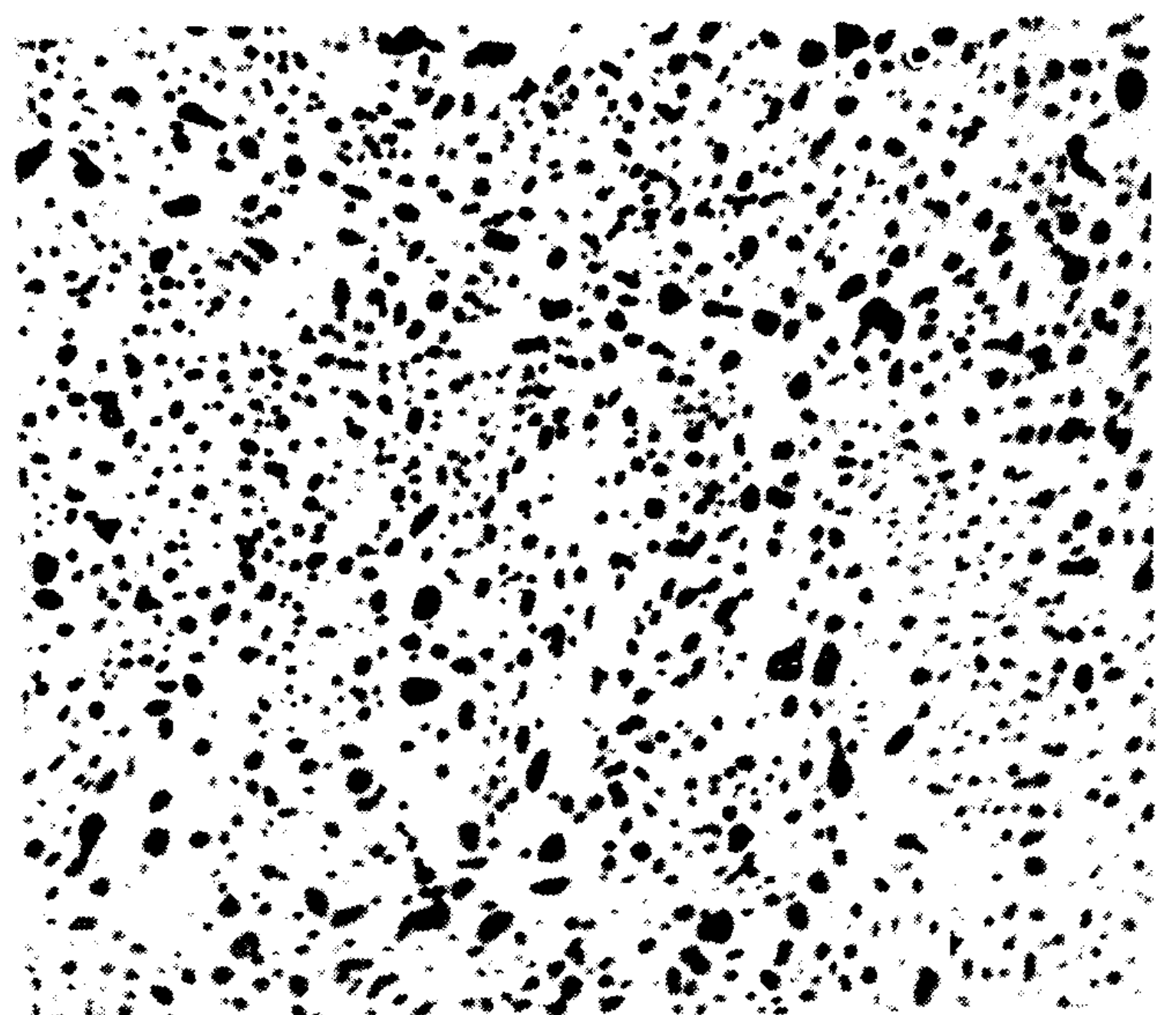
4% Picral



2% Nital

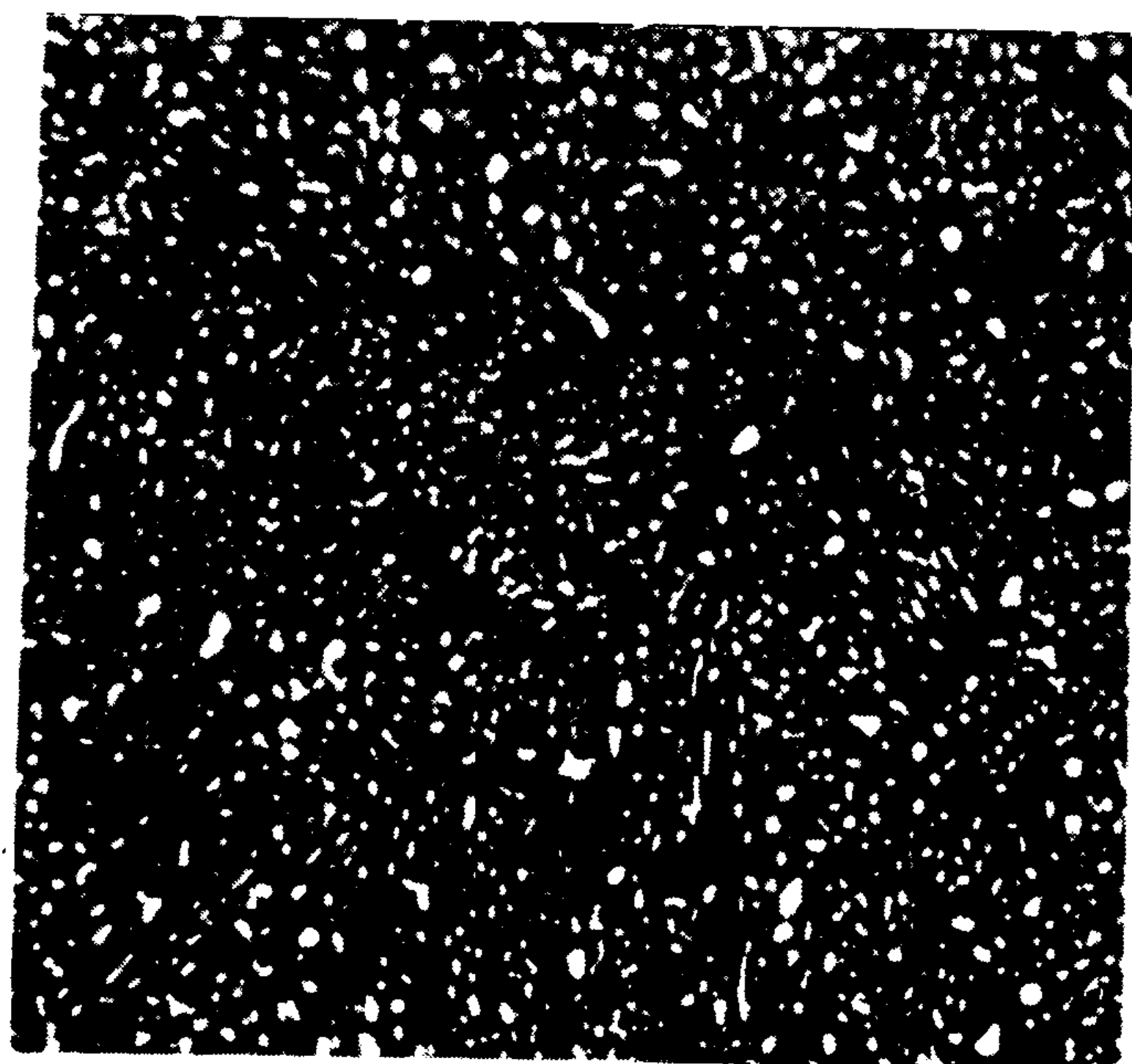


4% Picral/Klemm's I (etch 3a)

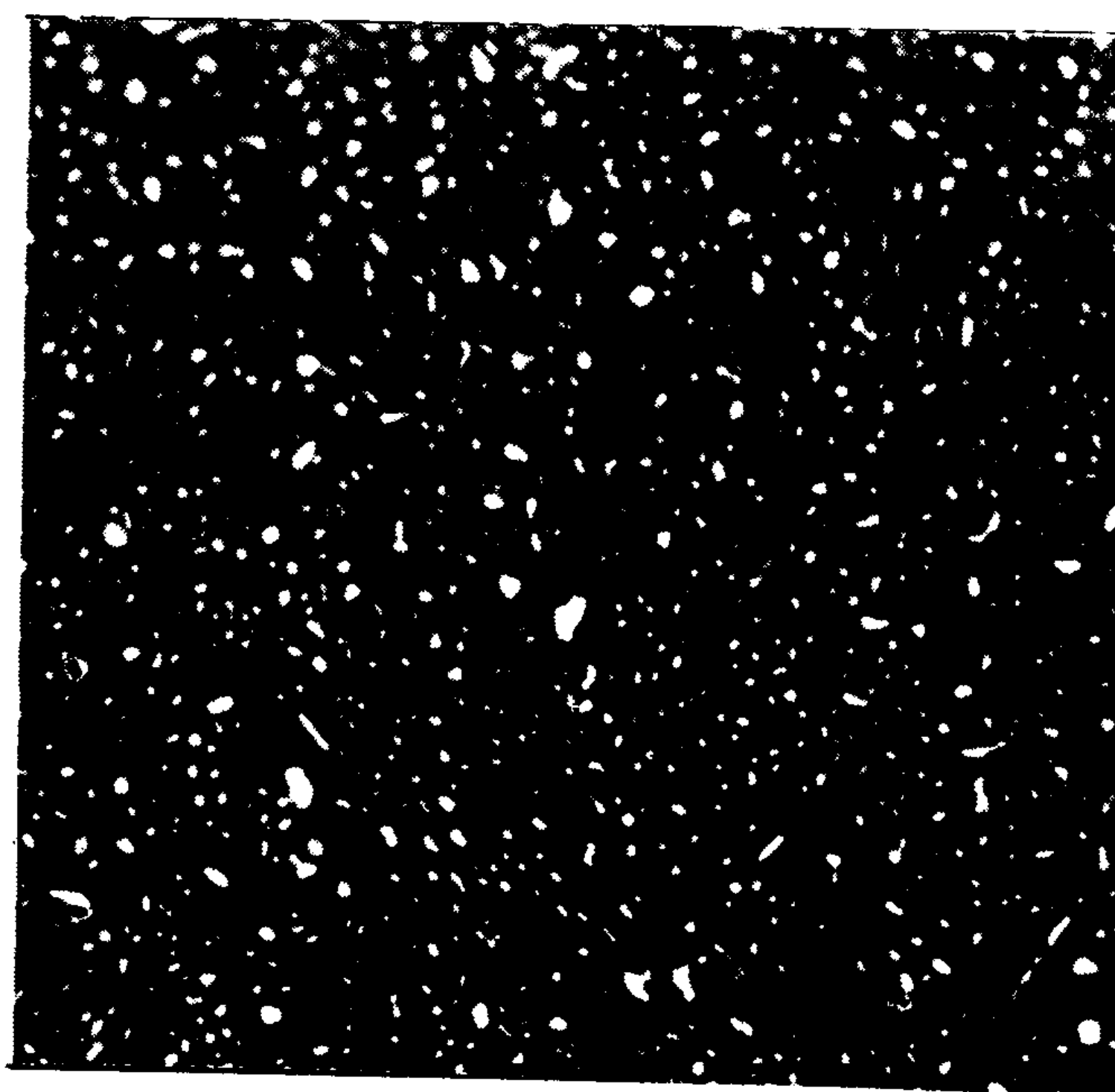


Boiling Alkaline Sodium Picrate
(etch 3g)

Fig. 1-10. Examples of selective etching of ferrite or cementite in spheroidized annealed AISI W2 tool steel compared to etching with standard nital and picral immersion etchants. (All at 1000 \times .) Tint etchants provide selectivity required for image analysis. See Table 1-1 for etch compositions.



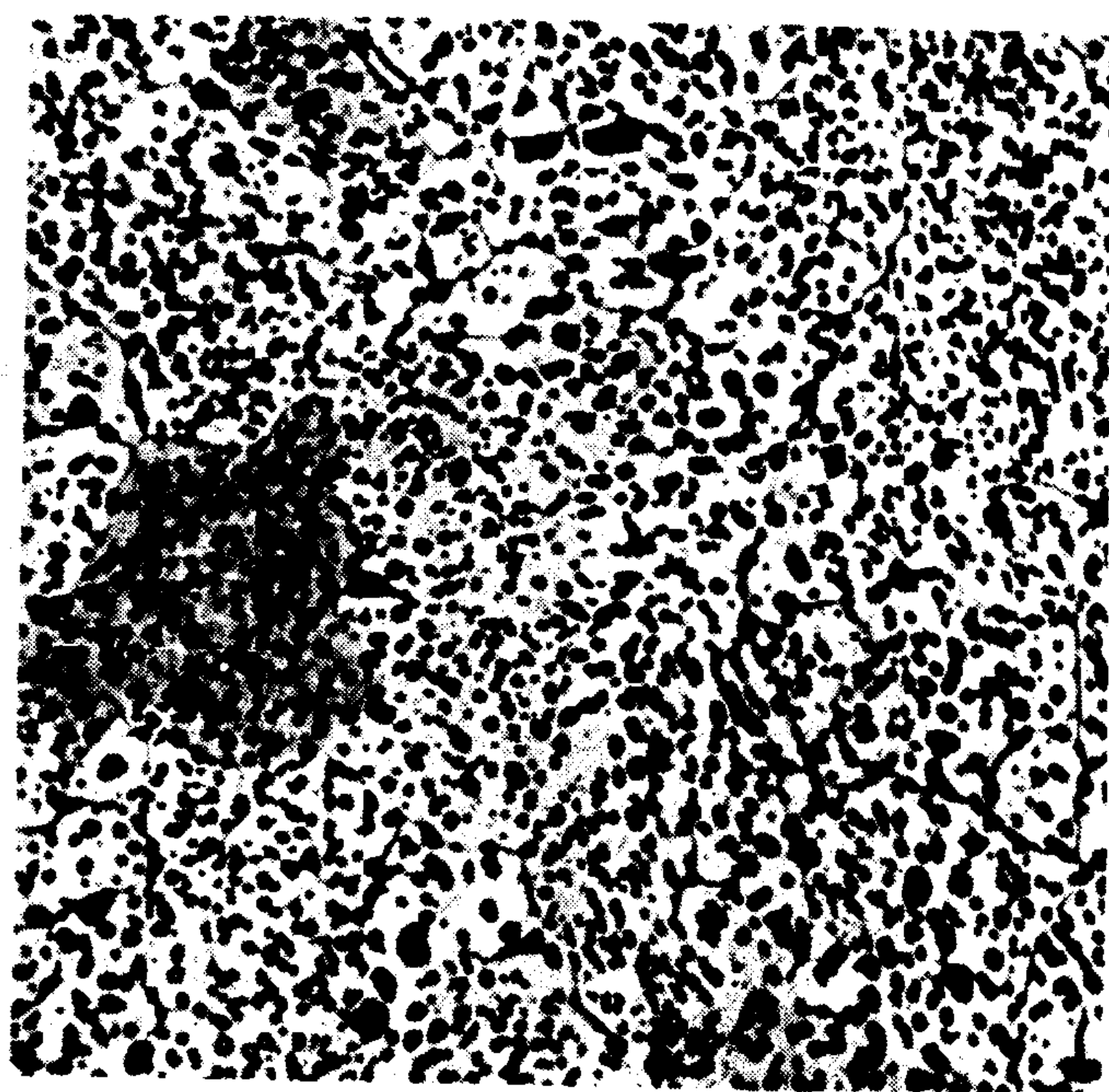
Sodium Thiosulfate-Ammonium
Nitrate (etch 3c)



Potassium Metabisulfite-HCl
(etch 3f)



Sodium Molybdate-Ammonium
Bifluoride (etch 3d)



Cadmium Sulfide Tint Etch
(etch 3e)

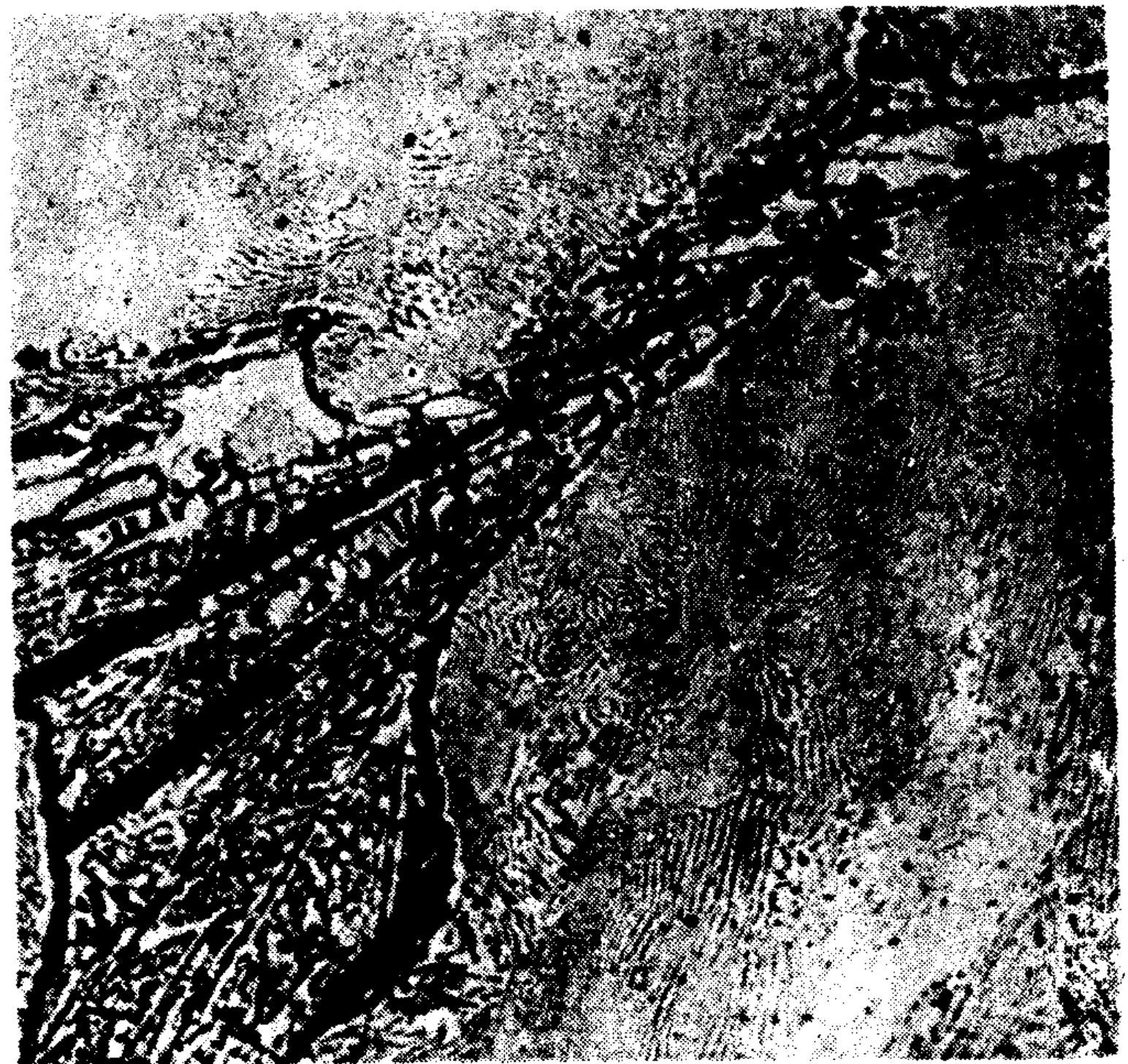
Fig. 1-10 (continued)

both preferentially color the cathodic cementite phase. Tint etch No. 3d colored the ferrite yellow and white and the cementite orange-brown. Longer etch times (30 to 45 sec) darkened the ferrite and reduced the contrast. Etch No. 3e colored the ferrite yellow and blue and the carbide brownish violet. Although Beraha recommended⁶ nital as the pre-etchant, the orientation sensitivity of this etch degrades tint-etch results, and picral is preferred for these structures.

Figure 1-11 shows the microstructure of gray cast iron (Fe-4%C-0.1%P-1.2%Si) containing the ternary ferrite-cementite-phosphide eutectic. Etching with picral and nital (sequentially) revealed the pearlite matrix and outlined the ferrite in the eutectic. There was no distinction, however, between cementite and phosphide. Boiling alkaline sodium picrate (etch No. 3g) colored the cementite only. Murakami's reagent (etch No. 3j, not illustrated) darkened the phosphide after about 10 sec and lightly



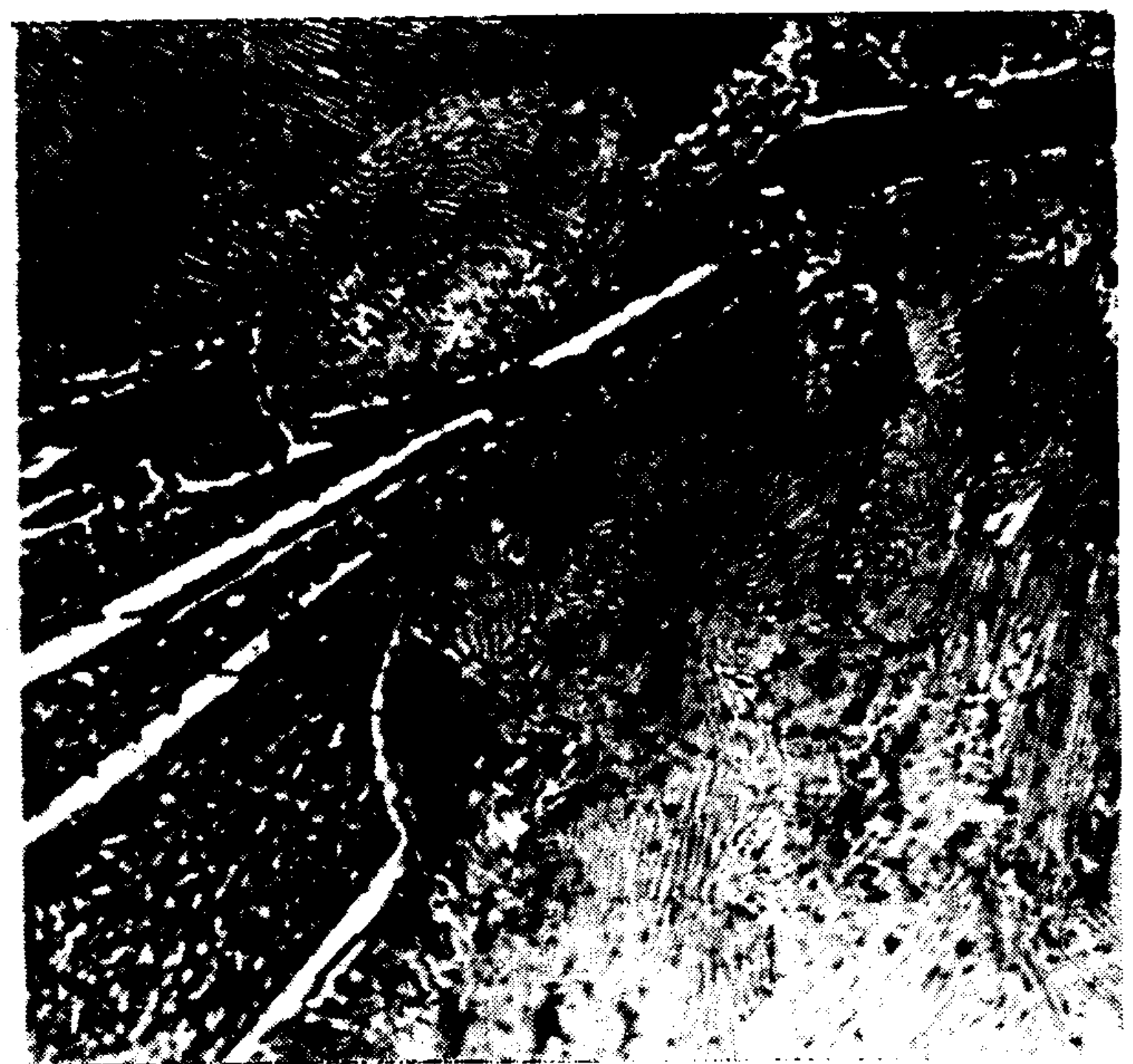
4% Picral/2% Nital
Outlines ferrite but does
not attack $\text{Fe}_3\text{C}/\text{Fe}_3\text{P}$ interface



Alkaline Sodium Picrate (etch 3g)
40 sec boiling, Fe_3C brown



Lead Sulfide Tint Etch
(etch 3h) Fe_3C pale blue



Cadmium Sulfide Tint Etch
(etch 3e) Fe_3C yellow-tan

Fig. 1-11. Examples of selective etching techniques for phase delineation of ternary ferrite-cementite-phosphide eutectic in gray cast iron. (At 500 \times .) See Table 1-1 for etch compositions.

colored the cementite after about 2 min in the boiling solution. Beraha's lead-sulfide reagent (etch No. 3h) colored both ferrite and cementite (darker of the two). Beraha's cadmium-sulfide reagent (etch No. 3e) colored all three phases: Phosphide shows up quite dark; cementite and ferrite are light with little contrast difference in black and white photography.

Beraha's lead-sulfide reagent (etch No. 3h) is exception-

ally useful for preferentially coloring manganese-sulfide inclusions. Figure 1-12 shows an as-polished sample of an alloy steel containing MnS inclusions and one darker oxide inclusion. The sample was etched with nital and then with the lead-sulfide tint etch, which deposited a white film on the sulfides.

Two alkaline chromate etchants^{8,9} have been developed to detect and reveal oxygen enrichment associated with

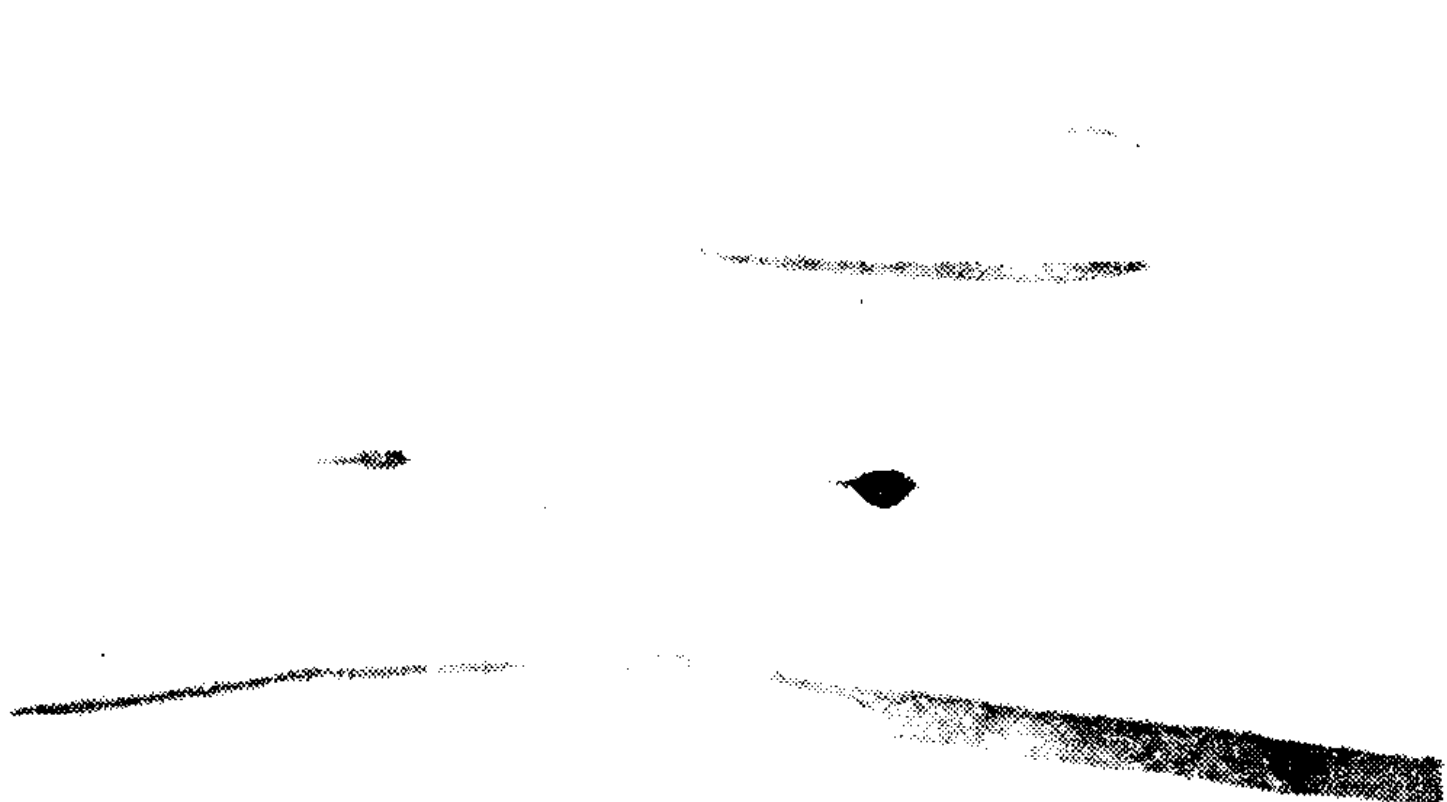


Fig. 1-12. Manganese sulfide can be positively identified and discriminated by the use of Beraha's lead-sulfide tint etch (etch No. 3h). Top: as-polished. Bottom: 2-percent nital pre-etch, lead-sulfide tint etch for 90 sec. (Both at 500 \times .)

defects in steels present at hot-working temperatures. One such etch⁸ (etch No. 3i) was used to reveal oxygen enrichment at a forging lap in an alloy steel, as shown in Fig. 1-13. The oxygen-enriched area is white, whereas the matrix was colored light green and pink.

ELECTROLYTIC ETCHING

Although many electropolishing solutions can be used as etchants by reducing the applied voltage at the end of the polishing cycle, none of these are noted for selectivity. A number of electrolytic etchants have been developed that do provide excellent selective etching action, but none of these are useful for polishing. Electrolytic etching solu-



Fig. 1-13. Oxygen enrichment at a forging lap in an alloy steel revealed by Fine's alkaline chromate etch (etch No. 3i). (At 100 \times .)

tions are often rather simple in composition as the applied potential replaces the oxidizer component in immersion etchants.

In nearly all work, the sample is the anode, and direct current is employed. Greater control of the etching process is achievable by selection of the electrolyte composition, etching time, voltage, temperature, and current density. Generally speaking, an underetched sample can be placed back into the electrolyte to strengthen the attack without repolishing. After some familiarity is gained, etching conditions can be easily reproduced.

Stainless Steels

Electrolytic etchants have been widely used in the study of stainless steels. The classic study of Gilman¹⁰ provided a clear understanding of selective etching of such steels. Simple hydroxide solutions will selectively color certain constituents. The stain can be removed by light repolishing, leaving the constituent outlined. The colors produced pass through a well-defined sequence: yellow, green, red, blue, and reddish brown. These colors are produced by interference effects. Strong hydroxide solutions—e.g., KOH—attack sigma phase more readily than carbides, whereas weak hydroxides—e.g., NH_4OH —attack carbides but not sigma. For hydroxides of intermediate strength, changing the voltage controls the attack, carbides being stained at low voltages and sigma and carbide being stained equally at high voltages. To identify phases in austenitic stainless steels, Gilman¹⁰ recommended that samples be pre-etched with Vilella's reagent (100 ml ethanol, 1 g picric acid, 5 ml HCl) to outline the phases. Next, the sample should be electrolytically etched with 10N KOH at 3 V dc for 0.4 sec; doing so colors sigma but not carbide. Then, the sample is electrolytically etched

in concentrated NH_4OH at 6 V dc for 30 sec to color the carbides.

Delta ferrite in martensitic or austenitic stainless steels can be preferentially revealed by electrolytic etching in 20-percent aqueous NaOH at 20 V dc for 20 sec (etch No. 3o).¹¹ Coloration is more uniform than with 10N KOH (etch No. 3n), which also colors delta ferrite (2.5 V dc for 10 sec). Figure 1-14 shows delta ferrite in solution annealed and aged 17-4PH stainless steel ($\text{Fe}-0.03\%\text{C}-16.5\%\text{Cr}-4\%\text{Ni}-3\%\text{Cu}-0.3\%\text{Nb}$). Since electrolytic 20-percent NaOH colors only the delta ferrite, the latter is easily observed at any magnification. Immersion etching with Fry's reagent (40 ml HCl , 5 g CuCl_2 , 30 ml water, 25 ml ethanol) revealed the martensitic microstructure very well and outlined the delta ferrite, but the results

were not as good as the electrolytic etch. Most simple immersion etches attack only the martensite in this sample.

Carbides in austenitic stainless steels are often selectively revealed by electrolytic etching with either 10-percent aqueous oxalic acid (6 V dc for 15 to 30 sec) or 10-percent aqueous sodium cyanide (6 V dc for up to 5 min). Since oxalic acid will also outline matrix phases in austenitic stainless steels and etch out the sigma phase, its action must be carefully controlled.

The electrolytic etchants are simpler and more reliable for phase identification in stainless steels than the Murakami-type reagents (etchants Nos. 3j to 3l). Etching results with Murakami-type reagents vary with etch composition, temperature, time, and phase orientation. When

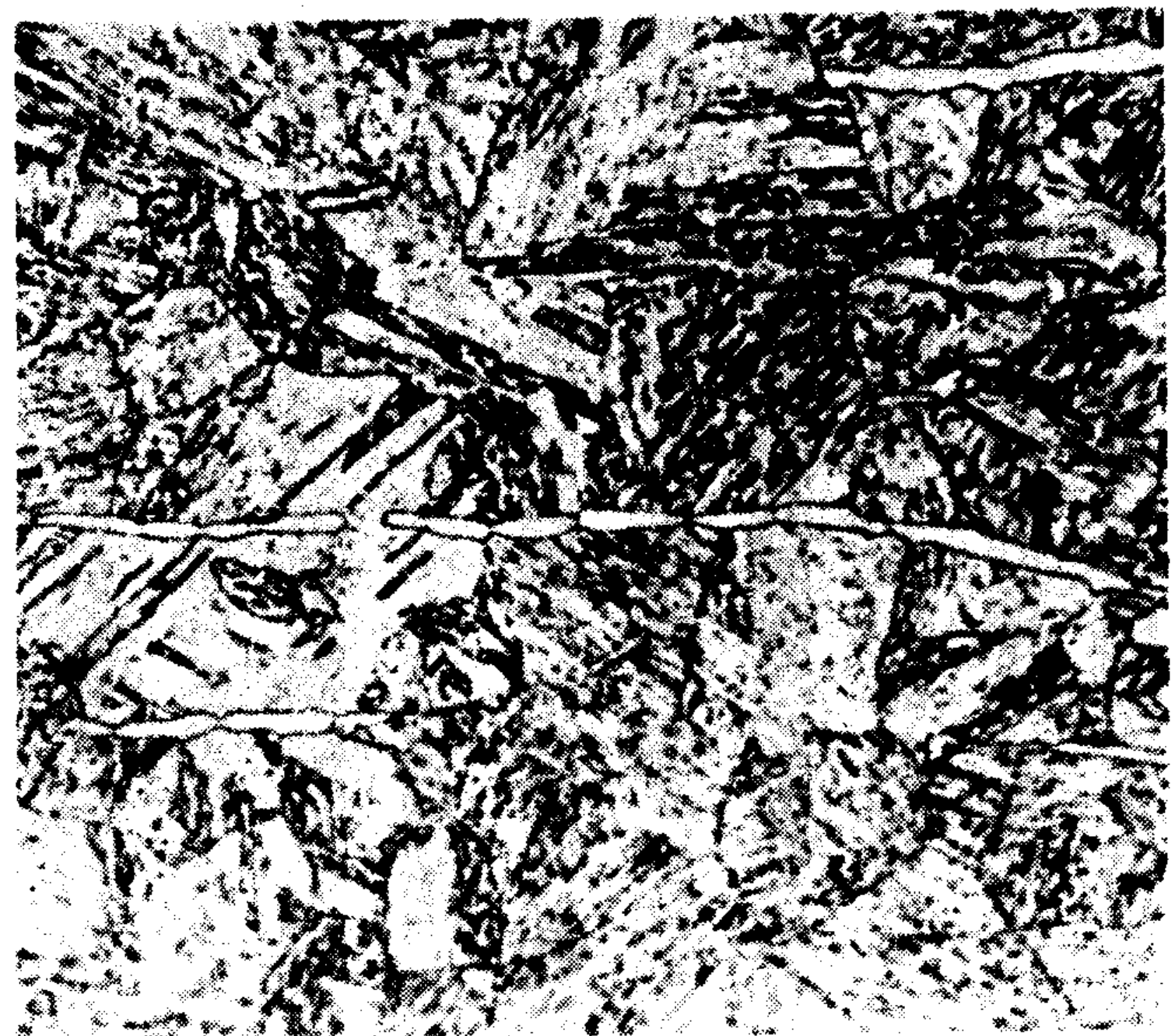
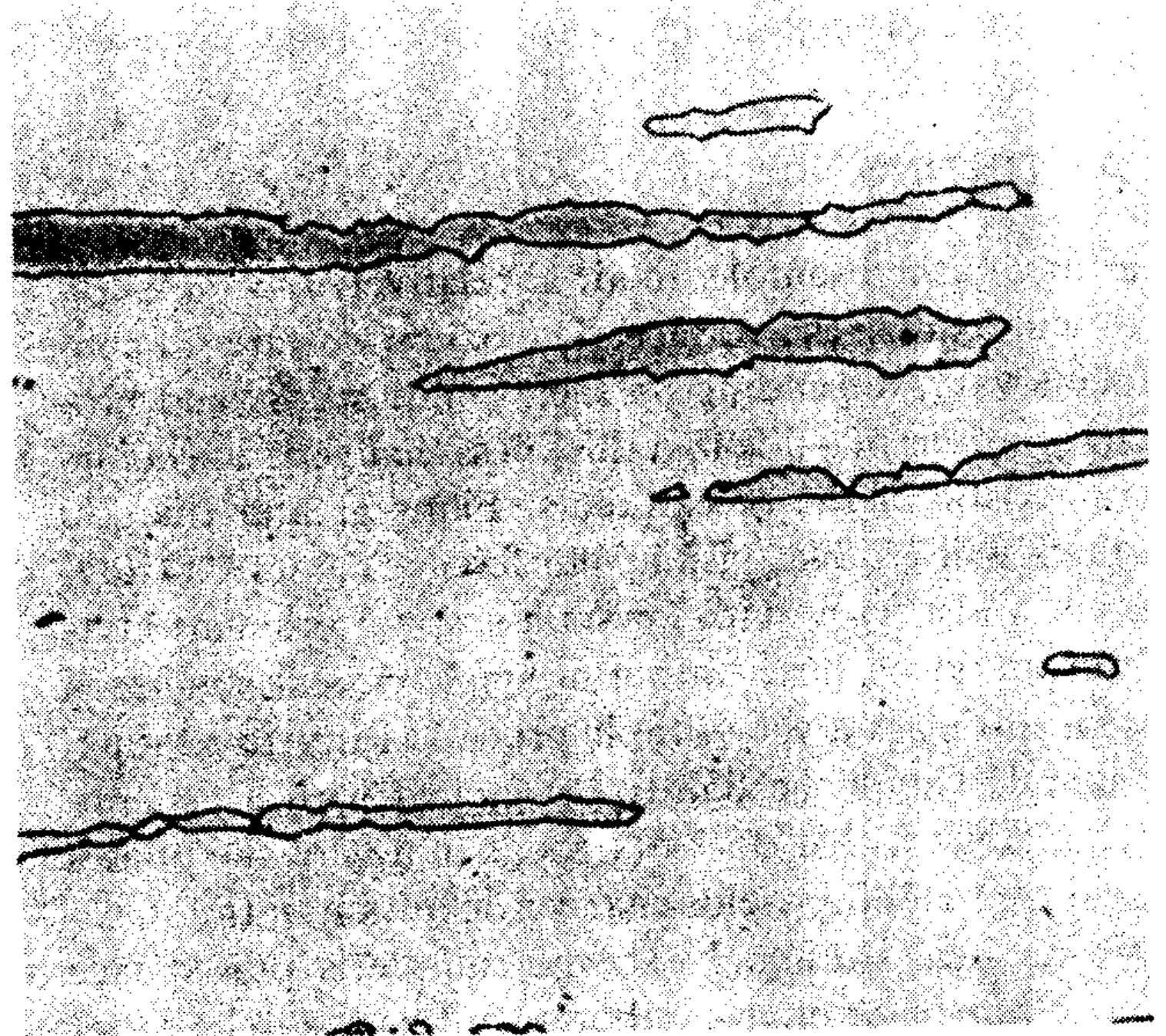
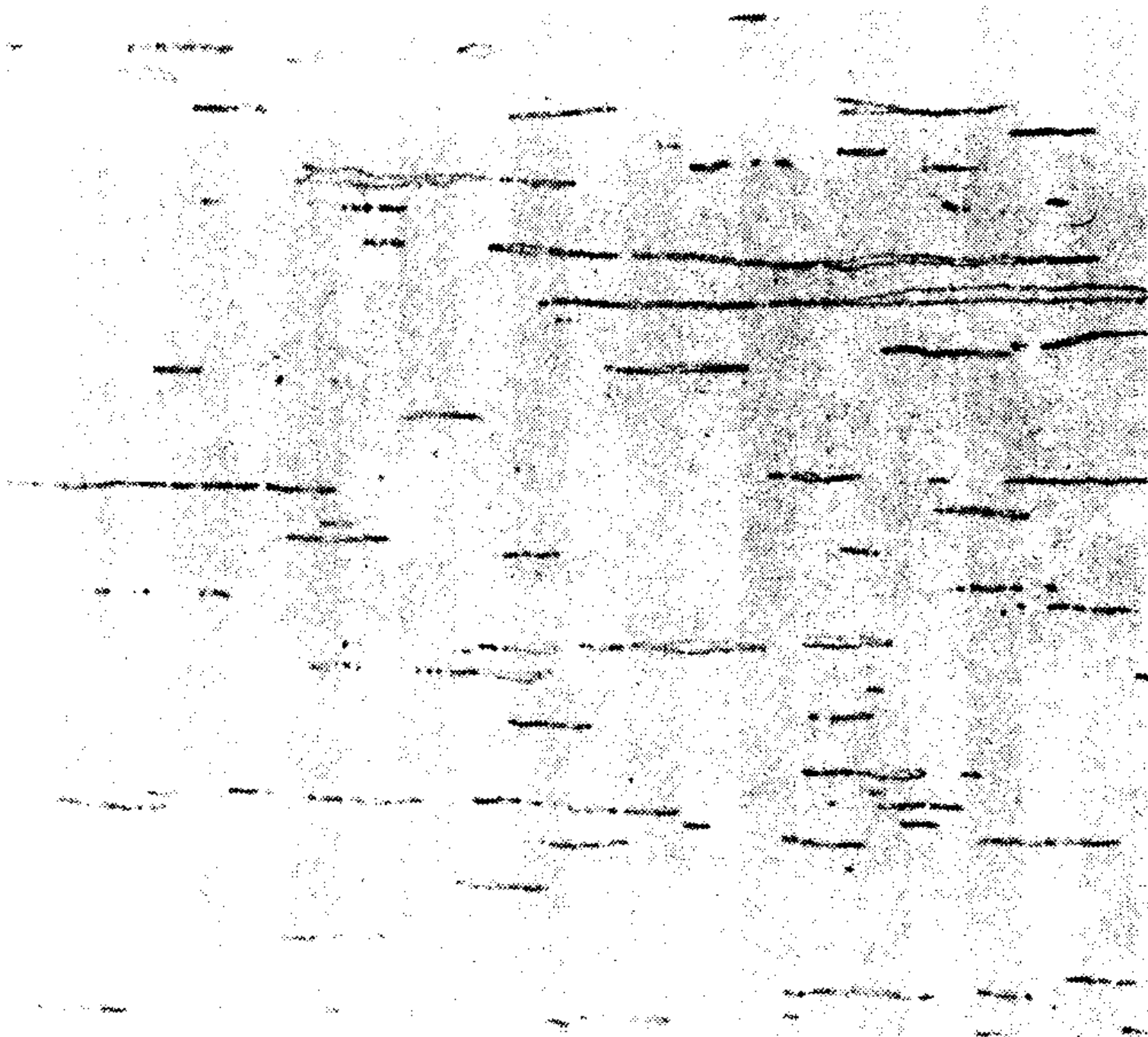


Fig. 1-14. Delta ferrite stringers in 17-4 PH stainless steel revealed (top) with 20-percent aqueous NaOH (20 V dc for 21 sec) and (bottom) by matrix etching with Fry's reagent. [100 \times (left) and 500 \times (right).]