PROGRESS IN METALLURGY: THE SCIENCE OF ALLOYS.*

BY

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The science of alloys is the motorcycle squad leading the parade of progress. From the earliest recorded alloy which appeared in Ur about 4000 B.C. until the present time, man's technological development has been limited by available materials, and the science of alloys, continuously providing new materials, clears the path for progress. The Electrum alloy of Ur made possible the first "modern" coinage system, and the X-ray target alloys of today make possible the latest system for locating the building blocks of organic chemistry in the complicated synthetic molecules. In the interim there has been a constant development of alloys for tools, instruments, machines, and electrical and chemical apparatus. A mere recital of the more common alloys would take more than the period allotted for this discussion, so that we will consider only those of more recent interest and those which best exemplify the principles of the modern science of alloys.

The everyday importance of the science of alloys is obvious, but man is so ready to accept the obvious that its significance is frequently lost. In general, the application of the alloys may be divided into four groups: master alloys for making other alloys, tools, instruments, and finished products for direct consumption. The master alloys are found only in the metallurgical industries. The tools are more apparent in everyday life. Those found in a modern kitchen well illustrate our dependence on alloys. Forks, knives and spoons are made of alloys of silver-copper, copper-nickel, nickel-zinc-copper, chromium-iron, or chromium-nickel-iron. The electric iron may have an iron-silicon-carbon or chromium-copper alloy base, and a nickel-chromium resistance element—all a result of alloy development. The mixing machine carries an

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electric motor built largely of silicon alloy steel, with a commutator which may be made of a silver-aluminum-copper alloy, and with phosphorus-tin-copper alloy springs. This motor drives a steel alloy shaft with a stainless alloy steel mixing blade—again a tool made possible by alloying.

As to instruments, a thermostat controlling the furnace may be seen in the adjacent hall. This is an assembly of parts made of alloys of copper and zinc, iron and nickel, nickel and copper, phosphorus and copper, and tungsten and silver. It is a measuring instrument of scientific accuracy, functioning as a controller and available to every household because of the development of alloys. And the telephone on the table is an instrument of a hundred alloys, each of which has been developed because of specific characteristics enabling it to fulfill a particular function.

Consider finished articles of direct use. The kitchen sink may be an alloy of nickel and copper or of chromium, nickel and iron. The faucets are alloys of copper, tin, lead and zinc. The stove may carry a high chromium-iron alloy top, and the refrigerator may be fitted with alloys of aluminum, copper, zinc and silicon, as well as alloys of iron nickel and chromium. If we step from the kitchen to the garage, we find the automobile which is built of some 125 different steel alloys and a host of non-ferrous alloys.

Thus it will be seen that the development of alloys is a matter of real importance in our everyday lives, and that the science of alloys has done much to increase our standard of living.

The question may well be asked "What is an alloy?" and indeed a truly satisfactory definition is difficult. In the broadest definition, a metallic alloy would simply comprise one metallic element plus one or more other elements mixed with sufficient intimacy. An alloy may be more effectively defined as an intimate mixture of one metallic element and one or more other elements which are or at one time have been mutually dissolved. Strictly speaking, this may not take into account synthetic mixtures of powders which have been compacted, but even in this case it may be considered that the compacting may effect surface bonding akin to alloying. The mutual solubility above mentioned may have

taken place only in the liquid phase, and after freezing there may be almost no mutual solubility. Still the intimate mixture which results is an alloy. Or again, powdered metals may be pressed together and sintered so that mutual solubility takes place along their borders, which solid solution may or may not continue to exist at room temperature. At any rate the intimate mixture is still an alloy. Broadly, alloys may

FIG. 1.
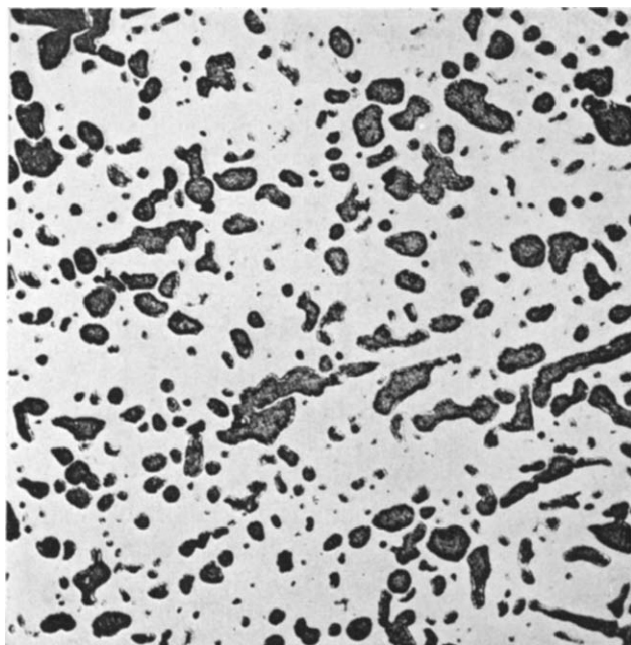
Emulsion type alloy. Copper containing 24 per cent. lead-unetched. 100 X.

be divided into four structural groups: solid emulsion type, solid solution type, precipitation type, and eutectic type.

The alloys representing the solid emulsion type are difficult to prepare if optimum properties are required. There is little need to describe such alloys, except to state that the object is to provide a mixture in the solid phase which is the analogue of an emulsion in the liquid phase. The alloys of copper and lead (Fig. 1), and of iron and lead are illustrative.

Copper-lead alloys may contain as much as 55 per cent. lead, although solubility is limited even in the liquid phase. Alloys containing up to this amount of lead are used for bearings, where the presence of the lead produces low frictional resistance. Compacted metal powders may approach this type. Lead in the iron-base alloys is a matter of very recent development, and the frozen emulsion which will contain some 0.2 per cent. lead is prepared with practically no liquid solubility. The object of adding the lead in this case is to provide small films of lead or lead compounds so distributed in the final rolled product that machinability is markedly increased.

The term "solid solution" has been used, and this is a concept essential to an understanding of the science of alloys. Metals in the solid phase exist in the crystalline form, that is, the atoms are located in a regular geometric pattern. Replacement of one of the atoms in a pure metal crystal by the atom of another element, for example, chromium in iron to give stainless steel (Fig. 2), results in a type of "mixture" of atoms known as a solid solution. Again, a stranger atom, such as carbon in iron to give ordinary steel, may simply exist as such in the space within the lattice instead of replacing an iron atom in a given position in a crystal lattice. This is another type of solid solution. In either case, we have a solid solution type alloy.

Suppose now solubility changes with temperature. The temperature is lowered between levels which permit certain atomic mobility. The stranger element or its compound is rejected from solid solution. The resultant alloy is an intimate mixture of small particles of the stranger element or compound surrounded by the crystal lattice of the solid solvent. The small particles of the stranger element may be large enough to see, or they may be submicroscopic. Such alloys are frequently known as precipitation type alloys. The alloy of copper and chromium is a case in point. At some 900° C. an alloy containing 99.5 per cent. copper and 0.5 per cent. chromium exists as a solid solution. As the temperature is lowered the solubility of the chromium in the copper decreases so that at approximately 300° C. less than 0.05 per cent. chromium remains in solid solution, the re-

mainder of the chromium existing as discrete particles, many of which are microscopically visible in the copper crystals.

The eutectic type of alloys results from a sudden change in solubility due to a phase change. This phase change may be from a liquid to a solid or from one solid phase to another. If sufficient solute is present in such alloys the solute is rejected from the solvent as the material undergoes phase

FIG. 2.
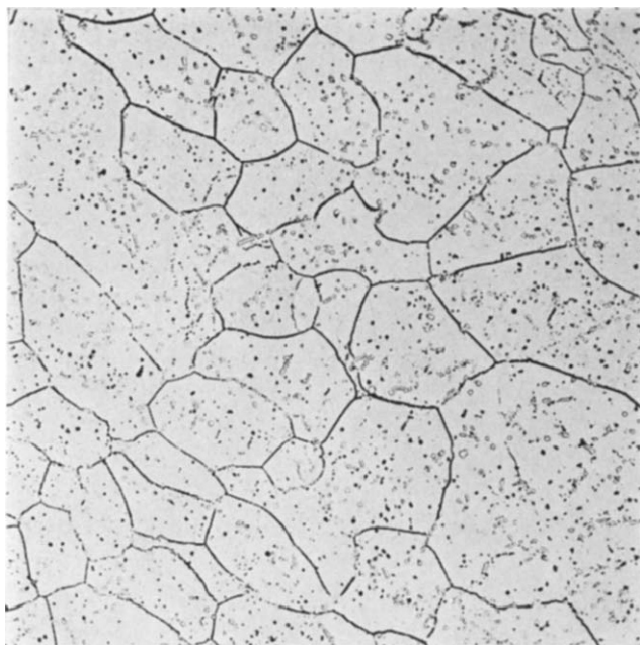
Iron-chromium solid solution and carbides (low carbon chrome iron) etched with aqua regia-glycerine.   250 X.

changes, generally due to lowering of the temperature. In binary alloys such phase changes generally take place over a very narrow temperature range if not actually at a fixed temperature, and it is common in such cases where time at temperature is sufficient to have the rejected solute present in the form of small plates interleaved with similar plates of the solvent (Fig. 3). When the amount of solute is such that the entire alloy consists of lamellar structure it is known as a

eutectic.   If the structure results from a phase change involving two solid phases the structure is similar in character and is known as a eutectoid.   We need not concern ourselves with the names given to these structures, but it is important that their nature be visualized.

The alloy of lead and arsenic is a case in point.   If we have some 3.3 per cent. arsenic in lead in the liquid phase at

FIG. 3.
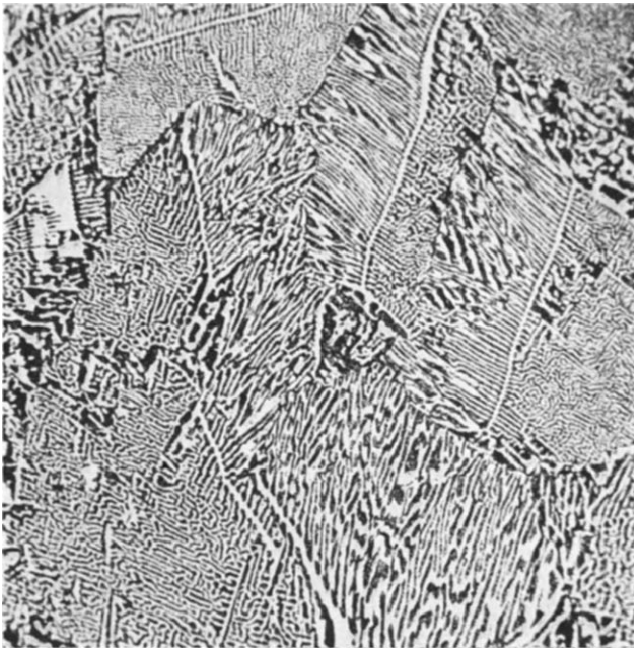
Eutetic alloy.   Bismuth-tin-etched with 25 per cent. HCl in alcohol.

300° C. and cool this liquid to 288° C. the liquid phase changes to the solid phase, giving an intimate though macroscopic mixture of lead and arsenic present as interleaved plates or lamellæ.   Not only may stranger elements be rejected from solution but such elements may form compounds with the main element and these compounds may be rejected from the solution.   In general, such a compound may be considered as a primary constituent similar to an element.   Iron-carbon is

a case involving solid phase changes.   If an alloy of iron containing approximately 0.9 per cent. carbon is held at 750° C. a complete solid solution exists, the iron being present as the gamma phase or face-centered cubic lattice.   As the temperature is lowered to approximately 725° a phase change takes place from gamma to alpha iron, that is, from a face-centered to a body-centered cubic lattice.   Solubility of the

FIG. 4.
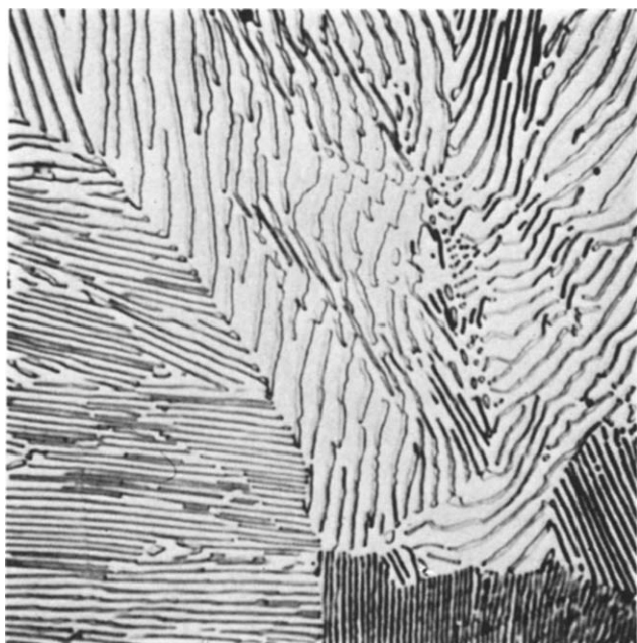
Pearlite in 0.90 per cent. carbon steel-etched with 5 per cent. picric acid in alcohol.   2000 ×.

carbon in the latter is very much less, so that carbon must be rejected from the solvent, alpha iron.   However, the carbon combines with iron to form a compound, Fe_3C, known as cementite, and this forms one part of the lamellar structure typical of a eutectoid, in this case known as pearlite because of its appearance (Fig. 4).

All of the above is representative of the slowly-cooled eutectic or eutectoid type of alloy.   If the change in phase is effected rapidly enough so that the rejection cannot take

place as described, intermediate, special structures occur, and correlative with such structures are special properties which may or may not be desirable. This rate of change of atomic arrangement may be influenced not only by the rate of change of temperature but also by the presence of other elements which due to their very presence affect the specific rate of the phase change.

This exposition may seem quite complicated to the layman. However, to one versed in the principles of chemistry and physics it is apparently nothing more than the common teachings of the phase rule, and to the metallurgist it is everyday behavior of his materials.

The purpose of alloying is to produce materials having specific properties or combination of properties. While occasionally we are primarily interested in one property, for example, electrical conductivity or coefficient of expansion, we are frequently interested in more than one property, and the combination of properties that is most important in most alloys involves strength and ductility. Metals may be strengthened by preventing deformation of the grain. Without going into the detail of various theories, we can summarize for our purpose by a few simple statements.

Solid solutions are stronger, but not necessarily much stronger than the pure metals, that is, the presence of a stranger atom as such in the lattice increases the tendency to resist distortion. Much more effective is the presence of stranger particles in the lattice which tend to prevent slip along atom planes. Likewise effective is the matter of grain size, small grains tending to prevent distortion by end blocking of the slip planes. Ductility in solid solution alloys is increased or unaffected; in eutectics it depends on the ductility of the least ductile constituent, and in precipitation type alloys it varies inversely with strength but not necessarily in proportion. As the limiting hardening effect is approached the ductility approaches zero. Thus, there are a number of definite ways in which strong, ductile alloys can be produced. As hardness generally goes with strength, the same is true of the production of hard alloys.

The alloys of the ancients, such as the coinage metals, the tool bronzes, and the Roman brasses, were predominantly of

the solid solution type. This is understandable, in that a simple melting of such alloys together with cooling in any fashion results in a structure having the properties desired. These older alloys were followed by those of the eutectoid type, where reasonably slow cooling resulted in the eutectoid structure. Here again there was great probability of achieving the desired result by simple fusion and normal cooling. In alloys requiring special heat treatments, however, a particular combination of circumstances was necessary to achieve the results, that is, the matching of alloying content and heat treatment. The probability that anyone experimenting in a hit or miss fashion would actually stumble upon the correct combination would appear to be small indeed, but even in 900 B.C. the effect of quenching steel had become apparent, and great progress in the production of new alloys in the period 1850 to 1890 was made in spite of the fact that the principles involved were not understood. This was the period of intensive application of chemical analysis and the tensile testing machine.

At the end of the last century with the advent of the metallurgical microscope, thermal analysis, and convenient hardness testing, the development of new alloys changed from an art to a science which has today reached a still higher level because of concepts made possible by X-ray analysis.

Consider some of the alloys which have been developed in recent years—alloys made possible by an understanding of the principles previously outlined. Duralumin was known but not understood. In the wake of X-ray analysis came Dr. Merica's theory of ultramicroscopic precipitation as a hardness-inducing phenomenon. Shortly thereafter Corson hardened copper with silicide precipitation, Dean hardened lead with precipitated antimony, Mudge hardened nickel-copper by precipitated aluminides, and Masing hardened copper by precipitating beryllides. Thus goes the roll call of modern alloying started by the impact of new understanding.

The copper and silicide story is one of the best examples. Copper dissolves a number of certain elements at high temperatures, and largely retains such elements in solution at low temperatures. By adding more than one copper-soluble

element of such character that the two elements might form a compound which is rejected from solution at low temperature, a precipitation type copper alloy results. Corson found that such elements as nickel, chromium or cobalt on the one hand and silicon or beryllium on the other, each readily soluble in copper at elevated temperatures, form a silicide or beryllide relatively insoluble in copper at low temperatures. Thus by adding proper amounts of these elements to the copper melt and holding the solidified alloy at an elevated temperature, approximately 900° C., a homogeneous solid solution is formed with the added elements well distributed throughout the copper lattice. Quenching retains these elements essentially in solid solution, so that the microstructure is not different from that of pure copper. Reheating at a low temperature, such as 500° C., increases atomic mobility and allows the compound to form with rejection from the solid solution. This results in copper crystals relatively free from atoms of the other elements and particles of the compound dispersed through the crystal. These particles prevent ready deformation of the grain proper, increase the strength and hardness, and retain this condition until the temperature of precipitation is approached. This makes possible the use of copper-base alloys with their naturally high thermal conductivity in such novel applications as combustion motor heads as well as for a wide variety of special applications such as resistance welding electrodes and electric switches.

The aluminum-silicon alloy with or without copper, now so widely used for automobile pistons as well as for a great variety of castings, illustrates the eutectic type of alloy. Here the maximum solubility in the solid phase is low (1.8 per cent.) and the eutectic is formed at a silicon concentration of some 10 per cent. This eutectic has a very peculiar property, in that the net volume change on solidification and cooling to a temperature at which the alloy has acquired strength is very small. Accordingly, molds and patterns are accurately filled and shrinkage stresses practically eliminated. For pistons, much more than 10 per cent. silicon is used in order to have hard silicon crystals to resist wear and lower the coefficient of expansion. The resulting eutectic structure carries with it the strengthening which could be expected

from the juxtaposed plates in each grain. These alloys have the particular property of low density combined with strength. Advantage is taken of low shrinkage in a 5 per cent. aluminum-silicon alloy used for welding aluminum-base articles.

A number of alloys developed to have some singular property are of interest. An alloy of copper, manganese and nickel containing approximately 12 per cent. manganese and 4 per cent. nickel is illustrative. In this alloy constant electrical resistance has been achieved as a function of temperature over the range found in usual living conditions, and in addition the alloy has a low thermoelectric force when coupled with copper. It is used in electrical measuring instruments similar to the meter whose reading determines your monthly electric light bill. Again, an alloy of nickel and iron which contains some 37 per cent. nickel possesses a coefficient of expansion that approaches zero over a limited temperature range, including the one in which we live, and is therefore used for surveyors' tapes, pendulum stems and thermostatic devices. The phenomenon is probably due to the same mechanism as that of the copper-manganese alloy previously mentioned, namely, a perfectly reversible formation and dissociation of intermetallic compounds within the solid solution—what the modern physicist would call "order disorder" variant with temperature. Iso-elastic is another case in point. This is an iron-base alloy with 37 per cent. nickel, 7.5 per cent. chromium and 0.5 per cent. molybdenum having a practically constant modulus, as a function of temperature—again over a limited but desirable range and likewise exhibiting extremely low plastic deformation and mechanical hysteresis. It was developed by deForest for accurate weighing mechanisms similar to those found in the modern butcher shop. Similarly, alloys of iron, chromium and nickel with manganese, vanadium, silicon or aluminum highly complex in character have been developed. These have coefficients of expansion approximating that of glass and are used for leads into glass bulbs containing electrical apparatus. The alloys having very great hardness are frequently based on a large proportion of hard particles of compound held in a small proportion of solid solution. Stellite, essentially compounds of tungsten, chromium and carbon in a

precipitation type cobalt base alloy, and the more recent tungsten-carbon-cobalt, essentially tungsten carbide in a cobalt-base solid solution, are typical. They are used for cutting tools and dies, having the property of retaining hardness at elevated temperatures.

A whole series of alloys, containing essentially 50 to 80 per cent. nickel, remainder iron, has been developed for maximum magnetic permeability with low hysteresis and remanence, and are used in long distance telephone and in cable lines. Another series developed for maximum remanence and hysteresis comprises iron, nickel, aluminum and cobalt, illustrated by the powerful permanent magnets used in radio speakers. In this field the metallurgist is still largely groping, having no comprehensive theory to explain the mechanism or to guide his work. These alloys are illustrative of another point, namely, that nature is often perverse. These permanent magnet alloys have so little ductility either at room or elevated temperature that they can be produced in usable form only by direct casting or by powder compacting.

Probably the most fascinating of all of the alloy systems are those based on iron as this is the only common inexpensive element which undergoes a solid phase change. The nature of this phase change in the simple iron-carbon alloy is fairly well understood, and has already been described to you by Dr. Johnston in his talk last year. Briefly, this phase change results in various types of mixtures of ferrite and iron carbide due to high solubility of carbon in the high temperature γ phase and low solubility in the low temperature phase, α. The particular type of mixture may be controlled by affecting the rates of phase change either by altering the rate of cooling of the article or by altering the specific rate of phase change for a given rate of cooling by means of alloy additions. The modern low alloy, high strength steels are a case in point. Such steels, in view of the fact that they are used as structural members of considerable magnitude, are not subject to heat treatment, but are used as cooled in the air from the rolling operation, or after a simple reheating and air cooling. Cranes, buckets and railroad cars (Fig. 5) are typical of structures built of these steels. The alloy addition is so adjusted with respect to carbon that a fine pearlitic structure results from

this type of cooling, which structure correlates with strength and ductility.   But even greater demands have been made on such alloys.   They not only must have increased strength and ductility, but also must retain this strength and ductility after specific heating operations such as occur in welding, and further, due to the fact that they are used in lighter sections, must show increased corrosion resistance.

There are many types of alloy steels intended for this purpose and all are based on the same general principles.

FIG. 5.
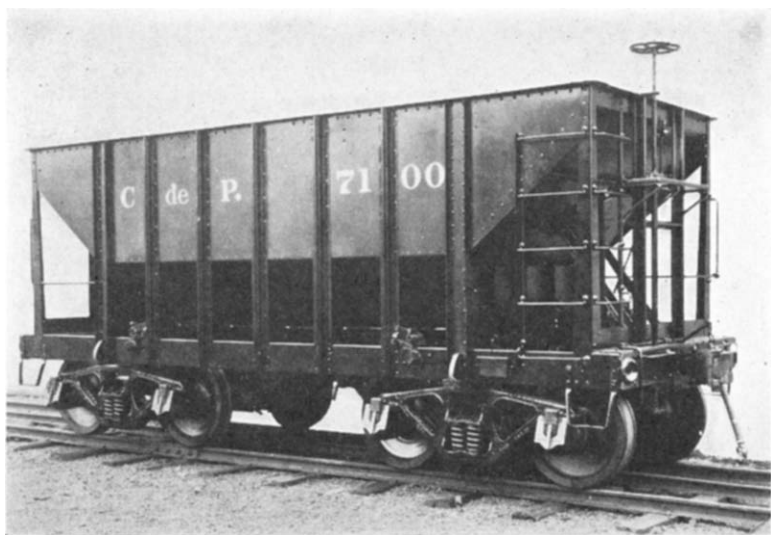
They all follow the same fundamental rules, namely, they must contain an element which primarily affects the transformation, such as chromium, manganese or nickel; an element to give corrosion resistance, such as phosphorus or copper, or both; and another element to control yield point or modify the transformation with different cooling rates, such as silicon, vanadium or molybdenum.

Consider one of the better known of the modern high strength structural steels.   To meet the welding requirements carbon must be kept low.   In general, it has been determined that in the structural alloy steels of this type no more than

0.14 per cent. carbon is permissible.   To get the type of fine
pearlite required with carbon at such a low level, chromium,
manganese or nickel may be added.   In view of the fact that
corrosion resistance is desired along with the other properties,
phosphorus and copper are used.   Phosphorus tends to have
an effect similar to carbon in producing fine pearlite.   There
will be a tendency for the pearlite to be too fine, which means
reduced ductility, and accordingly the carbon is held at a
still lower level, namely, 0.10 per cent. maximum.   The
copper tends to promote surface checking on hot working,
so that this element is restricted to 0.40 per cent.   In order
to obtain the required corrosion resistance with the copper
at this level phosphorus is increased to some value above
0.10 per cent., and to eliminate any embrittling effect of this
phosphorus, chromium is chosen as the strengthening element
and is placed at some value above 1 per cent.   Manganese
would tend to affect the transformation so as to get too fine a
pearlite, so this is kept to a minimum, at approximately 0.30
per cent.   In order to have a relatively high yield ratio, that
is, to have strengthening by solid solution affecting the
ferrite proper, silicon is carried at a relatively high level,
above 0.5 per cent.   All of this results in an alloy which at
first glance appears to be tremendously complicated.   It will
be noted that this steel contains maximum 0.10 per cent.
carbon, approximately 1.10 per cent. chromium, 0.30 per cent.
manganese, 0.11 per cent. phosphorus, 0.40 per cent. copper
and 0.6 per cent. silicon.   It will also be noted that there is a
very definite reason for each and every one of these alloying
elements and for their proportions, that is, the metallurgist
started out to get a combination of properties and by using
the elements as building blocks and noting and balancing the
effect of each he has been able to synthesize a steel having all
the required properties.

    Consider another of the low alloy steels.   Carbon has been
retained at 0.14 per cent. maximum to get the required fine
pearlite without too much hardening when cooled from a
very high temperature.   Chromium at approximately 0.5 per
cent. and manganese at approximately 0.8 per cent. work
together to affect the transformation.   Silicon is used at
0.7 per cent. to increased yield point, and copper at 0.4 per

cent. to increase corrosion resistance.   In addition, zirconium is added to improve ductility of the ferrite proper, again attention being paid to balancing the various alloying components.   And still another case, with carbon under 0.14 per cent., copper is placed at 1 per cent. or more for corrosion resistance, nickel is chosen at 1 per cent. or more as the strengthening element because it eliminates copper surface checking and if the pearlite is not sufficiently fine, depending on the amount of nickel, some 0.2 per cent. molybdenum may be further added—again the building and balancing process.

In the engineering steels used for automotive and machine tool construction the size and shape of the article are such that heat treatment is practicable, thus differing from the structural steels.   A variety of alloy steels is available, each with some particular property.   The plain chromium steels tend to form fine carbides which give wear resistance.   These are found in ball bearings.   Likewise in lower carbon ranges the fine pearlite induced by chromium promotes strength and ductility.   The nickel and nickel-chromium steels are readily carburized and are also found in parts where strength and ductility are of paramount importance.   Gears are typical. Vanadium is used to augment the carbide-forming effect and reduce grain size.   Molybdenum affects the transformation so as to give fine pearlite and is generally used in combination with other elements.

All of the foregoing refers to the problem of physical properties of alloys, but chemical properties, or more pertinently resistance to corroding media, are likewise of great interest and practical importance.   In general, there are two methods of obtaining corrosion resistance.   One is to use the so-called noble metals, or the highly passive element tantalum. Alloys of gold and silver or platinum and rhodium are illustrative.   In such alloys there is no chemical attack by a large variety of chemical media.   The second method is to so proportion and select the alloys that the products of corrosion act to protect the alloy proper from the corroding medium. This mechanism is based on which is commonly known as the film theory.   Chromium, for example, oxidizes readily, but the oxide film is tenacious and continuous so that attack may cease almost at once.   This phenomenon is the basis

for a most interesting series of alloys, commonly known as stainless steels.

The first stainless steel of the cutlery type was produced by Brearley, and contained some 14 per cent. chromium and 0.30 per cent. carbon. He found that corrosion resistance to oxidizing media was excellent when the material was in the heat treated condition, that is, when the state of heat treatment was such that the chromium was not tied up to the carbon in the form of carbide to such a degree that it could not act to form a continuous film. Cutlery is illustrative. Shortly thereafter it was found that lowering the carbon gave an alloy of the same degree of corrosion resistance without necessitating heat treatment, and further that increasing the chromium content increased the resistance to corrosion, particularly in oxidizing media. Such steels are found in hub caps, nitric acid handling equipment and many other decorative and chemical applications. Closer study of the phenomenon has led to the belief that the film is not entirely passive in nature but is dissolved slowly as a function to time, and that the rate of corrosion in a given medium is a function of the rate of removal and rate of reformation of the film and underlying alloy. Thus, the finding that the higher the chromium the greater the corrosion resistance is logical, as the increased chromium would undoubtedly increase the rate of film formation.

It was further found that in the higher chromium alloys not only was there a marked resistance to corrosion but also a marked resistance to atmospheric oxidation at elevated temperatures (Fig. 6). This had been previously noted in chromium-nickel alloys. This resistance to oxidation seems to follow the same general mechanism as resistance to corrosion, that is, the material oxidizes very rapidly at first and the products of oxidation protect the alloy proper, effectively stopping progressive oxidation. Furnace parts are illustrative. As the chromium is increased in low carbon iron alloys the well-known alpha-gamma transformation occurs over an ever more narrow temperature range, so that in the carbon-free alloys with over 12 per cent. chromium the transformation is completely suppressed, and with moderately small amounts of carbon the same is true at slightly higher chromium con-

tents.   Thus, one of the most valuable properties of the iron alloys is lost, namely, the ability to refine the grain without mechanical work.   This means that once such an article has been wrought to its final shape every high temperature heating operation serves to increase the grain size with correlative loss of ductility.   Inability to obtain grains in castings finer than the initial as-cast grain size, which is comparatively large, has seriously hampered the industrial use of these

FIG. 6.
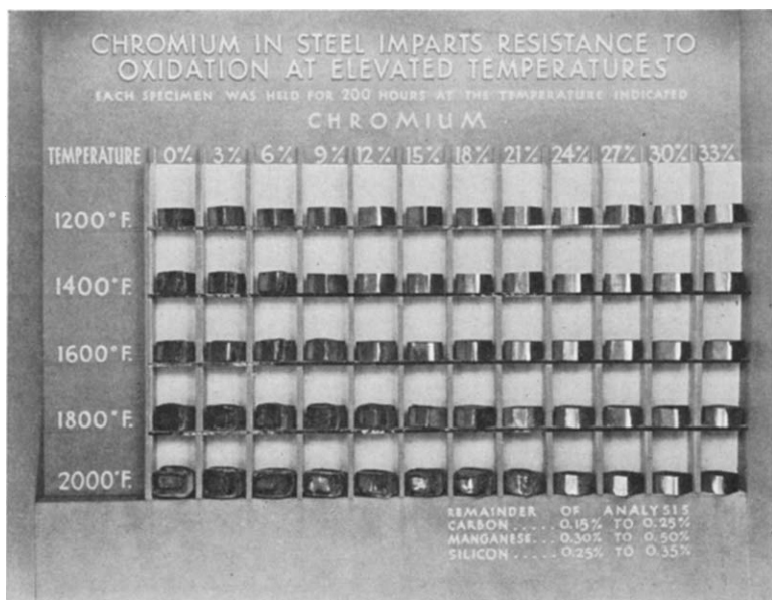
materials, and it is only more recently that this problem has been solved to a large degree by the addition of nitrogen. This results in material of very much finer grain (Fig. 7) and lesser tendency toward grain growth in a given heating cycle. The reasons for this nitrogen addition and its effect will be discussed at greater length together with master alloys.

One other attack on this problem has been the addition of further alloying elements which tend to restore the natural tendency of the iron-carbon base alloy to transform.   Just as chromium promotes alpha iron, other elements such as

manganese, nickel, copper and nitrogen, not to mention carbon, tend to promote gamma iron. Thus a balanced proportion of such elements together with the chromium results in high chromium steel which undergo transformation and are accordingly amenable to heat treatment for grain refinement or other purposes. By adding still larger amounts of austenite-forming elements such as nickel or manganese it is possible to produce a high chromium alloy which is completely austenitic at some elevated temperature and which undergoes the transformation so sluggishly that it is possible to suppress

FIG. 7.
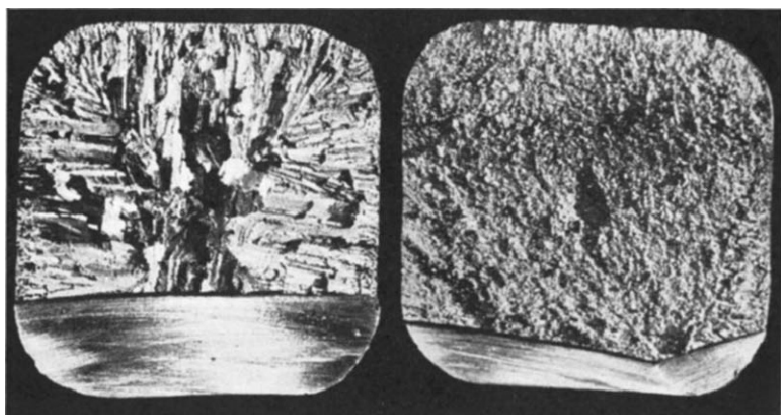
28 per cent chromium steel as cast, without and with a nitrogen addition.

it by rapid cooling. The austenitic structure possesses much greater ductility than the ferritic structure and facilitates such special operations as deep-stamping and cold forming.

The best known alloys in this class contain some 18 per cent. chromium and 8 per cent. nickel with low carbon. Alloys of this type are soft and highly malleable in the rapidly cooled state. They form the basis for equipment in the dairy and food industries, decorative trim and the chemical industry in general. Similar to many non-ferrous alloys, they may be cold worked to produce high strength without too great a loss of ductility. The "18-8" alloy in this condition is the essence of the modern light weight, high strength construction

found in the recent streamlined transportation structures such as railroad trains (Fig. 8), motor trucks and airplanes. These alloys contain comparatively small amounts of carbon, 0.07 per cent. maximum being a common specification. However, even this small amount of carbon may cause undesirable effects. Increasing the temperature to a point where there is sufficient atomic mobility so as to allow the structure

FIG. 8.
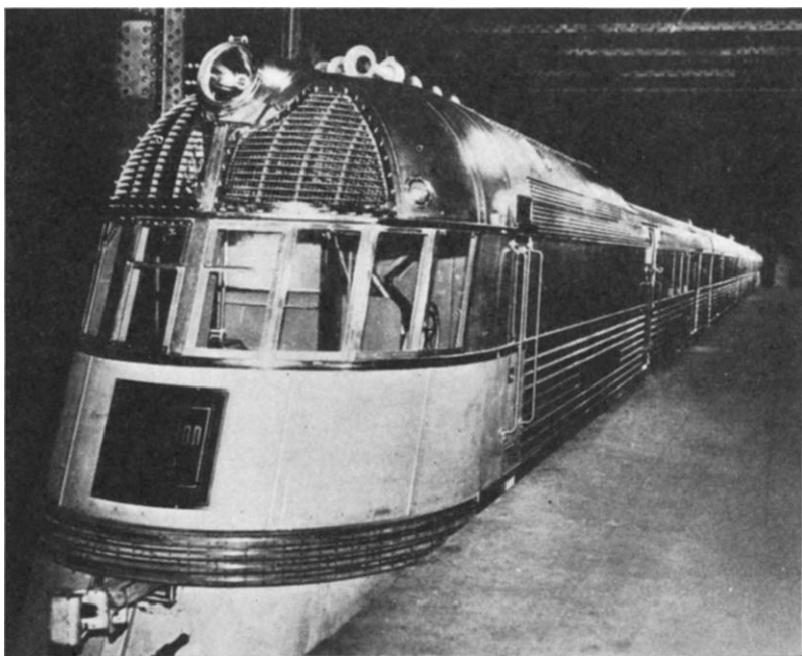
to change toward the equilibrium condition results in transformation of austenite to ferrite. Such transformation first takes place at the point of maximum internal stress, namely, the grain boundaries. Carbon being much less soluble in ferrite than in austenite is precipitated at these grain boundaries in the form of carbide. When these carbides are present in the grain boundaries the material exhibits lower ductility and corrosion resistance. In most applications of the standard 18-8 low carbon material the only exposure to heat

at the temperature implied above happens in welding, and
this is for such a short time that the degree of the precipitation
is slight.   Thus, for many engineering purposes the loss of
ductility and corrosion resistance is of such small magnitude
as to be inconsequential.   In fact, in the case of the high
speed resistance welding used extensively within walking
distance of this Institute the time at temperature is so short
that the intergranular phenomenon does not take place at all.
However, where corroding conditions are severe, where rela-
tively thick material involves a long time in the welding
operation, or finally where the material is used at the tem-
perature of precipitation the loss of ductility and corrosion
resistance may be serious.   The precipitation may be elimi-
nated by reducing the carbon to practically zero.   For this
purpose it is necessary to maintain a carbon content under
0.01 per cent., and this is not now commercially feasible.
Again the science of alloys comes to the rescue, it having
been found that a suitable amount of a very strongly carbide-
forming element, such as columbium or titanium, will form
carbides and practically eliminate carbon from solid solution
in the austenite.   Thus, there is no carbide precipitation on
heating to the precipitation temperature and no correlative
loss in corrosion resistance.   In other words, the phenomenon
of intergranular corrosion disappears in these steels when
columbium is present to the extent of ten times the carbon
(Fig. 9), and lesser amounts may be practically effective.
This is a boon to the chemical industries where many of the
recently developed reactions are carried out in stainless
welded equipment.

    Again, under certain corroding conditions where the media
are non-oxidizing in nature corrosion of the iron-chromium
alloys may take place at an undesirable rate.   The addition
of nickel to the extent above mentioned, namely 8 per cent.
or thereabouts, renders the film and underlying material
much more resistant to such media so that the net corrosion
resistance may be markedly increased.   This may be corre-
lated with the corrosion resistance of metallic nickel.   In some
media, particularly those containing halogen radicals, molyb-
denum has a similar major effect on corrosion resistance of
these alloys.   The use of 2 or 3 per cent. molybdenum to

improve corrosion resistance and the use of columbium to inhibit intergranular corrosion would seem to be mutually compatible, and indeed such steels have been made. However, both molybdenum and columbium are alpha-forming elements, with the result that when both of these elements are present in addition to the chromium it is difficult to retain the austenitic condition to a satisfactory degree. Again the science of alloying gives the answer, in that an increase in the

FIG. 9.
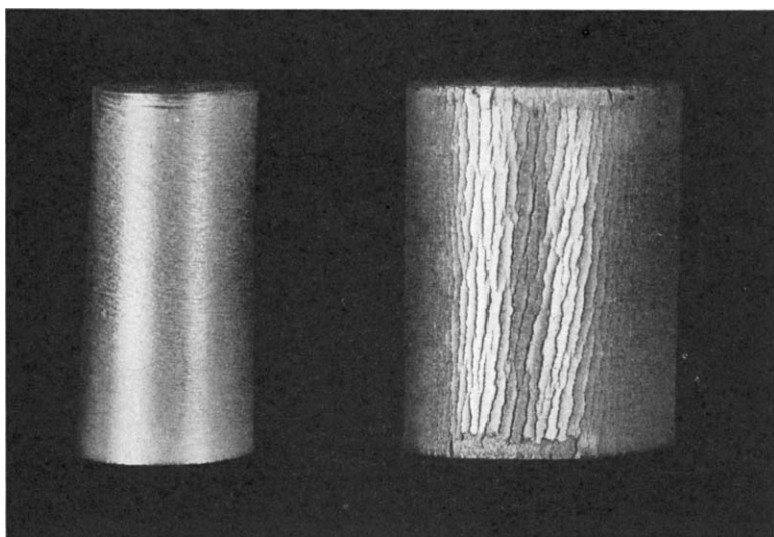
Effect of columbium on intergranular corrosion in 18-8 steel. Both samples heated at 650° C. four hours and air-cooled then immersed in boiling acidified copper sulfate solution for one and one-half hours and then bent. Sample on left was columbium-bearing, the one on the right a plain 18-8 steel.

austenite-forming elements, such as manganese as well as nickel, counterbalances this effect of the molybdenum and columbium and results in steels having the desired degree of austenite stability and correlative properties which render it suitable for use in a wider range of chemical equipment, and particularly improves resistance to sea water and brines.

The subject of master alloys mentioned in the earlier part of this discussion has been purposely left to the last as these alloys are primarily of interest to the manufacturing metal-

lurgist. The purpose of these alloys is to enable ready introduction of alloying elements whether for the direct purpose of alloying in line with objectives already discussed, for the purpose of eliminating undesirable matter, or for creating specific conditions leading to desired types of crystallization on cooling. The master alloys are industrially known either as hardeners or as ferro-alloys, depending on their composition. Typical of the hardeners are alloys of 50 per cent. silicon-aluminum, 30 per cent. silicon-copper, 30 per cent. manganese-copper, 10 per cent. chromium-copper, 15 per cent. phosphorus-copper and 10 per cent. nickel-aluminum. Typical of the ferro-alloys are 50 and 75 per cent. ferrosilicon, 70 per cent. ferrochromium and 80 per cent. ferromanganese, each with high or low carbon, and 40 per cent. ferrovanadium. In the melting of any alloy the problem of deleterious effects produced by unavoidable stranger elements is ever present. Oxygen from the air or from refining slags is most prevalent. Nitrogen from the air, sulphur from the ore or from reducing media, and phosphorus from the ore are typical.

In the manufacture of non-ferrous alloys deoxidation is generally unnecessary, copper and nickel being important exceptions. The addition of a variety of agents, the most common being phosphorus, silicon, calcium, and zirconium, is used in these cases. These combine with the oxygen in the melt to form oxides, which are either eliminated or harmless. Excess quantities of deoxidizers may, however, enter into a liquid solution and form either a solid solution or eutectic alloy. When this happens the material falls in the class of alloys previously described, and counterbalancing alloys and additions may be necessary, or changing the deoxidizer may result in elimination of the new problem. For instance, iron and chromium are reported to offset the small amounts of phosphorus which might otherwise be in solid solution in copper deoxidized with this element, and chromium may be used to offset similar effects of silicon.

The problem of deoxidizing non-ferrous alloys has been relatively simple. However, in the ferrous alloys, particularly the steels, the problem is much more complex and here the term deoxidation is so broad as to include reaction with other elements as well. For instance, oxides and sulphides

may be retained as a network in the initial grain boundaries of a casting and may seriously affect the ductility. In an ingot to be rolled the inclusions may be present as alumina, silicates or complex sulphides so that they roll to stringers in the steel and result in local weakness, initiating fatigue failure.

The science of deoxidizing steels so as to avoid undesirable types of inclusions is of comparatively recent origin. Herty has shown that in the initial deoxidation of a steel bath the use of a special alloy of silicon and manganese results in inclusions of just sufficient solubility and viscosity at usual steel bath temperatures so that they readily agglomerate and float out of the bath. The addition of zirconium to eliminate nitrogen from an active part in the final alloy by formation of zirconium nitride is another finding of more recent years. The use of manganese to eliminate iron sulphide by substitution of iron and formation of manganese sulphide is old in the art. It was long thought that steel could not be made without a manganese addition due to the ever-present sulphur. However, Becket has shown that zirconium may replace manganese in this respect, the mechanism being essentially the same.

After the steel is taken from the furnace a final deoxidation in the ladle is necessary. Silicon and aluminum are widely used for this purpose. This brings with it a certain danger of inclusion formation, but as a rule the oxygen content is sufficiently low so that this matter is not serious. However, when large additions of aluminum are used in order to obtain inherently fine-grained steels the inclusion problem may again become serious. This matter of fine-grained steels is illustrative of more recent developments. It has been found that if a large aluminum addition is made to the steel the tendency for grain growth in the austenitic phase is markedly reduced, the steels so treated being known as inherently fine-grained steels. Vanadium has been used similarly for many years, and without the correlative inclusion problem, but the cost of this element has discouraged its use in the less important alloy steels.

The mechanism of production of fine-grained steels has not been well established as yet. One theory holds that the

small grains are produced by the presence of small oxide or carbide particles acting as nuclei which give seeding action similar to that of dust in precipitation from saturated liquid solutions. Another holds that it is due to the actual presence of small amounts of the elements in question in solid solution. Regardless of the theory, we are faced with the need for an addition agent which will produce the fine grain, but at the same time not present an inclusion problem or an economic problem. As a result of a study of inclusion types, complex alloys have been developed. One of the more recent and effective of these contains silicon, aluminum, vanadium and zirconium in balanced proportions. This gives freedom from undesirable types of inclusions, and the combined effect of three grain-refining elements—aluminum, vanadium and zirconium—accomplishes the major objective by producing inherently fine-grained steel.

Master alloys, particularly those in the ferro-alloy category, may also be used for special purposes. It was earlier mentioned that nitrogen in high chromium steels resulted in a relatively fine grain in the cast state. This is effectively accomplished by adding the chromium in the form of a master alloy of iron, chromium and nitrogen, commonly known as high nitrogen ferrochromium. Whether because of the seeding action of the chromium nitride or for some other reason not explained the grain size of the cast structure is markedly reduced and tendency to grain growth on long exposure at elevated temperatures in service is likewise reduced. This also has a correlative effect on the hot working properties of ingots and billets, the fine-grained structure in this case being appreciably more ductile, particularly at elevated temperatures. As a result, the nitrogen addition is almost universally used today in high chromium irons.

Cast iron is a most complex alloy. In view of the fact that very little was demanded of cast iron in the past the real complexity of its nature was not appreciated. Only with the advent of high strength cast irons and short cycle malleable cast irons has the true nature of cast iron been investigated. There are two distinct problems in cast iron which are unfortunately interrelated. One is to produce a cast iron in which the graphite is suitably distributed, generally as rela-

tively fine graphite flakes.   The other is to affect the matrix, essentially an iron carbon alloy, by means of alloying additions in a manner entirely analogous to the way in which alloys affect steel proper.   It is not surprising that most of the alloying additions, such as chromium, manganese and molybdenum, when used in proper proportions tend to produce a pearlitic matrix.   However, most of these alloying additions likewise tend to form carbide rather than graphite, so that other alloying additions are necessary to balance this effect and prevent the alloy from forming a cementite mass rather than a gray cast iron.   The best known graphitizers are silicon, nickel and copper, although calcium, aluminum, and zirconium are also of interest.   Metallurgists have developed a number of master alloys, combining elements from each group. Many of these are ferro-alloys.   They are already industrially successful and with the increased understanding of the exact effect of each element, alone or in combination, even more effective addition alloys are to be expected.

From all of the above we have seen that alloying has progressed from an art to a science, and while we have learned much, particularly in the last twenty years, there is still a great deal to be learned.   The broad subject of solid solution and intermetallic compound formation, together with the previously mentioned concept of "order disorder," is still being intensively studied by the physicists, and as yet can hardly be said to have been applied in the science of alloys. Certainly within the next decade this concept will be reduced to the category of a tool for the metallurgist.   Again, the structure of the atom proper is under constant investigation by the physicist, and a better understanding of the significance of the nature of electron shells will do much toward answering the problem of why certain elements are soluble in each other in the solid phase under certain conditions and form intermetallic compounds under other conditions.   Further, while we have long realized the analogy between the reactions and phase changes of metallurgy and those that are normally considered in the field of chemistry, the effect of diffusion velocities on the specific rate of such metallurgical reactions is only now being given serious consideration.   The quantitative correlation of rates of diffusion and rates of transformation

will do much to increase the ability of the metallurgist to synthetically produce and control their behavior. Thus, we may look forward to a future of alloys tailor-made for specific purposes. Such alloys will result in much more efficient engineering and overall economy.

It has often been said that man has passed from the Stone Age, through the Bronze Age, through the Iron Age and is at present in the Steel Age. If we thus take man's more common materials to designate the Age in which he lives it is certainly true that we are just entering the Age of Alloys and that man's technological future is indeed bright.