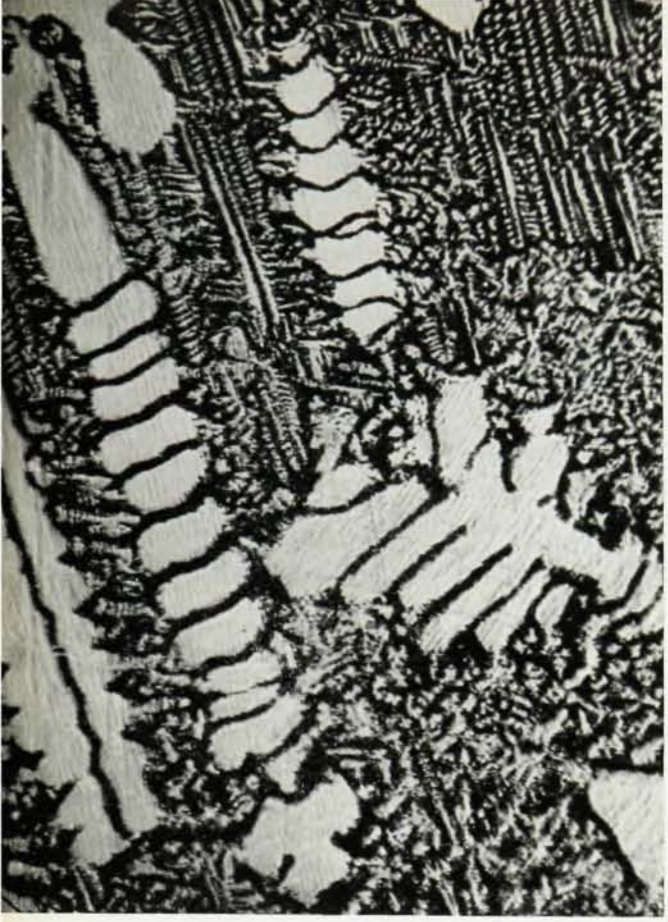


Figure 1. Photomicrograph of 50:50 antimony-bismuth alloy after sawing, polishing, and etching with a chloride solution. The white skeleton-like forms are dendrites, representing a phenomenon of growth generally characteristic of all organized matter, from crystals to plant and animal life. They contain excess antimony and resist chemical attack. Magnified 315 times.

The insides of METALS

by Carl A. Zapffe

The microscopic examination of fractured metal by a special "fractographic" technique is proving useful in revealing something of the manner in which metal coheres and in throwing some light on the nature of the minute subdivisions of metallic crystals.

Lost in antiquity are the origins of many methods used for examining metals, but the epochal discovery of the optical microscope a few hundred years ago originated the study of metals at high magnification. In its early stages, investigation with the microscope was limited to an exploration of surfaces. This was uninstructive because the principal service of metals lies in their strength, hence, in their internal constitution. The French scientist de Réaumur in 1722 and Sweden's Swedenborg in 1734 advanced the application of the microscope somewhat by studying the surfaces of fractures of metals, which disclosed some information regarding the manner in which metals are constituted. However, the difficulty of bringing the microscope lens close to the jagged surface of a fracture discouraged, for more than two centuries, these and all later scientists from developing such an application.

Among students of minerals, the microscope became a tool—and a great one—principally through the discovery in 1849 by Henry Clifton Sorby that minerals could be examined by transmitted light if they were sliced sufficiently thin. This introduced the thin-section technique, which is the bulwark of the science of petrography and mineralogy today.

Metals, in considerable contrast to most minerals, are completely opaque and do not submit to such thin-section study. Gold leaf has been beaten so thin that it transmits some light, but this is an exception which contributes nothing to the problem.

Carl A. Zapffe is a consulting metallurgist whose laboratory does work under contract with the ONR on fundamental metallurgical studies. He writes that he invented fractography as a result of research begun in *1938* at Batelle Memorial Institute on the behaviour of gases in metals. His curiosity was kindled by the radical changes in the macroscopic appearance of fractures when hydrogen was admitted. Steel cannot possibly recrystallize at temperatures less than red heat, yet many old hands say that the metal "crystallized" after pickling in an aqueous solution of sulfuric acid. One day, when his supervisor was not in the laboratory, he pushed a precious lens directly onto a rugged fracture face. A new world of phenomenon met his eye. Some fifty papers have issued from his laboratory on work in this field.

Figure 2. Fractograph—or photomicrograph of an unpolished and unetched fracture surface—for metallic bismuth, showing geometric markings which contain the story of deformation and fracture. Magnified 45 times.

Figure 3. Fractograph of a tough steel suitable for such construction as ship plate. The individual grain is very small, causing fracture to change its path much more frequently as it jumps from grain to grain; and the microscopic path through the grain itself is rough and torturous, as illustrated visually by this coral-like pattern of toughness. Magnified 1250 times.

It was at the close of the last century that metallurgists in Europe discovered the method of polishing and etching the surface of sections cut through metals to disclose their inner structure, and this has been the means of providing almost the entire body of technical information on the microscopic constitution of metals to date.

Polish-Etch Method

According to this method, a metal or alloy is simply cut with a saw through some section intended for study. The saw-cut surface is then ground flat and further polished with increasingly fine emery papers and buffing cloths until the polishing scratches are so minute as to be no longer visible at even relatively high magnification. Such treatment produces, of course, a superficial layer of highly distorted metal which completely conceals the true internal formations. This layer is then removed by carefully selected chemical reagents, determined through much research to provide certain characteristic effects depending upon the microscopic structure of the metal.

The reagent eats off the thin and disorganized superficial layer and then attacks the underlying metal—but to a degree dependent upon subtle differences in composition and structure. The result is a differentiated mottling, whose pattern is characteristic for the condition and hence is metallurgically informative. This is shown in Figure 1 for an alloy of equal parts of bismuth and antimony, at a magnification of 315 diameters. The specimen was cut with a saw, ground, polished, and etched with a solution of iron chloride in hydrochloric acid. The superficial layer was entirely removed, and the underlying metal was attacked in the elaborate manner shown. The peculiar light colored skeletons are known as dendrites because of their tree-like form, the word coming from the Greek "dendron", meaning tree.

Dendrites express a uniform peculiarity in the growth of crystals which causes them to grow from the fluid state in the form of branching growths. When an alloy—which is a mixture of two or more metals—solidifies from its liquid, the first solid to construct the dendrite is richer in the metal having the higher melting point. The remaining liquid is relatively rich in the metal of low melting point, and it is this which fills in between the branches of the dendrite. When an etching reagent is chosen which attacks one of the metals more than the other; the difference between the trunk and the interbranch material of the dendrite is made visible by the difference in chemical attack.

Fractographic Technique

While the polish-etch method has yielded a tremendous amount of information on the constitution of metals, it also has important limitations. For example, the remarks which have just been given will make it clear that the polish-etch technique would supply relatively little information

Figure 4. Fractograph of a steel which, in contrast to that in Figure 3, lacks toughness and is unsuited for such applications as ship plate. The facet of this individual grain is comparatively smooth, showing much less interruption of the progress of fracture than in the previous figure. Magnified 1250 times.

Figure 5. Unique fractograph of a molybdenum metal showing the exter surface of a grain—the grain boundary—with two intruding growths wh strongly affect the forgeability. The upper field has feathery forms which carbides necessary for forgeability. The lower field has a weedy-looking grov of oxide, caught in the act of invading the carbide area to form carbon ox gas which is removed by the vacuum treatment. The oxide growth causes grains to fall apart, preventing forging. Magnified 385 times.

for a pure metal. No constitutional differences exist, and attack by a chemical reagent would accordingly be uniform. About the only exception is a preferential attack at the boundaries of the individual grains and the fact that the separate grains are distinguished. Peculiarities existing within the grain itself, however, become for the most part unobservable.

About ten years ago, the centuries-old method of de Réamur and Swedenborg was tried again, this time with a fresh attack and with the benefit of modern improvements in the construction of the microscope. A special fractographic stage was designed which allowed the investigator to study nascent fracture surfaces, although this time not by exploring the general appearance of the fracture, but by exploring detail within the individual fractured grain. Metals are vast composites of minute crystals, called grains, and the older technique had done little other than view the surface of the entire assemblage. With modern fractography it is not the forest, but the individual tree which is being observed.

For the past four years fractography has been the subject of a special study in the author's laboratory, principally under the sponsorship of the Office of Naval Research, and the research from which this review stems has been largely conducted by F. K. Landgraf and C. O. Worden. Many fascinating new features of metals, also other crystals, have been discovered. Just a few of these will now be reviewed to show the astonishing elaboration to be found within the boundaries of the microscopic grain itself, and the many significant research fields inviting further exploration with this new tool.

In Figure 2, a fractograph of pure metallic bismuth is shown. The entire field of the photograph belongs to a single grain, as is proved by the fact that its markings have a common geometric relationship. If this specimen had been polished and etched, nothing would appear but a more or less blank surface, the grain boundary lying outside the field of observation.

On the other hand, one finds in the fractograph a wide assortment of markings. The most prominent of these are bands which are placed at exactly 60° with one another, forming equilateral triangles where all three directions appear. These are now known to be "twins", which means that the atoms throughout the region of the twin band have been forced into a certain special relationship with one another by the impact which fractured the metal. The fact that these twin bands lie at exactly 60° to one another is highly significant, for it reveals that the fracture has traveled along a special plane in the bismuth crystal—a crystal face which is the weakest link. This plane is the so-called basal plane, and is similar to the prominent cleavage plane that characterizes crystalline graphite, also mica. It has further been determined that the twin bands are intersections of three sloping crystallographic planes which form a low pyramid on the basal cleavage plane.

Figure 6. Fracture passing through a grain of molybdenum reveals a remarkable pattern which is probably the frozen record of the story of solidification and growth. Magnified 130 times.

Lastly, close observation will show some sharp cleavage edges, representing profiles of fractures on other crystal planes. The most prominent of these has been found to be a set also forming a pyramid, like the twins, but about twice as high. The story of deformation and fracture for this metal is thus written into the subtle markings on its fracture facets.

The Fracture of Steel Ships

From such observations of the path of fracture through the individual grains in a metal all these deductions can be made, and many more. A particularly important instance has to do with a problem involving both the loss of material and human lives.

During the recent war, more than forty of the welded steel ships made in this country fractured completely in two, and there were more than 4,000 reported cases of lesser fractures. The problem is one of an elusive property, simply called toughness, whose identification remains a great challenge in current metallurgical research.

Two steels, identical in virtually every respect so far as common analysis is concerned, will behave so differently when placed in service such as that of deck plate, as to cause shipwreck in one case and no trouble whatsoever in the other. Extensive researches conducted in many laboratories about the country, principally under sponsorship of the United States Navy, are now showing that the temperature range in which this change occurs is radically different for different steels. The fundamental reason for this difference remains unknown.

Nevertheless, fractographic study—as a new tool applied to the problem—has recently been shown to disclose a clear distinction between steel which will fail and steel which will not fail in service in a given range of temperature. Figure 3 is a fractograph of a steel which is known to be tough. At a magnification of 1250 diameters, an individual grain shows a pattern reminiscent of coral. The grain itself is very small—only a tiny fraction of the size of the bismuth crystal in the previous Figure 2—and there is no flatness anywhere in the fracture field. When this steel fractured, here due to a hammer blow at $-196°C$, the separation was continually impeded by the observed minute roughness as it traveled through the metal. The fractograph shows this pattern of roughness visually, which can therefore be interpreted as a pattern of toughness.

A sharply contrasting fracture facet is shown in Figure 4 for steel which is of similar composition to that shown in the previous figure, but is known by much mechanical testing to be inferior with respect to toughness. The magnification is the same as before, 1250 diameters; and the facets are seen to be about equal in size. A marked difference, however, lies in the comparative smoothness of the pattern in Figure 4, which gives visual evidence for the fact that fracture has traversed the grains in this steel without the consistent interruption experienced in the tougher steel.

While it is too early to point to useful application of this discovery with respect to the ship-plate problem, the contribution still being in the research stage, its promise is indicated by the fact that the contrast between Figures 3 and 4 is outstanding, whereas previous microscopic methods have revealed no detectable changes. In addition, the application of mechanical testing to this problem has involved the construction of huge testing machines at great cost, and much of the steel is destroyed in its testing. Fractography requires only a fractured chip and a microscope, and there is good reason to believe that the information obtained from the chip serves as well for the entire heat of perhaps 100 tons of steel.

Metals for Service at High Temperature

In the new and important field of metals for service at very high temperatures—gas turbines, rockets—there is an application of fractography which can already be described.

A pattern appears in Figure 5 which has some aspects of a good detective story, and has proved of great importance in the production of molybdenum metal. Molybdenum has one of the highest known melting points for any metal in the periodic system. At temperatures of white heat, where the strongest steel has not only melted, but begins to boil, molybdenum scarcely begins to melt. This fact simultaneously makes the metal a very attractive one for special services at high temperature, but one difficult to produce. A special furnace was finally designed a few years ago which melted molybdenum in vacuum by means of an electric arc. Castings of promising size and solidity resulted, but when they were subjected to the difficult forging operations they would often fracture.

To shorten a long research story, the metallurgists at the Climax Molybdenum Corporation in Detroit found that fractographic examination of a small chip broken from the casting with a hammer always reflected one of two characteristic patterns. The first was feathery in its appearance and connoted forgeable metal. The second was pearly and granular and always meant nonforgeable metal. Depending upon the presence of one or the other of these patterns, determined by a brief and simple fractographic examination, the processing of the ingots was directed either towards forging or remelting.

In the upper portion of the field in Figure 5, the "feathery" constituent is clearly visible. These small markings, resembling oatheads, are now known to be molybdenum carbide. In the lower half of this same field is a weedy-looking growth of the fine granular material now known to be molybdenum oxide. Both of these intruding constituents form in the boundaries of the individual grains—the carbide increasing cohesion, and the oxide destroying it. Here one is accordingly looking, as a special case, at the external surface of an individual internal grain—not its internal surface as in previous figures—and under the remarkable circumstance of finding both of the counteractive phases present. The carbide and oxide react, of course, to form carbon oxide gas, which is removed by the vacuum treatment. Here one can actually visualize the oxide caught in the act of invading a region of carbide feathers, destroying them as it advances.

The Micellar Theory

While such discoveries as the preceding readily lead to practical applications, a matter of far greater scope and interest is highlighted by fractographic patterns.

A century and a half ago, a great French mineralogist and crystallographer, Haüy, established what is now known as the Law of Rational Indices in crystallography and laid down a description for the physical constitution of crystals which endured for many years. Haüy spoke of the "molécules intégrantes", which were presumed to be minute building blocks—perfect microscopic crystals—which fitted together to comprise the macroscopic crystal. Virtually every scientist of that period accepted the theory that crystals were built of tiny crystallite units. The impact of the atomic theory and space-lattice theory in the latter 19th century, and particularly x-ray diffraction in 1912, temporarily shattered this picture to replace it with a conventional concept of regular atomic structure extending from the atom individual up to the boundary of the crystal or grain.

Nevertheless, in the past several decades, this picture of the homogeneous atomic lattice has come under sharp criticism from many angles of research in which crystalline substances persist in showing a markedly subdivided structure on a scale far more minute than the individual grain, yet much greater than the atom. Many theories have been advanced to explain this anomaly, and these can be reviewed in most current textbooks on physics. It is now becoming widely agreed that most crystals, if not all, have a finely subdivided structure. The nature and the origin of that structure, however, constitute one of the most hotly argued problems in metallurgy and physics today.

Briefly, the principal contention rests upon the question whether the subdivision results from imperfections and accidental submicroscopic cracking, or whether it is a fundamental result of the surfaces of previous submicroscopic units which come together at the time of freezing to form the solid.

For the first concept, "dislocations" currently provide the most popular picture. These are the result of vacant or improperly filled atomic positions in an otherwise regular lattice; and their propagation and motion throughout the body of the crystal is believed to develop the observed subdivided structure.

For both concepts, the term "mosaic" has been widely used, expressing a picture of a gross form built from small fragments, the misfits of the mosaic blocks creating the subdivisions in question. The mosaic block is usually pictured as the result of microcracking, but it has also been related to a pre-existence in the liquid.

Recently a theory has been proposed by the author in which the mosaic block is described as a *micelle* specifically originating in the liquid and having fundamental thermodynamic reasons for its separate existence. This word is borrowed from the organic chemists, and means a small repetitive arrangement of a given atomic or molecular species, having the form of a tiny crystallite. Such clusters are believed to be present, according to the micellar theory, in the liquid and even in the gaseous phase prior to solidification. The theory particularly postulates their existence within single homogeneous phases, such as that of a pure metal. A phenomenon of this type is known in colloid chemistry, the liquid being called an isocolloid.

As early as 1907, one of the founding scientists of colloid chemistry, P. P. von Weimarn, proposed a somewhat similar concept, and it has since been discussed by Alexander in America, Klyatchko in Russia, and Yoshida in Japan. The present micellar theory, published in 1949, differs in certain respects from those earlier described. It was designed specifically to explain the problem of imperfection structure in the solid state.

Without going into any of its technical details, the theory can be described as postulating the formation of clusters of atoms (or molecules) in the homogeneous liquid state as the result of a balance among four principal thermodynamic variables: 1) temperature, 2) pressure, 3) composition, and 4) surface tension. The net result is the production of a liquid which in effect is a mass of tiny solid particles swimming in their own debris. The size and form of the particles are determined by thermodynamic and crystallographic factors. When the temperature is reduced to what is known as the freezing point, these minute crystallites attach to one another, orienting their own atomic alignments with respect to one another so far as allowed by the freezing conditions, and thus form the solid. The mosaic block is now the micelle; and the subdivisional structure is the result of the persisting micelle boundaries.

Returning to fractography, Figure 6 shows the pattern of a fracture which passed *through* a grain of cast molybdenum—in contrast to Figure 5 where it traversed the boundary. This elaborate pattern is believed to represent a frozen record of the growth pattern during the time that the micelles of the liquid state were orienting and transfixing to form the solid. The roughly parallel bands are believed to result from pulsations in the solidifying front. This metal was cast—it will be recalled from earlier description—under the conditions of an electric arc at extremely high temperature, and it solidified in a water-cooled copper crucible. These are violent freezing conditions for a metal melting near 2620°C (4750°F). The story of solidification read from the fractograph in Figure 6 would show this grain to have formed from the upper right corner toward the lower left, the micelles rotating and orienting with one another sufficiently to produce a single crystal, but remaining slightly displaced from one another and misfitted sufficiently to set up a special pattern of weakness, which then showed itself fractographically by deflection of the fracture traverse in accord with the pattern misfit.

Finally, in Figure 7, a pair of fractographs adds further description to the micellar concept, and in addition shows an unusual application of the fractographic technique. A specimen of plain iron (Armco ingot iron) was annealed at 1250°C for two hours and slowly cooled in the furnace to remove effects

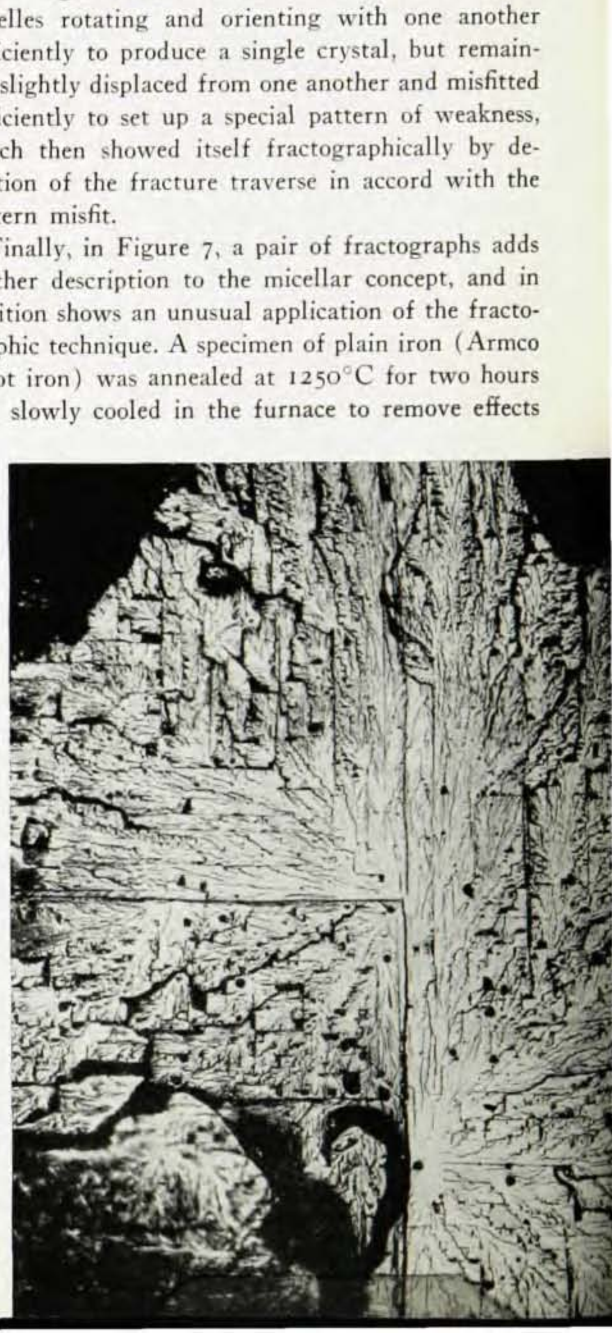
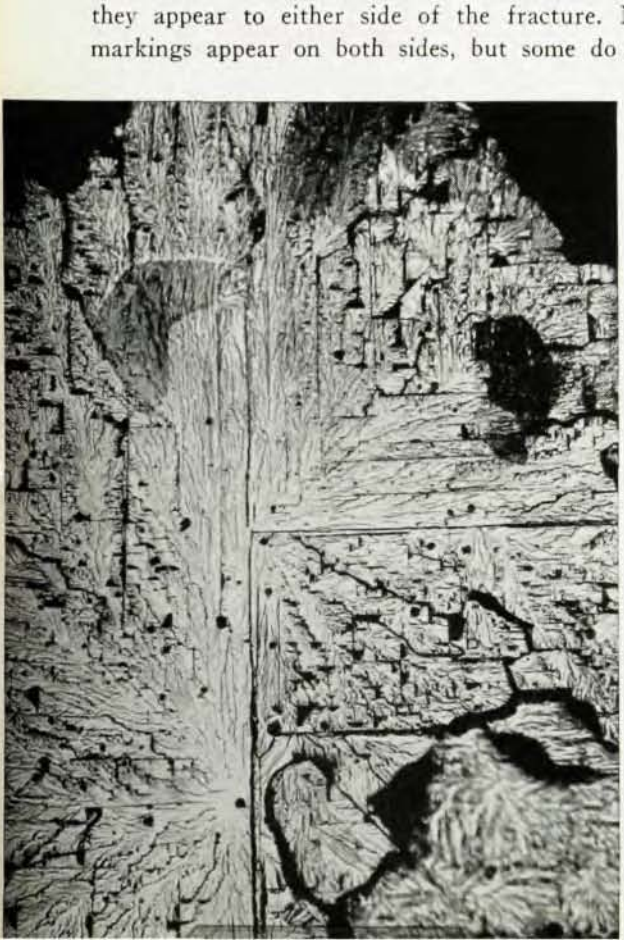


Figure 7. Obverse and reverse fractographs showing both matching faces of a fracture traverse through a single grain of iron. The sharp 90° angles prove this to be a cubic cleavage. The markings display an elaborate architecture within the grain, and their variations on the opposite surfaces are informative. Magnified 150 times.

of previous mechanical strain and to increase the grain size. The metal was then embrittled by forcing atomic hydrogen into its structure. This was accomplished by making the specimen the cathode (negative electrode) in an electrolytic cell. Iron absorbs hydrogen, but only atomic hydrogen; and, on the surface of the cathode, protonic or atomic hydrogen is deposited by the electric current passing through the solution—here ten percent sodium hydroxide. It is known from extensive research that this atomic hydrogen enters among the atoms of the iron, probably diffusing through interatomic interstices, and then later precipitates at certain well defined places within the body of the grain—the intermicellar boundaries, according to the micellar theory. The result is a marked loss of ductility; and it is said that the metal is suffering from hydrogen embrittlement.

The iron in Figure 7 was fractured while embrittled with hydrogen. The two fractured halves of the metal were separately mounted on the microscope, and a fractograph was taken of the same facet on the two matching halves of the fracture. These two fractographs are mounted facing each other in Figure 7, constituting obverse and reverse views of the fracture traverse through the single grain. Thus, one can follow the various markings as they appear to either side of the fracture. Most markings appear on both sides, but some do not; and there are provided some informative differences.



However, particular attention is called here to other matters. First is the fact that the outstanding markings are at exactly 90° to one another. This is because iron fractures on a crystal plane which can be described as the face of a cube. Just as the hexagonal-rhombohedral bismuth crystal in Figure 2 displayed equilateral triangles, so the cubic iron shows squares and rectangles. Here intersecting cleavages provide the cubic symmetry, rather than twins. Even the meandering markings will break down on close observation to show themselves as minute stepwise composites of 90° markings. The whole pattern, and particularly these tiny stepwise markings, give strong expression to an elaborate architecture existing within a single grain; and they certainly stand as impressive evidence in the favor of a general micellar theory. Little wonder that Haüy hypothecated his "molécules intégrantes". The grain is visually composed of tiny subgrains, or micelles, and without them it would be difficult to explain the pattern.

A New Era of Engineering Materials?

Many things must be left unsaid in a brief review of so vast a subject; but one particular issue follows from all this work which holds extravagant promise for future developments in engineering and hence in civilization itself. This is the fact that calculations, using many different approaches, all agree that the atoms of metals actually cohere with strengths of the order of several millions of pounds per square inch. Today the greatest achievement in engineering materials is of the order of two or three hundred thousand pounds per square inch. The reason that the observed strengths of materials are so vastly inferior to the theoretical atomic cohesion is generally agreed to be the subdivisional structure within the grain. The only thing not yet agreed upon is the nature and the origin of that substructure. The type of microscopic study here described greatly increases the information on this prize problem of solid state physics.

For a better understanding of the problem, the micellar theory has been offered. Right or wrong, the solution is certainly nearer; and, when the answer is found, it will bring with it a definite possibility of utilizing a new order of cohesive forces in developing the full theoretical strength of metals and perhaps other engineering materials.