# BINARY EUTECTOID SYSTEMS

By substituting other phases for the liquid and two solids of the eutectic reaction, related types of systems are obtained which differ only in the nature of the phases involved. One of the most important of these is the eutectoid reaction, involving three solid phases (Fig. 5-1). Upon cooling, one solid phase (γ) decomposes into two other solid phases (α and β), and with heating, the reverse of this reaction occurs.

$$\gamma \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha + \beta$$
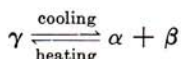
This type of system can be shown to conform with the requirements of the phase rule by applying the same arguments as those described in the case of eutectic systems. The form and directions of the phase boundaries which terminate upon the eutectoid reaction isotherm are also governed by the same consideration as those cited for the phase boundaries terminating upon the eutectic reaction isotherm. It should be noted that in the example of Fig. 5-1, both of the component metals undergo allotropic transformation; the A component transforms from α at low temperatures to γ at high temperatures, and the B component from β to γ; the γ's are isomorphous. Other examples in which the eutectoid reaction occurs without the presence of allotropic transformations will be mentioned later.
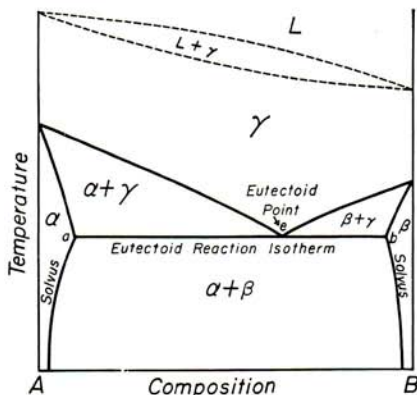

Fig. 5-1

Those portions of the diagram of Fig. 5-1 which are drawn with dashed lines are not involved in the discussion of the eutectoid. A liquidus and solidus are included merely to complete the diagram, but there are several other constructions that could as well have been used for this purpose.

No generally applicable names have been applied to the boundaries of the $\alpha + \gamma$ and $\beta + \gamma$ fields. In the iron-carbon system, Fig. 5-2, which includes a eutectoid reaction, the γ, or upper, boundary of the $\alpha + \gamma$ field is commonly called the A_3 line, and the γ boundary of the $Fe_3C + \gamma$ field (where Fe_3C corresponds to β) is called the A_{cm} line. No names at all have been given to the lower boundaries of these fields. In subsequent discussions these boundaries will be referred to as the γ (upper) and α (lower) boundaries of the $\alpha + \gamma$ field and the γ (upper) and β (lower) boundaries of the $\beta + \gamma$ field. The lateral boundaries of the $\alpha + \beta$ field are properly termed *solvus* curves, as in the eutectic systems. The *eutectoid reaction isotherm* is also known by the names *eutectoid line* and *eutectoid reaction horizontal* and, in the iron-carbon alloys, as A_1.

FIG. 5-2. Phase diagram of the metastable system iron-carbon.

Structure of the Eutectoid Alloy

Transformations involving the dissociation and reassociation of solid phases are much more sluggish than similar transformations involving one or more liquid phases because diffusion rates are much slower in the solid state. Nonequilibrium transformation assumes a correspondingly greater practical significance and must be considered in greater detail than was found necessary with eutectic alloys. In order to provide a logical starting point for this discussion, the structures produced by equilibrium transformation, corresponding to infinitely slow reaction, will be dealt with first.

The *eutectoid alloy*, composition e in Fig. 5-1, would undergo isothermal incongruent transformation in the "ideal" case. In every eutectoid system which has been studied it has been found that the high-temperature phase γ decomposes upon cooling to produce a lamellar, or "pearlitic," eutectoid constituent composed of the α and β phases (Fig. 5-3B). There is little to differentiate the equilibrium eutectoid and eutectic pearlitic structures in so far as appearance is concerned. Both form in so-called *colonies*, within which the lamellae are approximately parallel, and the crystallographic orientation of each of the two phases concerned is the same. In cast alloys the colonies tend to become elongated in the direction of freezing, while in the eutectoid structures the colonies are more commonly equiaxed (equal length and breadth), but there is insufficient regularity of behavior in this respect to make this difference a useful distinguishing criterion.

Hypoeutectoid and Hypereutectoid Alloys

The terminology applied to alloys on the right and left of the eutectoid composition parallels that used for the corresponding alloys of eutectic systems. Those alloys lying to the left of the eutectoid point, or on the side of the more important metal, are designated *hypoeutectoid;* those on the opposite side are *hypereutectoid.* Transformation in these alloys proceeds in two steps (Fig. 5-4): First, a proeutectoid precipitation of one of the low-temperature phases occurs over a temperature range, followed by an "isothermal" decomposition of any remaining portion of the high-temperature phase into the eutectoid constituent (Fig. 5-3A and C). Here the term *proeutectoid* is used with reference to the tranformation among solid phases in the same sense as is "primary" with respect to the freezing process.

If the hypoeutectoid alloy X, Fig. 5-4, is heated to T_0 and is held until equilibrium is obtained, it will be composed solely of crystals of the γ phase. Lowering the temperature to T_1 should cause an incipient precipitation of α crystals of composition α_1. Since the nucleation of precipitating phases is usually stimulated by surfaces, including grain boundaries, it is to be expected that there will be a marked tendency for the first crystallites of α_1
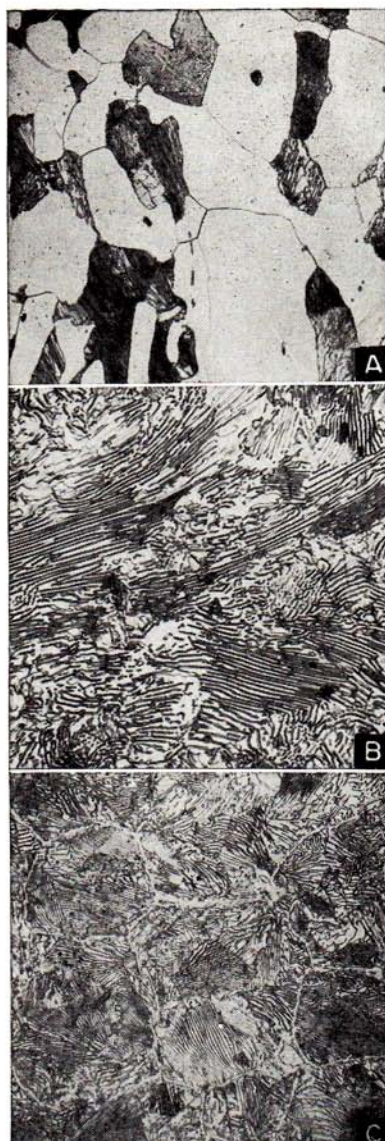
FIG. 5-3. (A) Hypoeutectoid steel, 0.3 % C. Light areas are proeutectoid ferrite (α); dark areas are the pearlitic eutectoid constituent ($\alpha + Fe_3C$). Magnification 500. (B) Eutectoid steel, 0.8% carbon, typical pearlite ($\alpha + Fe_3C$). Magnification 500. (C) Hypereutectoid steel, 1.2 % C. Thin bands of proeutectoid cementite (Fe_3C), light gray, outline the grains of pearlitic eutectoid constituent ($\alpha + Fe_3C$). Magnification 500.

to appear at the grain boundaries of the parent γ structure, and this is observed. As cooling proceeds, the phase diagram demands that the α crystals grow and at the same time change in composition along the α boundary of the $\alpha + \gamma$ field until the composition α_3 is reached at the
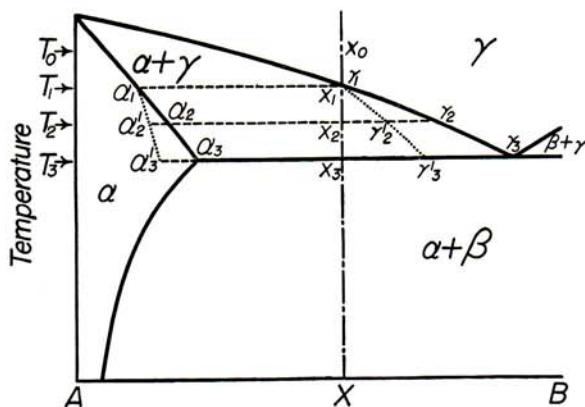
FIG. 5-4

eutectoid temperature T_3. Simultaneously, the γ phase, if it were to respond fully to the requirements of equilibrium, would change in composition along the γ boundary of the $\alpha + \gamma$ field until it attained eutectoid composition γ_3. All of the remaining γ phase

$$\%\gamma_3 \text{ (equilibrium)} = \frac{\alpha_3 x_3}{\alpha_3 \gamma_3} \times 100 \approx 45\%$$

should now be converted to the eutectoid constituent.

The resulting microstructure as exemplified by an alloy of iron with 0.30% carbon (equivalent to about 5% Fe_3C) appears in Fig. 5-3A. It will be noted that the eutectoid pearlite occurs in separate "patches" or "nodules," each composed of one or more "colonies." The patches of pearlite are surrounded by the white α phase, which is nearly continuous in the microstructure because it grew preferentially from nuclear sites upon the grain boundaries of the γ phase, which are now entirely gone.

A similar course of transformation in a hypereutectoid steel containing 1.20% carbon (equivalent to 18% Fe_3C) leads to the proeutectoid separation of Fe_3C (the β phase of Fig. 5-1). Because there is relatively much less of the proeutectoid constituent at this gross composition, it remains as a thin white network outlining the original γ crystals in Fig. 5-3C. All remaining γ has been transformed to eutectoid pearlite, as in previously considered cases.

By analogy with the natural freezing of hypoeutectoid alloys, it should be expected that in the transformation of a hypoeutectic alloy, the α

phase will fail to maintain its equilibrium composition and that its average composition will follow a path such as $\alpha_1\alpha_2'\alpha_3'$ in Fig. 5-4. The differences in compositions involved are so small in all the systems that have been investigated, however, that no information is available on the structural nature of the hypothetical "eutectoid coring." The γ phase, being crystalline, should also be expected to depart from its equilibrium composition during transformation, and a path such as $\gamma_1\gamma_2'\gamma_3'$ may be followed.

Transformations at Fixed Subcritical Temperature

Slow reaction in the solid state usually makes it possible to cool the eutectoid alloy to temperatures far below the eutectoid temperature without decomposition of the high-temperature phase, provided, of course, that the speed of cooling is sufficient. If the alloy is quickly cooled to and then held at a temperature somewhat below that of the eutectoid, transformation will proceed at a definite rate characteristic of that temperature. This may be done by removing the piece from the furnace in which it has been previously converted to the γ phase and immediately immersing it in a constant-temperature bath, such as a lead, salt, or oil bath, maintained at a controlled temperature. As the temperature of this kind of subcritical (below eutectoid) isothermal transformation is further and further decreased below the eutectoid temperature, the lamellae of the pearlite that is formed become thinner and closer together and the rate at
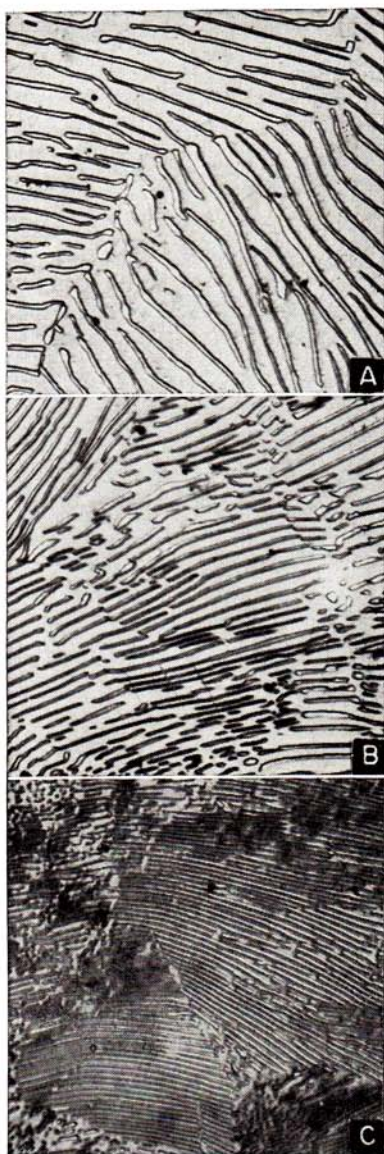
Fig. 5-5. Illustrates the variation in pearlite lamella spacing with temperature of formation: (A) formed at the highest temperature, (B) formed at an intermediate temperature, and (C) formed at the lowest temperature. Magnification 1,500.

which the transformation proceeds becomes more rapid. This change in
the "fineness" of the pearlite is illustrated, for a eutectoid steel, by the
series of photographs in Fig. 5-5, and the variation in the rate of trans-
formation with temperature of this steel is recorded in Fig. 5-6. In the
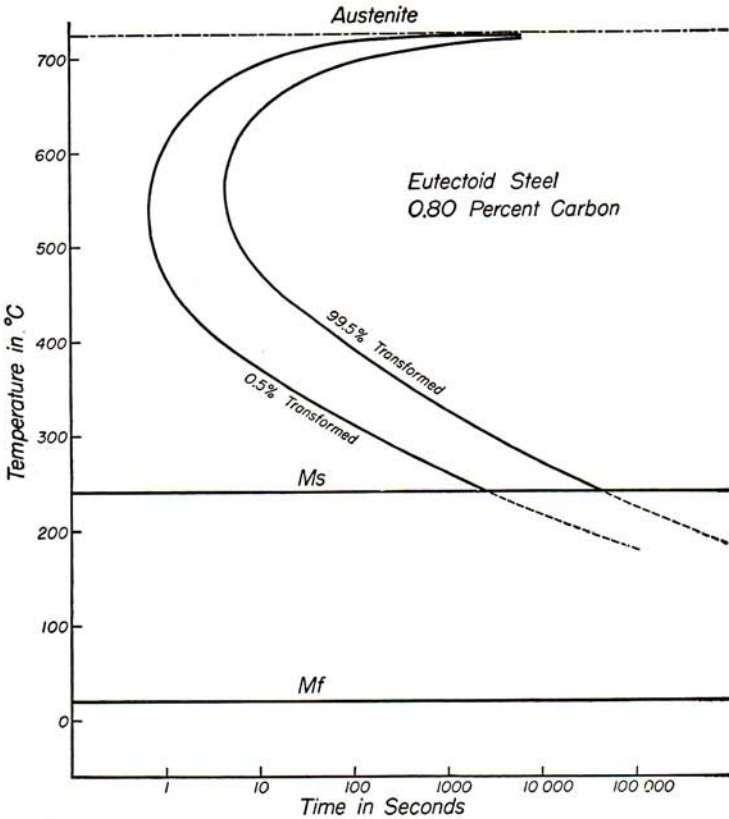latter diagram, temperature is plotted vertically, time of transformation

FIG. 5-6. Typical time-temperature-transformation (TTT) curve.

horizontally. The left-hand curve of the pair plotted represents the be-
ginning of transformation (i.e., 0.5% pearlite); the right-hand curve the
completion of transformation (i.e., 99.5% pearlite). In simple carbon
steels, pearlitic structures result from isothermal subcritical transforma-
tion at all temperatures down to the first reversal (knee) of the curves at
about 550°C. Pearlite nuclei form preferentially at the grain boundaries
of the γ crystals, and the rate of isothermal transformation is, accordingly,
the greater the finer the austenite (γ) grain size.

Below the knee of the reaction curves, shown in Fig. 5-6, a different
mechanism of transformation appears. The γ phase decomposes into

$\alpha + \beta$, but the resulting structure is not lamellar. Corresponding to the colonies of pearlite are acicular (needle-shaped) zones made up of $\alpha + \beta$ in a state of unresolvably fine distribution (Fig. 5-7). This structure in steels is called *bainite*. That the rate of this type of transformation decreases with falling temperature is shown by the curves of Fig. 5-6.

Finally at low temperature, the reaction curves are interrupted by a pair of horizontal lines (M_s and M_f) which correspond to the suppression of the $\gamma \to \alpha + \beta$ reaction and the appearance, in its stead, of a transformation of γ to an unstable transition phase, called *martensite* (Fig. 5-8). There is no "rate of transformation" of γ to martensite, no diffusion

FIG. 5-7. Bainite constituent in a partially transformed carbon steel. Magnification 1,500.
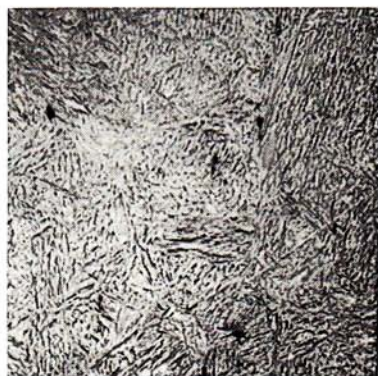
FIG. 5-8. Martensite constituent in a quenched low-carbon steel. Magnification 500.

being involved in this transformation. The reaction curves are horizontal; only with lowering temperature does the amount of martensite increase from zero at the "beginning line" M_s to 100% at the "ending line" M_f. At lower temperatures no further structural change is observed.

The entire graph of Fig. 5-6 is known as an *S curve* or, more properly, the TTT (time-temperature-transformation) curve. All the eutectoid alloys that have been studied have been found to transform in the same way, though with complications in some instances, and hence, a TTT curve may be used to describe the rate of each eutectoid transformation. Needless to say, the positions of the curves differ from alloy system to alloy system and also with composition change within any specific alloy system. Examples of TTT curves for hypo- and hypereutectoid alloys of the iron-carbon system are presented in Fig. 5-9. There is in this chart an additional curve showing the appearance of the proeutectoid (ferrite) constituent.

It should be clear that the TTT diagram is in no sense a phase diagram; it has been introduced here merely to describe the nature of eutectoid

transformation. The principles of equilibrium have no direct bearing upon transformation rates.
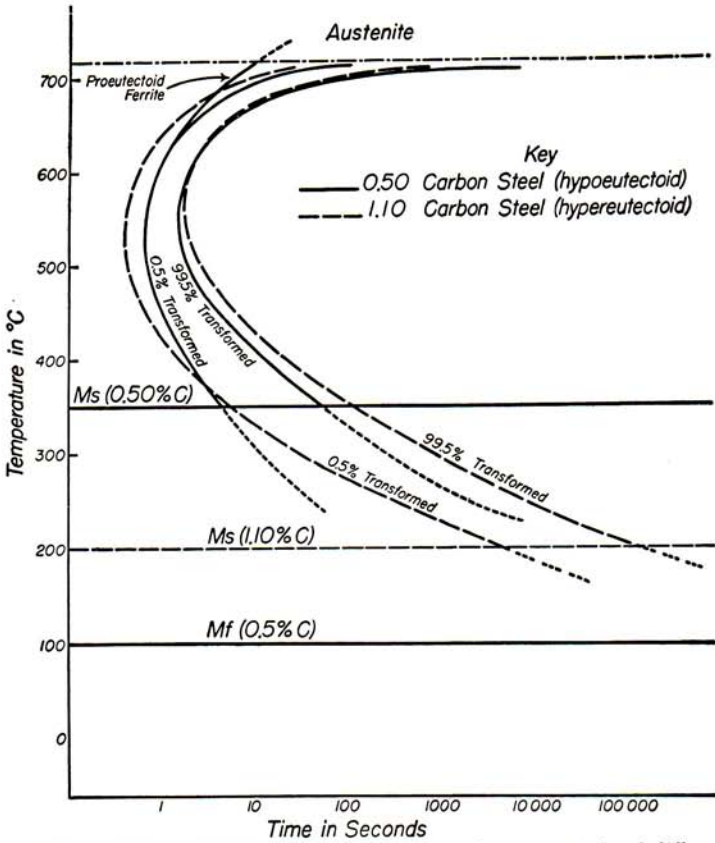

FIG. 5-9. Time-temperature-transformation diagram for two steels of different composition.

Transformation at Various Cooling Velocities

Heat treatments involving isothermal subcritical reaction, such as those just described, are of recent origin and still somewhat unusual; in the case of steels this type of treatment is called *austempering*. Most of the common heat treatments such as quenching, normalizing, and annealing involve cooling at a more or less definite rate from above the eutectoid temperature. Thus, if the eutectoid alloy is cooled at a rate described by the path of the dashed line designated as *a* in Fig. 5-10, the γ phase will be transformed to pearlite over a temperature range. The first pearlite formed at a high temperature will be coarser than that last formed at a
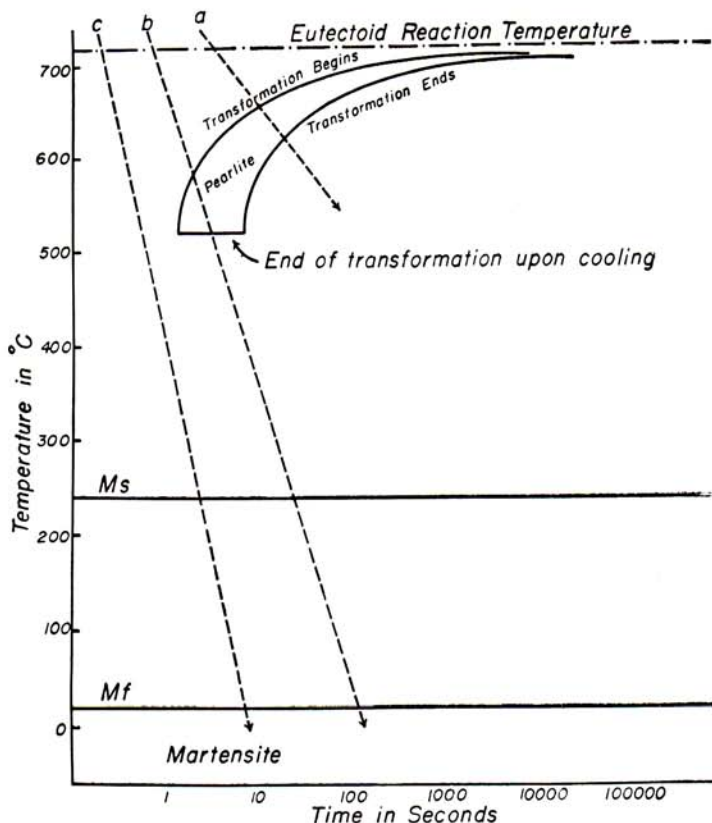
FIG. 5-10. Schematic transformation diagram for a eutectoid alloy. Dashed lines a, b, and c represent different cooling rates.

relatively lower temperature, so that a variation in the fineness of the pearlite will appear in the microstructure (Fig. 5-11). This type of transformation is typical of the annealing heat treatment, in which a very slow cooling rate is employed, or of normalizing, in which there is a somewhat faster rate of cooling obtained by permitting the metal to cool freely in the air.

A very fast rate of cooling, such as might result from quenching in cold water, is described by the dashed line c in Fig. 5-10. Here the transformation to $\alpha + \beta$ is suppressed altogether

FIG. 5-11. Pearlite formed during cooling through the transformation range exhibits a wide variation in lamellar spacing. Magnification 1,500.

and the alloy is transformed wholly to martensite. In many alloys the M_f line (completion of the transformation to martensite) lies below room temperature. When this happens, the conversion to martensite upon quenching to room temperature is incomplete. In either case, a tempering heat treatment, involving heating above the upper martensite line M_s, will cause a partial or complete transformation to $\alpha + \beta$, depending upon the time and temperature of tempering.

Curve b represents an intermediate cooling rate. Here, transformation proceeds part way, is interrupted, and then the balance of the γ is converted to martensite. The resulting microstructure is then composed partly of martensite (white) and partly of fine pearlite (gray) and a little bainite (dark) (Fig. 5-12).

Fig. 5-12. Eutectoid steel partly transformed by cooling at an intermediate rate through the temperature range of transformation. Light areas are martensite; dark areas are partly pearlite and partly bainite. Magnification 500.

The diagram of Fig. 5-10 is entirely schematic, being intended to picture the general relationships that have just been described. For precision it would be required that the "cooling curves" (lines a, b, and c) show arrests (with "recalescence") and that adjustments be made in the TTT curves so that they might apply to cooling rather than to isothermal transformation. A quenching TTT diagram, obtained by noting the first traces of transformation upon cooling, lies a little to the right and below the isothermal TTT diagram for the same steel.

Heat Treatment above the Eutectoid Temperature

The transformation of the $\alpha + \beta$ structure back to γ at supereutectoid temperatures is a nucleation and growth process implemented by diffusion and, therefore, may be expected to proceed the faster the higher the temperature and the finer the $\alpha + \beta$ structure, i.e., the shorter the diffusion distance. In the case of the Fe-Fe_3C eutectoid, it is necessary to exceed the equilibrium transformation temperature by many degrees in order to achieve complete transformation to γ within a reasonable time (austenitizing heat treatment).

Hypo- and hypereutectoid alloys must be heated correspondingly above the γ boundaries of the $\alpha + \gamma$ and $\beta + \gamma$ fields, respectively, in order to convert wholly to the γ phase. If the alloy is heated into and held within

the range of two-phase equilibrium ($\alpha + \gamma$ or $\beta + \gamma$), first the eutectoid constituent will be converted to γ, and subsequently, as much of the proeutectoid α (or β, as the case may be) as is required to satisfy the requirements of equilibrium at the temperature of heat treatment will also be converted to γ. Upon subsequent cooling, only that part of the structure which had been converted to γ will transform according to the mechanism described in the previous section. There will then be, in the structure, remnants of the original proeutectoid constituent plus products of decomposition of the γ of a kind dictated by the cooling rate.

Some Other Heat Treatments

Since eutectoid alloys are usually made by freezing from the melt, some nonuniformities, such as the coring that is characteristic of cast structures, are superimposed upon the normal eutectoid structure (Fig. 11-7). These may sometimes be reduced by a high-temperature heat treatment, wherein the temperature should be much higher than that required for the conversion to γ and should be held for a long time, because diffusion over relatively long distances is required. The most favorable temperature for homogenization lies a few degrees below the solidus temperature.

Spheroidization of the eutectoid constituent can be brought about by heating for an extended period at a temperature somewhat below that of the eutectoid (Fig. 5-13). No new principles are involved; spheroidization occurs by diffusion as in the case of eutectic alloys. This and the aforementioned homogenization treatment involve no phase changes, and the phase diagram is of service in guiding such treatments only in the information that it gives concerning temperature limits within which the treatments may be conducted.
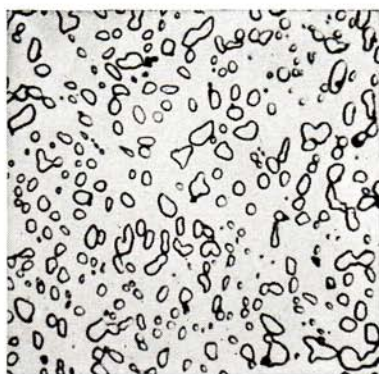

FIG. 5-13. Eutectoid steel in which the Fe_3C has been spheroidized by long heating at a temperature slightly below that of the eutectoid equilibrium; compare with Fig. 5-5A. Magnification 1,500.

A Note Concerning the Stability of Iron-Carbon Alloys

The fact that the usual iron-carbon phase diagram (Fig. 5-2) represents metastable equilibrium between iron and iron carbide has already been mentioned. The *stable* system iron-graphite (Fig. 5-14) involves the same

types of reactions on the iron side of the system, but with graphite substituted for Fe_3C where the latter appears in the usual diagram. Reversion to the stable state, known as graphitization, proceeds only at relatively high temperatures and very slowly. Although this transformation is not reversible, the metastable state may be reestablished either by remelting and freezing or, if the alloy falls within the composition range of the γ phase, by rehomogenization to γ with subsequent cooling to produce Fe_3C by eutectoid decomposition. From this it will be evident that references above to the formation of an $\alpha + Fe_3C$ eutectoid constituent by equilibrium transformation are not strictly correct; *true equilibrium transformation would yield a eutectoid constituent of α plus graphite.*

Alloying by Isothermal Diffusion

There are a number of surface treatments that are applied to iron and its alloys which involve the diffusion of an alloying element into the
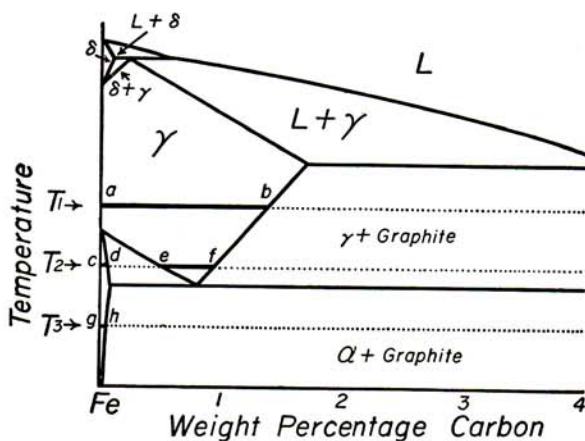

F̱ɪɢ. 5-14. Phase diagram of the stable system iron-carbon. Horizontal lines *ab*, *cdef* and *gh* are not part of the diagram; these have been inserted to indicate the composition ranges produced by carburizing treatment.

metal from an outside source. The principles of alloying by isothermal diffusion have been discussed in the preceding chapter, but some additional and important complexities appear in the eutectoid system iron-carbon owing to the metastability of Fe_3C.

The structures produced in this case by isothermal diffusion are those dictated by the stable system iron-graphite (Fig. 5-14), while structural evolution, accompanying the cooling of the γ phase, that has been formed by diffusion is predicted by the metastable phase diagram (Fig. 5-2).

Three basically different diffusion structures may be produced by

isothermally diffusing carbon into iron, depending upon the range within which the temperature of diffusion falls. Typical examples of each of these are designated in Fig. 5-14. At temperature T_1, above the α to γ transformation in pure iron, only layers of γ and carbon (graphite) can form, but the composition range within the γ layer will extend from pure iron (point a) to saturation with carbon (point b) if the material is examined before equilibrium has been established. If a lower temperature T_2 is employed, three layers are formed, namely, α, from c to d; γ, from e to f; and graphite. Here, as in previous examples, the $\alpha + \gamma$ and $\gamma +$ graphite regions of the phase diagram are represented in the diffusion sample simply as the interface between the layers of α and γ and of γ and graphite, respectively. Below the eutectoid temperature, at T_3, a two-layer structure is again formed: α, from g to h, and graphite. These, be it noted, are the structures existing at the temperature of isothermal diffusion; upon cooling to room temperature further changes occur.

Consider, for example, the sample that had been treated at T_1 (Fig. 5-14); upon cooling to room temperature, the alloyed surface layer will undergo metastable eutectoid transformation (Fig. 5-15). At the extreme surface, where the highest concentration of carbon exists, the material will be hypereutectoid (i.e., proeutectoid Fe_3C and eutectoid
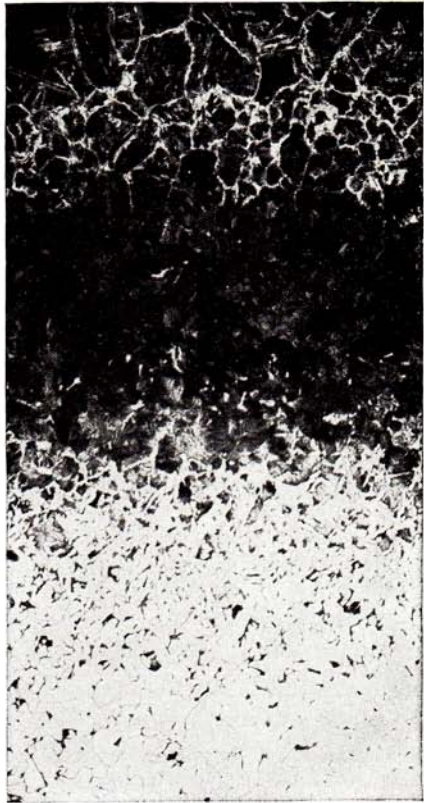

FIG. 5-15. Structure adjacent to the surface of a piece of carburized iron. External carbon-rich surface is at the top; unaffected iron at the bottom. Magnification 50.

$\alpha + Fe_3C$); somewhat below the surface the $\alpha + Fe_3C$ eutectoid will occur, and beneath that a hypoeutectoid zone. Thus, proeutectoid Fe_3C rather than graphite will appear at the surface. At the same time proeutectoid α (ferrite) is being rejected adjacent to and merged with the pure iron central portion of the piece, which is also converted from γ to α. The zone of the eutectoid constituent, instead of being infinitely narrow, is usually of finite width (Fig. 5-15) because of undercooling with respect to the pro-

eutectoid constituents over a composition range extending upon either side of the eutectoid point.

After cooling to room temperature, the structure of a piece of pure iron carburized at temperature T_2 fails to exhibit the sharp boundaries between layers that would have been apparent had it been possible to examine the material at the diffusion temperature. The layer of α remains virtually unchanged with cooling, but the γ layer, adjacent to the surface, decomposes into hypereutectoid, eutectoid, and hypoeutectoid zones as in the previous example. The only obvious structural difference between this example and the one discussed previously lies in the narrower composition range represented in the decomposition products of the γ layer.

The sample carburized below the eutectoid temperature at T_3 undergoes no significant structural change with cooling. At the diffusion temperature the metallic layer is composed solely of α (ferrite). Except for a very minor decrease in the solubility of carbon in α at lower temperatures, which can cause a slight precipitation of Fe_3C, the phase diagram does not predict any phase change for this case.

Exactly the reverse of the processes just described occurs if, instead of diffusing carbon *into* iron, carbon is diffused *out of* steel (decarburization). Additional factors are involved when other elements are diffused into or out of an iron-carbon alloy: these involve ternary alloy behavior, however, the principles of which will be discussed in a subsequent chapter.

Limiting Cases of the Eutectoid

It will be obvious that the terminal solid-solution range of either the α or β phase of the eutectoid reaction can be so narrow that it will appear to have zero width on the phase diagram. The eutectoid reaction isotherm will then appear to extend to the pure component. Occasionally the eutectoid point is located very close to one end of the reaction isotherm. The $\alpha + \gamma$ or the $\beta + \gamma$ field then becomes unrepresentably small and may be omitted in drawing the diagram. Where this happens, the user of the diagram must supply the missing region in his own mind in order to interpret the diagram correctly.

Mechanical Properties of Eutectoid Alloys

The wide variety of structures which can be produced in alloys of eutectoid systems by controlled heat treatment yields a correspondingly great diversity in mechanical properties. No new principles beyond those that have already been stated are involved, but the relative importance of the several controlling factors differs from those obtaining with solid-solution and eutectic alloys. The principle of the dominance of the con-

tinuous phase still holds good, as does that of solid-solution hardening. However, the effect of particle size in two-phase mixtures, which was of minor consequence in previous examples, becomes a major factor in controlling the properties of eutectoid alloys, where the range of sizes is very large and extends to extremely fine particle size. The finer the particle size, the greater the hardness and strength. Hence, pearlite formed at low temperatures is harder than that formed at high temperatures, and the acicular $\alpha + \beta$ structures (bainite) are still harder. The transition phases, such as martensite, appear to be extremely hard, as a general rule. Accordingly, alloys quenched from the γ range are the hardest of all. Tempering treatments, which cause the decomposition of the transition phase, reduce the hardness but increase the ductility, which normally increases as hardness decreases.

PRACTICE PROBLEMS

1. Demonstrate that Fig. 5-1 has been drawn in compliance with the requirements of the phase rule.

2. Consider the alloy X of Fig. 5-4, which upon normal cooling has transformed to a hypoeutectoid structure composed of proeutectoid α and eutectoid $\alpha + \beta$. If this alloy is next held for a long time at a temperature just below T_3, what changes will occur as the equilibrium state is approached? If this alloy were then quenched to room temperature and subsequently reheated to a temperature equal to one-half of T_3, what additional structural changes are to be anticipated?

3. A binary iron-carbon steel of eutectoid composition is subjected for a few minutes to decarburizing conditions at a temperature somewhat above that of the eutectoid but below the α-γ allotropic transformation temperature of pure iron and is then slowly cooled to room temperature. Deduce the microstructure of the affected zone in the steel.