Chapter IV

EFFECTS OF ALLOYING ELEMENTS IN FORMING AUSTENITE

In the previous chapter, steels were considered in the annealed (or ferrite-carbide) condition in which the alloying elements, according to their individual tendencies, are able to distribute themselves between the ferrite and carbide phases. The strengthening effect upon the ferrite of the several elements was shown to be a highly individual effect, differing greatly among the elements. The elements in the carbide phase exert an influence upon the form assumed by the carbide and hence upon properties, particularly abrasion resistance, but with respect to the tensile test the actual composition of any hard carbide constituent was seen to be of little consequence in any particular mode and fineness of dispersion. Far more potent influences of alloying elements are found. When steels are hardened and tempered, i.e., heat-treated, the presence of an alloying element may thoroughly alter the mode and end-product of austenite transformation in any particular treatment. The resulting structures, and hence the properties which depend so largely thereon, are thus tremendously responsive to the composition and grain size of the austenite.

Alloying Elements in Steel Rendered Austenitic for Hardening

Before the controlled rate of cooling of austenite (the essence of heat-treatment) can be applied to steel, it must be heated to form the austenite from which the desired microscopic architecture is to be finally built. The ferrite and the carbide react together to form the solid-solution in gamma iron only above a certain minimum temperature, the so-called Ac_3 point, and when the steel is so heated austenite formation proceeds at rates which increase with the temperature.

Importance of Appropriate Heating for Hardening — It is almost universal practice to harden steels with all the ferrite eliminated and generally with no carbide remaining in medium carbon steels, but with the higher carbon steels some carbide is often left unabsorbed; indeed, some useful compositions are such as to make impossible the complete solution of all the carbide; for example, high speed steel. The heating of the steel is an exceedingly important step in any process of hardening or heat-treatment and one which in some instances has probably had insufficient consideration. The final properties are profoundly altered by the degree to which the carbide phase is dissolved in the newly formed austenite and by the degree of homogeneity of the distribution of dissolved carbon and other elements. For many familiar steels, the optimum heating temperature has been established by long experience, but even here the actual period of time during which diffusion may occur is not much stressed and certainly not adequately prescribed in such instructions as the "one hour per inch of section" rule. No useful diffusion occurs until austenite is established (at a certain minimum temperature) and thereafter it occurs at a rate which increases very rapidly with increasing temperature of heating. Furthermore, the different varieties of carbide compositions diffuse at such different velocities that each composition, in principle at least, should be so heated as to assure, positively, in its makeup the required homogeneity of austenite.

The Formation of Austenite by Carbon Diffusion — Before reviewing the effect of the several elements upon the required heating time and temperature it will be helpful to observe in detail the sequence of events in the solution of carbide

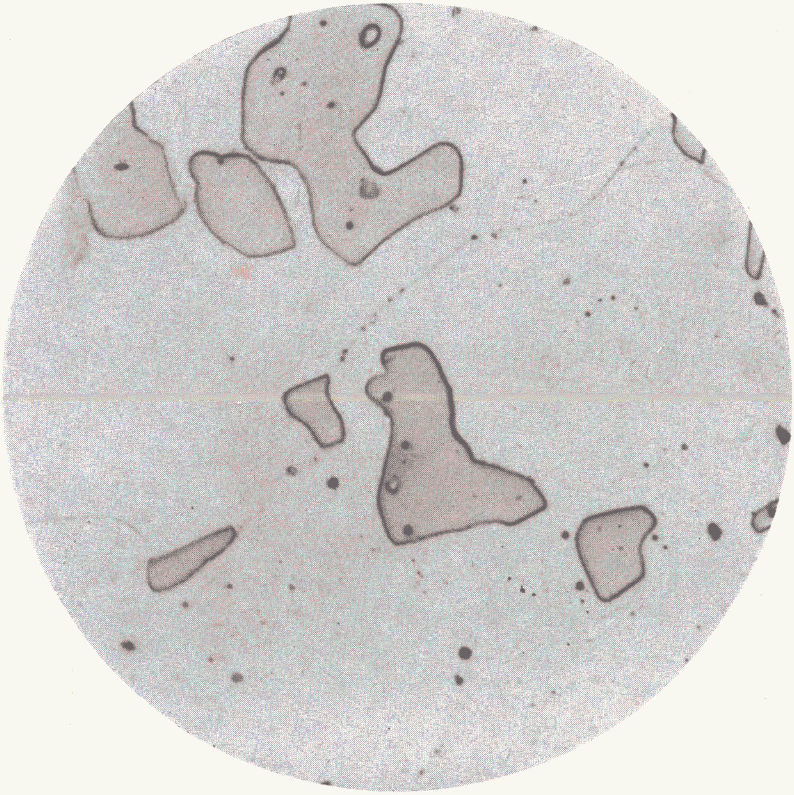

Fig. 58—Photomicrograph of a Spheroidized High-Carbon Steel; (2000×). *(Vilella).*

particles by means of the microscope. Carbon steel will illustrate the principle as well as any other, however different the actual rates may be, or the necessary temperature, for the other steels. Fig. 58 is a photomicrograph at 2000× of a coarsely spheroidized, pure, high-carbon iron alloy. The carbide particles appear gray in a white ferrite; there is a greater tendency for purely specular reflection in the former while the ferrite, slightly roughened, actually reflects more light into the objective lens. If small specimens of this material are plunged into a molten lead bath at a suitable tempera-

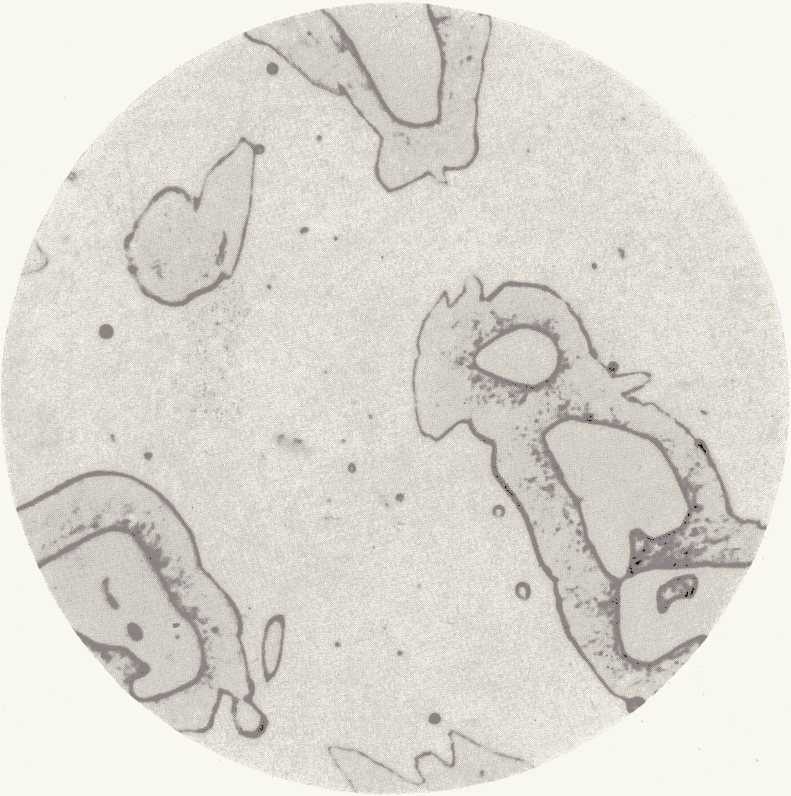

Fig. 59—Photomicrograph of Steel shown in Fig. 58 after Holding about 5 Seconds at 1375 Degrees Fahr. and Quenching. Note Extent of Carbon Diffusion to form Austenite (Now Martensite); (2000×). *(Vilella).*

ture, e.g., 1375 degrees Fahr. (745 degrees Cent.) the specimen almost instantly achieves this bath temperature and thereafter the reaction between the ferrite and carbide to form austenite is inaugurated. The reaction necessarily begins at the carbide-ferrite interface. To study this reaction it is necessary only to quench successive specimens after increasing time intervals at temperature, the quench serving to "fix" the reaction at the status reached in the various intervals. The austenite formed will be converted to martensite, while

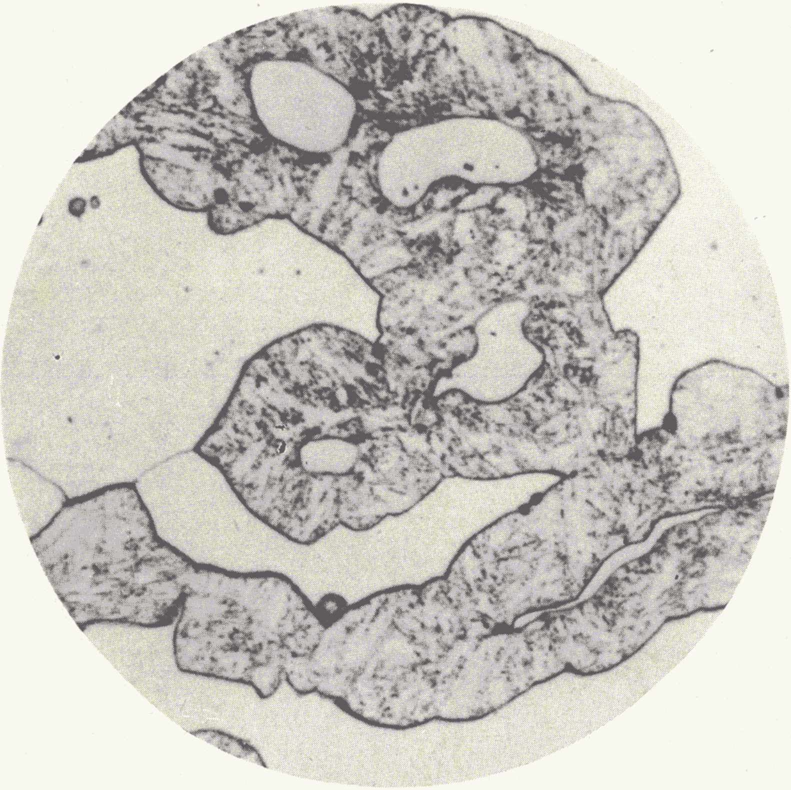

Fig. 60—Same as Fig. 59 except after 15 Seconds; (2000×). *(Vilella).*

any unaltered carbide and ferrite will remain unchanged by the quench to be recognized as such during subsequent microscopic examination. Figs. 59, 60 and 61 show the structures after 5, 15 and 60 seconds at 1375 degrees Fahr. (745 degrees Cent.). Fig. 61 is essentially the final structure remaining after any interval (actually 60 seconds) since the steel carried a carbon content in excess of that dissolvable at the temperature employed. The important feature is the comparative rapidity at which carbon migrates in pure carbon steel. The carbon originally in the carbide particles near the interface has moved out some 0.0003 inch in as short a time as 5 seconds

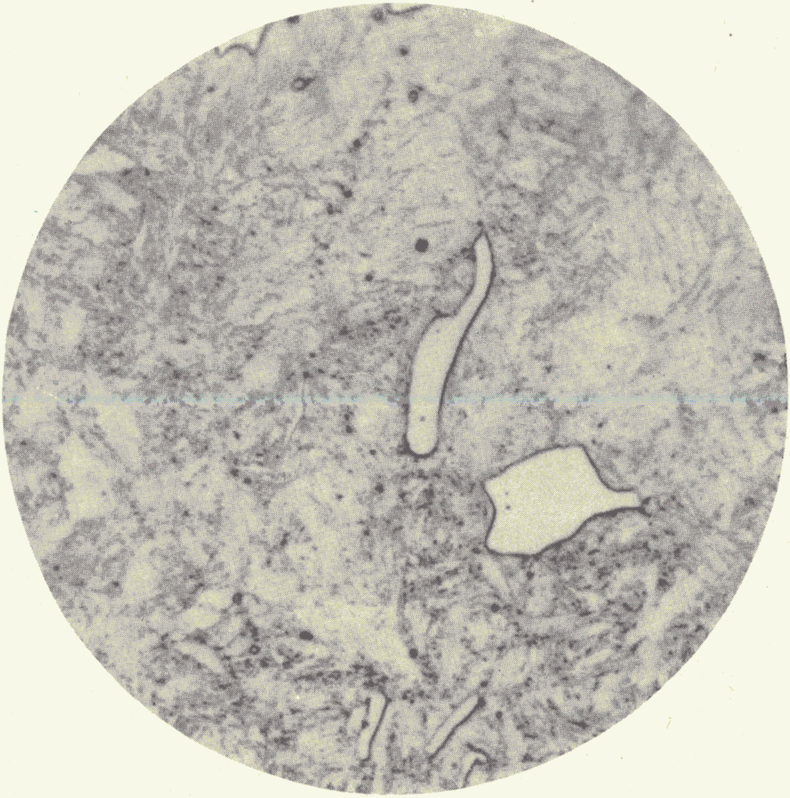

Fig. 61—Same as Figs. 59 and 60 except after 60 Seconds; (2000×). *(Vilella).*

and in 60 seconds sufficient carbon to form a complete austenitic matrix has diffused outward from the particles to a distance at least equal to half the spacing between carbide particles. But how much dissolved carbon is required to accomplish merely this? Really very little! Probably only 0.55 per cent carbon is necessary to permit the martensite formation seen in the photomicrographs. Perhaps slightly less is necessary to convert the entire matrix to austenite at the heating temperature. Thus, after heating at 1375 degrees Fahr. (745 degrees Cent.) one may quickly convert the steel

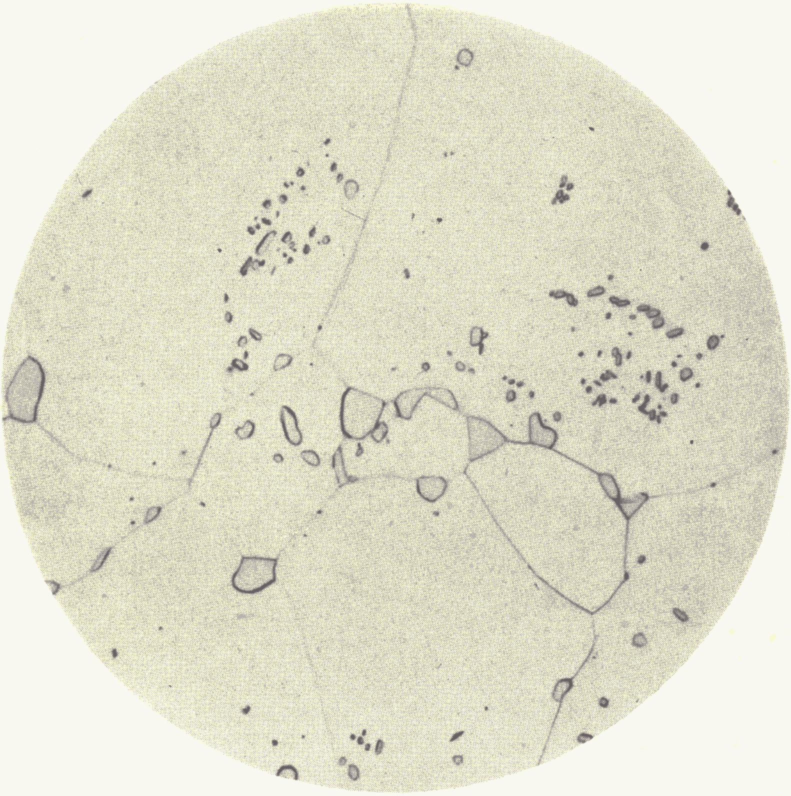

Fig. 62—A Spheroidized Structure in a 0.20 Per Cent Carbon Steel Employed to Investigate Solution of Carbon at 1550 Degrees Fahr. (845 Degrees Cent.); (1000×). *(Vilella).*

to a state of exclusive austenite and carbide and, upon quenching, develop martensite and carbide, but the product is far from that which may be secured by adequate solution of the carbide so as to secure a homogeneous austenite essentially wholly saturated with respect to carbon in cementite. At the moment when the last trace of ferrite just vanishes the austenite near the carbide particles contains about 1.1 per cent carbon, while the last to form carries only about 0.55 per cent. This steep concentration gradient is propitious for rapid carbon diffusion, but as it levels off the rate drops until

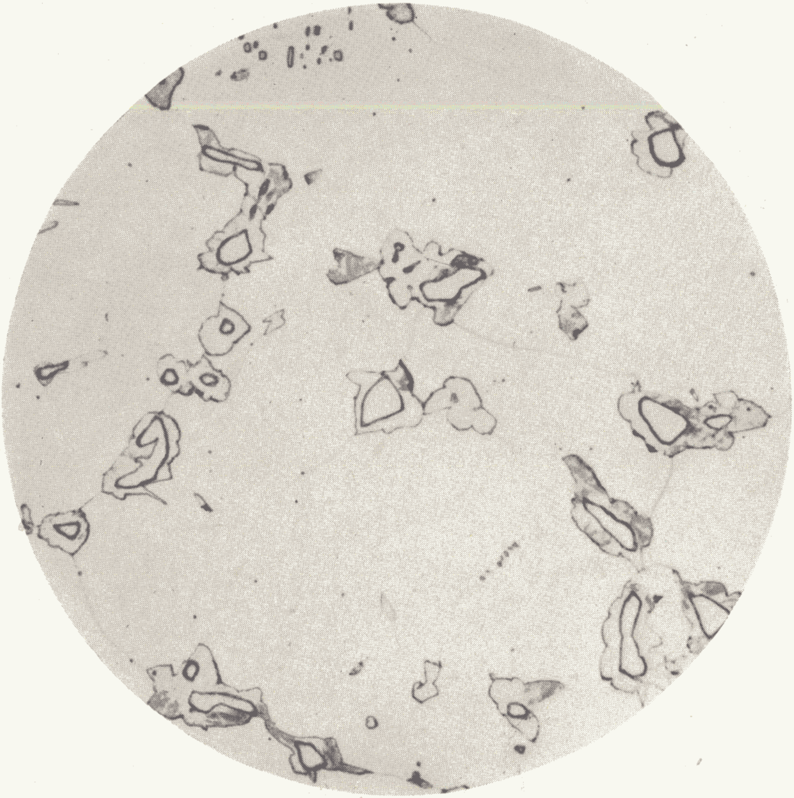

Fig. 63. Photomicrograph of the Steel of Fig. 62 after 5 Seconds at 1550 Degrees Fahr. and Quenching; (1000×). *(Vilella).*

the last solution and homogenization is slow indeed. Fortunately, however, the last degree of homogenization is likewise unimportant.

These circumstances are well illustrated also in the series of photomicrographs, Figs. 62 to 67 inclusive, which represent the process of carbide solution in a 0.20 per cent carbon steel at 1550 degrees Fahr. (845 degrees Cent.) beginning from the spheroidized structure of Fig. 62. The photomicrographs represent the diffusion of carbon, — as in the series for high-carbon steel,—but in this case the carbide particles

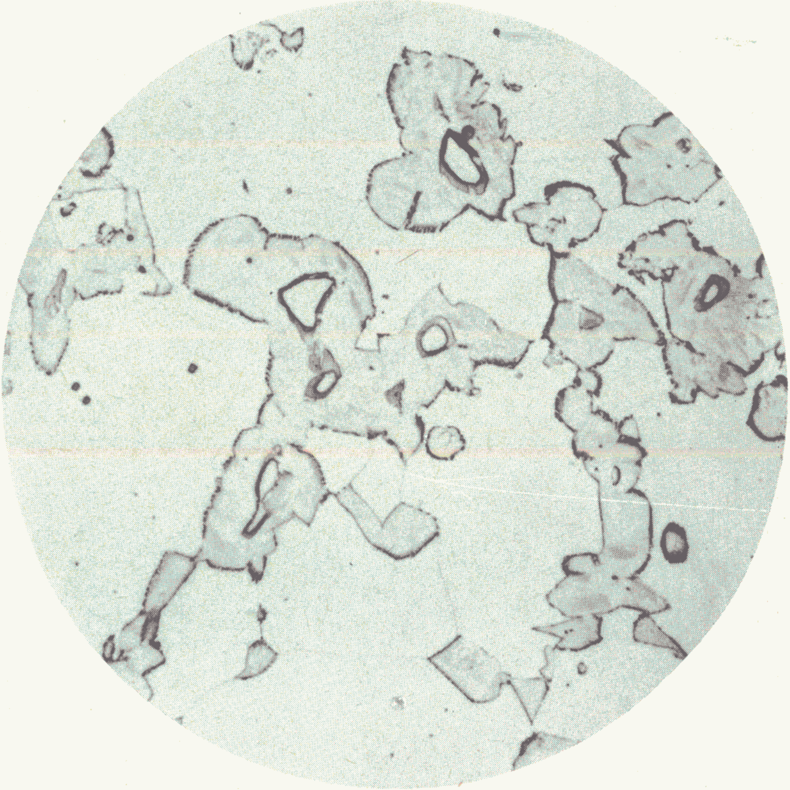

Fig. 64—Photomicrograph of the Steel of Figs. 62 and 63 after 8 Seconds at 1550 Degrees Fahr., Quenched; (1000×). *(Vilella).*

vanish before the ferrite is wholly eliminated. Homogenization within the austenite may therefore be well under way in an austenite-ferrite mixture. It will be noted that in this series the cooling rate was not sufficient to produce martensite exclusively and that a very low-carbon pearlite resulted from the quench. Although this circumstance brings out clearly that the purely pearlite structure may have a very low carbon content the pearlite is quite as useful a measure of diffusion distance as the martensite.

The hardness curves of Fig. 68 illustrate well the inferior

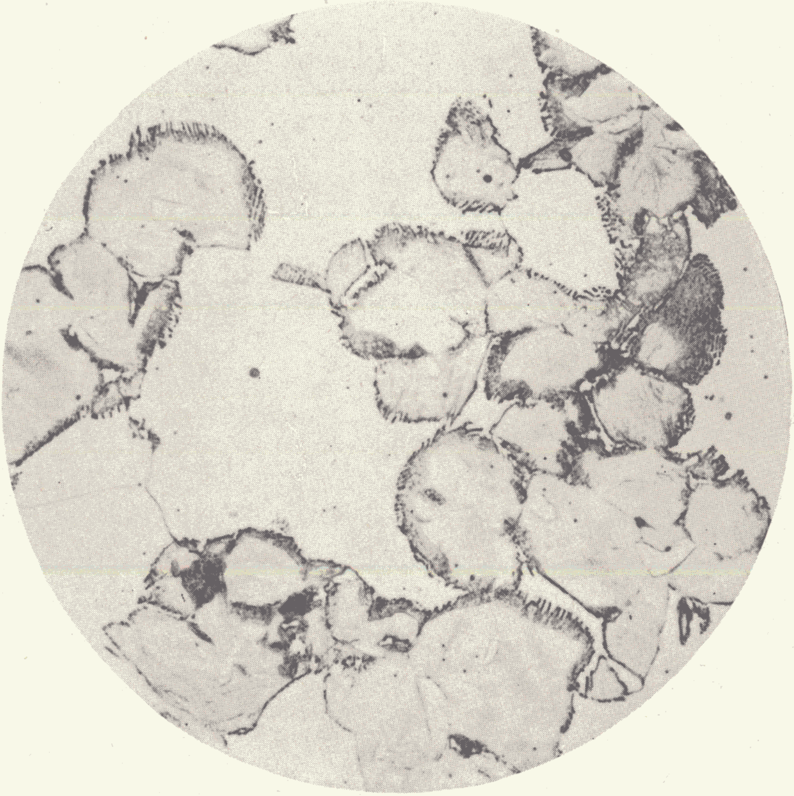

Fig. 65—Same as Fig. 64 except after 15 Seconds; (1000×). *(Vilella).*

average hardness of the structures resulting from unhomogenized austenite, and the approach to the maximum as a longer heating period induces a more nearly homogeneous austenite.

Regarding the solution of carbide in a quantitative way, it is desirable for the sake of simplicity to continue the study of this reaction at constant temperature rather than as it occurs in practice over a range of gradually increasing temperature. Fig. 69 shows the actual carbide remaining undissolved (expressed as percentage of the total mass of steel)

Fig. 66—Same as Figs. 64 and 65 except after 45 Seconds; (1000×). *(Vilella)*.

after increasing intervals of maintenance at 1600 degrees Fahr. (870 degrees Cent.). In these steels the initial proportion of carbide was about 15.5 per cent corresponding to 1.02 per cent carbon. It is interesting to note that some 80 per cent of the carbide is dissolved in 10 seconds, while 30 minutes did not suffice to dissolve the whole of it, indeed a trace of the originally largest spheroids remained after 1 hour at 1600 degrees Fahr. This curve is plotted from data secured by electrolytic separation of the carbide, which method was satisfactorily checked by area estimates made at the micro-

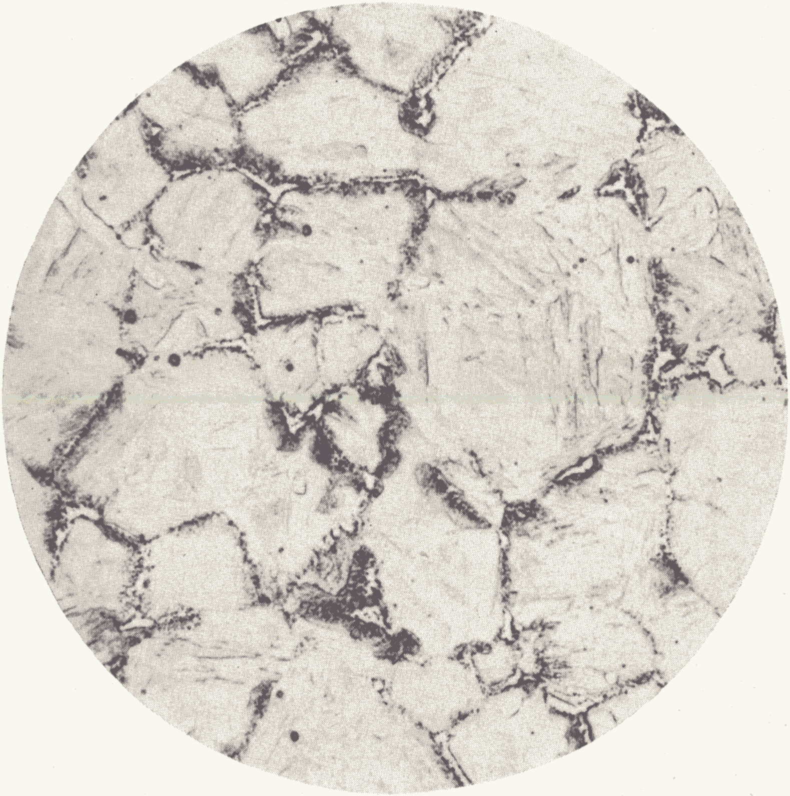

Fig. 67—Final Structure in Series of Figs. 62-66 after 8.5 Minutes at 1550 Degrees Fahr. (1000×). *(Vilella).*

scope by a reliable, but very time-consuming, method. The initial structure was essentially that of Fig. 70, a photomicrograph at 1000 diameters.

With this quantitative impression of the solution of carbide it is comparatively easy to reason dependably concerning corresponding reactions in alloy steels where only a few data are available. The important point is that once a temperature is established at which all, or a substantial, desired proportion, of the carbide is ultimately soluble, the solution will begin rapidly and then gradually slow up and the mechanism

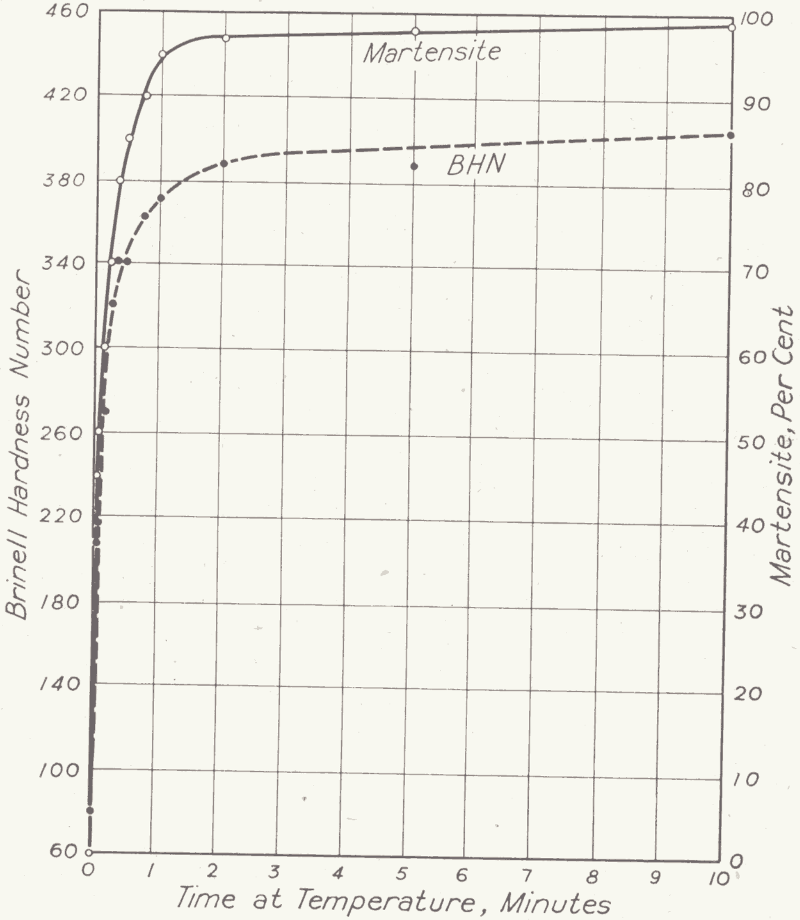

Fig. 68—The Increase in Hardness in the Quenched Steel of Figs. 62-67 with Extension of Heating Period. The Proportion of Martensite (Austenite) is also shown.

will be always substantially as shown for carbon steel, except for rate. Attention should now be directed to some regard of the temperatures at which such solution is possible in steels carrying various alloying elements, for this feature is very definitely controlled by alloy content.

Selecting the Heating Temperature—The selection of a thoroughly satisfactory heating temperature for the hardening or normalizing of any certain alloy steel composition can best be made on the basis of experimentation in which tests of the desired properties are carried out upon variously heated specimens. The time and expense involved in such preliminary studies should not deter one from this procedure and nothing brought out here is intended to dissuade anyone from such investigations. For the purpose of building up an understanding of the fundamental factors determining the optimum temperature of heating it is expedient to consider, however, the formation of austenite at elevated temperature in ternary iron-carbon alloys with increasing amounts of each individual alloying element alone.

Ternary Space Models and Their Sections—For this purpose it would be a happy circumstance if solid- or space-models of the ternary equilibrium diagrams[11] were available for all the systems. Actually such models as illustrated in Fig. 71[12] have not been discovered for any of the systems under discussion and, if they were at hand, they could not be used as lantern slides nor accommodated on two-dimensional pages of a book. Even photographs of such models are usually not very enlightening.

The ternary equilibrium systems for some of the elements have been well studied and sections are available for

---

[11] A supplementary word concerning 3-dimensional, or solid, models of ternary equilibrium diagrams may be in order. Fig. 46 illustrates the means of representing ternary compositions on a plane. If now it is desired to show at which temperatures any changes in constituency occur for the members of the ternary series, it is only necessary to erect perpendiculars upon composition plane and to measure off the temperatures, with suitable scale, upon these perpendiculars. With sufficient verticals (i.e., compositions) marked off by analogous points marking a common change in phase, surfaces may be passed which become then the phase boundaries.

Clearly a vertical plane may be erected carrying all compositions having a constant content of one component. The traces upon this plane of the phase boundary surfaces constitutes a typical section-diagram illustrated in Fig. 72. Three-dimensional diagrams are usually constructed from a sufficient number of these constant-component, section diagrams, rather than the reverse.

Fig. 71 shows idealized examples of the solid, ternary, equilibrium diagram for iron alloys. The two-phase zone, bounded by two warped surfaces, is schematically drawn; the two-phase zone is shown in A for the Iron-Nickel-Manganese Type; in B for the Iron-Tungsten-Molybdenum Type; and in C for the Iron-Nickel-Molybdenum Type.

It is important to bear in mind that the constant-alloy, section diagrams (as in Fig. 72) are employed to show only the phases which (at equilibrium) are established at the various carbon concentrations. Neither the composition nor the proportion of any phase in a heterogeneous field is in any way revealed in such sections. It should be unnecessary to add that any equilibrium diagram tells nothing whatever of the time interval required to bring about the changes in constitution which result from a change in temperature.

[12] Fig. 71 is drawn after the manner of Köster and Tonn, *Archiv für das Eisenhüttenwesen*, Vol. 7, 1933-34, p. 193-200.

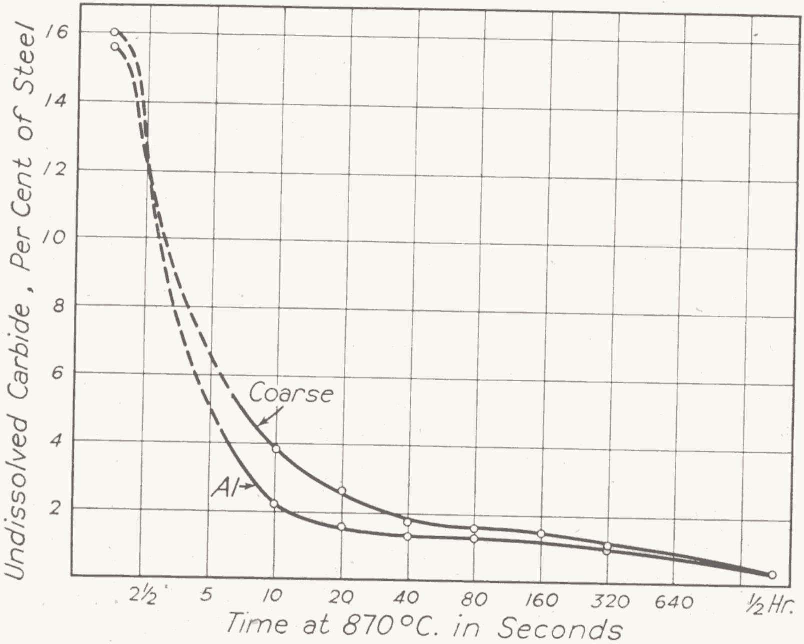

Fig. 69—The Proportion of Carbide remaining Undissolved in 1.0 Per Cent Carbon Spheroidized Steel after Various Heating Intervals at 1600 Degrees Fahr. Note Similarity of Fine and Coarse Grain Types.

a variety of alloy and carbon contents, for others the data are fragmentary or nonexistent. Thus in Fig. 72 the temperature (ordinate) -carbon (abscissa) section for iron-chromium-carbon alloys of 12 per cent chromium is shown in full detail. Obviously one may discover here not only the compositions and temperature of heating in which to secure ultimately a pure austenite, but also the conditions for the formation of the first trace of austenite in the three-phase zone, or the two-phase combinations with either ferrite or with carbides. The conditions for the cementite form and the special carbide crystal are also to be seen. This diagram is, however, complicated and admittedly may be confusing to one not acquainted with the use of such charts.

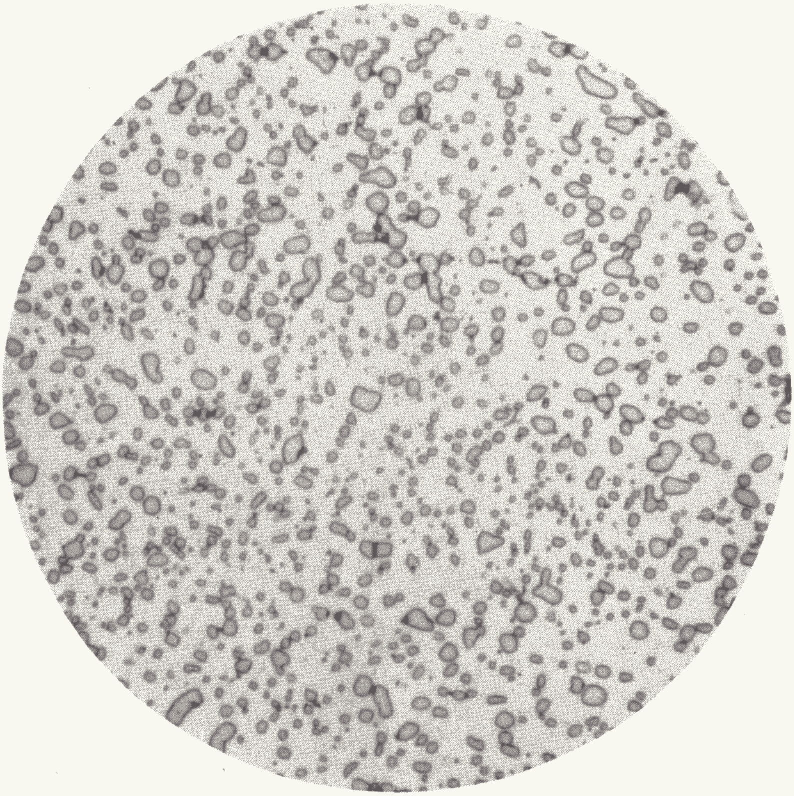

Fig. 70—Photomicrograph of a Spheroidized 1.0 Per Cent Carbon Steel such as Employed in Determination of Fig. 69; (2000×). *(Vilella).*

Abbreviated Temperature-Constant Alloy Sections — To gather a reasonable familiarity with the broad trends of the alloying elements a less detailed knowledge of the heating temperatures required to form austenite in various compositions may suffice. Accordingly a series of diagrams is presented which show only the compositions and temperatures within which pure austenite will result. To simplify further, several typical proportions of the alloying element are presented on a single chart so that the shift with increasing alloy content becomes readily apparent. In each chart a

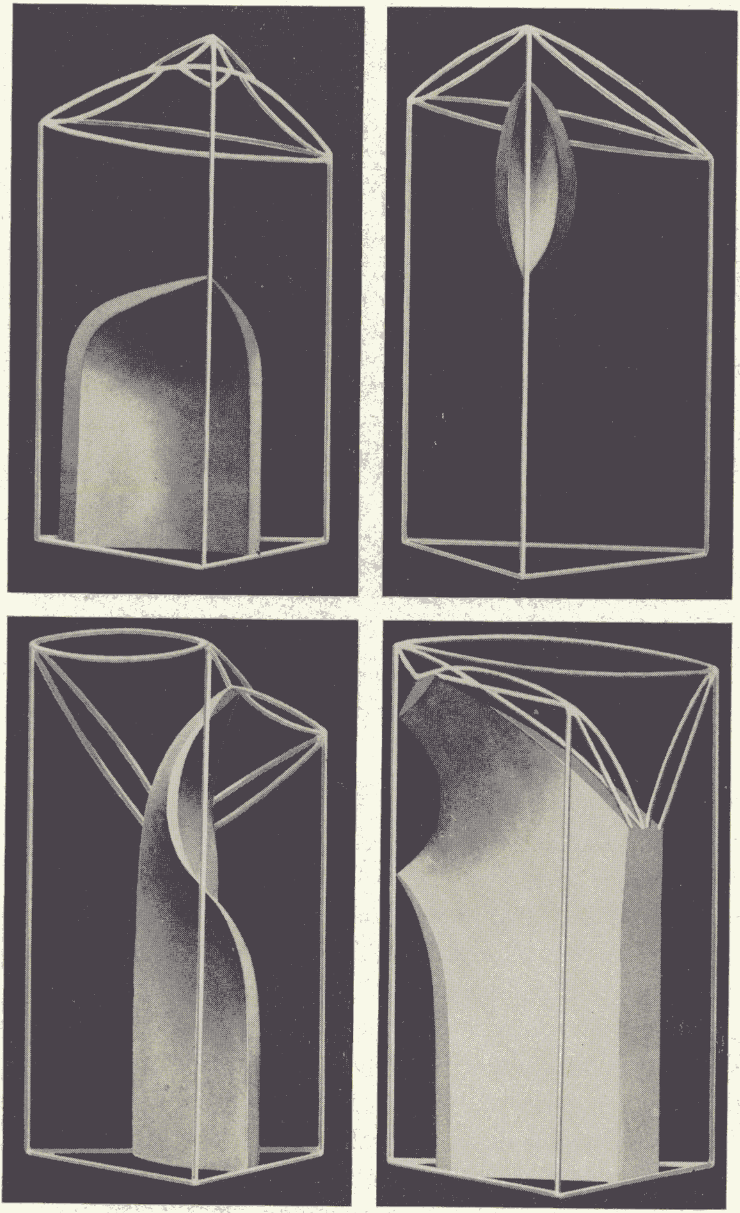

Fig. 71—Examples of the Appearance of 3-Dimensional Ternary Equilibrium Diagrams (Idealized)—A, Systems of the Iron-Nickel-Manganese Type; B, Systems of the Iron-Tungsten-Molybdenum Type; C, Systems of the Iron-Nickel-Molybdenum Type. The Solid Shape is the 2-Phase Region. *(After Köster and Tonn).*

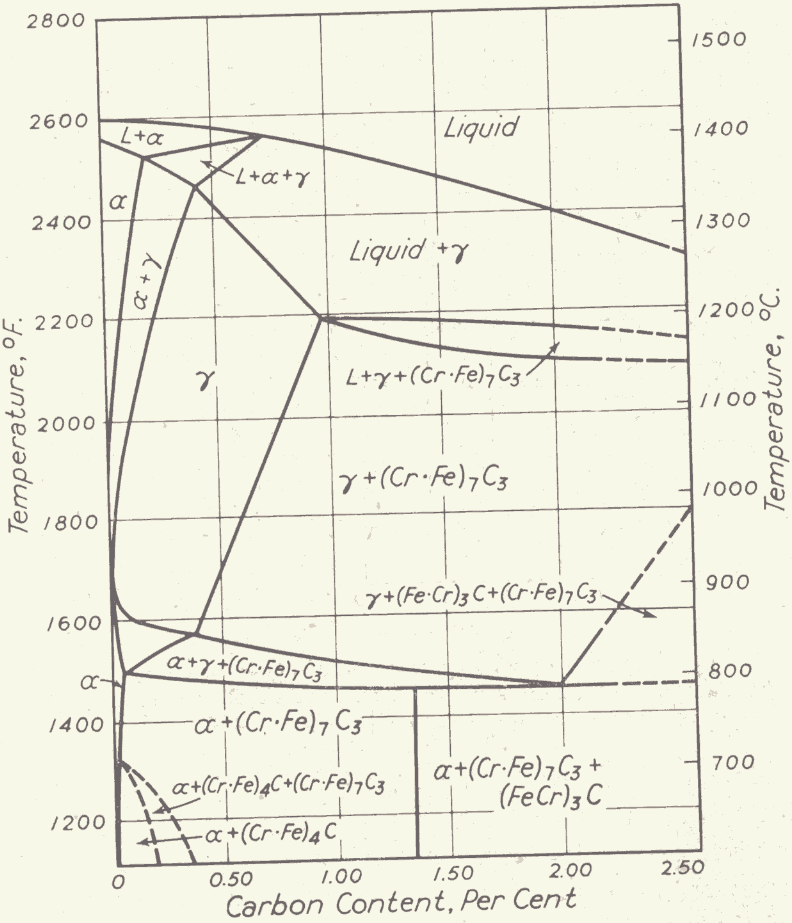

Fig. 72—The 12 Per Cent Chromium Section of the 3-Dimensional Ternary Fe-Cr-C Equilibrium Model. (Note that this is not a Binary Diagram and may not be used as such). *(Tofaute, Küttner and Büttinghaus).*

dotted line shows the field for austenite in ordinary carbon steels.

Fig. 73 for manganese[13] is typical also of the elements nickel and cobalt which are not more soluble in alpha iron than in austenite and not strongly carbide forming. The

---

[13] See Footnote 7.

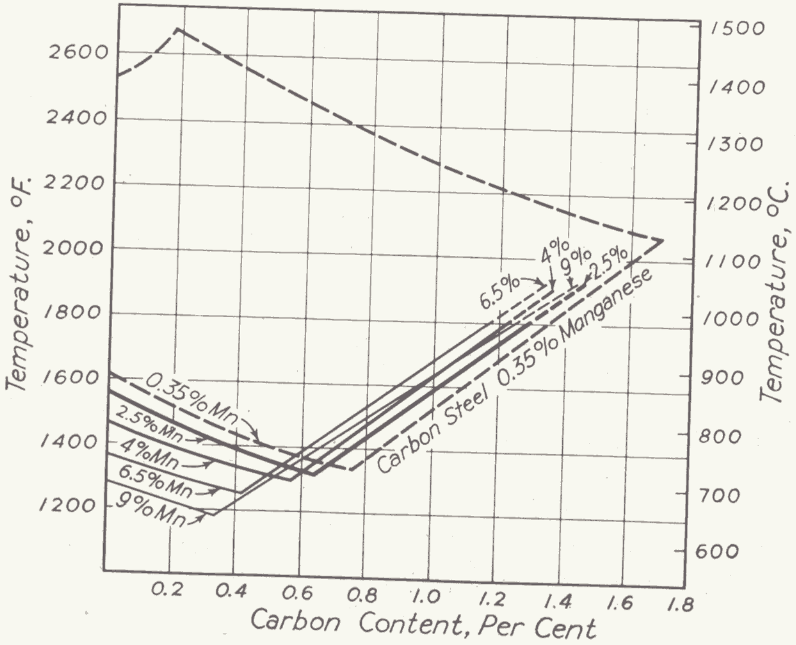

Fig. 73—Effect of Several Uniform Manganese Contents upon the Carbon Limitations for Pure Austenite at Elevated Temperatures. *(After data of Wells et al).*

minimum temperature for complete austenite formation shifts to lower temperatures with increasing manganese content and as in all systems the carbon content for this point decreases with increase in alloying element. Although, strictly speaking, the significance of the word "eutectoid" is lost in some compositions, the word will be employed to designate both the composition and temperature of these points of minimum temperature for pure austenite as shown on the diagrams. Fig. 74 indicates the shrinking of the pure austenite field by higher chromium[14] content and the final elimination of pure austenite as a possible exclusive constituent at about 20 per cent chromium. It should be noted that in low carbon compositions chromium first lowers the tem-

---

[14] See Footnote 7.

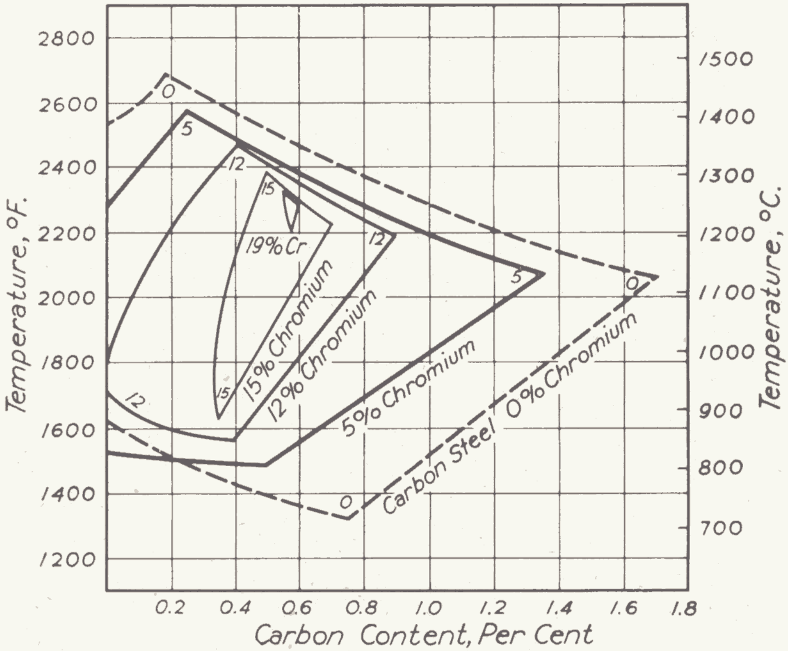

Fig. 74—Effect of Several Uniform Chromium Contents upon the Carbon Limitations for Pure Austenite at Elevated Temperatures. *(After data of Tofaute, Küttner and Büttinghaus).*

perature range for elimination of ferrite upon heating but at higher chromium raises this temperature. Fig. 75 for molybdenum[15] is not greatly unlike that of chromium except that only about 8.2 per cent molybdenum is compatible with pure austenite alone at any temperature. The transformation temperature upon heating is uniformly raised in all respects by molybdenum regardless of concentration. Molybdenum is very similar to tungsten in altering the formation of austenite, except that smaller proportions of molybdenum bring about the various restrictions in the austenitic field. About 12 per cent tungsten[16] suffices to prevent the complete austenitization of any iron-carbon combination in which it is

---

[15] See Footnote 7.
[16] See Footnote 7.

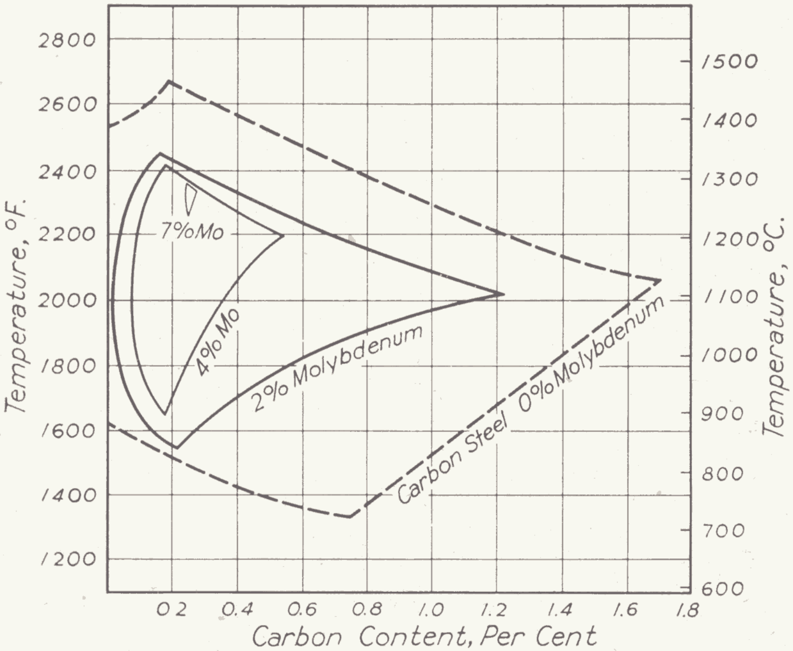

Fig. 75—Effect of Several Uniform Molybdenum Contents upon the Carbon Limitations for Pure Austenite at Elevated Temperatures. *(After data of Takei).*

present. Silicon, although not a carbide-forming element like tungsten and molybdenum, nevertheless rapidly constricts the austenite field until at 8.5 per cent silicon there is no longer any possibility of austenite as a sole constituent, as illustrated in Fig. 76.[17] Fig. 77 shows how rapidly the element titanium[18] shrinks the pure austenite field so that it vanishes at 1 per cent titanium. One may logically expect that vanadium might behave in a manner intermediate between molybdenum and titanium with a limit on pure austenite at some 4.5 per cent

---

[17] "A Metallographic Investigation of the Iron-Silicon-Carbon Alloys", by Sato, Technical Report, Tohoku, Vol. 9, 1929-30, p. 515-565.

"A Contribution on the Constitution of the Iron-Carbon-Silicon System", by Kriz and Poboril, *Journal,* Iron and Steel Institute, Vol. 122, 1930, p. 191-213.

"On the Constitution of the Iron-Carbon-Silicon System". Part II, Section Through the Tri-dimensional Diagram at 8 Per Cent Silicon. Collection of Czechoslovak Chemical Communications, Vol. 3, 1931, p. 61-72.

See Monograph, "Alloys of Iron and Silicon", by Greiner, Marsh and Stoughton, Engineering Foundation, McGraw-Hill, 1933.

[18] See Footnote 7.

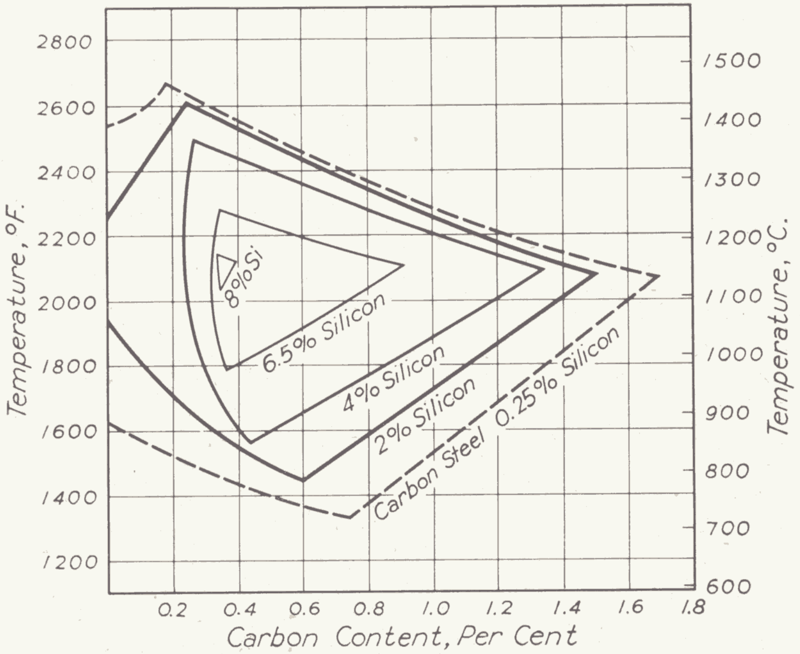

Fig. 76—Effect of Several Uniform Silicon Contents upon the Carbon Limitations for Pure Austenite at Elevated Temperatures. *(After data of Sato).*

vanadium and a carbon content in the vicinity of 0.25 to 0.30 per cent and a temperature of perhaps 1250 to 1300 degrees Cent.

In the use of all these charts showing the austenite field as a function of individual alloy content, it must be remembered that the field is for ultimate *pure* austenite formation at approximate equilibrium. Compositions lying progressively to the right of the "triangles" will be largely austenite with increasing amounts of carbide (or possibly graphite in the case of high silicon), and many steels employed for tools and abrasive wear are intentionally so constituted. Below the areas of pure austenite, that is at lower temperature, it will be found that a three-phase zone exists in which ferrite, austenite and carbide will persist together even at equilibrium.

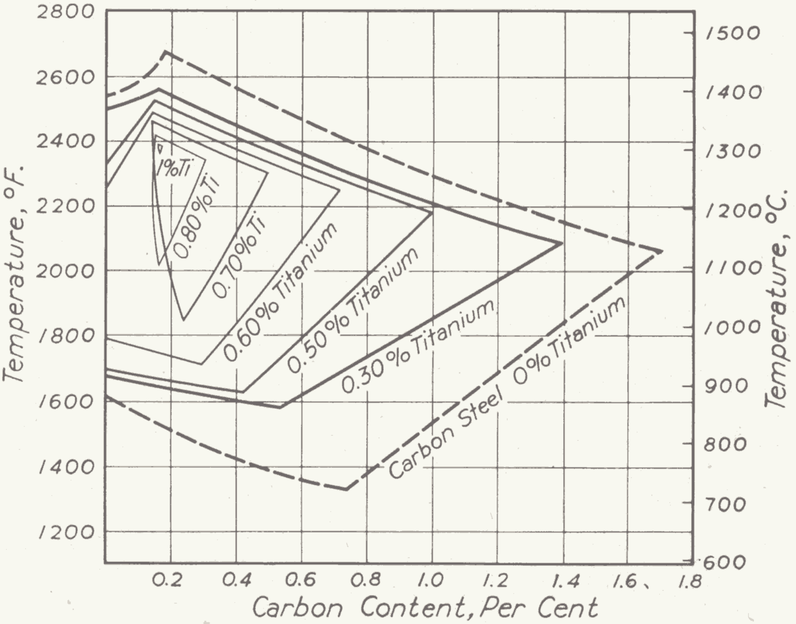

Fig. 77—Effect of Several Uniform Titanium Contents upon the Carbon Limitations for Pure Austenite at Elevated Temperatures. *(Tofaute and Büttinghaus).*

To the left of the austenite areas austenite with more or less ferrite (solutions in α or δ Fe) will be found.

Composition Range for Austenite at Constant Temperature — These vertical section diagrams, continually compared with the carbon steel diagram, will serve to develop an acquaintance with the effect upon austenite formation of the two broad classes of elements (1) those which rapidly restrict its limits and, (2) those which expand them or exert little influence such as manganese, nickel and cobalt. To fix this relationship still more firmly in mind it may be of value to regard the composition limits for austenite with respect both to carbon and the individual elements at some single high temperature. For this purpose one may choose the highest temperature at which carbon steel austenite, saturated

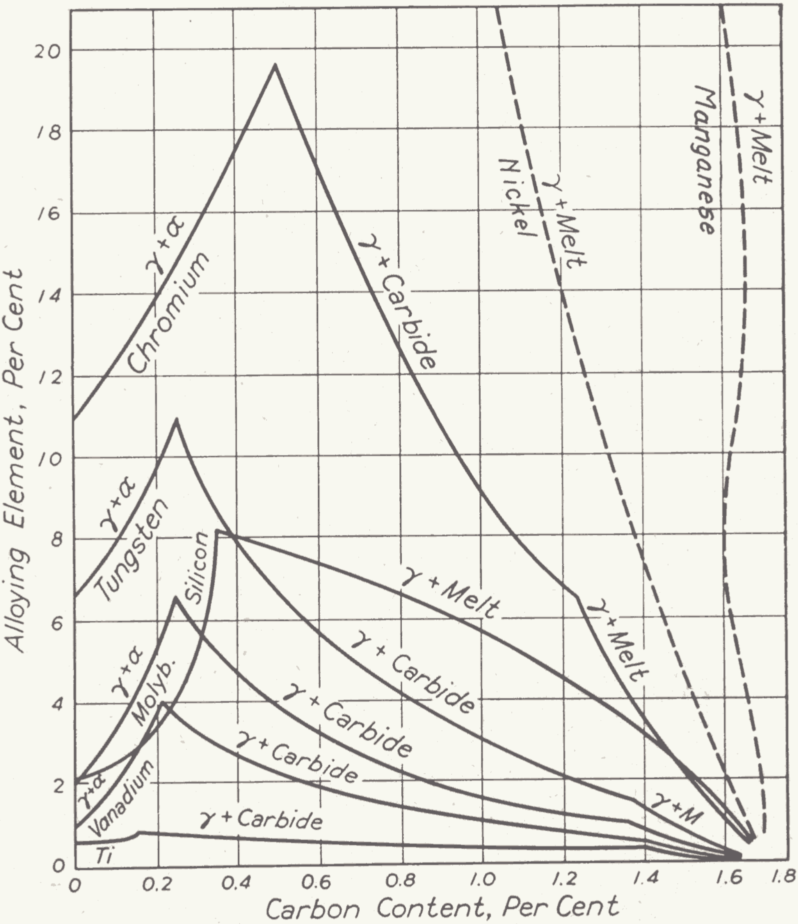

Fig. 78—Composition Limits for Pure Austenite at 2100 Degrees Fahr. (1150 Degrees Cent.) for a Variety of Elements. The Compositions Lying Under the Curve may be Rendered Austenitic.

with carbon, may remain wholly solid, or, in other words, the temperature of maximum dissolved carbon in austenite, which in iron-carbon alloys is at about 2100 degrees Fahr. (1150 degees Cent.). An area, then, on a composition plane at 1150 degrees Cent. can be plotted to show the limits of composition for austenite. As would be expected, increased proportions of chromium, tungsten, molybdenum, silicon, vanadium or

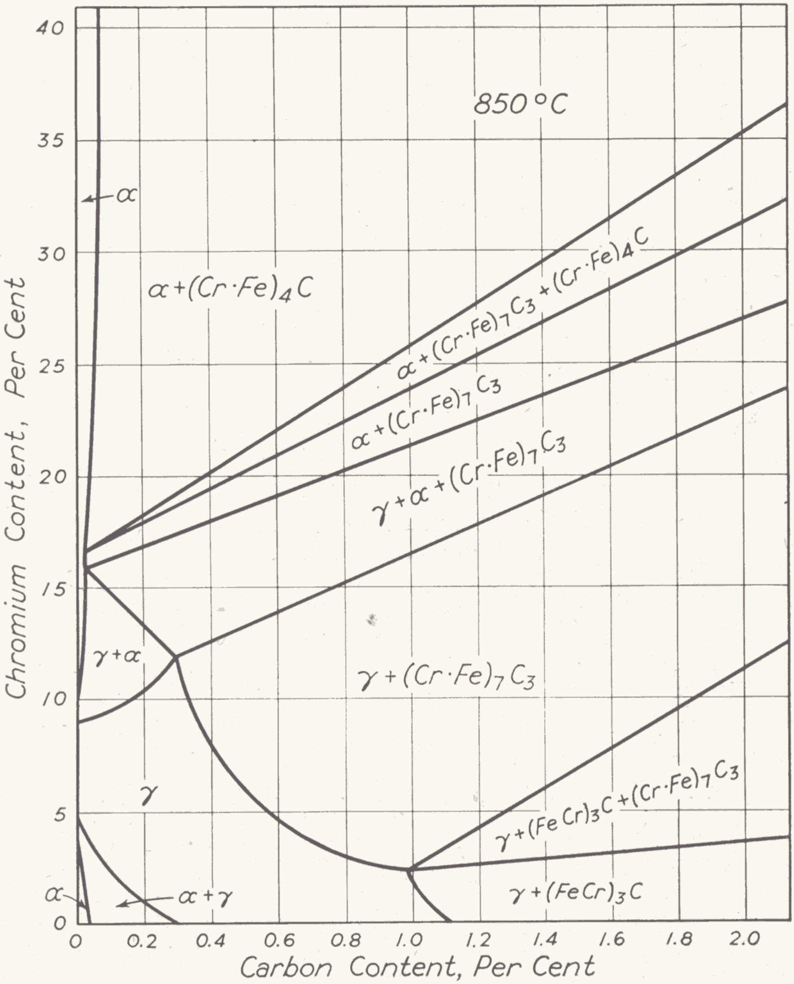

Fig. 79—Composition Limits for Various Phases in the Iron-Chromium-Carbon System at 1560 Degrees Fahr. (850 Degrees Cent.) *(Tofaute, Küttner and Büttinghaus).*

titanium restrict the carbon range in austenite and ultimately close the area while unlimited amounts of nickel, manganese or cobalt are possible in austenite. Fig. 78 is a chart showing this effect of the several elements. The chart is more useful as an illustration of a broad and important effect than as a

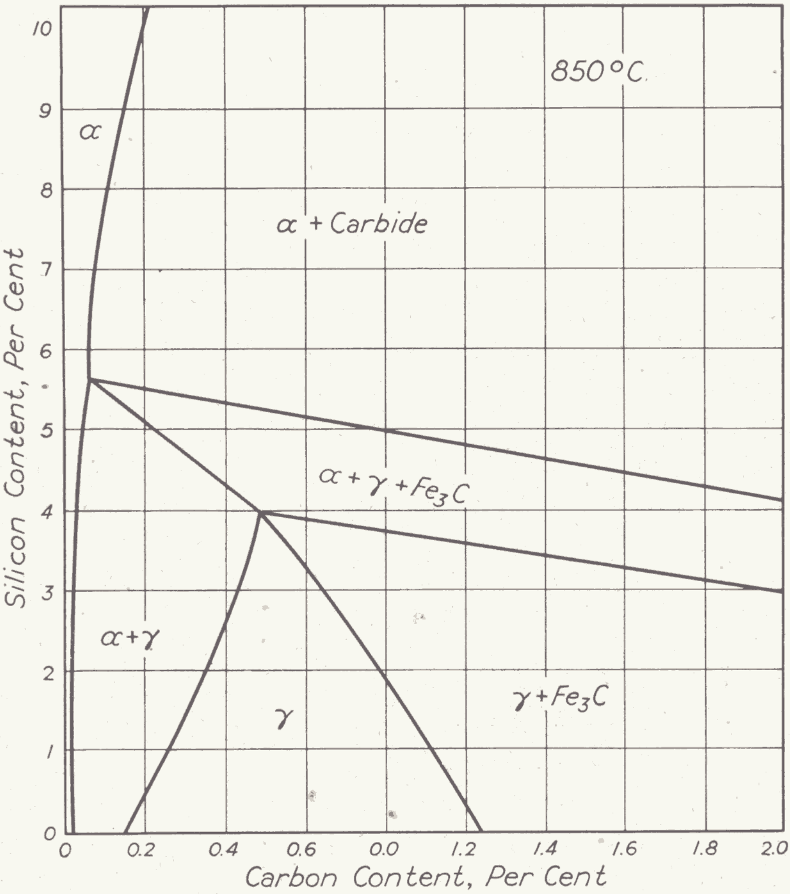

Fig. 80—Composition Limits for Various Phases in the Iron-Silicon-Carbon System at 1560 Degrees Fahr. (850 Degrees Cent.). *(Sato).*

reference for obtaining specific information, since few steels are heated to this temperature for heat-treatment.

It is to be regretted that there are not available a complete list of diagrams of the general type of Fig. 78 but carrying the full phase boundary lines for all useful compositions and, more important, based upon equilibrium at more significant temperatures. The range from 1500 to 2000 degrees

Fahr. (815 to 1100 degrees Cent.) is that most useful in heating medium-alloy steels, but for this range it is more difficult to deduce the precise equilibrium diagram from the incomplete records in reported work. Thus for chromium, which has been well studied by Tofaute, Küttner and Büttinghaus, the status of the constituents developed in a wide range of compositions at 1560 degrees Fahr. (850 degrees Cent.) is well developed as shown in Fig. 79. Similarly a corresponding diagram for the iron-silicon-carbon alloys is able to be shown in Fig. 80. At the risk of some slight inaccuracies it is recommended that students of the physical metallurgy of steel construct the most reasonable diagram possible from existing data on the other systems; aside from the acquaintance thus made with alloy systems the results will be definitely useful for first approximations.

Eutectoid Composition and Temperature in Alloy Systems — It is frequently desirable to know the proportion of carbon which, with a given alloy content, will result in the minimum temperature for complete austenite formation, that is, the "eutectoid composition". This series of compositions exactly corresponds in practical ways to the binary eutectoid composition in two component (e.g., iron-carbon) alloys, and is so designated here, even at the risk of a theoretical inaccuracy. Further, the actual eutectoid temperature is of interest. These are both shown graphically in Fig. 81 for a number of the more familiar alloying elements. It will be noted that while some elements lower the temperature of austenite formation and others raise it, none is found which shifts the eutectoid composition to higher carbon values. The precise effect, however, is highly individual and characteristic for each element.

In the case of steels which carry two or more alloying elements, systematic studies over a range of carbon have been made in only very few instances, notably in the case of

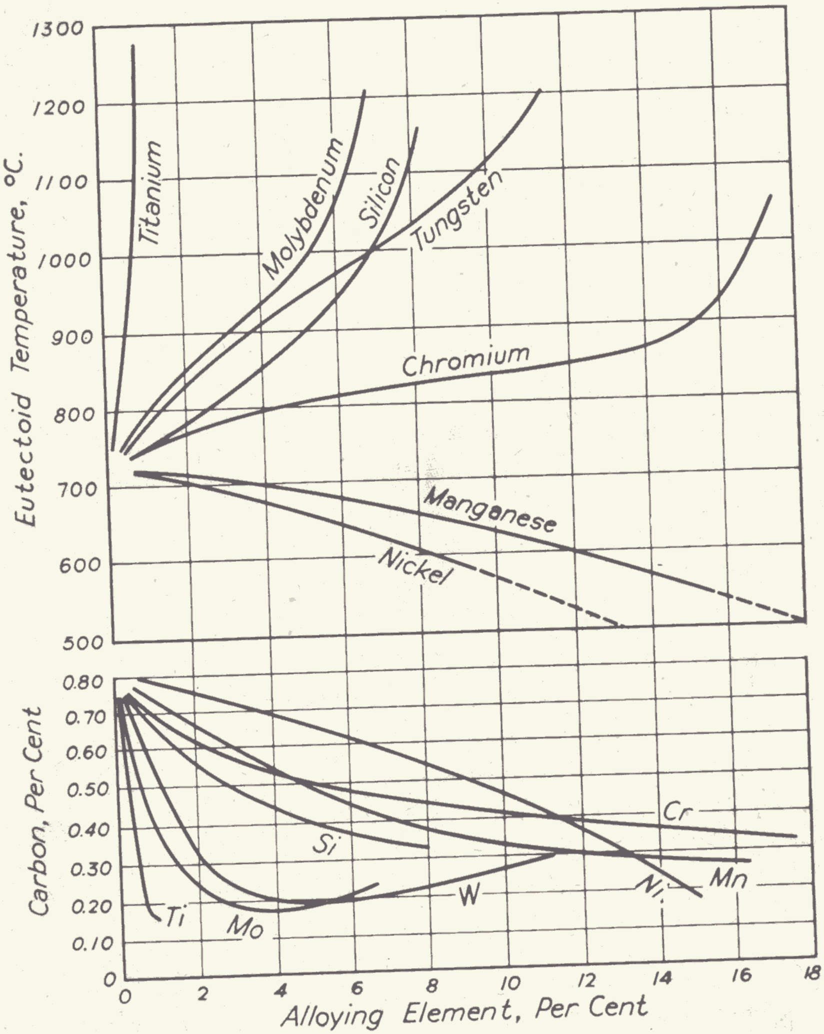

Fig. 81—Eutectoid Composition and Eutectoid Temperature as Influenced by Several Alloying Elements.

18 chromium, 8 nickel. When a first alloy raises the transformation temperature and the second one present lowers it, the aggregate effect generally is to make it possible to secure some austenite at a low-temperature characteristic of the

second element but to restrict the pure austenite formation to a fairly high temperature.

Remembering that the right-hand lines in the diagrams of Figs. 73, 74, 75, 76 and 77 actually reflect carbide solubility, it will be appreciated how a powerful carbide-forming element such as vanadium or titanium removes carbon from the austenite of any carbide-bearing compositions not heated into the fully austenitic temperature zones. Thus it will be seen that chromium or molybdenum will be forced into solid solution by titanium which forms a special, permanent carbide. In alloy steels carrying relatively large amounts of the carbide-forming elements chromium, tungsten, molybdenum, vanadium, etc., as well as silicon, it is practically impossible to have more than some 0.30 per cent carbon in solution.

From Fig. 78 it is possible to arrange the carbide-forming elements in a series which represents their relative effectiveness, weight for weight, in retaining carbon in combination. Inserting the more unusual elements in the series, based upon apparent increasing effectiveness, the order is approximately manganese, chromium, tungsten, molybdenum, tantalum, vanadium, columbium, titanium. Perhaps uranium might prove to be more effective than any (possibly excepting titanium) if it were thoroughly studied.

Equilibrium versus Rate of Solution (Diffusion)— Thus far the formation of austenite *at equilibrium* in steels carrying alloying elements has been considered. It must not be assumed that the special carbides may be dissolved in the time intervals employed with carbon steel. Carbon diffuses rapidly even at 1400 degrees Fahr. (750 degrees Cent.) ; and only carbon need diffuse much in the austenitization of carbon steels. In alloy steels the alloying element must likewise diffuse and the slow rate of migration of some of the metallic elements has been amply demonstrated. Thus in a particle of molybdenum-rich carbide, the so-called omega (ω) phase, the molybdenum content may be 80 to 90 per cent. Regardless of the constitution of the steel as a whole, molybdenum must diffuse away until only perhaps 8 per cent, at a maximum, remains at such a location before austenite may form there. Such a degree of diffusion may take place in reasonable time only at the highest possible heating temperature and accordingly the high heating temperatures prescribed for high-tungsten and high-molybdenum steels are easily explained.

As a matter of fact, in the case of steels carrying only a small proportion of these strong carbide-forming elements, homogenization of the austenite with respect to the alloying element is often not secured. It is often not necessary to dissolve the carbon held by the element since the carbon content is adequate to permit this reservation; the properties, however, would be altered by a distribution of the alloying element throughout the austenite. This matter of degree of solution of slowly dissolving alloying elements is an important one which almost certainly accounts for variable properties secured from the same steel under different conditions and will be discussed as a subject under hardening and tempering of alloy steels.

ALLOY DISTRIBUTION IN HEATED STEELS

In the furnace, ready for quenching, the alloy steels are usually so heated as to form a very large proportion of austenite. Relatively large amounts of all the elements are dissolved in austenite, and the five basic categories, listed for the possible location of added elements in unhardened or annealed steels, do not all seem necessary. In the main, the alloying elements are limited in their distribution as follows:

1. Dissolved in austenite.
2. Combined as carbide.
3. Combined as nonmetallic inclusions.

(Undissolved intermetallic compounds other than nitrides are not known among the alloy steels under discussion and as for elemental inclusions it is probable only that lead, above certain limiting concentrations, may exist as liquid inclusions).

We have seen that unlimited amounts of nickel, manganese and cobalt are soluble in austenite and that several per cent of any of the common metals save titanium may be dissolved. In the particular class of alloy steels to which present interest is specially directed (that is, those of moderate carbon content) the steels may be so heated as to render them almost wholly austenitic. Even the strong ferrite-forming elements which, in the absence of carbon, do not have a high solubility in austenite are able to have that solubility markedly increased by 0.20 to 0.30 per cent carbon.

Elements Dissolved in Austenite—Structurally, the austenite of alloy steel is seemingly not unlike that of carbon steel. It is, however, harder at any certain temperature than carbon steel and acts more "stiffly" in rolling and forging. If one could microscopically examine the austenite of alloy steels at elevated temperature there would probably be nothing to indicate the presence of alloying elements, except a tendency for a higher coarsening temperature and therefore generally finer grains at comparable temperature. The important difference among austenites of different compositions is latent and becomes manifest only in hardening, by virtue of the disparity in transformation rates.

Elements in Undissolved Carbide—It has been shown how undissolved carbides lower the concentration of carbon in the austenite below that of the steel as a whole. When alloying elements are present in the carbide phase in a proportion in excess of that of the steel as a whole obviously the austenite is thus impoverished to that extent. This is the state of affairs in steels carrying proportions of chromium, tungsten, molybdenum, vanadium and titanium, and to a small extent even in certain intermediate manganese compositions. With the vast majority of medium alloy, medium carbon steels the significance of this feature is not great, because so little carbide remains undissolved. The most familiar examples of the effect are the chromium steels carrying titanium in which the titanium-rich carbides, by remaining persistently undissolved, lower the available carbon or effective carbon to such a low value as to reduce hardenability almost to that of carbon-free material. Persistently undissolvable carbide particles are simply inert hard inclusions and play only a passive role in heat-treatment.

One of the circumstances contributing to the retardation of the approach to equilibrium in the solution of carbides and hence of producing a homogeneous austenite in steels carrying the carbide-forming elements lies in the carbide particle itself. During forging or rolling, when the steel is necessarily at a high temperature, much of the carbide, later rejected, is dissolved. Indeed economy and good rolling characteristics demand a high temperature for many alloy steels especially in the first break-down of the ingot. Mechanical work causes fragmentation of the larger carbide particles even if they are not dissolved. At this stage of conversion the high temperature permits considerable diffusion over the microscopic distances generally involved.

Accordingly, as the temperature first falls the most stable carbide may form, for combining tendency itself, not mere availability of atoms, dominates the reactions. Thus the special carbides of the various elements with iron will form first, as the high temperature begins to fall. Suppose, as is true in many commercial steels, that the carbide at equilibrium will be in part special carbide and partly cementite saturated with the alloying element. Then what occurs is almost to be expected. The "heart" of the particles, formed with the first gradual drop in temperature is of the special complex form,

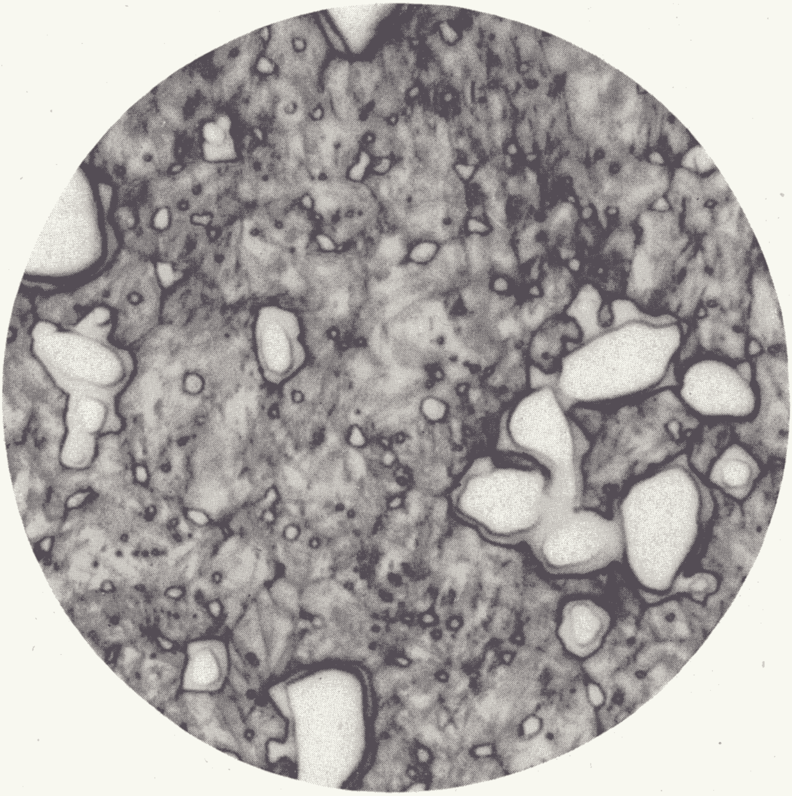

Fig. 82—Photomicrograph of "Duplex" Carbide Particles in a 5 Per Cent Molybdenum Steel. The Interior of the Particle is of the Special Carbide Type, Rich in Alloy; Exterior is Cementite, Lean in Alloy. *(J. R. Vilella, R. F. Campbell and J. W. Price, United State Steel Corporation Research Laboratory).*

while finally the cementite encloses the original particle and it is exposed to the austenite at the interface. Fig. 82 shows many such "duplex" carbide particles; the more angular special carbide is clearly visible at the center of essentially every carbide region, even of the very small ones. (Exceptions are doubtless the instances wherein only the surface layers are traversed by the polished surface.) Certain steels are prone to develop such "cored" carbide particles upon cooling from a high carburizing temperature.

In subsequent heating, the alloy-lean, iron-rich layer of carbide dissolves quickly enough; but with a "counter-pressure" of already dissolved carbon, the alloy-bearing interior of the carbide particle dissolves very slowly unless exceedingly high temperature is provided.

Persistent Carbides and Grain Size—One observes that the grain-size of steels which retain undissolved carbide particles coarsens only at exceedingly high temperature. In many steels, the grain-size quite promptly increases with the disappearance of most of the carbide particles. Thus, a composition such as provides a moderate dispersion of carbide particles still undissolved after desired austenite composition is achieved will in general produce a fine-grained austenite. Such steels are naturally regarded as being inclined toward fineness of grain as properly heated. Thus many tungsten, molybdenum and vanadium steels are automatically fine-grained as ordinarily heated although vanadium may act by other mechanisms also to restrain austenitic grain growth. It will be appreciated that in most instances a considerable portion of the carbide-forming element is dissolved in the austenite while a smaller portion remains with the carbide maintaining its reluctance or inability to dissolve. The influence of such elements is therefore dual in nature. We have seen how fine-grained austenite alone contributes toughness to its products of transformation; accordingly carbide-forming elements may at once influence austenite transformation characteristics by being in part dissolved and contribute toughness through restriction of grain growth.

Elements in Nonmetallic Inclusions — Iron-carbon alloys of extreme purity have been prepared with provisions against the possible acquisition of an oxygen or other content which could possibly result in the formation of nonmetallic inclusions. In such steels, the austenite grains coarsen markedly at relatively low temperature as soon as carbide particles are eliminated; the grain size is far coarser than that found in ordinary commercial steels when heated to corresponding temperature. The commercial steels regularly contain a sparse dispersion of minute, but usually detectable, refractory inclusions. The evidence seems convincing that these inclusions restrain grain growth in austenite and permit it to occur only at considerably higher temperature. It would be surprising indeed if this were not the behavior of austenite, for in other metals grain growth is effectively restricted to higher temperatures of heating by such dispersions of insoluble material. It is perhaps not altogether a misfortune that steel-making processes involve the solution of some oxygen in the molten steel which is later deoxidized; indeed the introduction of some well-controlled dispersion of these same products of deoxidation might otherwise be intentionally resorted to in many instances for the purpose of avoiding a too easily coarsened type of steel.

Usefulness of Nonmetallic Inclusions—There are, at any rate, refractory substances formed by the addition of manganese, silicon and aluminum or other deoxidizer to steel. Most of these products of deoxidation float out of the molten steel as particles. Some formed in molten steel may conceivably remain because of their fineness but, in the main, those which are found in the solid steel probably result from the reduction in solubility of oxygen with change from liquid to solid state. That they serve a useful purpose in preventing grain-coarsening can scarcely be questioned. On the other hand large inclusions are not desirable.

The grain growth characteristics of any certain steel composition probably depend very largely upon the nature and distribution of the finest of the nonmetallic inclusions. The larger inclusions exert a less marked effect upon grain growth. Various heating cycles applied to rolled steel have been found to alter somewhat the coarsening temperature or the grain size developed at some particular temperature. This circumstance points strongly to some alteration of the distribution or dispersion of nonmetallic particles in the solid state after their location has been first determined by freezing and hot working. The explanation for this circumstance almost certainly has to do with a certain solubility of some of the inclusions in austenite and a concomitant possibility for diffusion, reprecipitation and some coalescence.

Inclusions and Grain Growth — It would appear that *any* fine dispersion may have some restricting effect upon grain growth but that some inclusions are more effective than others. One behavior is quite marked; if grain growth is restricted at lower temperature and forced to higher temperature, the degree of abrupt growth then observed is all the greater for its having been restrained at the lower temperature. These behaviors may be illustrated by example.

One of the types of gradual grain growth is frequently encountered in the acid open-hearth steels of medium or high carbon content not deoxidized with aluminum. Presumably the inclusions, which are microscopically fine and well distributed, are of a siliceous nature. The grain size established after a moderately short heating interval at successively higher temperatures is indicated in Fig. 83 for two such steels. Under the microscope the distribution of grain-section sizes is such as to connote an exceedingly uniform size of the actual grains at any of the heating temperatures. (Actual grain size is, of course, under discussion, not a carburized grain size.) In general the initial grain size established upon full austenitization of steels of this type is not quite as fine as in steels of similar analysis but of the so-called fine-grained type. On the other hand there is no temperature at which an abrupt coarsening sets in.

Aluminum-Treated Steels and Grain Growth—In steels deoxidized with aluminum under specific conditions a some-

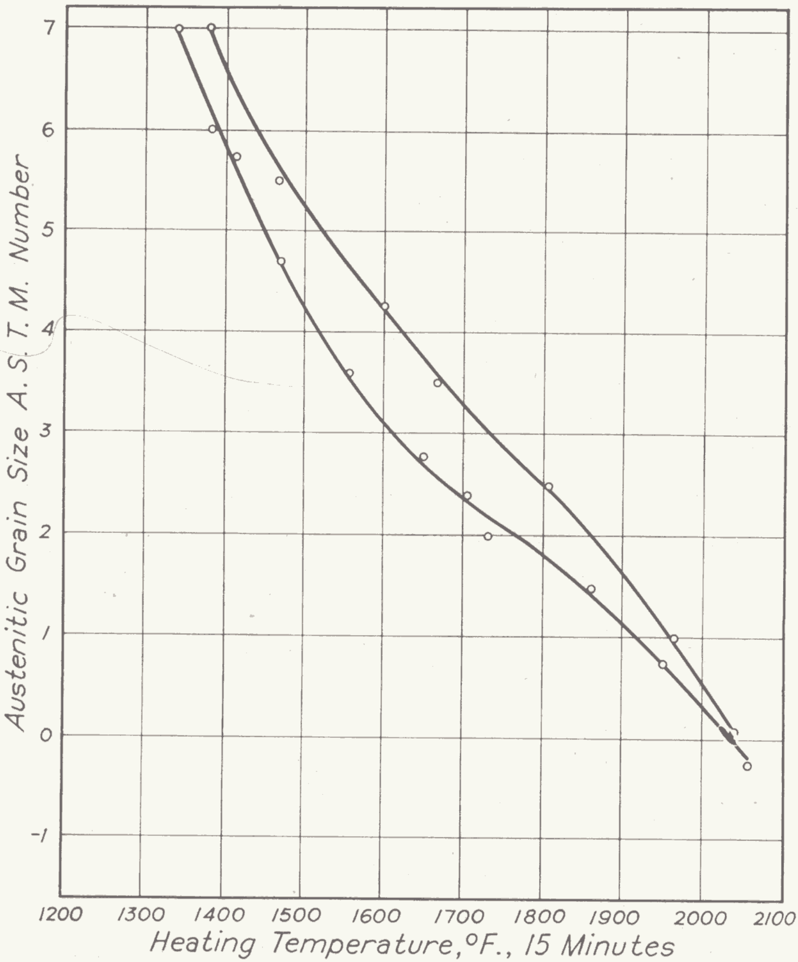

Fig. 83—Austenitic Grain Size established at Successive Temperatures in Two Steels of Gradually Coarsening Characteristics. Only a Narrow Range of Sizes Exist at any Temperature. *(L. R. Cooper and J. R. Vilella, United States Steel Corporation Research Laboratory).*

what different pattern of grain coarsening is encountered in which practically no change in grain size results from increased heating temperature until a certain coarsening temperature is reached. Above this temperature a short heating immediately starts the coarsening, usually to some definite

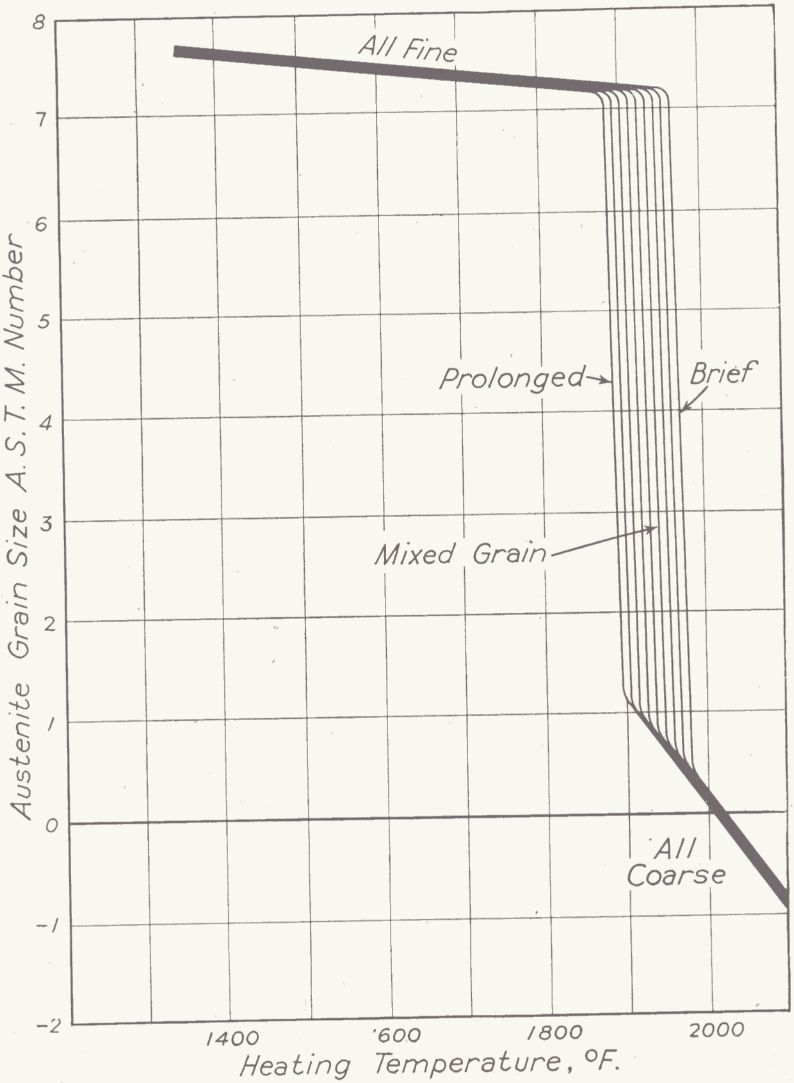

Fig. 84—The Response of Austenitic Grain Size to Heating Temperature in Steels of the Abruptly Coarsening Type, for example, Aluminum-Treated Steels. (Schematic).

grain size and prolonged heating converts all the grains into this same coarse grain size. A mixture of the two grain sizes exists after heating for such intervals of time and at such temperatures as inaugurate but do not complete the grain-coarsening action. Steels of this mixture of grain sizes are sometimes spoken of as "duplexed", though this word suggests a condition of inhomogeneity which does not exist in the steel. This abrupt mode of grain growth with increasing heating temperature is illustrated in Fig. 84. Probably examples of all degrees of abruptness of coarsening may be found lying between the behaviors of Fig. 83 and Fig. 84. If the particles acting to interfere with grain growth gradually dissolve or gradually coalesce then the grain growth should probably be gradual. If the particles remain, then the grain-growth forces probably overcome the restricting effect of particles rather suddenly although, similarly, the obstruction might also be abruptly eliminated.

It is not customary to regard the elements in nonmetallic inclusions as alloying elements nor to consider that such elements, when present in the necessarily small proportion, make alloy steel. Yet our interest is in the effects of the elements rather than in nomenclature and it seems therefore desirable to consider how it may be that some 0.03 per cent of aluminum added to steel may be able to bring about such marked modifications as result from grain-growth restriction. The researches of Brophy,[19] Mehl[20] and the author have shown that aluminum as dissolved in the steel exerts no significant effect upon grain growth. The mechanism must therefore relate to nonmetallic inclusions either of oxide, silicate or conceivably of nitride. Oxygen-free steels carrying various amounts of aluminum coarsen freely in a manner normal for so-called coarse-grained steels, as do steels deoxidized by an excessive amount of aluminum and therefore essentially oxygen free.

---

[19] "Influence of Aluminum on the Normality of Steels", by G. R. Brophy and E. R. Parker, Transactions, American Society for Metals, Vol. 25, 1937, p. 315.

[20] "Some Factors Influencing Austenitic Grain Size in High-purity Steels", by G. Derge, A. R. Kommel and R. F. Mehl, Transactions, American Society for Metals, Vol. 26, 1938, p. 153.

A number of observations have been made which point to a possible explanation of the elevated coarsening temperature found in steels to which a correct proportion of aluminum has been added under effective circumstances:

1. Aluminum must be added to steels carrying a certain minimum of oxygen (or possibly nitrogen).
2. A certain minimum of aluminum must be added, depending upon the condition of the steel with respect to oxidation.
3. Excessive amounts of aluminum result in easily coarsened steels unless other grain-growth restricting agents are present.
4. Migration of carbon is essentially unaffected by aluminum, either in ferrite or austenite.
5. Aluminum-bearing, coarse-grained steels may have the austenitic coarsening temperature raised by introduction of oxygen by diffusion. (Oxygen diffusion may occur in pack-carburizing, as may also nitrogen diffusion).

To account for these facts it may be assumed first that large inclusions, such as form immediately in liquid steel upon the addition of deoxidizers, either float out of the steel or, if retained, are ineffective so far as repressing grain growth is concerned. Similarly the inclusions formed during solidification are probably well able to acquire a size which renders them relatively inconsequential in the control of grain.

On the other hand, steels effectively rendered fine-grained by aluminum are frequently exceptionally clean microscopically and lead to the conclusion that the very small amount of aluminum operates to produce an exceedingly fine (sub-microscopic) dispersion of nonmetallic inclusions which alone could function so efficaciously. Although dispersions produced in the liquid state could scarcely be responsible for

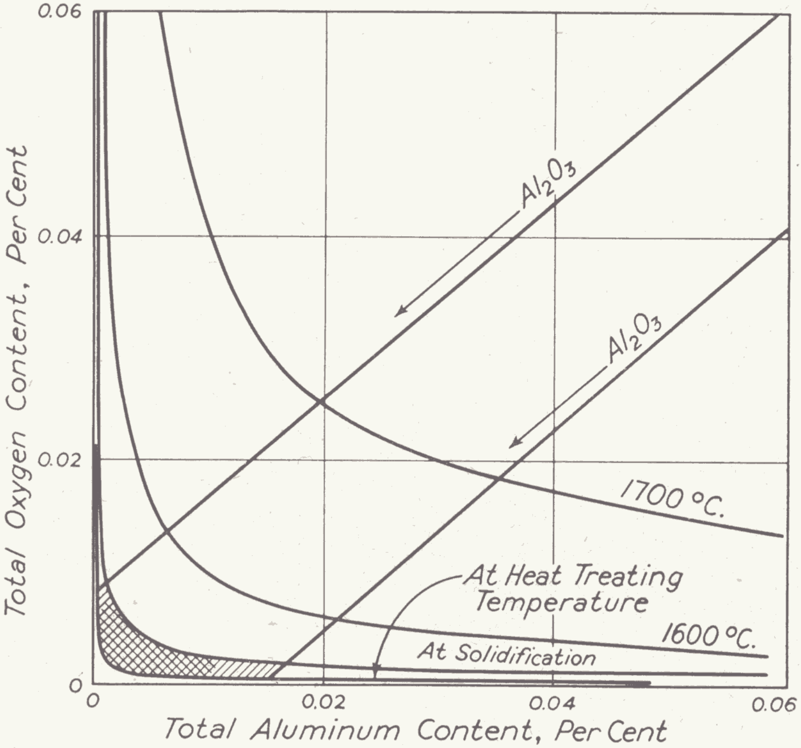

Fig. 85—The Mutual Solubility of Aluminum and Oxygen in Steel at Three Temperatures: (1) Liquid Steel; (2) Just Solidified Steel, and (3) (Schematic) Steel at Heat-Treating Temperature. Note that the Quantity of Rejected Alumina is Proportional to the 45 Degree Lines. The Most Effective Proportions Lie in Cross-Hatched Zone. *(1 and 2 from Wentrup and Hieber).*

the familiar degree of grain-growth restriction, a dispersion created in the solid state would be expected not to coalesce and therefore to remain tremendously effective. Thus it appears more than probable that alumina or aluminum-bearing oxide or silicate particles formed in the solid steel as it cools from the solidification to the heat-treating temperature are actually responsible for the success of the fine-grain steel practice utilizing well considered aluminum additions.

In Fig. 85[21] the relative solubility product of aluminum

---

[21] "Ueber Umsetzungen Zwischen Aluminium und Sauerstoff in Eisenschmelzen", by W. Wentrup and G. Hieber, *Technische Mitteilungen,* Krupp, Vol. 5, May 1939, p. 47

and oxygen is schematically shown at three significant temperatures: (1) at some representative ladle temperature, (2) at solidification temperature and (3) at heat-treating temperature. The rejected alumina is proportional to the length of lines drawn at about 45 degrees. It will be seen that the proportion of precipitated nonmetallic material is at a maximum for a certain proportion of oxygen and aluminum. With a given oxygen content above a certain minimum, the aluminum addition may be proportioned to bring the content of dissolved alumina into the range of maximum final precipitation. Presumably the required amount of obstructive particles is possible only when proportions fairly near the optimum are available, though the range is amply wide for commercial practice. This reasoning involving precipitation of an exceedingly minute, but finely dispersed, precipitate in the solid steel, while not easily verified, appears to explain all the observations including the ineffectiveness of too little or too much aluminum. The persistence of the obstruction to grain growth under many conditions of heat-treatment is a natural consequence of the exceedingly low diffusivity of aluminum even at elevated temperatures.

It should be mentioned that the mechanism of grain-growth obstruction has not been explained. Why grains should grow less readily in a metal carrying inert particles remains obscure. To speak of mechanical obstructions is merely to re-state the observation without offering any explanation. Nonetheless the effect has been so often observed in widely different materials that it is properly regarded as general or universal.

Perhaps a dispersion of particles in inhibiting grain-coarsening has done nothing more than to produce, at the last occasion for recrystallization, a copious nucleation. Such nucleation would assure the development of the most uniform possible grain size, which in turn would possess maximum stability and resist subsequent grain growth.

SUMMARY OF ELEMENTS IN STEEL AT AUSTENITIC TEMPERATURE

When steels are heated to the proper temperature range for austenite formation the principal interest centers in two conditions of the austenite: (1) its composition and (2) its grain size. On this basis the added elements naturally influence both as they are distributed in the heated steel.

All the elements as formerly dissolved in ferrite are, upon heating, dissolved in austenite except in the instances wherein so much of certain alloys and so little carbon are present as to render all or part of the ferrite stable at elevated temperature. These exceptional cases are not of primary importance here. The dissolved elements alter the properties of the austenite very little except to render it somewhat harder and hence "stiffer" in working. Dissolved elements have little influence *per se* upon grain size except possibly to slightly elevate coarsening temperature. Grain size is more dependent upon constituents undissolved in austenite. Both composition and grain size influence the behavior of the austenitic steel upon cooling with respect to its hardenability.

Alloying elements combined as carbide, and undissolved during heating, act to lower the carbon and alloy content of the austenite below that of the steel as a whole. The outstanding effect, however, is to restrain grain growth unless they are largely dissolved or until the steel is heated to exceptionally high temperature.

Elements combined as persistent nonmetallic particles act in a manner to force the temperature for austenitic grain growth to higher values during heating. Highly siliceous inclusions are somewhat dissolved in austenite and tend to coalesce somewhat and, perhaps for this reason do not inhibit grain growth as effectively as other, more inert inclusions. Alumina alone, or aluminum-bearing silicate inclusions perhaps, may remain in a fine state of dispersion and effectively prevent marked grain growth up to temperatures well above 1700 degrees Fahr. (925 degrees Cent.) and often to as high a temperature as 2000 degrees Fahr. (1100 degrees Cent.). The peculiar persistence of fine-grained austenite in aluminum-treated steel is possibly explained on the basis that a minute amount of Al_2O_3 is formed in the solid state, in which, coalescence being almost impossible due to the low diffusivity of aluminum, an effectively fine dispersion remains. The influence of fine-grained austenite upon properties was already discussed in connection with carbon steel in the second chapter, and these basic effects are manifest in the same way in alloy steel.