

A BRIEF HISTORY OF
The Science of Metals

by

ROBERT FRANKLIN MEHL, Ph.D., D.Sc., D.Eng.,
Doutor Honoris Causa (São Paulo)
Professor of Metallurgical Engineering
Director, Metals Research Laboratory
Carnegie Institute of Technology
Pittsburgh, Pennsylvania

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This slight volume

is dedicated to

Professor CHAMPION HERBERT MATHEWSON

long leader in the science of metals
and great champion of the young metallurgist

Preface

This brief account of the development of the science of metals was written upon the request of the American Institute of Mining and Metallurgical Engineers. It was originally intended that it should be included in a volume with other articles describing the progress of the other branches of metallurgy, published as part of the celebration of the seventy-fifth anniversary of the founding of the Institute. As the task was attacked, the subject grew in scope, somewhat beyond that initially intended, until ultimately the Institute decided to publish the account as a separate brochure, the little book now before you.

Proper organization of the material posed some difficult problems. In order to avoid a mere recital of the sequence of important events in each of the branches of physical metallurgy—a scheme which, though maintaining continuity in each branch, would suffer serious difficulty in showing the interrelations of the separate branches, and would fail to mark the important general movements—I have adopted several organizational devices.

I have used the date of the founding of the Institute as a fixed point. In order to show the status in that year, 1871, I have felt impelled to relate the events of the preceding period, though briefly. I have treated the following years up to 1900 as a chapter; this is happily convenient, for the latter three decades of the nineteenth century may readily be taken as a brief era, characterized by the gathering together of strands of information, and by recognition of many of the major problems, such as the nature of the hardening of steel, with the emerging and increasing coherence of a body of information and theory that began to create the subject of physical metallurgy as it is now recognized. I have written of this latter period from the point of view of the Institute, considering in some detail the publications in the *TRANSACTIONS*. I do not believe that this momentary transgression has jeopardized the impartiality of the treatment, for here and elsewhere I have tried to assign credit wherever, to whatsoever country, it is due.

By the turn of the century, in the years immediately preceding and immediately following 1900, when an extraordinary number of great figures emerged upon the metallurgical scene, the subject reached an early maturity, with the appearance of an extraordinary number of classic papers, in which good science began to be applied extensively. I have, accordingly, treated the turn of the century as a turn in the development of the science of metals, and have accorded it a brief chapter.

In writing of the period since the turn of the century I have felt constrained to write separate parallel accounts of the development of the several branches of physical metallurgy, for I can think of no way in which these stories may be told except separately; their interrelations are indeed very intimate, and one branch could not have lived and grown without the other, yet each branch has taken on distinguishing characteristics.

As noted in the text, I have attempted to restrict the major portion of this account to the development of ideas, to the evolution of the *science* of metals. This cannot be wholly successful, for the history of the production and treatment of metals is inextricably interwoven with the development of ideas on metallic behavior; each industrial development leads, through the new group of phenomena displayed, to the creation of new ideas—this is of course but an example of the effect that industrial and economic necessity has always exerted upon the development of science. Moreover, such correlative and background material, used mostly in the beginning, should add general interest for the general reader.

There is little to help the writer of such a document as this: there has been surprisingly little written on the history of the science of metals; there are no useful models. The possibilities of error, of omission, and improper balance are great. The article cannot have pretension to other than ordinary accuracy and completeness, as may result from one's familiarity with the literature of the field, growing through some three decades of interest. Any greater effort would require both extensive and minute, even meticulous, research. But though the account be remiss, the true history of the science of metals is one of extraordinary interest; much experimentation—easy to perform—still awaits the worker, inviting the young and even the old to partake in creating the new history in the new era.

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ROBERT FRANKLIN MEHL.

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The Preliminary Period—before 1871

THE record of the development of physical metallurgy since the founding of this Institute embraces by far the greater part of physical metallurgy as this subject is recognized today. Yet it is not to be supposed that the metallurgist interested in the properties and behavior of solid metals at the beginning of this period was without important and even fundamental information. He had an empirical knowledge of the behavior of solid metals which extended backward into prehistoric times and he had the early beginnings of many of the chapters in the science of metals. Industry was burgeoning in many directions, for methods had been developed, especially in the manufacture of steel, that provided materials in extremely large tonnages, permitting applications of metallic materials on a very widespread scale. These multitudinous new uses of metals created an increased interest in the behavior of metals, and provided the basis for the rapid development of a science of metals. Indeed, the development of science generally that accompanied the industrial revolution reached a flood tide toward the end of the century, furnishing the metallurgist basic principles in chemistry, physics, mechanics, and crystallography that would shortly be extensively applied to metallic behavior. In this account, the early developments in the wide metallurgical field will be traced, in order that the status of physical metallurgy in 1871, when this Institute was founded, may be clearly seen.

The subject of metallurgy in antiquity has been written upon frequently and at length. We shall here no more than indicate the main features that we need to define the position in 1871 and to provide a proper background for discussing subsequent developments. The writings of Pliny,¹ 23–79 A.D., to which Roberts-Austen³ fre-

¹ See Bibliography at end of book.

quently refers, are a good source of information on metallurgy in ancient times. The beginning of the scientific era brought renewed interest in metals and alloys. The writings of its chief progenitor, Francis Bacon,* in the early part of the seventeenth century, show this growing scientific interest, and serve to establish, with the writings of his near contemporary, Agricola,² the status of the knowledge of solid metals and alloys in that period. Bacon begins his essay with the paragraph:

“With what metals gold will incorporate by simple colliquation and with what not? And in what quantity will it incorporate; and what kind of body the compound makes?”

And then proceeds to answer these questions—questions which of course are the basic questions in alloying—for gold, and in order, for silver, lead, copper, iron; and he notes that information was available on the systems Au-Ag (the ancient “electrum” alloy), Au-Hg, Au-Pb, Au-Cu, Au-brass, Au-Fe, Au-Sn; Ag-Hg, Ag-Pb, Ag-Cu, Ag-brass, Ag-Fe, Ag-Sn; Pb-Cu, Pb-brass, Pb-Fe, Pb-Sn; Cu-Zn, Cu-Sn, Cu-Fe, Fe-Sn, etc.; and quotes copiously from the much earlier Pliny, correcting him at times. He notes the commonness of brass, bronze, pewter, and bell metal. And, foreseeing the difficulty of the student wrestling in a later era with ternary diagrams and the limitless number of alloys, he says, “The decomposition of three metals or more, are too long to inquire of!” Knowledge was available for all these systems as to the extent of alloying, and of the color, “plianthness,” and stability (volatility) of the alloys.

The familiar processes of forming and treatment were not new in the nineteenth century. The rolling of lead and of iron was practiced in the eighteenth century in England and France; Cort built the first rolling mill for iron in England in 1754. The heat-treatment of steels was practiced by the ancients, and quaint accounts are extant of the miraculous effects of certain quenching media. The historical writings on this period of Roberts-Austen³ are among the most interesting and valuable.

* The Works of Francis Bacon, 3 vols. Philadelphia, 1854. Parry and McMillan. Cf. vol. II, pages 33, 46, 116, 456–460. The important section is “Articles of Questions Touching Minerals, The Lord Bacon’s Questions, with Dr. Meverel’s Solutions,” in the section “Miscellaneous” and the subsection “Physiological Remains,” of “*Sylva Sylvarum; or A Natural History*,” first published in 1627.

MANUFACTURE OF IRON AND STEEL

The manufacture of iron and steel, ancient in its origin, was restricted to wrought iron and carburized iron until the invention of the crucible steel-melting method by Huntsman in 1740, producing for the first time a melted and cast steel, of a homogeneity characteristically greater than the blister steel that preceded it. Huntsman's steel was costly and was restricted chiefly to tool and allied applications. The early railroads were built with iron not steel rails, and much inventiveness was exercised to provide rails and rail design of tolerable quality. It is interesting to see how much writing prior to the first volume of the AIME TRANSACTIONS, and through many of the early volumes, was devoted to iron and later steel rails, reflecting the age of great railway expansion in this country.

The greatest impetus to the metallurgical industry, and indeed one of the greatest to the industrial revolution, came with the development of methods for the manufacture of great tonnages of cheap steel, first by Bessemer and by Kelly, and later by Siemens and Martin. In 1846, William Kelly discovered the pneumatic process for making "malleable" iron; in the course of his work, at the Suwannee Iron Works, near Eddyville, Ky., he observed that the iron was actually heated by the blast of air at a point where there was no charcoal; he demonstrated the idea, converting pig iron into steel, and made horseshoes and later plates of steel. Henry Bessemer was granted his first patent in England on the process that now bears his name (frequently and properly in combination with the name of Kelly); Kelly's American patents were granted in 1857. In 1856 Bessemer read his first paper before the British Association for the Advancement of Science, having just succeeded in converting a charge of a few hundredweight. The process, starting meteorically, was unsuccessful practically until Robert Mushet (in the same year) added spiegeleisen to the charge just after the blow, providing the necessary manganese, deoxidizing the blow, and replenishing the carbon content. In 1861 Bessemer patented the process of the addition of silicon as a deoxidizer, "to prevent blowholes" in castings.

The Bessemer-Kelly process then became successful rapidly, providing huge tonnages, and maintained its preeminence until surpassed by the open-hearth process in 1908. The bessemer process was rapidly established in France, when, in 1867, ferromanganese was

used in the process, and good steel plates were produced. The first bessemer steel produced in this country was made by A. L. Holley, at Troy, N. Y., in 1865. Control of Bessemer's patents had been secured the previous year. In 1871 the bessemer furnace was provided with an interchangeable bottom, by A. S. Dunning, of Ravenna, Ohio; in the same year bessemer steel and open-hearth steel were substituted for puddled iron in making wire, and the manufacture of bessemer rails became common.

The open-hearth process was experimented with even earlier, especially by Josiah Marshall Heath, but the process was not a success until the brothers Siemens, in 1856, developed the principle of regeneration as applied to a high-temperature furnace. In 1862, William Siemens made his first attempt to manufacture open-hearth steel, but the process was not practiced until the brothers Martin, in 1864, with Siemens' assistance, produced cast steel of good quality. It is interesting to note that the great Faraday, in 1862, in giving his last lecture to the Royal Institution, chose for his subject the qualities of the regenerative furnace. A few years later, in 1866, Siemens patented the use of ferromanganese in the manufacture of steel by his process. Rails were first made by Siemens in 1867, and in the following year the use of the open-hearth furnace on a true manufacturing basis was begun by John Ramsbottom at Crewe, England. In the same year a small open-hearth furnace was built by Frederick J. Slade at Trenton, N. J., and in 1870 substantial production was begun at South Boston, Massachusetts.

An improvement of forming methods accompanied this growth of steelmaking. John Fritz, in 1857, at the Cambria Iron Company's plant at Johnstown, Pa., invented the three-high mill; the cold-rolling of iron was first practiced by Bernard Lauth in 1859 and patented, the patents passing into the control of Jones and Laughlin, of Pittsburgh, Pa. Cold-rolling of steel has from its inception been peculiarly American. These are but examples of mill development; there were others, and many new ones were to follow in the next era.

The year 1871, seventy-five years ago, thus found society in possession of two hugely productive methods for the manufacture of steel, and the modern metallurgical age began, nearly coincidental with the birth of the AIME.

MEASUREMENT OF TEMPERATURE

It was apparent, of course, that control of these processes, as well as others in the treatment of solid metals, depended on control of temperature, and attempts to develop good pyrometers proceeded rapidly, based chiefly on earlier work. Musschenbrocks, in 1731, had proposed the use of the expansion of a metallic rod as a measure of temperature, and this was developed by John Daniell in London in 1822, who used a platinum rod encased in graphite with a mechanical lever as pointer, and later by Gauntlett. Seebeck, in 1821, discovered thermoelectricity, and this was available for temperature measurement, though surprisingly not used in practical pyrometers until 1888; its ultimate development was to mean much in physical metallurgy, as we shall see. In 1828, Prinsep described the gas thermometer; and had also shown the use of a graduated series of alloys whose melting indicated temperatures, a method much used later. In 1860, William Siemens suggested that the variation in electrical resistance with temperature of a platinum wire could be used to measure temperature, and in 1871 he reported to the Royal Society the completed electrical resistance thermometer.

NATURE OF STEEL

The history up to 1871 of the knowledge of the nature of steel could occupy a large volume. We shall here but indicate the development of the important fundamental concepts, for this historical article shall concern itself chiefly with the development of ideas.

A historical account* of this chapter of physical metallurgy should begin with a note on the work of Réaumur in 1722. Réaumur indeed promulgated ideas concerning steel (and made important contributions to French industry) which, in remarkable anticipation of modern knowledge, amounted to prescience. Réaumur assumed that when steel is heated "sulphur and salts" are driven out of the "molecules" into the interstices between them; on quenching, "sulphur and salts" are prevented from entering into molecules again by the rapid cooling, thus cementing the molecules firmly together, giving a hard, quenched steel; on tempering, the "sulphur and salts" partially return to the molecules and the metal becomes proportionately soft. If we interpret sulphur and salts as carbon, molecules

* *L'art de convertir le fer forgé en acier*. Paris, 1722.

as cementite, and interstices as the lattice interstices in the gamma phase, Réaumur is describing our modern knowledge with extraordinary accuracy. Or consider his deliberations on the grain size of blister or cemented steel: he invented a rough scale for evaluating the grain size of a quenched and fractured specimen, and found that this (fracture) grain size increased as the heating temperature increased, but, more than this, he anticipated much of the modern American studies of austenite grain size by observing that certain steels coarsened more easily on heating than others, and took it as obvious that the coarse-grained steel was inferior for tools.

An anonymous book published in Strassburg in 1737 provided an enlightened account of the nature of steel, and particularly of the importance of temperature, with respect to the quenching temperature and the rate of cooling during quenching. Bergmann, in Upsala, Sweden, in 1781 gave the first adequate description of the behavior of wrought iron, of steel, and of cast iron as manifestations of the effect of carbon; he thought that perhaps impurities might render steel allotropic, an anticipation of Yensen's recent suggestion! The cause for the difference between wrought iron and steel occupied a large place in the philosophical arguments of the day, and even phlogiston was invoked, by Becker, and Stahl, in 1786, and others—steel was supposed to gain phlogiston on quenching! But following Bergman, Vandermonde, Berthollet, Monge (1786), and, finally, Lavoisier (1788) laid the phlogiston ghost. Direct support of the carbon theory was furnished by Clouet (1798), by Pepys, working with Davy in 1815, who succeeded in making steel from iron and diamond, and finally by Margueritte in 1865, who showed that though steel can be made from iron and carbon in the absence of gases, it can more readily be made through the intercession of the carrier carbon monoxide—and it thus became recognized that the hardening capacity of steel depends upon the presence and the amount of carbon. Faraday studied steel in the annealed and the quenched conditions by dissolution in hydrochloric acid, finding the acid to leave a carbide on attacking annealed steel, a method to be followed later by much work, including the analyses of simple and complex carbides in steel, such as the work of Campbell at the University of Michigan on the relation of the chemistry of the dissolution reaction to the constitution of steel. In 1827, Karl Karsten, in Germany, isolated the carbide from soft steel and showed it to be a chemical compound of iron and carbon; Berthier, in 1833, isolated a carbide

which he believed to be Fe_3C ; it remained for F. Abel, in the year 1888, to dissolve steel in chromic acid, and to show that the residue carbide exhibited the formula Fe_3C .

THE ALLOTROPY OF IRON

The occurrence of allotropy in iron, later to prove of fundamental importance, was hypothesized early. In fact, in 1600 Gilbert discovered that iron loses its ferromagnetism when heated. This presented science with a conception that, confused later with phase-change allotropy, was to create near the turn of the century the beta-iron controversy, an era of difficulty in the theory of the hardening of steel. Barlow, in 1823, published a full account of the variation of ferromagnetism of iron with temperature. Much work was done in those early days using thermoelectromotive force, a physical property of considerable complexity in behavior, which sometimes led to uncertain and equivocal results. The idea of allotropy was often proposed, as for example by Bergmann in Upsala in 1781, by Jullien in 1865, but experimental evidence very shortly appeared, for Tchernoff in 1868 published his classic paper on heat-treatment, proving that steel cannot be hardened unless heated to or above a temperature a . Tchernoff was the father of the critical points in steel! Then Gore, in 1869, showed that steel previously heated momentarily elongates at a certain temperature on cooling, and Barrett, in 1869, repeating Gore's experiment, observed that the temperature suddenly increases when the momentary elongation occurs, and thus observed recalescence. And Tait, in 1873, employing thermoelectromotive-force measurements, showed the allotropy of iron. Thus, though little true information was available on the nature of the hardening of steel on quenching, the essentiality of carbon was known, the occurrence of a carbide had been recognized, and the principle of the critical point had been established. The problem was formulated, to receive effective answer in the next score of years.

THE MECHANICAL PROPERTIES

As physical metallurgy grew to an early maturity near the turn of the century, the analysis of the mechanical properties of metals received an increasing attention from those who called themselves metallurgists. The science of mechanics was allied to physical

metallurgy. The roots of the subject are deep in history. Common experiences with strength of metals are of course as prehistoric as the use of metals. And the hardening of metals by cold-work (and by alloying) was employed by the ancients, as were processes of annealing to relieve cold-work hardening. The first physical scientist to consider the nature of the resistance of metals to rupture was Galileo,⁴ who treated solids as inelastic. It is said that Galileo was the first to measure the tensile strength of a metal, determining the length of a copper rod that would fracture of its own weight. The great landmarks in the theory of elasticity were (and are) the discovery of Hooke's law in 1660 and the formulation of the general equations of elasticity by Navier in 1821. In 1817, Peter Barlow made determinations of the strength of materials including iron, and published his results in 1826. In 1807, Thomas Young, English physicist, described the modulus of elasticity.

In 1822, Thomas Tredgold, an English civil engineer, published "A Practical Essay on the Strength of Cast Iron and Other Metals," founded chiefly on Young's work. His work, and that of Duleau (and that of Barlow) were the first systematic and scientific investigations of the strength of metallic materials. The growing interest in iron bridges in that period led to the analysis, first, of the behavior of beams and girders under stress, by Eaton Hodgkinson in 1830, who presented a paper to the Manchester Literary and Philosophical Society, and, second, of stresses in framed structures, by Squire Whipple, of Utica, N. Y., in 1847. Whipple presented the first correct analysis, which supplanted the old empiricism in bridge building. It is said that the first real tensile machine was built at Woolwich Arsenal in 1837. The subject had grown to such importance by 1849 that a commission was appointed in this country to inquire into the application of iron to railway structures: the report (1850) was an early classic, giving experimental data on the elasticity and strength of metals, and leading to the introduction of specifications relating to working stresses and to strength values, and to the creation of testing laboratories. The common mechanical testing of metals was well established by 1871.

On the purely scientific side, Cauchy had discovered, by 1822, most of the elements of the pure theory of elasticity, showing that stress is expressible by means of six component stresses, and showing the existence of principal planes of stress. In the case of elastic anisotropy he found 21 independent constants, of which 15 are true

elastic constants and the remaining 6 express the initial stress and vanish identically if the initial state is one of zero stress (in 1855, Matteucci found the electrical conductivity of bismuth to be anisotropic). Wertheim, in 1849, showed that the value of Young's modulus is greater in cold-worked copper than in annealed copper. Poisson, in 1828, obtained equations of equilibrium for isotropic elastic solids identical with Navier's, and these were applied by Lamé and Clapeyron to numerous problems of vibration and static elasticity. Poisson, in 1829, considered the value of the ratio of lateral contraction to longitudinal extension of a bar under tension and deduced a value of $\frac{1}{4}$. Saint-Venant's principle, derived in 1855, constitutes the basis for the solution of elastic problems. By the year 1871, the theory of elasticity had been practically completely formulated, and many of the important problems had been solved; the elastic and inelastic behavior of the single grains in a metal aggregate, however, was not attacked until recent years, and is still in a somewhat parlous state.

The elastic after-effect was discovered by Wilhelm Weber in 1835, and was discussed by Maxwell and Boltzmann. Mechanical hysteresis was not to be discovered until 1881, when Bauschinger revealed what we now commonly call the Bauschinger effect. The beginning of extensive mechanical testing of metals in this period provided much new information concerning the behavior of metals under stress, a difficult subject to rationalize, then as now, but some basic facts were discovered, as, for example, the discovery of flow-lines by Lüders⁵ (to be worked on later by Hartmann⁶ and to be known as the Lüders-Hartmann lines). These lines were later to be shown as originating in the form of the stress-strain curve for steel—the "upper and lower" yield points—and were to prove of importance in the over-strain aging of steel. It is interesting that as early as 1858 Nogues⁷ observed that platinum wires heated repeatedly in a reducing gas flame developed a crystalline appearance on the surface, perhaps the first observation of recrystallization and grain growth.

The influence of repeated stresses, in the field we know as that of the fatigue of metals, was recognized as early as 1829, when Albert, in Germany, made tests on welded chains for mine hoists. Hodginson, in 1837, suggested that the study of the behavior of metals under repeated stressing might be important. William Fairburn made studies of repeated stress in 1864 on cast iron and forged

steel, and mentions earlier work by Captain James and Galton in which bars were subjected to repeated loadings by means of cams. The first comprehensive series of repeated stress tests were those of Wöhler, carried out in the years of 1860 to 1870, employing stresses in tension, torsion, and bending. Wöhler's work was brilliant; he demonstrated that metals will fail after a time by repeated cycles of stress, and developed the first S-N curve (Wöhler's "first law"). He gave limiting endurance stress values for wrought iron and cast steel; he showed that the effect of stress cycles with the average stress above zero is to reduce the safe range of stress (his "second law"): and he noted the deleterious effect of notches.⁸

CRYSTALLOGRAPHY

As remarked elsewhere, the work of crystallographers and mineralogists profoundly affected the development of scientific thought upon metals, as indeed it has continued to do. The subject of crystallography was advancing rapidly in this period. Hessel, in 1830, and Bravais, in 1849, had demonstrated the 32 crystal classes, and the descriptive knowledge of crystals and their behavior grew to a large volume. Some of this work was later to be employed by metallurgists as their problems became more completely recognizable, particularly with respect to the plasticity of metal crystals; for example, the work of Reusch in 1867 on slip lines and twinning in minerals⁹ and that of Sohnke in 1869¹⁰ on cleavage in sodium chloride.

THE DEVELOPMENT OF ALLOYS

It is not easy in brief form to note the early developments in alloys and the study of their structure and constitution. Bacon's comments reveal that many alloys were known in the early seventeenth century. In 1820, Faraday and Stodart prepared a number of alloys, by welding and annealing wires of the component metals; for example, alloys of iron and platinum.¹¹ They observed that etching will develop the "grain" in these alloys, a comment that will recall Réaumur's experiments on austenite grain size. A full exploitation of the subject of grain size remained for the development of the metallurgical microscope. In the same year Pierre Berthier prepared alloys of iron and chromium. In 1855, tungsten steel was first prepared, by Jacob, in Austria; and two years later, Robert Mushet worked on tungsten steel and invented the important

air-hardening steels, employing a steel with 7 to 12 per cent tungsten and 1.5 to 2.0 per cent carbon. The alloy-steel era was beginning in 1871, to be brought to full prominence by Robert Hadfield 10 years later with the production of manganese and silicon steels.

METALLOGRAPHY

The development of metallography—the study of the structure of metals and alloys—grew out of the work of mineralogists and crystallographers in the early nineteenth century. Crystallography has remained ever since an important subject in the study of metals. The full realization of the crystalline nature of all metals and alloys came after 1871 though it was more than half suspected before that.

The study of meteorites played an extraordinarily important role in the development of the knowledge of the structure of metals. This era began in 1808, when Alois de Widmanstätten, Director of the Imperial Porcelain Works in Vienna, polished and etched a surface of a meteorite known as the Agram Iron, and observed the beautiful geometrical structure since known as the Widmanstätten figure or structure. Widmanstätten apparently attempted no explanation of this structure, and in fact did not publish an account of his discovery, yet it shortly became known among crystallographers and mineralogists. Since the Agram Iron was known to be an alloy of iron and nickel, the accurately geometric character of the Widmanstätten figure gave an early clue to the inner crystallinity of metals. Rose, in 1863,¹² demonstrated that the (kamacite) plates in iron meteorites of the Agram Iron type are in fact arranged with respect to each other as the faces of an octahedron, and since that time meteorites that exhibit this type of geometric crystallinity have been known as octahedral in type, as octahedrites.

In 1849, Henry C. Sorby, of Sheffield, founded the science of petrography, having prepared the first thin rock section for examination under the microscope by transmitted light. Sorby knew of the Widmanstätten structure in meteorites, and wondered whether similar structures might not occur in steels. In examination of polished and etched samples of bessemer steel and of a cast-steel ingot, it became clear that no structure was visible to the unaided eye but he applied his newly developed technique of petrography to these samples, of necessity using reflected light, and did indeed observe the Widmanstätten figure.

Before proceeding to a full discussion of Sorby's work, we should note that though he is properly described as the father of modern metallography, he was not the first to examine a metallic object under the microscope. As far as the record goes, that distinction appears to belong to Robert Hooke, author of "Micrographia," published in 1665, who examined the edge of a razor blade and made a drawing. He proposed that it is difficult or impossible to obtain a true polish on a hard substance by means of powder abrasives, since each particle, however fine, cuts its own minute groove; he began at this early date the long discussion of the nature of the polishing operation which has remained a major subject in physical metallurgy. Hooke suggested that the hardening of steel originates in the formation of a glassy (amorphous) phase; and anticipated modern methods of thought by considering the structure of solids as composed of the regular piling of spheres—atoms. Réaumur examined the fractures of many kinds of steel by the use of a lens, and used the lens to rate "grain sizes." Over a century later, and just before Sorby, J. R. von Fuchs¹³ examined cleavage surfaces, and concluded that iron can be either cubic or rhombohedral. Belaiew¹⁴ pointed out that P. Anosoff had used the microscope in 1841 to observe the watered patterns of damascened steels, and in attempting to imitate this structure developed etching methods. This does in fact appear to be the earliest instance of the use of the microscope in examining polished and etched metals, but as it was published in Russian it did not become known outside Russia. Anosoff, however, enlisted the interest of Tchernoff, and greatly influenced his work.

Sorby's original work aroused surprisingly little interest in England. Independently, Martens,¹⁵ in Germany, undertook the study of metallographic microscopy, embarking upon a detailed program of the study of fractured surfaces, of methods of polishing and etching (he invented heat-tinting), and of the microscopic structure of metals, particularly pig iron. Martens' contribution to metallographic microscopy was important, and very influential, especially in Germany and France. It led to Wedding's work,¹⁶ which in turn helped to renew Sorby's interest in the subject. Wedding published colored drawings of metal samples; he studied the formation of grains, and the fibrous appearance and directional properties of metals. Sorby published his well-known classic in 1887, as related below. Following this, Sorby's participation in the development of metallography apparently ceased.

THE HARDENING OF STEEL

Tchernoff's famous paper on the critical temperature,¹⁷ though not published until 1880, was read before the Imperial Russian Technical Society in 1868. Tchernoff described the dendritic structure of steel ingots, and the effect of repeated heating on structural alteration. In studying this effect, he investigated the temperatures at which structural alteration occurs, but lacking any methods to measure temperatures, he gauged them only by colors. He found it necessary to heat above a certain temperature in order to provide hardening. His discovery of the critical temperature became very well known and formed the basis for the later work of Osmond and others. Osmond adopted Tchernoff's designation of the critical temperature as α , which, now capitalized and with suitable subscripts added by Osmond, Portevin, and others, is the basis of our modern nomenclature.

Twenty years ago Benedicks¹⁸ pointed out that the Swedish Patriotic Society in 1777 published an article by J. F. Angerstein relating experiments carried out to improve cutlery steel, and the next year a second paper on the hardening of steel. This work, published somewhat obscurely, clearly anticipated much work commonly attributed to those who worked a century or more later. Angerstein said:

As a continuation of my experiments on the improvement of cutlery steel, I beg to state the safest way of obtaining the best hardening, probably of all sorts of steel. The hardening has earlier necessitated the most careful attention, until now the glowing of the steel has betrayed the secret moment, at which it has to be quenched at once. This betrays itself to the eyes of many, when the piece of steel is big enough, but only to the trained eye when it is small as a kind of fluttering, as if a cloud of dust or a faint shadow were rapidly flitting over it.

This is clearly decalescence, and Angerstein thus not only may be said to have discovered the critical temperature but also to have recognized its essential role in the heat-treatment of steel.

PHYSICS OF METALS

The work of Matthiessen, published in this period, and known now chiefly for its contributions to the knowledge of the electrical conductivity of metallic solid solutions—used later by the early

metallographers, especially Kurnakov, Tammann and Guertler, as a fundamental method to determine the constitution of metal systems, and still used—has a wider importance in the history of the science of metals than is generally recognized. Long before a clear recognition of solid solutions was common, Matthiessen said:¹⁹

In nearly all cases two metal alloys may be considered as solidified solutions of one metal in the other. There is, however, an important point in the definition of the term solid solution which must not be overlooked, namely, that the components are most intimately mixed together; in fact, they are homogeneously diffused in one another, and to the extent that even under the most powerful microscope, it would be impossible to distinguish the components of a solid solution.

Matthiessen goes on to say that the occurrence of definite crystalline forms in alloys is no proof of chemical combination in the sense of compounds, quoting Cooke on the point, and referring to alloys in the systems iron-carbon and antimony-zinc.

This century saw a rapid growth of physics, providing information on the physics of metals that Matthiessen had available to apply to alloys. Even in the preceding century, Achard, in 1784, had suggested the close alliance of the thermal and the electrical conductivity of metals; in 1853 to 1859, Wiedmann and Franz expressed this alliance in their well-known ratio; Seebeck discovered thermoelectricity in 1821; and in general the physical properties of the metals were rather well understood. Matthiessen was the first to extend this knowledge to alloys. Graham,²⁰ in 1866, discovered the occlusion of gases in metals, a subject to be pursued actively later by Sieverts. The importance of gases in the behavior of metallurgical materials was perceived early.²¹

THE BIRTH OF THE MICROSCOPY OF METALS

Sorby's major papers were published in 1886²² and 1887,²³ following his lecture to the Iron and Steel Institute in 1885. He employed magnifications up to 650 diameters; in addition to the study of many diverse samples of iron, steel, spiegeleisen, etc., he devoted most of his enthusiasm to the "pearly constituent," which Howe later renamed, mineralogically, pearlite: he correctly identified its constituents as iron free from carbon and "the intensely hard substance." He believed iron and carbon at a high temperature associate in a compound, which on cooling breaks up into iron free

from carbon and a compound of iron and carbon. He noted that such structures might occur even when the microscope cannot resolve them (much controversy might have been saved later if this had been taken more to heart). He thought the orientation of the pearlite plates might have been determined by the previous crystalline structure, and thus anticipated future studies on the Widmanstätten figure. He observed quenched (martensitic) steel and noted the lack of carbide, believing that the particles might have been too fine, or perhaps the high-temperature compound so "fixed" by the sudden cooling as to give high hardness. And he noted, revealingly, that the effect of tungsten in Mushet's steel may have been to prevent the separation of pearlite from the high-temperature compound. Sorby spoke familiarly of the grain structure of metals, which had indeed been recognized by Réaumur more than a century previously. He noted that tempering gave separation into carbide and soft iron. In his second paper he noted the occurrence of recrystallization, remarking that the cold-worked state is one of unstable equilibrium. Reasoning on the behavior of steel, he correctly associates structure changes, recalescence, and hardening with the critical temperature. It is difficult to leave Sorby without at least mentioning some of his other important observations: that metals may fracture intergranularly or intragranularly; that fatigue does not crystallize a metal—it was crystalline before and no more crystalline later; and many others.

IN 1871

The extent of the knowledge of physical metallurgy in 1871 may be judged from the foregoing, at least with respect to the major subjects, if not with respect to the innumerable details of the behavior and properties of the many metals and alloys available. The book by Percy,²⁴ lecturer on metallurgy at the Royal School of Mines—a book that is one of metallurgy's important classics, deeply influencing the profession for many years—summarizes the knowledge available at that time. Percy describes the metals common in his day. The crystalline structure of metals was recognized, though whether metals were wholly crystalline was uncertain; the occurrence of iron carbide was admitted, though its formula was uncertain, despite the work of Berzelius, Karsten, and Gurlt.²⁵ On the hardening of steel Percy has much to say, referring to the volume changes, to the

work of Caron,²⁶ who found the hardness of steel to vary with the rate of cooling on quenching, varying inversely with the square of the time of cooling (!), to the effect of hardening and tempering upon the fracture characteristics of steel, even microscopically,²⁷ to the increase in grain size with increase in heating temperature, to the basic question of the theory of hardening, whence he says: "Why carbon should produce this result (convert iron into steel) is a mystery; why carbon, thus introduced, should cause iron to retain its magnetism is a mystery; why it should admit of tempering is a mystery—and yet these are well-known distinctions between iron and steel." He notes that tensile tests were common, quoting a chromium steel with a tensile strength of 198,910 psi, and giving results on tensile, transverse, deflection, torsional, and crushing tests. He suspected that bessemer steel might replace wrought iron; he wondered whether a use might be found for molybdenum; he notes the heat-capacity and expansion pyrometers then available.

In a book published in this country by Osborn²⁸ in 1869, a book owing much to Percy's, we discover that the crystalline state of iron was clearly recognized, from fracture studies, as was that of zinc. Osborn writes at length about fiber in forgings; he quotes revealingly on the state of powder metallurgy, for, following the early work of Wollaston, objects were made, medals struck, from powders of copper, silver and gold, and unusual damascene effects were obtained by imperfect mixtures of silver and gold. He lists the important alloys of iron. The comprehensive book by Kerl may be employed in like manner.²⁹ Kerl notes the availability of the thermoelectric pyrometer, which he ascribes to Steinheil and Pouillet, and to Becquerel.

2

1871 to the Turn of the Century

THE TRANSACTIONS of the Institute for the early years display but little interest in physical metallurgy—indeed, it is striking how thoroughly process metallurgy absorbed attention until quite recent years. The first volume carries no article that can be strictly described as physical metallurgy, unless one on the rolling and hammering of ingots be doubtfully so described. Nor does the second volume contribute more—the interest then was in mining, and in production methods, both ferrous and nonferrous, with much attention to the new methods of making steel. The third volume records papers on: the condition of carbon in gray and white iron, a paper devoted to chemical rather than microscopic analysis; the annealing of spiegeleisen; phosphorus and carbon in iron and steel, similarly chemical. Much attention was given, and continued to be given for years, to the manufacture and behavior of rails. The question of the nature of steel appeared early (Vol. II)—What is Steel, by A. L. Holley—where arguments on nomenclature were already active; and Holley also bemoans, in modern spirit, the Inadequate Union of Engineering Science and Art; Pearse wrote on cast iron for guns (reflecting again the ironic beneficence of war in metallurgy), and said that Captain Walbach was the first to insist on chemical analysis of gun irons; he quotes Major Wade's study of comparative hardness, using penetration hardness measurements (Brinell was to come later), and quotes the important Reports on the Strength and Other Properties of Metals for Cannon, by H. C. Baird, Philadelphia, 1855, in which the advanced state of tensile testing at the time is shown.

Hewitt, in Vol V, comments upon the function played by technical schools and technical societies upon the growth of metal-

lurgy.* Henry Marion Howe appropriately writes on the nomenclature of iron, as he does from time to time in later volumes; and Billings relates his studies of a remarkably extensive series of iron alloys, Fe with Ni, Cu, Pt, Al, Sb, Bi, Mo, Zn, Pb, Ag, Co. In Vol. VIII, Kent, following Wöhler, investigates repeated stressing—and in the process “crystallizes” his metal! In that same year Kent wrote “On Some Curious Phenomena Observed in Making a Test of a Piece of Bessemer Steel,” a curiously interesting paper, indeed, for it is in fact disclosure of the phenomena of over-strain aging in steel, the knowledge of which is commonly thought to be of later origin. Kent noted that cold-work lowers the elastic limit, removes the yield point and the elongation (and the “drop of the beam”) at the yield point, with aging restoring the yield point at a value higher than the initial.†

In that same year, Egleston reported that rail wear produces plastic flow; that punch marks, filed away, nonetheless leave their mark that can be revealed by etching, anticipating the FBI!; and he speaks familiarly of recrystallization; he worries, as we still do, about the nature of fatigue.

Bayless, in 1882, refers to Martens’ work on metallographic microscopy (and Martens’ prediction that microscopy might some day be as important as chemical analysis—which Bayless doubted!) and to Sorby’s work, and contributes to this subject himself; he derides the idea of fatigue causing crystallization and underestimates the toughness of an idea! Abbott, in Vol. XII, describes the status of tensile testing, stating that Fairbanks built the first testing laboratory in this country, in New York City, using a multilever type of machine in 1863, followed later by Riehle Brothers, and then Emery in 1880. Bayless, in Vol. XIII, observes, cogently, the inadequacy of chemical analysis in evaluating the quality of steel, and says, “The key to

* The early TRANSACTIONS of the Institute carry a surprisingly large number of papers on metallurgical education. They read well today! And they somewhat shame the modern educator in his silence on pedagogical matters.

† Roberts-Austen³³ wrote: “I may remind you, however, that much of what is both interesting and full of suggestion, even at the present day, is to be found buried in the treatises of the old writers whose work we inherit and continue.” However trite it may sound, it still must be said that modern metallurgical writing suffers, at times woefully, from an ignorance of that which has already been done; however arduous, substantial literature research must accompany experimental research, else the latter will expend itself in already conquered territory, and has too frequently done so.

the mystery seems to lie in the structure of the metals." Garrison, in Vol. XIV, published what appears to have been the first photo-micrograph in an American journal, at 50 diameters. Smith, in Vol. XVIII, produced a paper on Aluminum in the Drawing Process, with sheet obtained from Hunt, and forecasts the use of aluminum for pots and pans in the kitchen. Papers on aluminum bronze (described earlier by Percy) appeared; and Hunt, Langeley, and Hall described the properties of aluminum in detail. The Hall process was under-way, and other papers on aluminum were to follow.

In subsequent years, following 1890, articles on microscopy, on alloy steels (especially nickel and manganese-alloy steels), on pyrometry, and heat-treatment appeared in increasing numbers; and the names of Howe, Sauveur (the latter first in 1893), Martens, Roberts-Austen, Hadfield, became familiar. Sauveur, in 1893, showed that the grain size of austenite increases as the temperature to which austenite is heated increases; his observation, and the much earlier one of Réaumur, might well have led then to ideas of the effect of austenite grain size on depth of hardening that are modern, but for the surprising lack of knowledge and even of interest in the phenomenon of the depth of hardening. The Institute held a symposium on Physics of Steel in 1894, which led Sauveur many years later to observe, somewhat drily, that "physics of metals" was not new; Sauveur related his experience in applying microscopy practically in steel-plant work.

These historical notes, restricted largely to the TRANSACTIONS of this Institute, may be taken as an indication of the nature of progress in other countries as well in the years to the turn of the century; the turn of the century is a natural historical division in physical metallurgy, for the end of the nineteenth century saw a sudden spurt in this subject, which we shall relate. The metallurgists, chemists and physicists in the European countries undertook the study of metals with great seriousness in the early years of the twentieth century and were much advanced in this respect compared with their counterparts in this country in physical metallurgy (note, however, not in production metallurgy), as parallel studies of English, French, and German literature will show—and as we shall see subsequently in this article. Although the drawing of historical boundaries awkwardly lacks preciseness, it may be said that but little work was done in this country on physical metallurgy until the middle of the second decade of the twentieth century,

and that progress became rapid only in the following decade. The TRANSACTIONS show only one article on the constitution of metal systems in this time period, that by Fay and Gillson in 1901 on alloys of lead and tellurium and of antimony-tellurium, despite the great volume of similar work done abroad. The energies of metallurgists in this country in this period, and the attention of the profession, were absorbed in expanding the metallurgical economy.

3

The Turn of the Century

THE turn of the century was marked by the appearance of a series of greatly important pieces of research that became the foundations of modern physical metallurgy. It is, of course, somewhat misleading to ascribe the growth of a science, or a branch of engineering, to the work of a few men, as it is to write history generally in terms of great men, for this approach neglects background development, and tends to overemphasize the importance of immediately subsequent events; the correlative and steady growth of the basic sciences added to the resources of the new science of metals—developments in basic science years later were to appear in their application to metal systems. Yet it is useful to emphasize the importance of these relatively few pieces of research.

THE PHASE RULE

The work of Willard Gibbs on heterogeneous equilibria, which included the derivation of the phase rule, was published obscurely in the journal of the Connecticut Academy.³⁰ Unearthed by the German physical chemists (evidently by van der Waals, to use Ostwald's phrase, "aus dem staubigen Fundort"), its importance to the study of alloys was pointed out by Jüptner,³¹ and by Le Chatelier; its application to polycomponent systems, and to metal systems in particular, was developed by Rijn van Alkemade (1893), by Le Chatelier,³² and especially by Roozeboom (1899–1900).

The work of Raoult on the depression of the freezing point by solutes led to the study of the phenomenon in amalgams and shortly to metal systems. Work was done, by Roberts-Austen and others, on the initial freezing temperatures of binary alloys—the liquid, data applicable to Raoult's work. Van't Hoff in 1890 had pointed out

the analogy between solid solutions and liquid solutions, as had Matthiessen much earlier. Moreover, the work of Tchernoff¹⁷ on the critical points in iron was followed by Roberts-Austen's study³³ of the constitution of iron-carbon alloys, in which the solution characteristics of the gamma phase was recognized, as it had also been by Jüptner, and in Osmond's⁶⁷ classic work on critical temperatures in steel. This work of Osmond, of profound effect in metallurgical science, requires and deserves somewhat detailed mention.

Methods of measuring temperature were developed in the latter half of the nineteenth century, as already noted. Although the possibilities of the use of thermoelectromotive force were recognized, the invention of the platinum-platinum-rhodium thermocouple by Le Chatelier in 1888³⁴ made available an easy and highly accurate and dependable method that was to play a role of extraordinary importance in the study of alloys. Osmond used this thermocouple, applying it with a chronograph in 1890 to the determination of the critical point in a series of steels of carbon content varying from 0.08 to 1.25 per cent C. He found that a hypoeutectoid alloy possessed not one critical point, but two, and when including the magnetic change, sometimes three, which, following Tchernoff, he designated as a_1 , a_2 , a_3 , he found these points to be different on heating and on cooling, and introduced the a_c and a_r terminology; and, moreover, he found these critical points to vary in temperature with the rate of heating and of cooling, noting also, finally, that they varied not only with the carbon content but also with the percentage of alloying elements present. Sauveur plotted these points on a diagram, with temperature as ordinate and percentage carbon as abscissa.³⁵ While this diagram cannot be called an "equilibrium diagram," it was in fact the first recorded approach to the equilibrium or constitutional diagram.

Roozeboom employed the work of Roberts-Austen,³³ and of Osmond on the thermal examination of the steels, applying the phase rule of Gibbs, and, in a metallurgical classic, produced and published an equilibrium diagram for the iron-carbon system.³⁶ This diagram, now seen as obviously in error in some points, owing to inadequate information, was of great importance in the development of the study of the constitution of alloys. The phase rule offered a guiding principle, simplifying experiment, and greatly simplifying interpretation—it excluded an infinite number of possible explanations for complex and uncertain facts originating in

lack of or slow approach to equilibrium. Roozeboom³⁷ derived the possible types of binary, *t-c*, diagrams, with which all systems, including metallic, must comply.

THE CONSTITUTION OF ALLOYS

Roozeboom's work was applied by Heycock and Neville to their results on the constitution of the copper-tin system. It showed that the liquidi experimentally determined by Heycock and Neville must be accompanied by solidi, and led to correction in the explanation of solid-solid equilibria (see note, *Metal Progress*³⁸). Heycock and Neville employed quenching from a fixed temperature as a method of studying constitution, a method used earlier by Howe.³⁹ Their work, together with that of Matthiessen, formed the orthodoxy of constitutional studies for many years, and remains much of it today.

Research on the constitutions of other alloys—e.g., the brasses—followed. The chief subsequent development, however, was the appearance of the first paper,⁴⁰ in 1903, from what was later to be familiarly known as the "Tammann school," at Göttingen. Tammann was a figure long to remain a dominant one in the development of physical metallurgy. Turning his attention to one subject after another, through a long life, he breathed good science into physical metallurgy, and added fundamental knowledge to an unbelievable number of subjects: the nature of freezing, thermal analysis, oxidation, corrosion, recrystallization and recovery, and alloy constitution; and he trained many students, soon to become leaders in metallurgy in Germany and elsewhere. His early work was devoted to the thermal analysis of a great number of binary metallic systems; he employed methods developed earlier, and added some new ones; e.g., the method of the duration of the eutectic arrest. In subsequent years many papers appeared from his laboratory on the constitution of binary systems; Tammann's chief purpose in this work was to make a wide survey of many systems, rather than an intensive study of a few, for his objective was not the precision determination of alloy constitution but generalizations concerning the chemical constitution and nature of the phases formed in alloy systems.*

* Tammann⁴¹ said, "Before the turn of the century alloy meant the intimate mixture of two chemically different substances. Views concerning the structure of this mixture varied widely and since precise methods of determining con-

The work of Heycock and Neville,³⁸ especially on copper-tin alloys, established good practice in precision investigation of the constitution of alloy systems. It was followed by a long series of investigations, at first largely on the systems Cu-Zn, Cu-Sn, Cu-Al, and Fe-C. Cooling-curve techniques were developed: Osmond employed the inverse-rate curve in 1887, Roberts-Austen the differential curve in 1899, and Rosenhain, later, in 1910, the derived differential curve. Fixed thermometric points, based on the gas thermometer, were available in 1900 up to 1775°C. Heyn, at Charlottenburg, did much to improve metallographic techniques. The work on constitution diagrams was to lead to Bornemann's compilation in 1909, to be succeeded by Bauer's in Landolt-Bornstein, and in recent years by M. Hansen's. The problem of the instability of Fe₃C was recognized (cf. Stansfield⁴²) and the representation of this instability upon the constitution diagram—the so-called double diagram—was proposed.⁴³ Delta iron, foreshadowed by Ball and Gontermann (1908), was demonstrated by Ruer and Klesper in 1914.^{44*}

THE HARDENING OF STEEL

The theory of the hardening of steel was a favorite subject about which to write in this period. Sorby had observed the constituent martensite, though he appears to have misinterpreted its nature. Osmond named it in honor of Martens; Osmond also named

stitution were lacking (and also a knowledge of the relationships among the phases), views differed. That many metals are crystalline at least in part, was recognized early, but knowledge of the composition of the phases was unknown—as to whether pure metals or compounds." In defending his work on the constitution of alloys, which appeared largely in the years 1904 to 1913, and chiefly in the *Ztsch. anorg. Chem.*, Tammann said (*op. cit.*): "By repetition of work on individual equilibrium diagrams with purer materials and by careful reexamination of questions raised in the first investigation, deviations of a secondary nature have been found in a few cases. . . . To obtain a survey of a wide field the goal will be reached more rapidly the more the attention is concentrated on the principal point and the more it is possible to distinguish between the principal and the secondary consideration." Tammann's work has been subjected to a somewhat unsportsmanlike criticism, and his reply is in warmth, and in turn a little extreme, for subsequent investigations have often shown the results of the first studies of alloy systems to require very extensive revision.

* For a summary of much of this work, see W. Campbell: Last Twenty-Five Years in Metallography (Howe Memorial Lecture). *Trans. AIME* (1926) 1135.

austenite, for Roberts-Austen. Much had just been learned concerning the constitution of the steels, as related above, and this led to very extensive theorizing. As we see it today, the information available on the kinetics of reactions in the solid state was far too scanty to provide any reliable basis for theorizing. Indeed, misconceptions concerning constitution itself were not infrequent—iron-carbon equilibrium diagrams occasionally termed the field austenite “martensite.” Sauveur was much engaged in the controversies concerning the hardness of martensite; the first Howe Memorial lecture, delivered by Sauveur, was devoted to the beta-iron theory of hardening; these controversies are ably summarized by W. Campbell (see footnote on page 24). Campbell notes that acicular products similar to martensite had been observed by Howe (and others) in the bronzes on quenching.

It is not easy to review these theories today: they involved, in general, concepts of retention of phases and of stress; Osmond, Roberts-Austen, and Howe held that retained allotropic forms gave martensite its hardness, especially beta iron which, *ad hoc*, was conceived as hard; Le Chatelier and Guillet held the hardness due to alpha iron; Humphrey believed (as had some earlier and some later workers) that the hardness of martensite is due to the “amorphous” condition of martensite; Arnold and Hanemann argued for the presence of a special carbide $Fe_{24}C$ in martensite; and others argued for hardness as caused by great internal stress. The minds turned to this problem were able, indeed brilliant minds, but the problem was exceedingly abstruse and the basic information available very meager.

The Reports of the Alloys Research Committee by Roberts-Austen (published by the Institution of Mechanical Engineers) in the years 1891–1899,⁴⁵ are very engaging reading, for apart from the important role they played in the development of physical metallurgy in this period, they suggested lines of research that were to prove of much significance in the future. Roberts-Austen was much concerned with the effect of small amounts of alloy upon the properties of a metal, and believed that this should be studied from the point of view of the periodic table—a point of view to be developed later in a very fruitful fashion. He noted the extreme effects of some impurities: that 0.003 per cent antimony changes the rate of oxidation of molten lead, that 0.05 per cent lead makes gold brittle, that 0.5 per cent iron reduces the electrical conductivity

of copper 60 per cent. He tended to ascribe such effects to ubiquitous allotropy—a view that was to plague physical metallurgy until recent years, a view that Le Chatelier opposed with much intelligence, ascribing the effects on mechanical properties to structure instead. Roberts-Austen devoted much attention to the application of recently developed solution laws to the melting points of alloys; he believed that the effects of alloy in steel could be ascribed to a change in the rate of allotropic change; and he reported his important work on diffusion, etc.

Other transformations were being studied at this time. Cohen had made important observations on the alpha-beta tin allotropic change (the rate of which was to be measured by Tammann years later).⁴⁶ And interest in the mechanism of the freezing process began, again on the stimulus of Tammann, who wrote on the operation of nucleation and growth in freezing, a process found later to be widely applicable in the metallurgical field.⁴⁷

PLASTIC DEFORMATION

The study of the nature of the plastic deformation of metals, and the relation of this to the crystal structure, though not entirely a new subject at the turn of the century, as the account already given shows, received a very marked impetus in these years. Twinning of metals was observed, first by Neumann in the ferritic kamacite phase in meteorites in 1848 and later by Prestel in commercial iron. Neumann identified the plane along which these mechanical twins occur as $\{112\}$; in iron these mechanical twin bands became known as Neumann bands.

Ewing and Rosenhain,⁴⁸ in 1899, in studying the plastic deformation of metals, especially lead, showed deformation to proceed by slip on crystal planes, evidently on equivalent sets of planes, for the "slip lines" were observed to intersect. This provided the first important evidence for slip in metals and for the block movement that accompanies deformation. The so-called slip interference theory of hardening was at least implicit in this work, for manifestly any effect making slip more difficult must render the metal more difficult to deform; that is, harder. This work is thus the cornerstone in the science of the plastic deformation of metals.

Shortly after, Mügge⁴⁹ studied these slip lines crystallographically, showing them to follow the $\{11\}$ planes in copper, gold, silver,

and lead; he showed the Neumann bands in ordinary alpha iron to be on the {112} plane. This work is the first of the great number, still current today, on the crystallography of slip. (See reference to Osmond's work below.)

MECHANICAL METALLURGY

In 1900, Brinell published a description of the method of measuring hardness that bears his name,⁵⁰ which attracted Howe's attention on a trip to Europe. Although penetration methods were not new—Hertz had earlier considered theoretically the problem of penetration by a needle, and Auerbach had experimented with it—they found little practical use until the superior Brinell method appeared.

Deshages had already plotted the tensile strength of steel against the percentage of carbon and of manganese. Shortly Izod (1903) and Charpy (1904) gave impact testing to the profession, a subject that was to remain one of discussion and of some uncertainty, up even to the present day. The nature of tensile elongation was considered at length during this period, with the development of high-quality measuring devices, and with the application of the principles of mechanics to the problem. Considère⁵¹ observed that the attainment of the highest load in the tensile test is concomitant with necking. Kalakoutsky⁵² considered the measurement of internal strains, and (to select only a few of the many references in this period) Le Chatelier⁵³ studied the effect of temperature upon the tensile values for nonferrous metals, observing the general decrease in strength and increase in ductility. In 1904, Bach reported the occurrence of an "upper" and a "lower" yield point in steel.⁵⁴ Adamson,⁵⁵ in 1878, had shown that brittleness occurs after cold-working; Ridsdale,⁵⁶ in 1898, observed the influence of the working temperature on the generation of brittleness, and finally, Martens,⁵⁷ in 1890, in a systematic study, fully demonstrated blue brittleness in steel, confirmed in 1907 by Stromeyer.⁵⁸ In 1904, Le Chatelier⁵⁹ made the observation, which later was to prove of much importance, that the temperature at which blue brittleness manifests itself depends upon the speed of testing. Although blue brittleness was discovered by Martens in 1890, its relationship with over-strain aging was not to be recognized until many years later. The Lüders-Hartmann lines in iron formed by local yielding ("stretcher strains") were further studied by Hartmann in 1896.⁶⁰ Howe recognized the ob-

struction microconstituents can offer to flow, devising the "obstruction principle," the precursor to slip interference.

ANNEALING

The study of the effects of annealing metals following cold-work, after the preliminary investigations of Nogues (noted on page 9), was undertaken by Kalischer in a remarkable study published in 1881-1882.⁶¹ Kalischer observed that zinc sheet develops large visible grains on heating, and found this occurred only in rolled zinc; he explained this by saying that the crystalline structure formed on freezing is destroyed by rolling, then recreated on heating to a temperature exceeding the rolling temperature; he widened his observations to include many metals and alloys, finding similar behavior in silver and gold, failing in other cases; he observed that the physical properties change upon recrystallization, and actually reported a density increase of 0.04 per cent.

Ledebur⁶² found that the grain size after recrystallization is the greater the higher the annealing temperature and the longer the time of annealing. Stead,⁶³ in 1898, made the important observation that recrystallization proceeds by nucleation and growth. Ewing and Rosenhain⁶⁴ observed that lead will recrystallize at room temperature, as Campbell showed for zinc.⁶⁵ Following 1902 there appeared many papers reporting recrystallization temperatures, frequently determined under experimental conditions we now recognize as badly defined; perhaps the stubborn idea that a metal has a fixed recrystallization temperature in the sense that it has a melting point originated in this period; work that was soon to appear showed that the temperature at which a metal will recrystallize is subject to many variables, not the least of which is time. Thence followed a series of observations on the effect of temperature upon grain size; for example, Charpy,⁶⁶ who succeeded in demonstrating recrystallization in alpha brass, Osmond,⁶⁷ Sauveur,⁶⁸ Heyn⁶⁹ and others. Behrens,⁷⁰ in 1894, studied the temperature limits for the recrystallization of tin in some detail. In 1904, Campbell showed that cold-working elongates the grains of copper, but not of lead because of simultaneous "equiaxing." While it is difficult to say when the conception of the production of amorphous metals by cold-work was first introduced among metallurgists—we have seen that the idea of amorphous metal had been employed by those attempting to ex-

plain the hardening of steel—it has been credited to Brillouin;⁷¹ this hypothesis as forwarded later by Beilby and Rosenhain was long to remain a point of controversy.

IN 1900

Osmond published his well-known text, "The Microscopic Analysis of Metal," in 1904.³⁶⁴ It was in essence a summary of his original researches, and may be taken as a statement of the position of physical metallurgy at the turn of the century. Roberts-Austen's book, published a few years before, is a more general treatise; Desch's book, which has occupied a position of importance in this field for decades, was first published in 1910. Osmond gives detailed directions in metallographic microscopy; the details are those we still extensively employ today; heat-tinting, used earlier by Martens in 1878, is described; scratch methods for determining relative hardnesses of microconstituents, also used earlier by Martens, were familiar, and much discussed; Osmond had invented the polish-attack method; he studied silver-copper alloys, and might have discovered age-hardening if the hardening in that system were not so feeble; he was confused as to whether a eutectic composition should be regarded as a chemical compound; he relates his important work on the crystallography of iron, noting cleavage, slip lines, Neumann bands, indentation figures, allotriomorphic and idiomorphic crystals, and inclines, surprisingly, to the belief that there is much amorphous material in metals. Stead, in 1898, had shown that etching may reveal crystal facets in iron-silicon alloys, and Ewing and Rosenhain had shown the same thing for tin; Osmond demonstrated that etch pits in iron are cubic, that indeed idiomorphic iron, reduced from solution, is cubic. Osmond's crystallographic work on iron⁷² was of very great importance: he showed the slip plane in gamma iron to be $\{111\}$, and found the slip lines in alpha iron to be curved, making their determination difficult, though he (correctly) believed that $\{111\}$ and $\{100\}$ are not active slip planes; he confirmed $\{112\}$ as the twinning plane in alpha iron; and he believed (without the advantages of more modern knowledge of lattices) that both alpha and gamma iron are cubic.

4

Since the Turn of the Century

THE extraordinary volume of work done in this period, and the multiplicity of subject matter, make a year-by-year historical account undesirable, if the account is not to be an assembly of unrelated fragments. We shall, instead, undertake to narrate the development in this period of each of the branches of the subject separately, hoping that their interrelations will be self-evident.

There is a certain arbitrariness in the selection of subject matter in the following sections. The development of important engineering alloys—for example, high-speed steel—is disregarded, for it is the primary purpose of this account to relate the advances in ideas, the growth of the science of metals; other historical accounts relate these parallel advances. Nor are advances in techniques stressed, though occasionally the most important are noted; nor is the progress described in allied fields such as welding, cutting, etc.; for though these developments have very frequently made possible the advances herein related, they are far too numerous to recount in anything short of a ponderous volume. There is a more serious arbitrariness, however; it is not an easy matter to draw the boundaries of physical metallurgy, and some contiguous subjects have been omitted that perhaps should have been included, such as, for example, corrosion, gases in metals, the magnetic behavior of metals and alloys, and certain other fields in the physics of metals.

REACTIONS IN ALLOYS—DIFFUSION

Many of the reactions occurring in alloys proceed by the operation of the process of diffusion in the solid state: the annealing of mixed powders to form alloys, the homogenization of castings or forgings, the freezing of alloys, the treatment of clad metals, the loss

of volatile constituents on annealing, are all examples of simple diffusion; the formation of pearlite from austenite, and the aging of alloys, involve diffusion in connection with the process of nucleation and growth, by which heterogeneous reactions characteristically take place. In organizing this account of the development of physical metallurgy, it will be convenient to discuss this large section of the field as a unit.

Diffusion in Solid Metals

It has been noted in the foregoing pages that Faraday and Stodart had prepared alloys by annealing packed wires, a process requiring diffusion in the solid state. Roberts-Austen's classic work on determining the value of the diffusion coefficient for gold in lead, also noted before, showed the amenability of this process to measurement, and demonstrated, contrary to current views, that the process take place with high velocity.

Little attention was devoted to this subject in the early years of the present century. Van Orstrand and Dewey, in 1915,⁷³ re-measured the rate of diffusion of gold in lead, confirming Roberts-Austen. The field became very active in the early '20s, particularly as a result of the work done on the related problem of the electrical conductivity of ionic crystals, and that of von Hevesy⁷⁴ on the use of radioactive isotopes in measuring diffusion, including self-diffusion.

Methods were developed for measuring the diffusion coefficient D ; Stefan⁷⁵ had given solution to Fick's⁷⁶ law of diffusion (derived by analogy from Fourier's law of heat flow) and applied these to Graham's⁷⁷ measurements on diffusion in liquid solutions; Stefan prepared tables facilitating the calculation of D , which were later amplified by Kawalki⁷⁸ and by Jost.⁷⁹

Measurement of Diffusion Coefficient

Early work was done on the measurement of D in alloy systems by Grube;⁸⁰ this showed D to vary with concentration, which led Matano⁸¹ to apply Boltzmann's solution to the case of varying D ; it was found that D does indeed often vary markedly with concentration. Specific experimental techniques were devised; the obvious one of machining layers for analysis from a diffusion couple remains the standard one, though several methods of chemical analysis

were and are used, such as the spectroscopic, and the determination of lattice dimensions by X-ray diffraction; the radioactive tracer technique, already noted, has been extensively used, and, with recent developments in the production of radioactive isotopes, bids fair to become extremely important; the thermionic technique, employed by those interested in vacuum tubes, has provided much information otherwise difficult to obtain. Short-cut methods have frequently been used, but rarely give unambiguous results.⁸² The variation of the diffusion coefficient D with temperature is great. An exponential relationship was proposed by von Hevesy in 1920,⁸³ by Tammann and Schönert in 1922,⁸⁴ and by Weiss in 1923,⁸⁵ and the present form, in which the process is shown as an activation process, was given by Dushman and Langmuir in 1923.⁸⁶ The later equation permits an approximate calculation of the temperature coefficient from one D -value.

Chemical Affinity in Alloys

Evidence accumulated in the early years of the century for a state of partial ionization in alloys. Kremann,⁸⁷ in a long series of studies, showed that liquid alloys may be electrolyzed; Seith and Kubaschewski⁸⁸ showed that solid solutions may likewise be electrolyzed. von Hevesy and Seith⁸⁹ showed that in lead-base alloys the greater the chemical difference between solute and solvent—and therefore, presumably the greater the chemical affinity—the greater the rate of diffusion, and work since on silver-base alloys⁹⁰ and copper-base alloys⁹¹ showed the same effect. In general these measurements too rarely consider the variation of D with concentration; when such measurements have been made it is observed that D increases as the solid solubility limit is approached.⁹¹

Application to Alloy Constitution

Guillet⁹² showed in 1914 that solid solution formation is necessary for diffusion, a rather self-evident fact though not always understood. Diffusion in a given phase will continue until that phase is saturated, providing a method to determine solubilities, especially small solubilities, a circumstance occasionally though not frequently enough employed; Seith and Etzold⁹³ in this way determined the solubility of gold in lead, and Ziegler studied the solubility of carbon

in alpha iron.⁹⁴ Guillet's principle leads to the generalization that the number of alloy layers developed in diffusion is that which the equilibrium diagram shows to be stable at the temperature concerned; this principle seems valid, though recent work by Hickman, quoted in the section on oxidation (p. 38), questions it. The rate at which intermediate alloy layers form was studied by Tammann and Rocha,⁹⁵ and by Heindlhofer and Larsen;¹²⁰ and studied definitively by Lustman;¹¹⁸ these rates should be derivable from diffusion laws, producing a parabolic behavior, but the results show only an approximate parabolic behavior, disturbances arising perhaps from special phase orientations. These simple facts have given methods by which the constitution of binary alloys may be more readily studied; the principles of diffusion in ternary alloys are still in need of definitive study.

Anisotropy

Investigations of the variation of electrical conductivity with crystal direction in noncubic crystals showed an anisotropy.⁹⁶ Using the radioactive tracer technique, Seith⁹⁶ showed that self-diffusion in rhombohedral bismuth is sharply anisotropic. Evidence for anisotropy is available on alloy diffusion,⁹⁷ but the field badly needs exploiting.

Imperfections—Cold-work

Studies on the degree of perfection of crystals, of special importance for structure-sensitive properties⁹⁸ such as the mechanical properties, have been extended to the imperfections resulting from cold-work, and to the effect of cold-work on diffusion. This, of importance to those processes such as age-hardening that involve diffusion, is difficult to investigate directly. The development of electron diffraction, however, which makes available a method for the study of minute amounts of diffusion (and thus avoids annealing at high temperatures and resultant loss of cold-work distortion), especially by Finch, Quarrell and Roebuck,^{99,100} have shown that distortion increases the value of D . Other evidence,⁸² points in the same direction, both as regards the effect of cold-work and that of ordinary imperfections.

Grain Size

It has not been easy to obtain information on the effect of grain size on the D -value. There is, however, evidence that a grain-size effect occurs, at least in some systems.⁸² Rhines and Wells⁹⁷ believe the effect to be general, with the difference between the rate of grain-boundary diffusion and of diffusion within the grain decreasing as the temperature approaches the melting point. The best measurements on grain-boundary diffusion are those of Langmuir¹⁰¹ and of Fonda, Walker and Young,¹⁰² who used thermion emission from thorium in tungsten, showing the D -value to be much the greater at the grain boundary, with a much smaller activation energy. In other cases, however, it has not been possible to detect an effect of grain size upon the overall rate of diffusion, as, for example, in Wells' work on the diffusion of carbon in gamma iron.¹¹⁰ The thermionic field has provided data on the rate of surface diffusion, the existence of which was originally demonstrated by Volmer,¹⁰³ and data for several systems are available, including thorium in tungsten (where D is greater than in grain-boundary diffusion and the activation energy less), but unfortunately those systems do not include any of direct interest to metallurgists. Both grain-boundary diffusion and surface diffusion are much in need of study for metallurgical purposes.

Use of Radioactive Isotopes

The increasing availability of radioactive isotopes, from the cyclotron, and now from the atomic pile, offers much in this field. Self-diffusion coefficients in pure metals, of interest in rate processes such as creep, have been derived (using isotopes from the cyclotron and other "atom-smashers"),^{104,105} though others, as in the case of alpha iron and gamma iron, are still lacking. Darken¹⁰⁶ in recent years has proposed that activity coefficients should be employed instead of concentrations, and while it may not appear that the variation in D noted in many systems merely reflects a variation in solution activity, Darken has shown that diffusion will occur in the direction of an activity gradient and against a concentration gradient. The atomic mechanism of diffusion remains a difficult subject, with experts in this subject inclining toward a mechanism in which vacant lattice sites play a predominant part.⁹⁹

Diffusion of Carbon—Carburizing

The process of carburizing, in solid or gaseous media, has long been recognized as an example of diffusion in the solid state, as noted before. Bramley,^{107,108} subjected the process to detailed study and from his results calculated D -values for the diffusion of carbon in gamma iron. Theoretically the rate of carburizing should depend upon the equilibrium concentration of carbon established upon the surface of the piece carburized and upon the rate of diffusion inward. Recently Stanley¹⁰⁰ analyzed commercial carburizing from this point of view with much success, employing the data of Wells¹¹⁰ on the diffusion of carbon in gamma iron, in pure and alloy steels. Wells showed the diffusion coefficient to increase rapidly with increase in carbon, a circumstance that may probably be shown to explain the full shape of the carburizing curve.

OXIDATION

The observation of scaling of metals, is, of course, very old. And the observation of the formation of temper films on metals must also be very old, for steel was quenched and tempered by the ancients, and it is likely that the colors produced were used to measure the amount of tempering desired. Little scientific progress was made, or could be made in the study of these phenomena until Lavoisier, in 1774 to 1777, demonstrated the true nature of oxidation. Following this work, the nature of oxide scales became clear, but the nature of temper films, because of their extreme thinness, was more difficult to recognize. Newton, much earlier, had shown the origin of interference colors of oil films on water (and in other cases), and the similarity between these and those of temper films was apparent.

Temper Films

The identification of temper films as oxide layers was made by Humphry Davy in 1813.¹¹¹ But in succeeding years there was much controversy concerning the nature of the film. Barus, in 1886,¹¹² thought that oxygen molecules penetrated only a few thousand atom diameters, and that their passage through the film was by a process allied to that of liquid diffusion. He noted that the film increases in thickness more rapidly at higher temperatures (though evidently

he did not clearly recognize this process as a rate process), and that films which are thin oxide layers (taken usually as below 2000Å in thickness), pass gradually to scales, which are thick oxide layers (taken as above 2000Å). Barus also defined the use of temper colors to measure temperature.

Tammann's work on temper films, published in 1922,¹¹³ gave impetus to the field. Tammann used the temper-film color, though a simplified optical analysis, to appraise the film thickness. He proposed that oxide (and other) reaction films on metals, when in the temper-film range of thicknesses, form at an exponential rate with time, whereas thick films—that is, scales—form at a rate parabolic with time. The parabolic rate was shown to be very simply deducible from diffusion laws, assuming that the limiting oxygen (or metal) concentrations on the inside and the outside of the scale remain constant during oxidation, but the exponential rate for temper films remained, and still largely remains, inexplicable.

The work of Evans and his coworkers* in the following period on oxide films on metals has become a classic. Evans and others showed that all metals that oxidize in air form a film at ordinary temperatures, and that this film is of essential importance in determining the behavior of the metal, especially its electrochemical and corrosive behavior. Evans was able to separate the film from the metal, and to study it. Most of his work concerns corrosion, a subject which, though allied to physical metallurgy, cannot be considered in this account. Reaction films other than oxides were studied, and their formation shown to be entirely analogous. Much of the difficulty in studying the rate of formation of thin oxide films lies in the uncertainty in the method used for measuring film thickness; optical methods have been favored, but have interpretive difficulties (Evans, *op. cit.*); and more direct methods have been employed; the subject has, by slow degrees, reached today a fairly satisfactory state; optical methods are evidently now valid (Lustman,¹¹⁸) and direct gravimetric methods have been developed to a satisfactory point.¹¹⁴

* These papers are very numerous. They are all listed and reviewed in *Metallic Corrosion, Passivity and Protection*, by U. R. Evans. London, 1937. Arnold and Co.

Scaling

Pilling and Bedworth, in 1923,¹¹⁵ also proposed the parabolic function to express scaling rate, in one of the most important papers in this field. They observed, however, that while some metals, like copper, follow this parabolic behavior, yielding scales which, parabolically, increase in thickness with time at a rate diminishing with the scale thickness, and thus oxidize "protectively," other metals, like calcium, oxidize linearly with time, and thus oxidize "non-protectively." They associated the protective behavior of the oxide scale on copper with the coherency of the scale maintained by the volume expansion accompanying the formation of the oxide, and associated the nonprotective behavior of the oxide scale on calcium with the cracking of the scale occasioned by the shrinkage of volume on scaling. This generalization has been said to have exceptions,¹¹⁶ and the subject requires further study; Gulbransen, and Rhines and Leontis¹¹⁷ recently showed that magnesium, a metal that ordinarily oxidizes nonprotectively like calcium, does in fact oxidize protectively at low temperature.

With an oxide scale recognized as a diffusion layer, it is to be expected that it should exhibit characteristics derivable from diffusion behavior generally. It seems generally true that the number of diffusion layers formed in a system is equal to the number of phases stable at the temperature of diffusion, and that each should increase in thickness parabolically with time. Lustman has studied this, finding it in general approximately true, but occasionally such layers, in a multilayer case, are so thin as to be difficult to detect.¹¹⁸ Recently Hickman,¹¹⁹ employing electron diffraction, finds reaction layers in oxide films and scales containing phases not stable at the temperature of formation. Generally, however, the principle is good, at least in first approximation; Heindlhofer and Larsen¹²⁰ studied the oxidation of iron and found it to exhibit the predicted phases, the layers growing in thickness parabolically with time.

Rate of Oxidation

Diffusion laws would predict that the oxidation-rate constant should increase exponentially with time, that is, should show Arrhenius activation behavior. Dunn¹²¹ showed this to be the case. The activation energy, however, cannot be the same as for diffusion alone, for solubilities changing with temperature are involved; in

fact, few data are available on the rates of diffusion in oxides, and a fully satisfactory quantitative treatment is thus far lacking. Involved also, as noted below, is the identity of the atom that diffuses.

The study of intermediate phases showed that certain lattices are defect lattices; that is, exhibit vacant lattice positions. The phase "FeO" is a notable example. Such phases have been shown to depart from stoichiometric proportions to a degree that the ostensible formula cannot be applied; familiar phases, such as "FeO"¹²² and "CuAl₂"¹²³ fall in this category. "FeO", possessing vacant lattice sites of iron, might be expected to show a more rapid diffusion rate for iron rather than for oxygen. Could growth of such a scale result from the diffusion of iron rather than of oxygen atoms, as instinctively assumed? Pfeil,¹²⁴ in studying the rate of oxidation of iron, adduced experimental evidence to this effect; and the same circumstance seems to apply to Cu₂O. It may be very widespread.

Wagner and Schottky,¹²⁵ working in the parallel field of the electrical behavior of solid salts, showed that the electrical (electrolytic) conductivity is associated with rates of diffusion, and, by studying ionic transport, formalized the theory of the diffusion of defects and oxidation rates.¹²⁶

The rate of formation of thin films displays many peculiarities, not yet resolved by theory.¹²⁷ It was shown in 1934¹²⁸ that oxide layers bear a fixed orientation relationship to the metal crystal on which they form, as had been anticipated earlier from the topographical geometry of scales. It might, then, be expected that the rate of oxidation would vary with the crystal face oxidized, and this has been shown to be so. Thin films of Cu₂O on copper form at quite different rates on different crystal planes;¹²⁹ these rates, disappointingly, vary with orientation in a complex and inexplicable fashion; and, moreover, the variation with orientation does not remain the same as the temperature varies—the matter is unresolved at this writing; and, finally, the exponential plot of the rate of film formation on copper shows two branches, of uncertain significance. Not all films on metals grow exponentially with time, however; theory is not in good shape, and the field requires reexamination.¹³⁰

Oxidation of Alloys

The metallurgical engineer, of course, is primarily interested in the oxidation of alloys, for experience has long shown, especially

with the stainless steels, that alloying is necessary to improve oxidation resistance. There have been many studies of the oxidation of alloys, particularly those by Dunn,¹³¹ who found small percentages of aluminum very greatly to decrease the rate of oxidation of alpha brass; by Portevin, Pretet, and Jolivet,¹³² who studied the oxidation behavior of iron with alloy of chromium, silicon and aluminum; and by Fröhlich,¹³³ on copper-base alloys. The phenomena are exceedingly complex: concentration gradients occur in both metal and scale; occasionally only the solvent oxidizes, as in the copper-tin alpha solid solutions. It is clear, as it has been for some time, that oxidation resistance is conferred by alloying with a metal of greater oxidizability, and this remains a useful principle in practice—the oxidation resistance is imparted by the characteristics of the initial film, not directly by the properties of the metal or alloy.

Arguing from Wagner and Schottky, Price and Thomas¹³⁴ proposed that to give good oxidation resistance to an alloy a metal should be added, which, when appearing on the surface as an oxide would have a high electrical resistivity. Their immediate problem related to preventing the tarnishing of silver; they recognized that films of Al_2O_3 or BeO would have the desired electrical characteristics (that is, diffusion characteristics) and proceeded to create these films by oxidizing dilute silver-aluminum and silver-beryllium alloys in mixtures of water vapor and hydrogen; the result is a product of very low tarnishing tendency. The creation of such films on this and other materials, and their tendency toward or against self-repair constitutes an important part of corrosion science (cf. Evans, p. 37). The effect of mixed atmospheres presents a new series of complications, from which generalizations issue reluctantly.¹³⁵

The fact that scaling is accompanied in some cases by diffusion of oxygen into the alloy itself, with reaction there to oxide of the more readily oxidizable solute, was recognized some years ago. This "internal oxidation," proceeding by the growth of a layer inward in which all solute is oxidized (called the "subscale") has been subjected to careful analysis by Rhines,¹³⁶ who, studying many alloys, showed the rate of inward growth of the "subscale" to follow diffusion laws.

DECOMPOSITION OF AUSTENITE

Under this heading will be included all matters relating to the heat-treatment of steel.

Supercooling

Following the work of Osmond on the critical points, Howe and Levy,¹³⁷ in 1916, studied the A_{r1} point of a eutectoid steel, as varying with the rate of cooling, and with the temperature to which the steel had been heated initially. They demonstrated that the points of recalescence occur at lower temperatures the faster the rate of cooling, and that this curve of recalescence temperature versus cooling rate lies at a higher temperature the lower the temperature of austenitizing. They observed that the higher the A_{r1} point, the coarser the pearlite, as Stead had observed earlier.¹³⁸ This indeed is the upper part of what we now call the quenching S-curve; further pursuit along these lines might well have led to the full S-curve at this early date. The austenitizing temperature was conceived as affecting the homogeneity of austenite, and thus in turn the A_{r1} temperature; this, of course, is true in part, but the effect of austenitizing temperature upon austenite grain size was missed.

Split Transformation

The next important step was that taken by Dejean¹³⁹ and Portevin and Garvin.¹⁴⁰ These workers extended the work of Osmond, using steels varying in carbon from 0.10 to 1.45 per cent. They made precision determinations of the critical temperatures, from A_{e1} to room temperature, at differing cooling rates obtained by varying the size of the specimen cooled. They reaffirmed Osmond and Howe on the effect of the rate of cooling upon A_{r1} . They observed that the formation of martensite is manifested thermally at a low temperature; and they discovered the "split transformation," on which both pearlite and martensite form, and the critical quenching velocity—that at which pearlite is just avoided. They measured depth of hardening by cooling rounds of different diameter at a constant cooling rate—a phenomenon later to be analyzed quantitatively by Grossmann. And they observed the effect of carbon and of manganese in decreasing the critical quenching velocity. In 1924, French and Klopsch¹⁴¹ studied this split transformation, and the effect of quenching media, in detail.

Chapin¹⁴² continued these studies, directing attention particularly to the rate of the reaction between the pearlite and the martensite points, and found a very slow rate of decomposition of austenite

just above the martensite point, employing the appearance of ferromagnetism as a criterion of decomposition. This work, and the preceding, especially that of Portevin, set the stage for work on the isothermal decomposition of austenite.

S-curve—Principles of Hardenability

The extraordinarily fruitful work on the isothermal decomposition of austenite was undertaken by Bain and his collaborators, especially Davenport, in the year 1929. Davenport and Bain¹⁴³ adopted a method of quenching small pieces directly into a thermostated lead bath, following the course of the reaction either continuously by the use of a quenching dilatometer or by successive removal of small pieces for quenching and planimetric evaluation of the extent of reaction. The course of the reaction, plotted on a temperature-time diagram, produced the now familiar S-curve, recently somewhat more properly described as the TTT-curve (the time-temperature-transformation curve). Bain demonstrated the relationship of this curve to quenching, to hardenability,¹⁴⁴ and showed that the effect of austenite grain size upon hardenability, as demonstrated by McQuaid,¹⁴⁵ lay in the displacement of the S-curve toward longer reaction times, owing to the circumstance that pearlite nucleates at austenite grain boundaries; and he showed, in this and in later publications, the effect of alloying elements in displacing the S-curve toward longer times of reaction, thus providing deeper hardening. Much work was done on the principles controlling grain size; as McQuaid noted, "killing" with aluminum was found to give fine austenite grain size.

Grossmann, in 1933,¹⁴⁶ demonstrated that fine-grained hypoeutectoid steels on heating in the austenite range encounter a temperature at which they rapidly coarsen. It has been customary to ascribe the influence of aluminum deoxidation in controlling grain size to the grain-growth-inhibiting characteristics of alumina, though the evidence leaves much to be desired.

It may be said that Bain derived the rules of hardenability.¹⁴⁷ Davenport later¹⁴⁸ extended this work to alloy steels, finding that a simple S-curve may be modified into a double S, with two "knees" of rapid reaction. The constituent formed below the pearlite "knee," not readily obtainable on simple quenching of unalloyed steels, though familiar in alloy steels, has now come to be known as

“bainite.” This work has made it possible greatly to simplify the nomenclature of steels, previously a badly muddled subject.¹⁴⁹ These workers appraised depth of hardening by hardness traverses in rounds, a method used later by Grossmann, but now largely superseded practically by the simpler end-quench method of Jominy and Boegehold.¹⁵⁰ Shepherd, in 1934,¹⁵¹ has developed the P-F test for tool steels, measuring at once the penetration (depth) of hardening and the grain size on fracture, a clear appreciation of the importance of austenite grain size.

The extensive work of Wever and his colleagues,* undertaken nearly simultaneously with that of Bain, need not be pursued here in detail; it followed similar lines, though somewhat more narrowly. Electrical and magnetic methods were employed to measure the extent of reaction. The form of reaction curves derived were similar to those of Bain. Wever undertook the study of alloy steels earlier, finding the two “knees,” and observing the phenomenon of incomplete reaction noted since by Bain’s followers. Strangely, grain size was not considered as a variable affecting the reaction rate. Robertson¹⁵² published simultaneously with Bain upon somewhat similar subjects, though his excellent work was brief and not so quantitative as that of Bain.

The past 20 years has seen an extraordinary interest in hardenability and related topics. As a result of the work on S-curves, the whole subject of the heat-treatment of steel has been rationalized, set into a form that permits quantitative treatment. Bain’s work marked the beginning of a new epoch in the old subject of the heat-treatment of steel.

Burns, Moore and Archer¹⁵³ demonstrated that the hardness of martensite (as contrasted with the depth of hardening) is dependent upon the percentage of carbon only, and varies little with carbon above 0.6 per cent, a fortunate circumstance that greatly simplified experimental analysis. Janitsky and Baeyertz¹⁵⁴ showed that the tensile properties of all steels are essentially equivalent; that is, if a steel is fully quenched and tempered to the same hardness or yield strength as another, all tensile values are the same in the two steels. Apart from the variation in heat-treatment needed to get the same hardness or yield strengths, heat-treating steels are thus essentially equivalent in their ability to develop the common tensile properties; selection among steels must be made and is made upon other bases.

* Published in the *Mitteilungen K-W-I Eisenforschung*, 1930 ff.

Depth of Hardening

The factors of chemical composition, of grain size, and of the quenching power of quenching media, were subjected to detailed and quantitative analysis by Grossmann, Asimow and Urban¹⁵⁵ and by Grossmann,¹⁵⁶ in several papers, which, with the earlier ones of Bain, constitute the modern classics in this subject. Both groups of papers have led to innumerable others—that acid test of quality. Particularly is this true with respect to the detailed study of reaction characteristics and microstructures of a wide selection of heat-treating steels, as revealed by isothermal studies, and with respect to a detailed study of the chemical factors which determine the depth of hardening, a subject that Grossmann has placed upon a true scientific and engineering basis, taking the final step to remove it from art.

Martensite

The formation of martensite had long been studied by the use of cooling curves, by Portevin in 1919,¹⁴⁰ French in 1930,¹⁴¹ Esser and Eilender in 1930,¹⁵⁷ Wever and Engle in 1930,¹⁵⁸ and others. This work, and that of Carpenter and Robertson in 1939,¹⁵⁹ showed that the temperature of martensite formation is not influenced by cooling velocity, and, indeed, does not form isothermally, but only upon temperature decrease. Greninger and Troiano¹⁶⁰ developed this point in detail, devising methods to determine the martensite point with precision, which have proved of great usefulness. In the hands of Payson and others, the effect of alloying elements upon the martensite point has been determined,¹⁶¹ with both the temperature of the start of martensite formation and of the finish ascertained. This work provided an important modification of the lower portion of the TTT-curve. The acicular martensite, forming by a shearing process from austenite, appears to form “needle” by “needle” (actually plates) with great velocity; very probably in a time period less than 0.002 seconds.¹⁶²

Crystallography

Osmond had shown the cubic characteristics of ferrite and austenite. Apart from Belaiew's¹⁴ contribution to the crystallography of the segregation processes in austenite, little progress was made or

could be made until X-ray diffraction methods became available. Hull,¹⁶³ in 1919, showed the lattice of alpha iron to be body-centered cubic. In 1922, Westgren and Phragmén published the first of their important contributions to the lattice structures of alloys, and showed that alpha, beta and delta iron are all body-centered cubic, whereas gamma iron is face-centered cubic, and that the solid solution austenite is an interstitial solid solution.¹⁶⁴ The recognition that alpha and beta iron have the same lattice structure, and that any density difference between them is so slight as to be uncertain, led to the final abandoning of the beta-iron hardening theory, and beta iron became recognized as a nonferromagnetic form of alpha iron, with A_2 as a magnetic change (spread over a temperature interval) and not as an ordinary phase change.

In 1929, Fink and Campbell¹⁶⁵ discovered that the lattice of the martensite "needle" is body-centered tetragonal, a slightly distorted form of alpha iron, presumably distorted by the presence of unrejected carbon atoms. In discussion to this paper, Bain proposed an atomic-crystallographic mechanism by which gamma iron may transform to martensite and to alpha iron, the first suggestion of a transformation mechanism.*

Studies on the Widmanstätten structure, carried out in the early part of this century by Belaiev,¹⁶⁶ were undertaken anew in 1930,¹⁶⁷ with a view to determining the atomic-crystallographic mechanism by which solid-solid transformations occur. In 1933, the observation by Belaiev¹⁶⁸ that ferrite forms on the octahedral planes of austenite was completed by a determination of the orientation of the ferrite lattice with respect to the austenite lattice, information from which the mechanism of atom movement during transformation can be derived. Kurdjumow and Sachs, in 1930,¹⁶⁹ had subjected martensite to such an analysis, showing the orientation relationships and indicating the sets of shearing processes by which the austenite lattice may be converted into the martensite lattice. Pearlite and bainite were subjected later to a similar analysis, with the result that bainite and martensite,¹⁷⁰ and proeutectoid ferrite, were found to bear one relationship, whereas pearlite was found to bear a quite different relationship, which was interpreted to mean that pearlite is nucleated by cementite—for which there is much other evidence—and bainite

* The mechanism proposed by Bain is now known to be correct, though it is incomplete in the sense that it does not provide the correct number of alpha orientations; cf. Kurdjumow and Sachs.¹⁶⁹

by ferrite. Complete crystallographic analysis by Greninger¹⁷¹ and by G. V. Smith¹⁷¹ of the composition plane along which martensite—and bainite—forms shows that the shearing process is complex, not simply related to the orientation relationships, leaving an unsolved problem.

Nucleation and Growth

The conception that pearlite forms from austenite by a process of nucleation and growth is by no means new. As a heterogeneous reaction, it was implicit in Gibb's work³⁰ that this should be true. Arnold and McWilliam¹⁷² and Benedicks in 1905¹⁷³ stated the fact, and Stead,⁶³ and Howe and Levy³⁹ assumed it; Bain¹⁴⁴ clearly recognized it. Formulation of the isothermal-reaction equation was given in 1939 by Johnson,¹⁷⁴ and detailed experimental measurements on the rates of nucleation and growth by Hull and Colton soon followed,¹⁷⁵ together with a detailed study of the structure and mode of formation of pearlite.¹⁷⁶ The so-called "nodular troostite," formed near the knee of the S-curve, has surrendered to the superior resolution of the electron microscope, and shows itself to be fine pearlite, as Benedicks claimed.¹⁷³ Attempts have been made to explain these rates of nucleation and growth,¹⁷⁴ and though some of the fundamental facts concerning them are being learned, the subject is not yet on firm ground theoretically.¹⁷⁷⁻¹⁷⁸ Nucleation theory¹⁷⁹ is difficult in its application to solid-solid reactions. These studies have been extended by Roberts to the formation of austenite from cementite-ferrite aggregates; and the factor of austenite heterogeneity in hardenability is now on a better quantitative basis.¹⁸⁰ Much remains to be learned concerning the mode of formation of bainite.

Tempering

The process of tempering of martensite, studied by Kurdjumow and Sachs¹⁶⁹ by X-ray methods, has been subjected to minute study by Cohen and his collaborators, with the discovery of a transition lattice between the tetragonal martensite and the final ferrite, and with new facts concerning the stability of martensite and austenite on tempering.¹⁸¹

AGE-HARDENING

A decrease in terminal solid solubility with decreasing temperature was not an unthought idea in the early part of this century; Roozeboom³⁶ drew binary temperature-composition diagrams exhibiting it; Roberts-Austen³³ demonstrated the decreasing solubility of Fe_3C in gamma iron with temperature; and Goerens' text¹⁸² on metallography, published (in English) in 1908, shows several *t-c* diagrams which exhibit decreasing solubility with temperature. The study of such systems, some of which are now known to age-harden substantially, did not, however, disclose the age-hardening phenomenon, presumably because the thought did not occur to the workers that quenching followed by aging might produce desirable property changes.

In 1906, Alfred Wilm, in an attempt to produce an aluminum alloy that might compete in strength with brass, added 0.5 per cent magnesium to an aluminum alloy with 4 per cent copper and small amounts of manganese, and quenched from 520°C . An immediate determination of the Brinell hardness gave disappointing results, but an intruding week end delayed further hardness testing; on continuation of the testing it was found that the hardness had assumed a much higher value as a result of the intervening aging. This work, published in 1911,¹⁸³ was the first disclosure of the phenomenon of age-hardening.*

Early Precipitation Theory

The fundamental cause of the age-hardening of duralumin was unknown to Wilm (who was unable to find any structural alteration under the microscope), and remained unknown until the work of Merica, Waltenberg and Scott¹⁸⁴ in 1919. These workers demonstrated the decreasing solubility of copper in aluminum and proposed that age-hardening results from precipitation, suppressed by quenching and occurring on aging after quenching. The aging process was not, however, accompanied by any microscopically visible precipitation, with the techniques employed at that time, and it was postulated that the precipitate particles are submicroscopic

* R. F. Vines and E. M. Wise (Symposium, Age Hardening of Metals, American Society for Metals, October 1939) report that the art of age-hardening was practiced earlier with precious metal alloys, though apparently without clear recognition of the essential steps of annealing, quenching, and aging.

in size, blocking slip, and therefore hardening, by reason of their number and by reason of their interaction with the matrix. The essential part of this theory is that of the requirement of decreasing solubility with decreasing temperature. No finer example occurs in the history of physical metallurgy of the importance of theory to practice. Following Wilm, and up to the time of Merica, Waltenberg and Scott, very little progress was made in this field, for it was not clear what alloys might be expected to show age-hardening behavior; following the development of the theory, progress was very rapid, for the theory defined the necessary conditions, and the search for new age-hardening alloys became susceptible to intelligent approach.

Complexities

The initial difficulty with the theory lay in the fact that no evidence of precipitation could be obtained microscopically, and theories were developed that discarded the conception of submicroscopic precipitation and instead postulated a process of pre-precipitation association of solute atoms. This latter idea received ostensible support from the type of property changes that accompany age-hardening, changes that were viewed as anomalous for simple precipitation.

In 1920, Fraenkel¹⁸⁵ observed that the electrical conductivity of duralumin on aging at low temperatures decreases instead of increases as the decomposition of a solid solution requires. In 1926, Schmid and Wasserman,¹⁸⁶ and later, in 1930, v. Göler and Sachs,¹⁸⁷ discovered that the lattice constant of quenched duralumin does not change during the period when marked hardening occurs. And in 1930, Tammann¹⁸⁸ noted that the intensity of magnetization of copper-iron alloys does not increase during aging, when, presumably, ferromagnetic alpha iron is precipitating. Hengstenberg and Wassermann,¹⁸⁹ in 1931, obtained diffraction effects from aging alloys that were interpreted as indicating an aggregation of the solute atoms in the aging solid solution rather than a precipitation. Fraenkel,¹⁹⁰ in 1929, demonstrated that age-hardening produced on incomplete low-temperature aging is partially lost on subsequent aging at a higher temperature, the so-called "retrogression phenomenon," which led to the assumption of a fundamental difference between low-temperature and high-temperature aging, with the low-

temperature aging held to be different from "simple" precipitation. The occurrence of double (or triple) peaks on the age-hardening curve¹⁹¹ has been regarded as anomalous and frequently has been cited as evidence for complicated mechanisms of precipitation. For a time those theories of pre-precipitation association of atoms prior to precipitation held sway; Merica¹⁹² accepted them, at least tentatively, in 1932, describing the pre-precipitation aggregates of solute atoms as "knots," ascribing hardness to the slip interference which they were presumed to afford.

Resimplification of Theory

In 1936, Fink and Smith restudied the complexities of age-hardening behavior, reporting in a series of papers¹⁹³ that have done much to simplify thought in this field. They employed the best of metallographic technique and were able to demonstrate the onset of a microstructural alteration in the early stages of hardening, and thus concluded that the inertness of the lattice parameter to aging change can signify only that change in the lattice parameter is "no criterion of precipitation"; they showed that double aging peaks can result from a heterogeneity in the aging process—the aging process proceeding more rapidly in some regions than in others, providing overlapping hardening curves and thus multiple peaks; and they regarded the other "anomalies" as resulting from a very fine precipitate particle size accompanying "simple precipitation." This latter point of view was becoming the conventional one in this period. Masing and Koch¹⁹⁴ showed that there is no clear distinction between "hot" and "cold" aging, that the phenomenon of retrogression occurs whenever the temperature is raised and is thus dependent only upon temperature change, not upon absolute temperature.

Transition Structures

Renewed studies of the aging process by X-rays furnished several new points of view. In 1935, Wassermann and Weerts¹⁹⁵ discovered the occurrence of a transition lattice, intermediate between the lattice of the matrix and the equilibrium precipitate "CuAl₂," which Fink and Smith¹⁹³ showed to bear a simple geometrical relationship to the matrix lattice.

In 1937-1938, Guinier and Preston independently¹⁹⁶ showed the occurrence of streaks of Laue patterns during the hardening of age-hardening alloys, which indicated the occurrence of aggregates of atoms of the solute (possibly with atoms of the solvent) concentrated upon certain matrix lattice planes, the so-called "Guinier-Preston zones." These aggregates, on further aging, were observed to grow to a size that would afford three-dimensional diffraction. These zones apparently are the early stages of the transition lattice of Wassermann.

Strain Theory

The systematic studies of the Widmanstätten structure in age-hardening alloys, undertaken initially to throw light on the age-hardening problem,¹⁹⁷ had demonstrated that precipitate lattices have a simple orientation relationship to the parent lattice. The work of Wassermann and that of Guinier and of Preston, combined with this, presented a body of evidence upon which present-day age-hardening;¹⁹⁸ the loss of coherency implies the loss of hardening. lattice alteration, in which precipitation is conceived as beginning when the lattice movements begin that will, when completed, convert the matrix to the equilibrium precipitate; in the early stages these small regions are held in lattice coherency with the matrix, which in some cases requires the occurrence of a transition lattice, and this forced coherency produces strain, which is the cause of hardening;¹⁹⁸ the loss of coherency implies the loss of hardening. Subsequent research by Geisler appears to confirm this conception¹⁹⁹ and begins to provide ideas concerning the factors that in some systems afford great hardening, even when the solubility change with temperature decrease is small, as in alpha iron-carbon, and in others only slight hardening even when the solubility change is great, as in magnesium-tin. The analysis of the strain is not simple, though the studies of Mott and Nabarro²⁰⁰ are beginning to resolve this problem. This, of course, is a departure from the older ideas of simple particle dispersion-hardening, in which hardening was attributed to simple geometrical obstruction without particle-matrix interaction.

The number of age-hardening alloys developed since Merica's first paper is great. Low-melting alloys, such as lead-calcium, will age rapidly at low temperatures; high-melting alloys, such as copper-

beryllium, iron-molybdenum, and iron-tungsten, require high temperatures for age-hardening.²⁰¹ Stainless steel can be modified to produce age-hardening.²⁰² The possibilities of producing age-hardening are ubiquitous, and the phenomenon can thus be invoked by the metallurgist in alloy development with remarkable freedom. For many complex age-hardening alloys the constitutional changes involved in precipitation are but poorly understood; for instance K-monel. Since very small solubility changes can cause great effects in some cases, the phenomenon thus frequently occurs when least suspected.

Blue Brittleness

Early studies on the effect of working at elevated temperatures, or of tensile testing at those temperatures, disclosed a characteristic brittleness in steel in the neighborhood of 250°C—the “blue-brittleness” phenomenon. It was observed by LeChatelier²⁰³ in 1909 and by Reinhold²⁰⁴ in 1917 that the temperature range of blue brittleness as shown in the tensile test at elevated temperatures is the lower the slower the speed of elongation; similar results were observed in impact testing, where, in “static” notch-bar tests a brittle range occurred in the neighborhood of 250°C, but in impact tests was observed to be displaced to 550°C,²⁰⁵ a phenomenon studied in some detail by Bauer.²⁰⁶ Early work on the effect of cold-working and aging, either at room temperature or at elevated temperatures, showed embrittlement, as noted early in this account. Fettweiss, in 1919,²⁰⁷ showed that strain aging and blue brittleness are but different aspects of a strain-aging process: that on tensile testing at 250°C the aging process is rapid enough to take place during the test; at lower temperatures the time is inadequate, and at higher temperatures the time is sufficient for overaging, thus rendering the temperature of 250°C optimum. Bach and Baumann, in 1921,²⁰⁸ showed that full tensile curves taken in the blue-brittle region display a characteristic jaggedness, which was explained as rapid strain aging on successively active slip planes. Fry²⁰⁹ showed that the results of strain aging in the interior of a piece of steel could be revealed by proper etching.

Quench Aging

Over-strain aging appeared to bear some relationship—though a difficult one to define—to quench aging. Many of the phenomena of strain aging are those that would be expected from an ordinary age-hardening process. Fry's etching agent acts equivalently on specimens strain-aged or quench-aged. It has been assumed that the solid solubility of a constituent is decreased by cold-working, providing a precipitation potentiality, or that straining greatly accelerates precipitation.

The nature of the aging agents in each of the two cases, however, still remains somewhat uncertain. Generally it has been usual to ascribe quench aging to the precipitation of iron carbide. Pfeil²¹⁰ observed over-strain aging in steels extremely low in carbon, and reasoned that the aging agent must be oxygen; this point of view received ostensible support from the development of deoxidation techniques for the manufacture of steels with low over-strain aging sensitivity, as in the case of the product Izett, and a latter product.²¹¹ But despite careful recent studies²¹² the question is not satisfactorily resolved.

CRYSTAL STRUCTURE

The study of the structure of metals and alloys in the first two decades of the present century was restricted to the use of the methods of the older crystallographers—observations and measurements of the form of idiomorphic or natural crystals, of etch pits, of various deformation structures such as twin bands and slip lines, in which geometrical symmetry principles were employed. These methods yielded much information, as employed by Osmond, Belaiew, Mügge, Ewing and Rosenhain, and others, as noted in the foregoing pages. These methods are limited, though still very usefully employed for many purposes. The discovery and application of X-ray diffraction methods greatly stimulated the field.

X-ray Diffraction

In 1912, following a discussion in a seminar on the nature of X-rays, Max von Laue had his student Friedrich pass a beam of white X-ray radiation through a crystal, and observed that the beam

formed diffraction spots on a photographic plate held behind the crystal, at once proving that X-rays were light waves, and providing a method for the determination of lattice structure.²¹³ W. H. and W. L. Bragg,²¹⁴ in England, immediately undertook the study of this phenomenon, devising new techniques and doing much to clarify the principles of the method. In 1917, Hull²¹⁵ in this country and Debye and Scherrer²¹⁶ in Germany invented the very useful powder method of crystal analysis, which in time was to constitute the most useful method of crystal-structure analysis for metallurgists. Development in techniques and methods followed rapidly, methods that permitted the full determination of the structure of any of the 230 space groups.

Structure of Alloys

The lattice structures of the common metals were shortly determined, and early light was cast upon the problem of the relationship of the behavior of metals to their lattice structure. Bain, in 1923,²¹⁷ undertook the study of alloys, particularly solid solutions, discovering superlattices, demonstrating the maintenance of the solvent lattice type in primary solid solutions, and the variation of the lattice spacing with variation in solute concentration. Westgren shortly entered this field, and with his coworkers studied the structure of a wide range of alloy systems.²¹⁸ The similarity of the phase diagrams of the alloys of copper (and of silver and of gold) with the metals of the B-subgroups in the periodic table—zinc, cadmium, aluminum, tin, etc.—had been recognized in the early days of the century. Westgren showed that these systems, the so-called “structurally analogous” systems, exhibit the same lattice types for corresponding phases (the beta, gamma, etc., phases); he determined the lattice structures of many intermediate phases, some of which are so complex that they did not surrender easily to analysis. Information on lattice structures and dimensions built up rapidly by the labors of a very large number of investigators—X-ray diffraction became fashionable! Intermediate phases received much attention, as in the work of Hägg on borides, nitrides, carbides, hydrides;²¹⁹ and intermediate phases in metallic systems responded to study, with a great increase in factual knowledge. The classic argument of Dalton and Berthollet on the law of definite proportions was remembered, and Berthollet supported the observation that inter-

mediate phases are often not stoichiometric, nor of a single composition, but with a range of composition.

Structural Analogies

The determination of the lattice types of alloy phases, chiefly by Westgren, was taken by Hume-Rothery and rationalized on the basis of atomic structure. Hume-Rothery showed that the structurally analogous phases are characterized by a fixed ratio of the number of atoms and the number of valence electrons present.²²⁰ He also showed that the extent of terminal solid solubility is related to the relative atom sizes, to chemical affinity effects between the unlike atoms, and atom-valence-electron ratios; and extended this direction of thought to a consideration of the intermediate phases, the somewhat misnamed "intermetallic compounds," and to solidus and liquidus temperatures.²²¹ The studies on intermediate phases have been extended by many others, especially Norbury²²² and Preston.²²³ Jones²²⁴ invoked the new electron zone theory of metals in an analysis of the factors determining alloy composition.

Iron Alloys

In 1931, Wever, interested in the fact that certain elements when alloyed with iron widen the gamma field whereas others narrow it, showed that this behavior is related to the position of the elements in the periodic table; group VIII metals widen the gamma field; the alkali and alkaline earth elements are insoluble; and most of the intermediate elements narrow the field.

The application of X-ray methods has given an immense body of information concerning the nature of metals and alloys, growing by degrees, and much not readily assignable to a few individual workers: the nature of substitutional and interstitial solid solutions; methods for the determination of alloy constitution including solvus curves; techniques for the determination of preferred orientation, and for the determination of strain; the nature of cold-worked metals, and of imperfections in crystals; mechanisms of transformation and precipitation in the solid state; methods for the analysis of phase constituents, especially carbides in alloy steels and in carbide tool materials; etc. The major items in this group will be noted in the appropriate sections.

Constitution of Alloys

Methods for the study of alloy constitution were developed and established rapidly in the early part of this century. The relationship between electrical conductivity and constitution was formulated by LeChatelier²²⁵ and by Guertler,²²⁶ on the basis of the early work by Matthiessen and the later by Kurnakov and Zemczuzny.²²⁷ Apart from the development of X-ray diffraction for this purpose, the subject was developed to a point of maturity, and attention was given to details, especially by Rosenhain, in order to increase accuracy. The investigation of the constitution of alloy systems remains extremely laborious, and no method that will afford substantial saving in time and effort has appeared. Despite great volumes of work on the constitution of alloys, the information on many important systems is distressingly inadequate; for example, the alloy steels.

Distribution of Microconstituents

Microstructural studies of the distribution of constituents in alloys, resulting either from the freezing process or from constitutional changes in the solid state, have grown in this century by slow accretion. The matter is of fundamental concern in the consideration of the mechanical properties of metallic materials; it cannot be reviewed in brief compass here. Nor can the extraordinary development of alloy compositions, of heat-treating steels, heat-resisting alloys, age-hardening alloys, both nonferrous and ferrous, stainless alloys, tool compositions, nitriding steels. The use of sintered and bonded carbide compositions for tool materials should be noted; for example, Widia, first invented in Europe and developed in this country;²²⁸ and the great growth of powder metallurgy from its early origins over a century ago should be mentioned; though the techniques are new, no new metallurgical principles are involved.

Superlattices

Solid solutions have usually been considered as exhibiting purely random distribution of solvent and solute atoms. In an attempt to explain the phenomenon of "resistance limits"—the abrupt change in a solid solution, with increasing concentration, from one that will

completely resist the attack of an acid to one that will completely surrender to it—Tammann,²²⁹ who discovered this phenomenon and studied it in detail, postulated a departure from this randomness, with atoms taking “ordered” positions to each other. Subsequent study showed Tammann’s theory inapplicable,²³⁰ the phenomenon originating in a different cause—yet ordering does take place in some alloys. Bain, in 1923,²³¹ observed extra diffraction lines in the copper-gold system, “superlattice lines,” explicable on the basis of an ordering of copper and gold atoms, with these atoms forming interpenetrating superlattices. This was confirmed by Johansson and Linde²³² in 1925.

Since then superlattices have been found in other systems. Continued study, especially by the physicists, has disclosed the details of these; since their formation involves a change from a disordered to an ordered distribution, and their destruction on heating involves the reverse process, the subject is frequently designated as “order-disorder.” In some cases the formation of superlattices involves no change in lattice symmetry, but only in order, whereas in others a change in symmetry also is involved, and at times this is substantial. In the extreme case it is difficult to distinguish the ordering process from true phase changes.

The theory has been considered by a host of workers, including Bragg and Williams,²³³ and Bethe.²³⁴ These theoretical studies have considered the interaction energy between like and unlike atoms, and methods have been derived to determine the degree of order. This order is now recognized as of two types, “long-range” and “short-range.” The short-range order may exist at temperatures above the familiar critical temperature for the decomposition of the superlattice, giving a departure from randomness; indeed, evidence is accumulating that departure from randomness is to be considered the rule.²³⁵ Continued work has provided a large body of information in the property changes accompanying ordering. At the time of this writing it is conventional to speak of order-disorder changes as distinct from ordinary phase changes, and not, in this sense, similarly subject to the principles of heterogeneous equilibria.

Electron Diffraction

The diffraction methods for the determination of lattice structure were greatly augmented when Davisson and Germer,²³⁶ in

1927, demonstrated that lattices will diffract an electron beam. This method is alternative to the X-ray method for studies of ordinary structure (though much more difficult), but bears a special advantage for the study of very shallow layers—films, or surface layers—owing to the fact that, in contrast to the X-ray, the electron beam penetrates only a few atom layers and accordingly the diffraction result originates in a thin layer only. This makes the method awkwardly sensitive to surface films in ordinary work: and, conversely, constitutes it an excellent method for studying those films. Using it, workers, especially in the school of G. I. Finch,²³⁷ have studied the nature of the polish layer, of diffusion in the polish layer, of pseudomorphism in deposited layers. The results obtained in these fields are noted in other sections.

Advances in Microscopy

Advances in the microscopy of metals since 1900 have consisted chiefly in the improvement of microscopes and of polishing and etching techniques. In 1926, Lucas²³⁸ applied ultraviolet light, and described the best technique available at the time, procuring higher resolutions than were possible before. This technique advanced in 1935 with the introduction of electrolytic polishing by Jacquet and Rocquet.²³⁹

The electron microscope, developed in this country by Zworykin (there were parallel developments in other countries), in which a superior resolution has clearly been attained, found ready application to the study of the structures of metals and alloys. For such purposes, the use of replicas is necessary, for the method requires that transmission photographs be made. The limit of theoretical resolution has not nearly been approached in metal micrography; the electron microscope, already proved of value,²⁴⁰ will benefit greatly when a reflection design, not requiring replicas, becomes available.

PLASTICITY OF METALS—MECHANICAL METALLURGY

The beginning of the twentieth century saw this subject in a very active state of development. Among conventional metallurgists there was, however, then, even as to some degree now, a predilection to regard physical metallurgy as consisting nearly exclusively of the

study of microstructure (though metals are never used simply because of their possession of a certain type of microstructure!). Mechanical metallurgy grew as a somewhat independent strain, though with increasing cross linkages. This large subject we shall pursue by giving brief, separate accounts of the several branches of the subject.

Amorphous Metal Theory

The hardening resulting from cold-work presented, and still presents, a theoretical problem of considerable magnitude. Beilby, following the work of Rayleigh on polish layers, set forth the amorphous-metal theory of hardening in 1911;²⁴¹ he thought that the crystalline arrangement of atoms was not the densest possible (X-ray diffraction had not yet appeared, to yield the true values of packing density), and thus thought the crystalline state to be one of "great mechanical instability," and accordingly of low strength. He conceived mechanical disturbances to destroy the crystalline arrangement, causing momentary melting and subsequent freezing of the molten portions to a rigid, strong structure.

Rosenhain²⁴² supported this view and extended it,²⁴³ assuming that the last traces of metal to solidify on freezing are equally attracted by competing grains, and, in this state of balance, form an amorphous intergranular layer which serves to bond the crystals together, providing grain-boundary strength. This hypothesis is hard to confirm or deny, for it assumes a condition characterized by the absence of a quality, that is, crystallinity. When X-ray diffraction became commonly available, it was soon found that the most drastically worked metals give diffraction, showing at least that most of the metal is crystalline; but this also does not prove the absence of substantial amounts of amorphous metal. The argument has been revived in recent years upon the use of electron diffraction for the study of polish layers—for electrons penetrate much less than X-rays and thus will successfully examine the most drastically worked outer surface of the polish layer—Finch²⁴⁴ reporting that success in the preparation of polish metal with no diffraction, and Germer²⁴⁵ disputing the validity of the argument. Cochrane²⁴⁶ was able to prepare thin films of polished gold which gave no crystalline electron diffraction. Modern tendencies have been to assume great distortion and strain as the primary cause of work-hardening, picturing the

effect of slip in distortion as creating grain fragmentation and finally creating a crystalline debris.*

Nature of Cold-work—Slip Interference Theory

Work on the plasticity of single crystals soon began to give information on the processes of lattice movement accompanying distortion, and provided evidence for lattice rotation and for the creation of internal strains. Ludwik²⁴⁷ believed the source of work-hardening lay in lattice distortion, whereas Heyn²⁴⁸ conceived internal stress as the prime factor. Studies on line widening have led Wood²⁴⁹ to assume that cold-working does indeed fragment metal grains severely, but not below a size of about 1000Å. Struck by Merica's theory of age-hardening, and by the observation of the effect of grain size on the hardness, Jeffries and Archer²⁵⁰ formulated the so-called "slip interference" theory. They accepted much of the Rosenhain amorphous-metal hypothesis, but thought the hardening role assigned to amorphous films to have been exaggerated, believing that the great portion of cold-work hardening originates in the small grain size produced by fragmentation; and they generalized the theory to include all hardening as originating in interference to slip, whether by cold-working, by precipitation, or by alloy structure generally, grain boundaries or particles of a second phase "keying" and thus blocking slip lines. Apart from the general qualitative knowledge that small-grained material is harder than coarse-grained, there was available at this time the careful work of Bassett and Davis,²⁵¹ which had shown the quantitative dependence of Brinell hardness upon grain size in alpha brass. Subsequently, Edwards and Pfeil showed a similar (though smaller) dependence of tensile strength upon grain size in the case of alpha iron²⁵² and Ishigaki for the dependence of hardness of alpha iron on grain size.²⁵³ This dependence is most clearly seen, however, in the comparative tensile and hardness values for single crystals and for aggregates, as shown by Schmid's school.

Lattice Imperfections—Dislocation Theory

The problem was and remains complex. Recent theorizing has been devoted chiefly to the dislocation theory, proposed by Orowan,²⁵⁴

* Desch once remarked that modern theories picture metals so greatly distorted as to be indistinguishable from amorphous!

Polanyi,²⁵⁵ and Taylor.²⁵⁶ This is based upon the original difficulty concerning the strength of metals, which is observed to be far less than theory calculates it to be. Griffith,²⁵⁷ working on glass fibers, showed the predominant influence of fine cracks—imperfections—in causing failure at low nominal stresses. Smekal²⁵⁸ believed crystals are far from perfect, containing departures from perfect lattice geometry originating in the initial growth process, and assuming that regions of imperfection are also regions of stress concentration where flow will be easy. These assumptions have at least in part been supported by Burgers and Koref's²⁵⁹ demonstration of growth imperfections, and by Joffé, who showed that the tensile strength of sodium chloride is increased a hundredfold by measuring under water, which presumably acts to dissolve the surface and remove the surface imperfections.²⁶⁰ This line of attack was extended to form the dislocation theory, which, in a word, provides for the overcoming of the cohesive forces by moving atoms one at a time along a line of stress. This theory, though very fashionable, possibly suffers at the moment from a too great facility and a lack of critical experiments; Masing²⁶¹ believes it inadequate to account for work-hardening. Knowledge of the cold-work condition of metals, unfortunately, is still not deep, and our inadequacies embarrass us in this and other connections, as in the theory of recrystallization.

Work-hardening

The increase of hardness upon cold-working is an old fact. Detailed studies furnished a great deal of quantitative information on this fact, in terms of the new Brinell numbers, and in terms of the tensile values. Meyer,²⁶² in 1918, furnished an analysis of the Brinell hardness which gave an exponent measuring the rate of work-hardening. Analysis of the true-stress: effective-strain diagram, devised by Ludwik,²⁶³ and to receive much attention later, similarly furnished a measure of work-hardening in the slope of the straight section of the curve following the beginning of necking. Early in the century Ludwik demonstrated the effect of the speed of tensile loading on zinc,²⁶⁴ and Stribeck studied the effect of the rate of loading at various temperatures on a modified brass,²⁶⁵ showing the elastic limit and the tensile strength to lie at higher values at the higher rates.

Single Crystals

The development of methods for the preparation of single crystals of metals, near 1920, led to a great volume of very important work; such materials made it possible to study the behavior of the individual grain. This work has been done in many fields, but found perhaps its greatest opportunity in the study of the plasticity of metals. Methods were developed by Tammann,²⁶⁸ Obreimow and Schubnikow,²⁶⁷ Bridgman,²⁶⁸ Czochralski,²⁶⁹ Gomppez,²⁷⁰ and others for the preparation of single crystals from the melt; by Koref²⁷¹ and van Arkel,²⁷² employing deposition from a vapor; by Carpenter and Elam,²⁷³ making use of the principle of critical strain in recrystallization, and by Schaller and Orbig,²⁷⁴ who devised a method involving proper sintering of tungsten powder. Moreover, methods were devised to determine the orientation of single crystals, some employing the new X-ray diffraction methods and others the older crystallographic methods, which made it possible to study the crystallographic details of many processes in a relatively simple way.

Plasticity of Single Crystals

The work done by Polanyi and Schmid was especially notable. These workers studied the behavior of single crystals in great detail, chiefly with zinc, cadmium, tin and bismuth. The sum of their work constitutes one of the most important chapters in physical metallurgy; it shows the great power of systematic research in this field, a lesson that metallurgists apparently need to relearn periodically. Observing that the extension of single crystals produces slip lines, which are ellipses in a round bar, they were able to identify the planes of slip for many metals, and, moreover, to demonstrate that slip takes place in a fixed direction in that plane;²⁷⁵ they showed the occurrence of rotation during slip and of the bending of atom planes; they were able to express work-hardening upon a more fundamental basis than formerly, by measuring the shear stress necessary to continue slip as a function of the amount of preceding shear; they showed the operation of a critical resolved shear stress to initiate slip;²⁷⁶ they demonstrated the effect of velocity of loading upon the tensile properties, and showed the relation of recovery to this;²⁷⁷ and they determined the critical normal stresses for cleavage and for twinning.²⁷⁸ Taylor and Elam took up this work in England;

they similarly derived the critical resolved shear-stress law²⁷⁹ and studied the deformation of aluminum, inventing a new analytical method resting upon a study of the change of outward shape,²⁸⁰ a technique particularly useful on aluminum owing to its multiplicity of slip systems.

This work was paralleled by the definitive work done on twinning in this country by Mathewson,²⁸¹ which afforded a complete analysis of the formation of mechanical twins in iron, zinc, and copper. These studies have been followed by a host of others; information is now available on the active slip, twinning, and cleavage planes for a large number of metals, and also for solid solutions. Whereas simple lattice geometry should provide a prediction of the direction of slip and the consequent lattice rotation in a single grain, the important work of Barrett²⁸² on "deformation bands," observed early, especially by Howe, show that some grains develop lamellae within one grain, with the crystal in alternate lamellae rotating in one direction upon deformation and that in intermediate lamellae rotating in another; this unexpected complication remains largely unexplained.

Preferred Orientations

The generation of preferred orientations as a result of deformation became apparent as a necessary result of the crystallographic mechanism of slip as demonstrated by Schmid, but the recognition of their occurrence preceded this. References may be found far into the nineteenth century of directional properties in wrought materials, though usually these refer to the "fiber" in wrought steel. The presence of preferred orientations in natural rocks was shown by Sander,²⁸³ and their presence in metals was predicated by Lehmann²⁸⁴ and by v. Moellendorf and Czochralski.²⁸⁵ The first determination of preferred orientations appears to be that of Polanyi in 1921 for the limited fiber texture in cold-drawn wires.²⁸⁶ There then followed a great mass of published information on preferred orientations in sheet, in torsion specimens, and in specimens having suffered complex deformation; usually these results were obtained by X-ray diffraction, though other methods have been used—for example, the orientation of etch pits²⁸⁷ and light-reflection phenomena.²⁸⁸ The introduction of the use of pole figures for expressing the results of orientation studies, by Wever,²⁸⁹ now the usual method, assisted greatly in the quantitative treatment of the subject.

Preferred orientations, however, have turned out to be not so simple as was anticipated, for differences occur between two metals whose slip mechanisms appear to be identical.

The occurrence of preferred orientations implies a directionality in the properties, and indeed this is an old fact in the field of the drawing of metals, as, for example, in the formation of ears in drawing brass. Directionality in the strength properties of zinc was recognized in 1906 by Meyer.²⁹⁰ Studies of the correlation of directional properties and of preferred orientations were shortly undertaken; anisotropy in Young's modulus in rolled copper was shown by Goens and Schmid²⁹¹ in 1931 and by Weerts,²⁹² in 1933; and many papers followed on the directionality of the plastic properties, including the common tensile properties:

The recrystallization of materials with preferred orientations was observed frequently to yield a product showing a "recrystallization structure;" there are many data available on this, but the subject is an obdurate one, for the origin of the recrystallization structure in the parent preferred orientation is not clear. This problem, still under active discussion, remains largely unsolved.

Internal Strains

The occurrence of internal strains in metals had been assumed very early in the development of the subject. The work on plasticity clearly showed the occurrence of strains on a microscopic scale, as many had predicted in the last century, particularly in connection with the decomposition of austenite; but grosser, macroscopic strains had also been hypothesized and methods for the relief of stress considered.²⁹³ It remained for Heyn, in 1911,²⁹⁴ to demonstrate and measure these, showing the very substantial magnitude of the macroscopic "Heyn strains," produced by cold-work, and showing that they are additive with external loads and thus important in the behavior of material. Heyn's work led to extensive studies; he wrote, in 1914, on season-cracking; in 1927, Sachs²⁹⁵ devised a sectioning method by the use of which the complete three-dimensional internal stress system can be computed—though many short-cut methods have been invented, including the X-ray method, this remains the only complete method of analysis. Scott²⁹⁶ considered the internal stresses generated in steel by heat-treatment, and Bühler, Buchholz and Schultz²⁹⁷ applied the Sachs method in a systematic study of

the stresses generated by quenching in a series of steels of various compositions.

Impact—Notches

Early in the century the prevalence of notches and their apparent importance in engineering structures, together with the evidence that some materials are peculiarly brittle in the notch test, led to a series of systematic experiments through two decades, by Barba, Fremont, Charpy, Ast, and others, on devising a reliable notch-bar impact test. These experiments were reported by Charpy to the International Association for Testing Materials²⁹⁸ and by Ehrensberger to the German Society for Testing Materials.²⁹⁹ This provided a standardized test (to be followed by that of Izod). Very extensive work showed that the test would distinguish between two steels that are indistinguishable in the tensile test—one of Charpy's tests showed a difference in such a case of 44 to 2.7 mkg. This early work has led, in the intervening years, to much work, in which the variables in the testing method, and metallurgical variations in the materials tested, have been studied, particularly in Germany. The rapid falling off in impact value in steel in the neighborhood of zero degrees centigrade was studied³⁰⁰ and was found, in the early part of the third decade of this century, to be associated with the state of deoxidation of steel,³⁰¹ with killed steels maintaining higher impact values to lower temperatures. The translation of this test to service conditions has remained a point of some uncertainty, but data on the failure of machine parts appear to show a correlation. Notch sensitivity is involved, a matter of importance also in fatigue. Information is still too scanty to correlate impact data with microstructure, though recent work on ordnance materials and on ship plate promise an empirical solution.

Calculations on the theoretical strength of metals show that metals in ordinary tests do not nearly approach the theoretical, presumably because of imperfections, as already noted. Kuntz³⁰² has studied the problem of cohesive strength experimentally by the use of notches of increasing sharpness and increasing depth, hoping to approach a state of uniform three-dimensional stress and thus the ultimate cohesion; but despite voluminous data, the whole problem remains in a state of uncertainty.³⁰³

Fatigue

Studies on fatigue have largely followed the lines of attack laid down in Wöhler's study. In 1900, Ewing, Rosenhain, and Humphrey³⁰⁴ showed the formation of slip bands during fatiguing; Gilchrist³⁰⁵ showed fatigue to occur by progressive fissuring; data have been accumulated on the generation of heat during fatiguing, and on changes in physical and mechanical properties. The plot of the fatigue curve as stress against cycles was modified by plotting the values on double logarithmic plots, by Basquin³⁰⁶ and by Moore and Seely.³⁰⁷ The latter developed many S-N curves for steel, a type of plot that clearly shows an endurance limit for steel³⁰⁸ and the lack of one for nonferrous materials; for example, Monel.³⁰⁹ The early demonstration by Wöhler that fatigue life is adversely affected by notches has been developed, on the one hand by using notches of various design and on the other by studying the effect of surface preparation; that is, by studying the effect of fine notches. The importance of surface preparation was shown by Heyn³¹⁰ and by Leon,³¹¹ and studied by Thomas;³¹² the field of corrosion-fatigue was broken open and exploited by McAdam.³¹³ Despite the great volume of work, good theory has been reluctant to emerge. The origin of the fatigue crack is extremely localized, and it is unlikely that gross measurements will reveal much. One has the feeling that the restriction of materials for study to those of engineering interest has been unfortunate to the development of theory and that an attack on a broader base might more successfully produce the requisite clue.

Creep

The interest in the mechanical properties at high temperature and at differing rates of loading, which was high early in the century, led to the study of creep in metals. Chevenard was an early investigator in this field;³¹⁴ the first tests of long duration were those of Dickensen.³¹⁵ Hanson³¹⁶ contributed important studies on the effect of grain size in aluminum, showing large-grained material more creep-resisting; and Clark and White,³¹⁷ in a long series of studies, identified metallurgical variables affecting creep in steels, including austenite grain size. Creep was shown to occur in three stages, and a mathematical formulation of creep curves has been given by McVetty.³¹⁸ The physics of creep, treated as an activation problem, have been discussed by Kanter,³¹⁹ by Dushman,³²⁰ and by

Kauzman.³²¹ The greatly increased interest recently in alloys for high-temperature service, in the gas turbine, in superchargers, and in rocket propulsion devices, had led to the development of many new and better alloys. This work has been largely empirical; the metallurgical variables of solid solution formation, of precipitation, of grain size, and others, require definitive study. The study of the variables in structure in relation to the mechanical properties has proceeded more by separate and sometimes random observations than by systematic study, with only a few notable exceptions.

Solid Solution Hardening

Rosenhain, in 1923,³²² proposed a general theory of solid solution hardening, relating to the effect of atom size, compressibility, and interatomic attraction upon lattice distortion and thus upon solid solution hardening. This attractive theory has led to surprisingly little direct study of distortion in solid solutions, even admitting the task as difficult. Norbury³²³ related chemical affinity in copper-base alloys, as measured by separation of the component metals in the periodic table, to solid solution hardening, and later showed the electrical conductivity to be similarly dependent upon the effect of chemical affinity.³²⁴ Frye,³²⁵ working with Hume-Rothery, employed the Meyer analysis of the Brinell hardness of silver-base and copper-base alloys in like fashion, producing highly interesting periodic variations. Similar work has been done by Lacy and Gensamer³²⁶ on iron-base alloys, utilizing the true-stress:effective-strain diagram. The work on the plasticity of single crystals provided results on solid solution hardening in terms of the critical resolved shear stress for slip, by Rosbaud and Schmid³²⁷ for the terminal solid solutions of cadmium and tin in zinc, and by Sachs and Weerts³²⁸ for the isomorphous system silver-gold. Admittedly, the variations of mechanical properties in age-hardening systems are very difficult to rationalize;³²⁹ but for steels, in which well-defined products may be produced by isothermal reaction, the experimental problem is not difficult; a beginning on this has been made by Gensamer.³³⁰

RECOVERY, RECRYSTALLIZATION, AND GRAIN GROWTH

At the beginning of this century some of the fundamental facts about recrystallization were already known, as related in the foregoing pages. Recrystallization had been noted and studied; it had

been proposed that the process proceeds by nucleation and growth; some "recrystallization temperatures" had been determined; the influence of temperature upon grain size (a matter of considerable practical importance) had been investigated for several metals and alloys; grain growth had been noted. The subject came under active study, in 1909, when Gard published, and has remained active since.

Softening

Gard³³¹ prepared softening curves for cold-rolled copper and alpha brass, and noted that recrystallization occurs at a lower temperature the greater the degree of deformation; such softening curves became nearly standard with investigations in this field, with the implication that recrystallization proceeds quantitatively with softening, an assumption now known to be only an approximation; many of the "laws" of recrystallization, however, have been built on this assumption—they would be better termed "laws of softening."

Critical Strain

Charpy,³³² in 1910, performed the "Brinell impression experiment" for the first time; he annealed a piece of steel upon which a Brinell impression had been made and observed a region of abnormally large crystals; LeChatelier reported a similar study in 1910³³³ and stated that these crystals grew in the most deformed region; Sauveur³³⁴ repeated this experiment in 1912, adding bend and tensile tests, and, differing with LeChatelier, believed he had demonstrated a critical strain at which large grains formed on recrystallization, with no change in grain size at smaller or larger deformations; Chappell, in 1914–1915,³³⁵ undertook the same investigation, showing, properly, that the recrystallized grain size at deformation above the critical progressively decreases upon increasing deformation, and is not critical in Sauveur's sense—he also studied the effect of time and of temperature of recrystallization; he confirmed earlier observations that the mechanism is, as in freezing, one of nucleation and growth, and recognized that the relative values of these quantities determines the final grain size; and he appears to have been one of the first, if not the first, to have recognized the process of recovery. So much work has been done using softening curves, with only passing mention of microstructure, that it is

not easy to assign the discovery of the phenomenon of recovery. Chappell also recognized the distinction between recrystallization and the subsequent process of grain growth, and his work was well conceived and competently interpreted; it created a new era in these studies.

Variables—Effect of Deformation and Temperature

Heyn³³⁶ showed, in 1912, that the temperature at which recrystallization occurs is the lower the greater the degree of deformation. Robin³³⁷ continued earlier studies relating to the origin of the new recrystallized grains, reporting, in the same year, that they begin as nuclei at grain boundaries and twin bands, both places of high localized strain. Czochralski's³³⁸ important work began in 1916, when, practically simultaneously with Chappell, he demonstrated the progressive change of recrystallized grain size with deformation, and published the first of his well-known three-dimensional recrystallization diagrams, upon tin, plotting final recrystallized grain against percentage deformation and temperature for constant annealing periods. Czochralski gave a fairly complete argument concerning the operation of nucleation and growth. Following this, many three-dimensional diagrams appeared, for many of the common metals and for some alloys; for example, Oberhoffer's work on iron.³³⁹ Hanemann³⁴⁰ later developed comparable recrystallization diagrams for hot-work, with subsequent recrystallization at the temperature of working, finding the diagrams to be the same in type, though displaced somewhat owing to a lesser effectiveness of hot-work as contrasted with cold-work. Mathewson and Phillips'³⁴¹ very important work on the recrystallization of alpha brass appeared in the same year; they observed the functional relationship between final grain size and degree of deformation, observed the effect of temperature upon this relationship, and noted the effect of time upon the process of recrystallization. They confirmed what others had observed, that recrystallized grains originate preferentially at grain boundaries, twin bands, and slip lines.

Carpenter and Elam³⁴² published, in 1921, one of the important papers on this subject. They studied the recrystallization of aluminum isothermally; they observed recovery; they observed the migration of grain boundaries during grain growth in a series of experiments characterized by much elegance in performance. Jeffries and

Archer, in 1923,³⁴³ assembled the knowledge that had been accumulated to that time into a general statement of the laws of recrystallization and grain growth, adding their own important observations, especially with respect to the impeding effect of thorium oxide in tungsten on grain growth. Many of the functional relationships were known, at least roughly, by that time, as noted in the preceding paragraphs.

Single Crystals

The beginning of the work on the plasticity of single crystals offered new opportunities to study the stages of recovery, recrystallization, and grain growth. Schmid,³⁴⁴ in 1925, recovered slightly strained single crystals, showing the loss of work-hardening and the retention of the entity of the single crystal without recrystallization. Schmid appears to have been the first to apply the word "recovery" in this connection. Czochralski,³⁴⁵ in the same year, twisted a single crystal of aluminum and observed that "untwisting" decreased the tendency to recrystallize, a phenomenon not yet adequately explained. Karnop and Sachs³⁴⁶ showed the same effect for polycrystalline copper. They demonstrated the effect of prior grain size on recrystallization in an especially forceful manner by comparing the recrystallization of deformed single crystals with similarly deformed aggregates. It had now become evident that recrystallization depends not upon percentage deformation, but upon the strain-hardening this entails, which is known to decrease as the initial grain size increases. The effect of grain size was studied by Griess and Esser³⁴⁷ on iron, and they showed the critical deformation to decrease with increasing initial grain size at constant degrees of deformation.

Tammann³⁴⁸ studied the effect of the processes of recovery, recrystallization, and grain growth upon the physical and mechanical properties, demonstrating the fundamental nonparallelism of these changes in properties, doubtless the origin of earlier confusion on the separation of the three processes.

Recovery

Much work was done on recovery employing X-ray diffraction, in an endeavor to learn the basis for recovery. It must be admitted

that the results are not yet clear; recovery appears to be the release of certain strains, though clearly not all strains, for recovery does not destroy the tendency to recrystallize.

Rates of Recrystallization

Rates of recrystallization were first approximated by Czochralski,³⁴⁹ who employed the reciprocal time for complete recrystallization as a measure of rate; he plotted these against temperature. Van Liempt³⁵⁰ treated the rate of the recrystallization process as an activation process, and thus began the modern era on theory. Bailey³⁵¹ had earlier employed the exponential plot to represent the temperature dependence.

Isothermal rates of recrystallization were first studied by Sauerwald and Globig,³⁵² who evaluated the fraction recrystallized as a function of time. Analysis of these curves had to await a derivation of a reaction-rate equation for processes of nucleation and growth, which appeared in 1939.³⁵³

Nucleation and Growth

It became clear two decades ago that the basic approach to the problem of recrystallization is through a measurement of the rate of nucleation and the rate of growth of recrystallized grains. Polanyi and Schmid were the first to make measurements on the rate of growth, working with tin, in 1925,³⁵⁴ and measurements on other metals followed, such as those of Karnop and Sachs³⁵⁵ on copper. Hanemann made similar measurements on alpha iron. The work was taken up by Kornfeld in a long series of papers³⁵⁶ on a number of metals, beginning in 1934, and he showed that the rate of growth varies exponentially with the temperature, and calculated activation energies, for aluminum.

Measurements in the rate of nucleation proved much more difficult to measure. Karnop and Sachs³⁵⁵ approximated them for copper. Kornfeld measured the rate of nucleation and considered the variation of the rate of nucleation with temperature and with the degree of deformation, though possibly with some uncertainty.

Derivation of the rate equation for recrystallization³⁵³ gave an opportunity for a full treatment of recrystallization rate in terms of the basic factors of the rate of nucleation and the rate of

growth. It was first applied by Stanley³⁵⁷ to the recrystallization of silicon ferrite, and later by Anderson³⁵⁸ to aluminum. Anderson developed full functional relationships (for the first time) between the rate of nucleation and the rate of growth, on one hand, and time, percentage deformation, temperature, and initial grain size on the other; he showed both the rate of nucleation and the rate of growth to be activation processes; he derived the activation energy as a function of degree of deformation.

The effect of prior recovery on recrystallization has been studied by a number of workers. The results are uncertain—both an increase and a decrease in the rate of nucleation have been observed; occasionally, as with Anderson's work, no effect appears. The subject needs systematic study.

Effect of Composition

Compositional variables remain to be studied on this basis; Stanley³⁵⁹ has found that silicon in solid solution decreases both the rate of nucleation and the rate of growth in silicon ferrite. But most of the information available at the moment is on the basis of softening curves. These show that solid solution formation increases the softening temperature (presumably decreasing the rate of nucleation and the rate of growth), as, for example, in copper-nickel solid solutions, as shown by Jones, Pfeil, and Griffiths.³⁶⁰ The many observations on the effect of solid solution impurities do not respond easily to summarization; it may be that generalizations based upon the chemical affinity and valence electron concentration effects in solid solutions may prove useful, as they have in many other cases, for Smart and Smith³⁶¹ and C. S. Smith have shown the softening temperature of copper to be increased by solutes roughly in proportion to the solute valency.

Grain Growth

The laws of grain growth have not responded readily to investigation. The use of constant annealing times in the derivation of three-dimensional diagrams superimposed grain growth on recrystallization at higher temperatures, where the time for recrystallization was very short compared with the annealing time, so that the final grain sizes on such diagrams is deceptive—at high temperatures it

does not represent the as-crystallized grain size, but this somewhat increased by grain growth, as French³⁶² has demonstrated recently.

The increase of grain size during grain growth has been variously ascribed to a tendency toward minimum surface energy, to growth resulting from small strains residual upon the completion of recrystallization, and, very recently, by Harker and Parker,³⁶³ to a striving toward solid angles of the grain faces of maximum stability.

CONCLUSION

Engineering and scientific societies play an essential role in the advancement of engineering and science. This is not only the obvious role in the publishing of the results of study, but also in providing the opportunity for communion among workers, in lending dignity and a sense of importance to the profession, and particularly in maintaining standards of achievement. The American Institute of Mining and Metallurgical Engineers has long asserted and supported these propositions.

Whereas, in the early years, physical metallurgy occupied a relatively small part of the activities of the Institute, the growth of this subject in the last three decades, especially the last two, has been remarkable. Active in the whole of the metallurgical field, the Institute has long held a leading position in nonferrous metallurgy, both process and physical; it has emphasized the importance of good science in the physical metallurgy of both ferrous and nonferrous metals and alloys. The record is clear in physical metallurgy, as it long has been in other fields, that the study of the basic behavior of material, of however little immediate usefulness, does indeed lead to the most important engineering advances. It is necessary to take the long view. This Institute has held this view throughout its history. Its wisdom has never been clearer than it is now, when research has finally come of age in society, in the year 1946.

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