Non-metallic Inclusions in Bronze and Brass*

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IN the literature of metallography there is a large amount of material describing the various non-metallic inclusions found in iron and steel, and the appearance of sulfides, silicates, oxides, or alumina in steel under the microscope is fairly well known. The inclusions found in non-ferrous metals are, however, not so well known, at least judging from published writings, and the author has been interested in examining small castings of copper, brass, or bronze with certain inclusions purposely mixed with the metal, to see what was the characteristic appearance of each kind of inclusion, and if they could be readily distinguished from one another.

The method employed in most cases consisted in overheating and oxidizing a small charge of copper, then cooling it somewhat, and adding a suitable amount of the element whose oxide it was desired to observe. This element was stirred in well and given time to react with the oxygen in the copper, then the melt was poured in a sand mold in the form of a cylinder about $2\frac{1}{2}$ in. (63 mm.) in each dimension, with a sprue about $1\frac{1}{2}$ in. (38 mm.) in diameter and 3 in. (76 mm.) high on top of the cylinder, the sprue forming the only riser. Samples for examination were cut sometimes from the center of the casting, and sometimes from the sprue or riser. A few of these samples were cast in chill molds. The appearance of sulfides was studied in an alloy containing 10 per cent. each of tin and lead, with which a flux of plaster of Paris was used. The appearance of foundry sand was studied in several alloys, one of them having sand stirred into the metal intentionally, and others having cut into the molds badly when poured, so that the castings were spoiled by included sand.

As all this work was done on alloys having copper as the chief ingredient, the natural starting point was copper oxide, the appearance of which in a micro-section is well known. Cuprous oxide is soluble in molten copper, but separates out in freezing and forms a eutectic containing 3.5 per cent. Cu_2O, or 0.39 per cent. oxygen. If there is less

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oxygen than 0.39 per cent., primary crystals of copper are embedded in the eutectic; and if more than 0.39 per cent. oxygen is present, the eutectic surrounds primary crystals of Cu_2O. Fig. 1 illustrates the former condition and Fig. 2 the latter, both showing unetched samples. The oxide particles are light blue when examined by white light and contrast strongly with the red background of copper.

Copper absorbs oxygen very readily when melted, but when other elements are alloyed with it, the copper oxide is always reduced and the added element is oxidized. Tin is one of the most common additions to copper, being used in all true bronze, and its oxide takes the form of angular crystals or needles of a very dark bluish gray color, as shown in Figs. 3, 4, and 5. The first two show views of the same casting poured in sand, but Fig. 5 is a view of a chill-casting, in which the tin-oxide crystals are much smaller. Special care was taken to avoid contamination of either of these heats by anything except copper, tin, and oxygen, and in the other cases to be described later equal care was taken to keep the heats free from any undesired element. The poor polishing qualities of these tin-oxide crystals are noteworthy, as they always appear more or less pitted and standing out in relief above the metallic surface with heavy black outlines. This probably indicates that they are hard and brittle. After etching with ammonia and hydrogen peroxide, as in Fig. 4, they appeared still more pitted, as if this reagent had attacked them or partly loosened them from the metallic surface.

It has been suggested that tin oxide occurs as films surrounding the primary crystals of the bronze; and although some of these films are seen in Fig. 4, the writer believes that they were caused by gas dissolved in the metal. The reasons for this view are: the angular crystalline form is characteristic of inclusions known to be tin oxide; the inclusions are idiomorphic and scattered through the bronze crystals rather than between them; the chilled sample (Fig. 5) did not show any of the films; and similar films were found in samples containing no tin, but zinc and phosphorus, the oxides of which are volatile. The common oxide films found so frequently in commercial bronzes are therefore thought to be caused either by the volatile oxide of zinc or phosphorus or by dissolved gases thrown out of solution when the metal solidifies. These films are illustrated in Figs. 6 and 7, the latter being an extreme case, where the unsoundness was very evident before the specimen was etched. The more usual oxide films, as shown in Fig. 6, do not appear distinctly until after etching, as the polishing seems to make the metal flow over and hide them.

Several unsuccessful attempts were made to examine inclusions of zinc oxide in brass, but, at first, the only result obtained was an apparently clean though unsound metal with films and cavities like those shown in Figs. 6 and 7. Finally, some typical inclusions were obtained
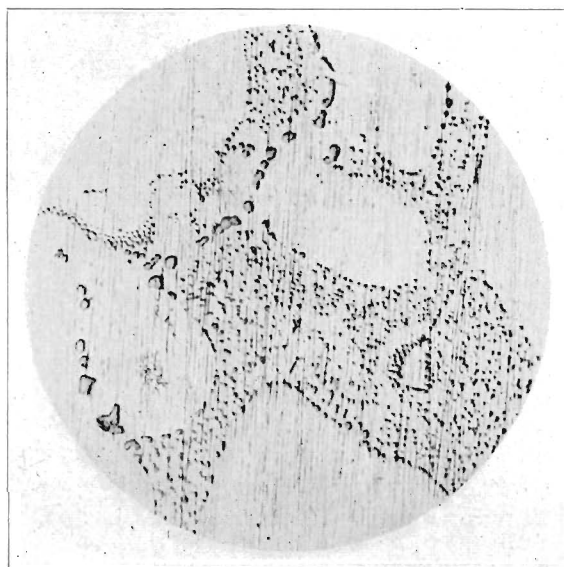
FIG. 1.—ELECTROLYTIC COPPER INGOT, SHOWING OXIDE EUTECTIC, UNETCHED. × 400.

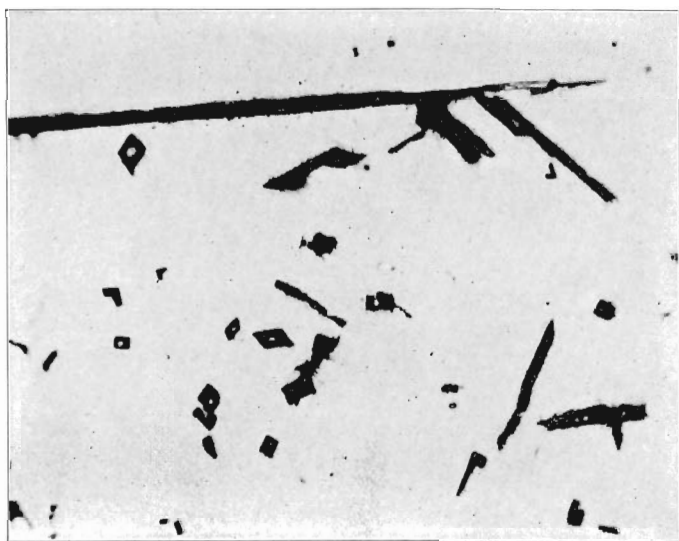FIG. 2.—BADLY OXIDIZED COPPER, SHOWING OXIDE CRYSTALS AND EUTECTIC, UN-ETCHED.   × 200.

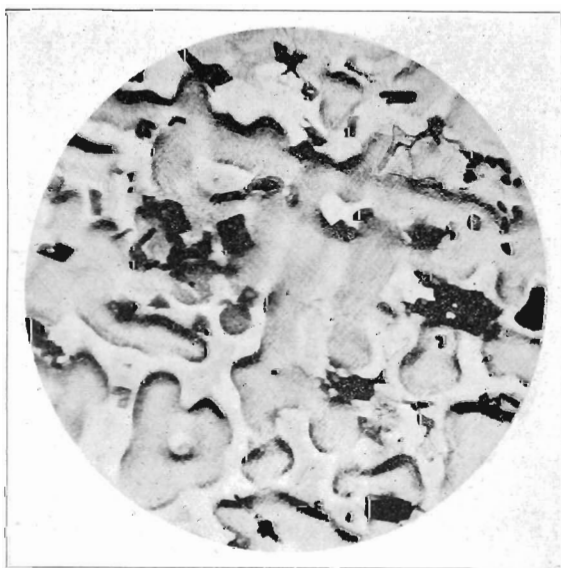FIG. 3.—TIN-OXIDE CRYSTALS IN OXIDIZED COPPER TREATED WITH 10 PER CENT. TIN, UNETCHED. × 200.

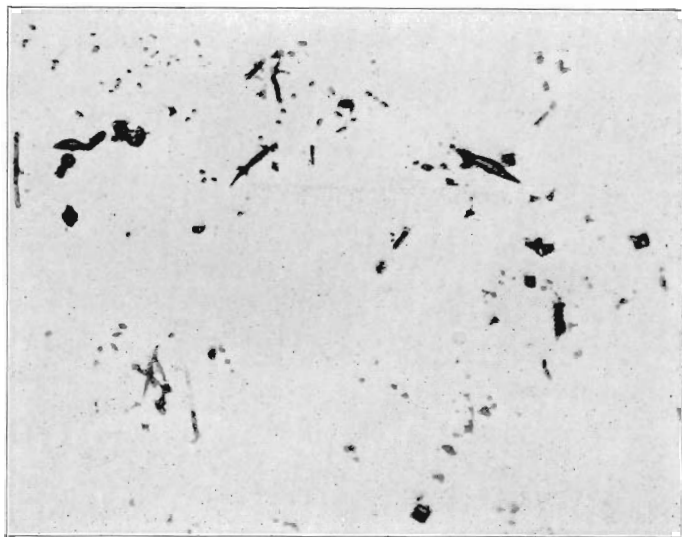FIG. 4.—SAME SPECIMEN AS FIG. 3, AFTER ETCHING WITH AMMONIA AND HYDROGEN PEROXIDE. × 100.

FIG. 5.—TIN-OXIDE CRYSTALS IN ANOTHER HEAT OF BRONZE MADE AS IN FIG. 3 BUT CAST IN A CHILL INSTEAD OF SAND, UNETCHED.   × 400.
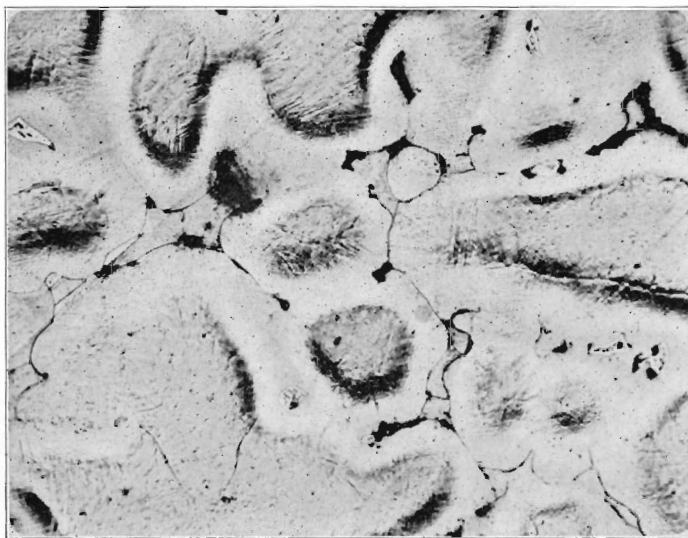

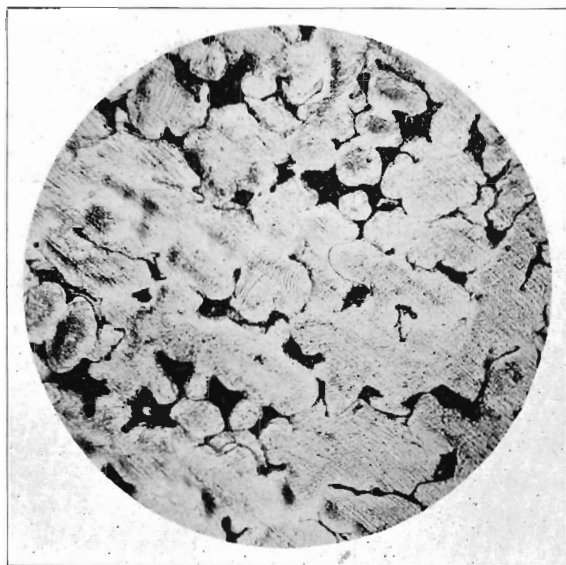FIG. 6.—TYPICAL OXIDE FILMS AND SPOTS IN GUN-METAL BRONZE CASTING, ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE.   × 400.

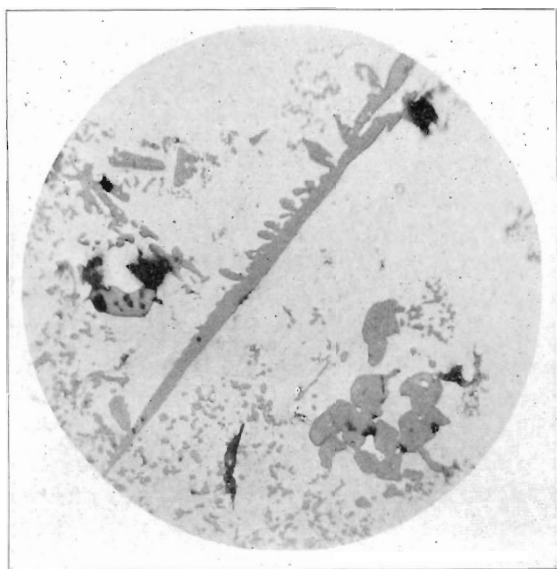FIG. 7.—VERY UNSOUND SPOT IN BRONZE CASTING WITH 12 PER CENT. TIN AND 6 PER CENT. ZINC, ETCHED LIKE FIG. 6. × 100.

FIG. 8.—ZINC-OXIDE INCLUSIONS IN OXIDIZED COPPER TREATED WITH 30 PER CENT. ZINC, UNETCHED. × 200.

in three cases, as shown in Figs. 8, 9, and 10. Some of these appear idiomorphic, but they are distinguished from tin-oxide crystals by their lighter color, smoother surface, without very dark outlines, and more rounded form. Fig. 10 shows metal cast in a chill, hence the inclusions are much smaller in it than in the others, which were cast in sand.

Manganese and phosphorus, when added to oxidized copper, gave results like those first obtained with zinc; that is, no typical inclusions were found although the castings were not sound. Fig. 11 shows the intercrystalline films produced when 0.5 per cent. of phosphorus was used to deoxidize some normal copper. These cavities seem to follow along the lines where the copper-oxide eutectic would be expected, had the metal not been deoxidized. Films that have been described as tin oxide are exactly similar to these, which were caused by the volatile oxide of phosphorus. Fig. 12 shows some badly oxidized copper after treatment with 2 per cent. of phosphorus. The phosphide eutectic was abundant here, but no non-metallic inclusions were found, the black spots shown being merely cavities.

While on the subject of phosphorus, it might be of interest to describe the writer's experience in identifying the phosphide in bronzes, although of course this cannot be considered a non-metallic inclusion. In specimens containing copper-tin eutectoid (or delta) and phosphide, these two hard bluish substances were found to be indistinguishable when etched with ammonia and hydrogen peroxide, or with ferric chloride. But before etching, the phosphide could be distinguished from the eutectoid because it was darker in color and stood out in relief above the rest of the alloy on account of its greater hardness. Also after etching with the above-mentioned reagents, if 50 per cent. nitric acid was applied the eutectoid was slightly attacked leaving the phosphide perfectly bright. As little as about 0.1 per cent. phosphorus can be detected in bronzes in this way. Figs. 13, 14, and 15 illustrate the appearance of phosphide in the presence of eutectoid when the same specimen is treated in different ways.

These three photomicrographs illustrate the appearance of sulfide as well as phosphide in bronze, for the alloy that they represent was made with a flux of plaster of Paris covering it in the crucible. The analysis of the alloy showed 79.3 per cent. copper, 9.9 per cent. tin, 9.8 per cent. lead, 0.4 per cent. phosphorus, 0.36 per cent. sulfur. In the unetched section, the sulfide looked rather dark blue, but when the bronze was made dark brown by the etching reagents, the sulfides appeared very light by comparison, as none of the ordinary reagents attacked them. They had more regular rounded shapes than the phosphides, which had the typical form of a eutectic, as illustrated in Fig. 15. These two substances can also be readily distinguished by the darker color of the sulfide either in an unetched section or after etching with ammonia and
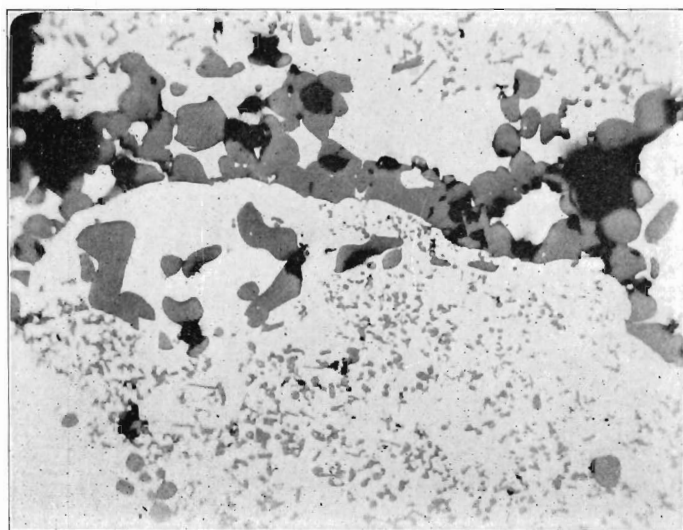
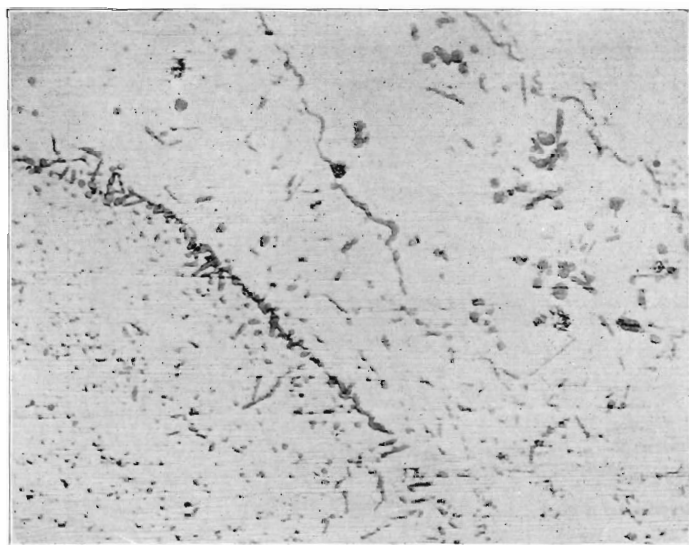FIG. 9.—ANOTHER VIEW OF ZINC-OXIDE INCLUSIONS, LIKE FIG. 8.

FIG. 10.—ZINC-OXIDE INCLUSIONS IN ANOTHER HEAT OF BRASS MADE AS IN FIG. 8, BUT CAST IN A CHILL INSTEAD OF SAND, UNETCHED.   × 400.
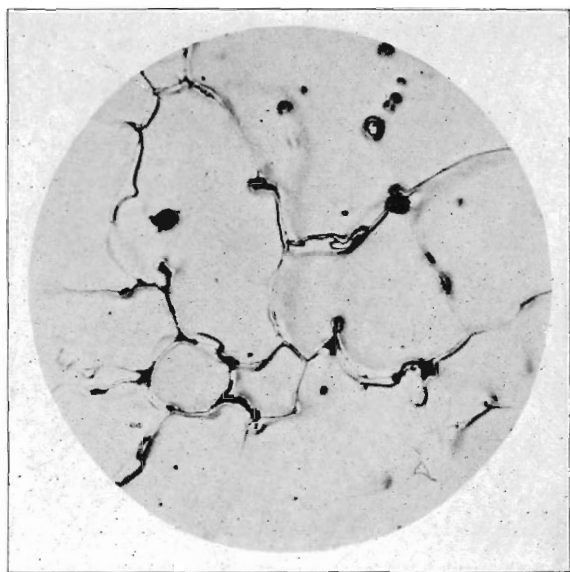
FIG. 11.—OXIDIZED COPPER TREATED WITH 0.5 PER CENT. PHOSPHORUS ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE, THEN REPOLISHED.   × 100.
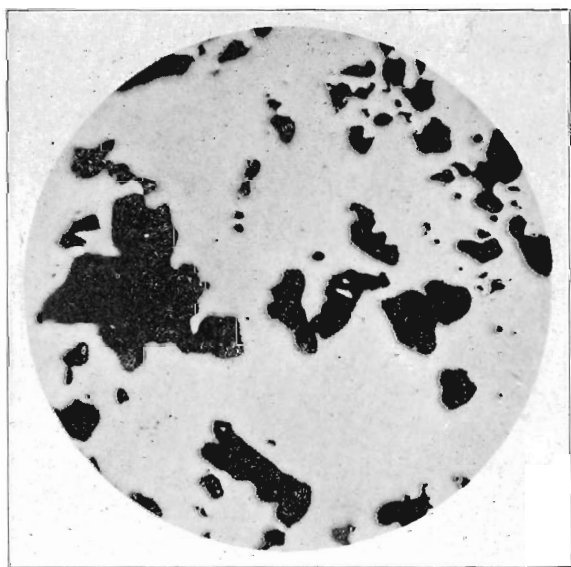

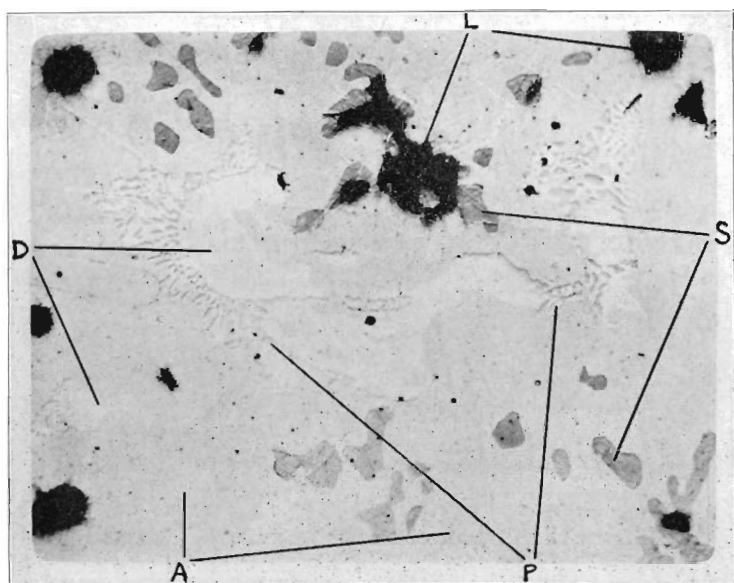FIG. 12.—BADLY OXIDIZED COPPER TREATED WITH 2 PER CENT. PHOSPHORUS, UNETCHED.   × 20.

FIG. 13.—PHOSPHOR-BRONZE SHOWING BLACK SPOTS OF LEAD L, DARK GRAY SULFIDE S, BRIGHT DELTA D, AND LIGHT GRAY PHOSPHIDE P, IN FINE PARTICLES STANDING OUT IN RELIEF ABOVE THE DELTA D, AND ALPHA A.   UNETCHED. $\times$ 400.
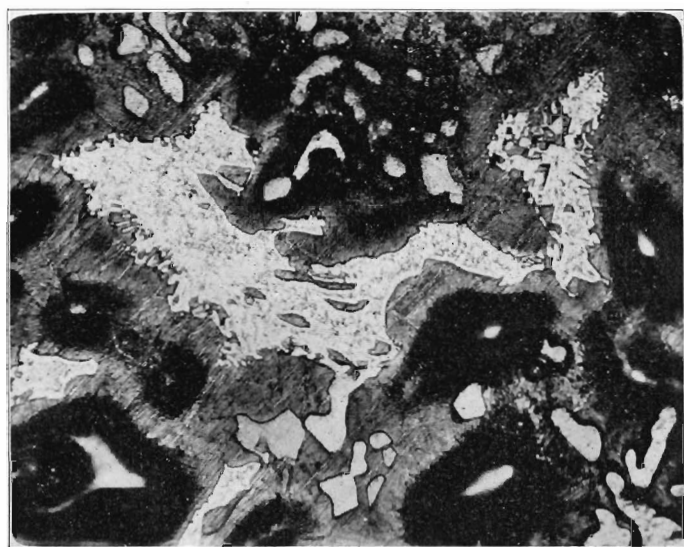

FIG. 14.—SAME SPOT AS FIG. 13, TAKEN AT SAME MAGNIFICATION AFTER ETCHING WITH AMMONIA AND HYDROGEN PEROXIDE, FOLLOWED BY FERRIC CHLORIDE.   THE SOFT CORES OF THE ALPHA CRYSTALS ARE HERE SHOWN BLACK LIKE THE LEAD, AND THE PHOSPHIDE CANNOT BE DISTINGUISHED FROM THE DELTA OF THE EUTECTOID.
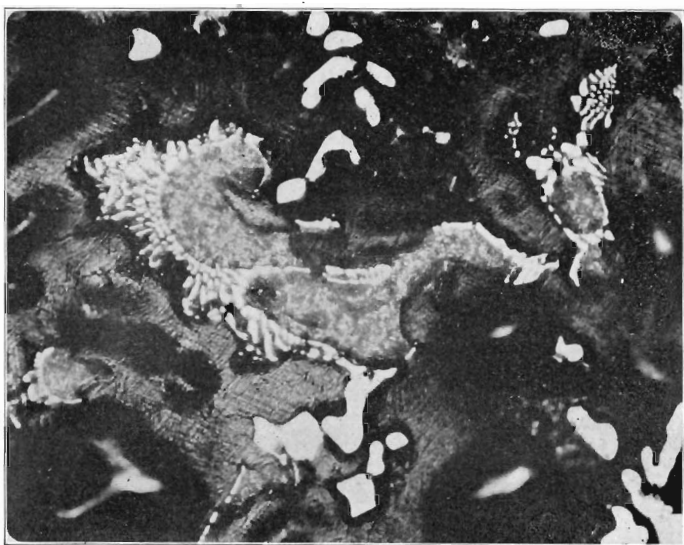
FIG. 15.—LIKE FIG. 14, BUT AFTER FURTHER ETCHING WITH STRONG NITRIC ACID. THE EUTECTOID IS HERE DISTINCTLY DARKER THAN THE PHOSPHIDE, AND THE SULFIDES APPEAR LIGHTER BY CONTRAST WITH THE DARKENED ALPHA.
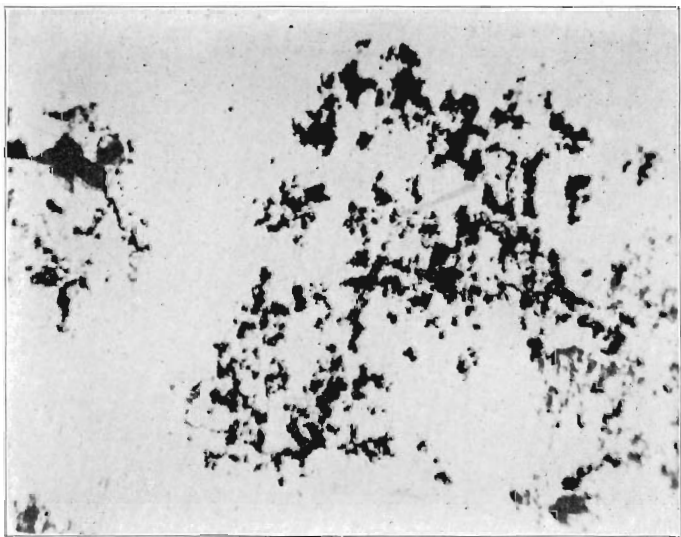

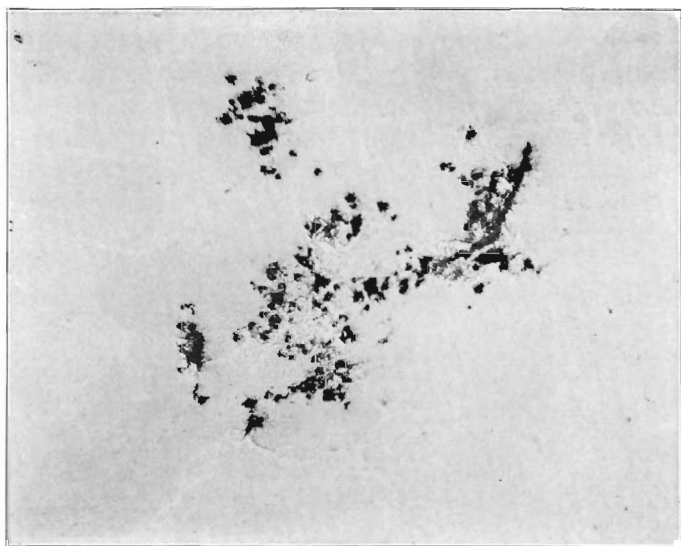FIG. 16.—ALUMINA INCLUSIONS IN OXIDIZED COPPER TREATED WITH 8 PER CENT. ALUMINUM, UNETCHED.   × 200.

FIG. 17.—ALUMINA INCLUSIONS IN A CASTING OF 10.7 PER CENT. ALUMINUM BRONZE
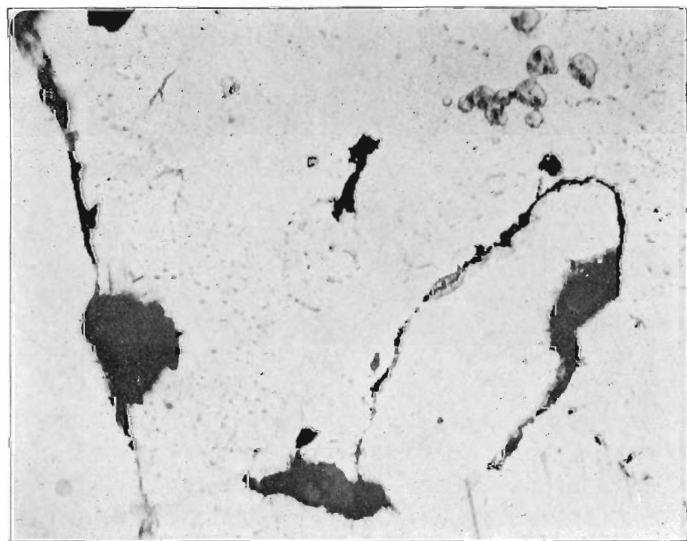UNETCHED.   × 200.

FIG. 18.—SILICATE INCLUSIONS AND STREAKS ALONG BOUNDARY BETWEEN COPPER
CONTAINING OXIDE SPOTS AND COPPER DEOXIDIZED BY ABOUT 4 PER CENT. SILICON,
UNETCHED.   × 200.

hydrogen peroxide. Sulfide inclusions in bronze look very similar to the few samples of zinc oxide in brass that have come to the writer's attention, but the latter were readily attacked by strong nitric acid, while no reagent has been found that darkens the sulfides in bronze.

The oxide of aluminum, alumina, has exactly the same appearance in bronze as in steel, and Figs. 16 and 17 show typical examples, the former having been made to contain alumina intentionally and the latter showing these inclusions in a regular aluminum bronze casting. The black specks shown are probably pits in the polished surface, where particles of alumina have fallen out, as these particles themselves are rarely seen in a
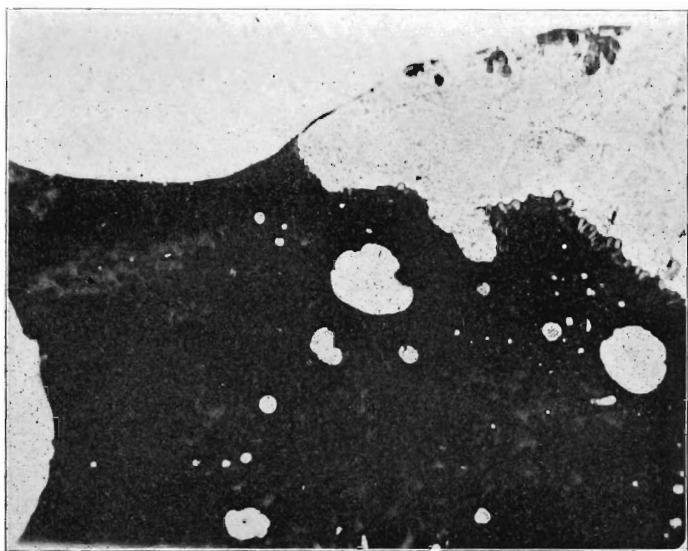

Fig. 19.—Mass of silicate slag formed by remelting oxidized copper and silicon copper together, unetched.   × 200.

polished section. The very dark color, small size, close grouping yet lack of coalescence, irregular shape, and rough edges due to pitting are characteristic of alumina in bronze or cast steel.

It was thought that silica might have the same appearance in bronze as alumina, but the writer has been unable to secure any evidence in support of this view. Several attempts to produce silica in copper by oxidizing the metal and adding silicon were not very successful, and no typical silica inclusions were found. Fig. 18 shows one of the results from these attempts. Part of the view shows oxidized copper, with pale round spots of Cu_2O, and part shows silicon copper, clean and sound. Between the two are streaks and spots of a very dark material, most of which has apparently fallen out of the section in polishing. This may be
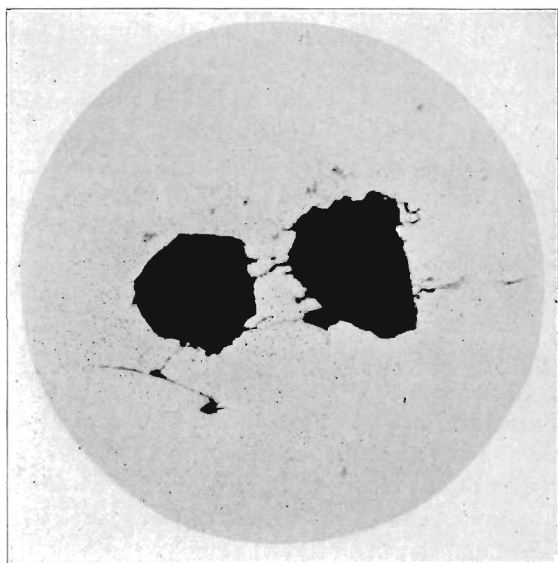
FIG. 20.—TWO SMALL GRAINS OF SAND IN ALUMINUM BRONZE, UNETCHED.   × 200.

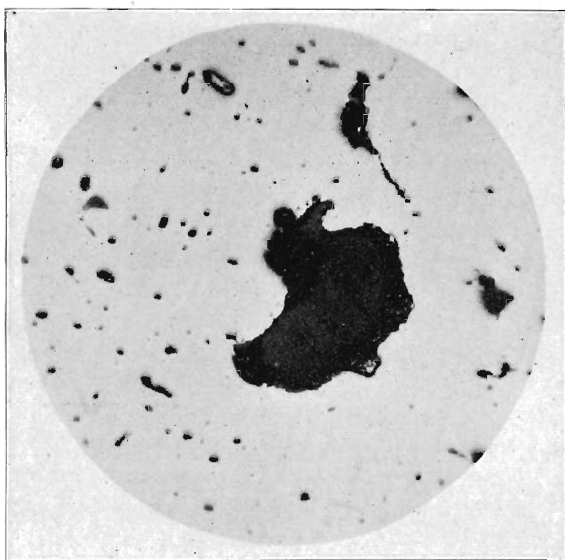

FIG. 21.—A LARGER GRAIN OF SAND IN A BRONZE CASTING WITH 9 PER CENT.   LEAD,
UNETCHED.   × 50.

silica or a silicate.   It has no resemblance to alumina, but resembles slag
in steel quite closely.   Fig. 19 shows a mass of silicate or slag included
in a chill casting made of oxidized copper and silicon remelted together
several times.   Some copper oxide is still present in this specimen,
but most of the material had been deoxidized by the silicon, and the
oxidized product or slag had coalesced into fairly large masses and left
the silicon copper clean.   The slag here is not homogeneous, but seems
to contain particles of copper oxide or some similar substance.

Figs. 20 and 21 show specimens of foundry sand included in bronze
castings, the former being aluminum bronze with sand stirred in in-
tentionally and the latter an ordinary leaded bronze that had burned
into the mold excessively and so become mixed with sand at the surface.
The angular form of the inclusions in Fig. 20 would indicate that they
were grains of sand and not slag formed in the metal, but this distinction
is not always so clear.   In general, it is probably reasonably safe to
say that where smooth dark-gray inclusions like these are angular in
shape or have convex sides, they are sand grains; and when their sides
are concave, they are slag inclusions.   The writer is not aware of any
other distinction between slag inclusions and grains of sand either in
bronze or cast steel.   It should be noted in this connection that it is
more difficult to polish a sample of bronze containing sand than a similar
sample of steel, without having the sand fall out leaving merely a pit
or cavity in the finished section.   The cavities thus left cannot generally
be distinguished from cavities caused by shrinkage, gas, or a volatile
or powdery oxide of some element like phosphorus or zinc.   Another
point that might be noted in regard to sand inclusions is that when a
casting containing sand beneath the surface is machined, the tool natur-
ally pulverizes the sand, and the white powder thus produced may readily
be mistaken for an oxide in the metal, such as alumina.   The particles
of alumina in bronze or steel, however, are so fine and so intimately
mixed with metal, as shown by the microscope, that in machining, while
the point of the tool may be dulled by them, it is very doubtful if they
ever break out of the metal chips in sufficient quantity to be recognized
as a white powder.

In presenting these notes the writer does not claim to have made
any remarkable discovery or to have found the best method for identify-
ing the non-metallic inclusions in non-ferrous metals, nor does he claim
to be able to identify every inclusion that may occur in a bronze.   It is
hoped, however, that the notes may be of some interest or possible
value to other metallographists, and may bring out criticisms or further
suggestions along these lines which will accelerate progress toward the
the true interpretation of everything that we see in metals with the
microscope.