3. Thermodynamics in a phase diagram

3.1 Phase diagram

In chapter 2, we have discussed the order-disorder transition in alloys. In this chapter, we study a fundamental thermodynamics in a phase transition and develop it into a phase diagram.

Supposing that Au-Ag ingot is put in a crucible and kept as high as 1100 °C, it melts soon at this temperature. Then, when the crucible is cooled down to 900 °C, the melt starts to be cooled down as well. The temperature of the melt as a function of the cooling time is shown in Fig. 1(b). As for a pure Au, the temperature stops dropping for a while at 1064 °C, and then a plateau is detected, indicating that the melt is supplying some amount of the latent heat that is almost comparable to that to be released out. After releasing the latent heat, the temperature drops monotonously again. The similar temperature dependence is observed for a pure Ag, and the latent heat is detected at 960 °C. As shown in the cooling curve for the alloy with the atomic composition of Au : Ag = 25 : 75, a kink within a gentle slope line is detected at the point of b and c, although no obvious steps like a pure Ag or Au appear. The kink b and c in Fig. 1(b) are plotted as B and C in Fig. 1(a), respectively. Additionally, for the composition of Au : Ag = 75 : 25, the kink b’ and c’ are plotted as B’ and C’, respectively. The temperatures of kinks with various compositions are then plotted again to draw a leaflet loop in Fig. 1(a).

At the temperature range above B-B’ curve, only a liquid is detected, while just a solid is detected below C-C’. Then, how about the phase within the BB’C’C loop? When the melt with the composition of Au : Ag = 25 : 75 is cooled down from the temperature A to B which is just on the loop, some amount of fine particles are detected. With slowly cooling down the melt to 990 °C, the particles grow larger and the amount of the liquid decreases as well. Here, we quench the melt into ice water, then the melt suddenly

![Fig. 1 Ag-Au binary alloy; (a) phase diagram, (b) temperature of a melt with various composition as a function of a cooling time.](image)
gets frozen, keeping the phase that may be stable at 990 °C. This is what we call a meta-stable state. Fig. 2 shows a cross section image of the alloy obtained here. An elemental analysis indicates that the atomic composition of the particles corresponds to that of the solid in Fig. 1(a), while the rest area solidified in quenching corresponds to that of the liquid. In the same way, the composition of the particles produced at 1000 °C corresponds to that of D, while the rest area corresponds to B. At 980 °C, all in the crucible is solidified, and several single crystals grow larger and/or form aggregates as shown in Fig. 2(b). When slowly and carefully cooled down, a fine grain grows with a uniform composition of C. As mentioned above, even if the same composition at melt, the composition of the obtained alloy strongly depends from which temperature and how it is cooled. In other words, we can easily control the hardness and other mechanical properties by this technique. In industry, a heat treatment is accompanied by a mechanical one. One of the examples of the cross section of the alloys thus obtained is shown in Fig. 3.

Let us consider a more complicated phase diagram in Fig. 4. Consider the composition $x$, where the melt is cooled down to the point E at $T_1$, which is the lowest point on the liquidus. The liquid phase at E is in the equilibrium state with the solid phase F as well as G. In other word, two species of the solid phase, abbreviated as $\alpha$- and $\beta$-phase herein, are crystallized simultaneously. That is;

$$\text{Liquid E} \rightleftharpoons \text{Solid Solution F(\alpha-phase)+Solid Solution G(\beta-phase)}$$

The coexistence of two species of the solid phase is called an eutectic, and $T_1$ is called an eutectic
temperature. Since the α- and β-phase crystallize simultaneously at $T_1$, both phases consist of fine particles and are mixed together. When it is cooled down, the diffusion of A atoms into the α-phase as well as B atoms into the β-phase may occur together, changing the composition in the solid. For example, the composition of the α- and β-phase at $T_2$ correspond to b and b’, respectively, and each amount approaches to $\frac{D}{C}$ with cooling down to $T_3$ in equilibrium.

Consider the composition $y$, where the melt is cooled down to the temperature $T_4$, at which the α-phase with the composition of c starts precipitating. The phase detected at the temperature range from $T_4$ down to $T_1$ is similar to that of the complete solid solution in Fig. 1(a). At $T_1$, the amount of the solid solution in the α-phase with respect to the liquid is estimated to $\frac{CE}{CF}$, although some amount of a liquid phase is left in the system. Additionally, the solid solution in the β-phase starts crystallizing at $T_1$, then, this is called an eutectic crystal. On the other hand, the first crystallized α-phase particles at $T_4$ is called a primary crystal. Because the primary crystals have already been formed before crystallizing the eutectic ones at $T_1$, the eutectic crystals precipitate with covering the surface of the primary crystals. After solidifying completely, the temperature of the system starts dropping. When cooled down to $T_5$, the large α-phase primary crystals are surrounded not only by the fine α-phase crystals with the composition of C, α(C), but also by the β-phase with the composition of D, β(D). The amount of the α-phase with respect to the β- is estimated to $\frac{yD}{Cy}$ according to a lever rule.

Then, consider the composition $z$. When cooled down to $T_5$, the β-phase stars crystallizing, and the liquid phase disappears with cooling down to $T_6$, leaving just the β-phase as a solid solution, which is similar to a typical behavior for a complete solid solution. When crossing $T_7$ on the line at the point d’, corresponding to the solid solute limit, the α-phase with the composition of d, α(d), starts precipitating on the β-phase with the composition of d’, β(d’).
Finally, at the composition $u$, this is almost similar to the complete solid solution at the temperature range from $T_4$ to $T_5$.

Fig. 6 shows the cooling curve for alloys with the composition of $x$, $y$, $z$, and $u$. At the eutectic temperature, because the temperature is constant until the liquid phase disappears completely, the eutectic reaction in the system exhibits a plateau on the cooling curve.

### 3.2 Solid solution

A solid solution is classified into two types, an interstitial type and a substitutional type. The interstitial type that B atoms diffuse into A may occur when the ionic radius of B is considerably smaller than that of A, and then the matrix B does not cause a significant deformation in the crystal structure. For atoms with a small ionic radius such as C, N, H, and B, an interstitial solid solution is formed, expanding the volume of the unit cell.

The $a$-axis of a cubic Austenite iron increases when carbon is introduced, while a tetragonal Martensite iron increases the $c$-axis but decreases the $a$-axis. In the case of the complete solid solution, the lattice constant reveals a linear relationship to the composition of foreign atoms, which is called Vegard’s rule, and many metallic solid solutions follow this rule.

![Fig. 7 Lattice constant of Martensite and Austenite iron as a function of carbon content.](image)

![Fig. 8 Complete solid solutions that follow Vegard’s rule.](image)

### 3.3 Solid solution and lattice constant

In a binary alloy, the lattice constant changes with the composition of the foreign atom until the solid solute limit, and remains constant beyond. Let us consider the phase diagram as shown in Fig. 9(a). The lattice constant of the $\alpha$-phase quenched from $T_1$ shows a typical compositional dependence as shown in Fig. 9(b). The intersection point at the composition $x$ between $bc$ and $de$ curves corresponds to the solid solute limit of the $\alpha$-phase at $T_1$. When the alloy No.6 is kept at $T_2$ for a while and then quenched to room temperature, the alloy contains the $\alpha$-phase saturated with B, which is a stable phase only available at $T_2$. Assuming that the lattice constant at $T_2$ is $a_\alpha$, we can easily estimate the composition of B in the $\alpha$-phase to
Fig. 9 Phase diagram for AB alloy (a), and the lattice constant and solute limit (b).

Here, we consider the XRD patterns for an imaginary alloy as shown in Fig. 11. The solid solution of A and/or B atoms into the intermediate γ-phase can be ignored in this system. The crystal structure in α- and β-phase is fcc, and that in γ-phase is bcc. Furthermore, the size of B atom is larger than that of A. The lattice constant at room temperature is shown in the bottom of Fig. 10. The details are as follows;

1. Pure metal A with the crystal structure of face centered cubic, fcc.
2. α-phase with almost saturated with B. The diffraction angle 2θ shifts to lower due to the expansion of the unit cell according to Bragg’s rule.
3. Coexistence of the α- and γ-phase. Since α-phase is saturated completely with B, the lattice constant shows the maximum and is constant with increasing B.
4. The same pattern as 3, however, the intensity of the α-phase decreases, while that of the γ-phase increases with increasing B.
5. Pure γ-phase of body centered cubic, bcc.
6. Coexistence of the β- and γ-phase. Since β-phase is saturated with A, the lattice constant shows minimum and is constant with increasing B.
7. β-phase with a little larger lattice constant.
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In a certain system in an alloy, Gibbs free energy $G$ is given as follows

$$ G = E + pV - TS = H - TS $$

(1)

where $E$ is an internal energy, $H$ is an enthalpy, $S$ is an entropy. Supposing that both $H$ and $S$ varies with a parameter $a$, (3-1) is expressed as

$$ H(a) = TS(a) + G(a) $$

(2)

As shown in Fig. 12, eq. (2) is treated as a linear function, and the slope and the intercept to the axis corresponds to $T$ and $G(a)$, respectively. At a given temperature $T$, the slope is defined as a constant. At this time, we can find the contact point $a_0$ on the $H$–$S$ curve, and the slope of the tangent is defined as $T$ to give the free energy of $G(a_0)$. Since the $H$–$S$ curve is convex to a downward, $G(a_0)$ shows the lowest energy at $T$. That is, $a_1$ other than the contact point $a_0$ gives a relationship of $G(a_1) > G(a_0)$ at $T$. On the other hand, when the $H$–$S$ curve is convex to an upward as shown in Fig. 13(a), the contact point $b_0$ gives the highest free energy $G(b_0)$ at $T$, corresponding to a system with an unstable state. Moreover, at the inflection point $c_0$ in Fig. 13(b), $G(c_0)$ indicates a boundary between a stable and unstable state, or practically a nonexistent region.

At higher temperature, the slope of the tangent is increasingly steeper, and the contact point moves gradually to the upper on the $H$–$S$ curve as shown in Fig. 14, and the intercept $G$ becomes lower as well to give a typical $G$–$T$ curve in Fig. 15. The entropy $S$ should always be a positive value and increases with $T$, corresponding to the tangent slope on $G$–$T$ curve is steeper with $T$. Supposing an ideal alloy under the constant pressure of $p = p_0$, the alloy presents two phases of $\alpha$ and $\beta$, and the enthalpy and entropy corresponding to the phase is referred to $H_\alpha$, $H_\beta$, $S_\alpha$ and $S_\beta$. At $T_0$, we can draw a common tangent line at the contact points of $a_0$ and $a_\beta$ with the slope of $T_0$ on $H_\alpha$–$S_\alpha$ and $H_\beta$–$S_\beta$ curve. In this case, $T_0$ corresponds

5. Pure metal B with the crystal structure of fcc.

Fig. 12 $H$–$S$ curve convex to a downward.

Fig. 13 $H$–$S$ curve (a) convex to an upward and (b) that with an inflection point.

At higher temperature, the slope of the tangent is increasingly steeper, and the contact point moves gradually to the upper on the $H$–$S$ curve as shown in Fig. 14, and the intercept $G$ becomes lower as well to give a typical $G$–$T$ curve in Fig. 15. The entropy $S$ should always be a positive value and increases with $T$, corresponding to the tangent slope on $G$–$T$ curve is steeper with $T$. Supposing an ideal alloy under the constant pressure of $p = p_0$, the alloy presents two phases of $\alpha$ and $\beta$, and the enthalpy and entropy corresponding to the phase is referred to $H_\alpha$, $H_\beta$, $S_\alpha$ and $S_\beta$. At $T_0$, we can draw a common tangent line at the contact points of $a_0$ and $a_\beta$ with the slope of $T_0$ on $H_\alpha$–$S_\alpha$ and $H_\beta$–$S_\beta$ curve. In this case, $T_0$ corresponds
3. Thermodynamics in a phase diagram

Fig. 14 Tangent lines in $H$-$S$ curve with various temperatures.

Fig. 15 Typical $G$-$T$ curve.

Fig. 16 $H$-$S$ curves in an ideal alloy presenting two phases of $\alpha$ and $\beta$; (a) a common tangent line at $T_0$, and (b) two tangent lines at $T'_0 < T_0$.

Fig. 17 Typical $G$-$T$ curve with $\alpha$- and $\beta$-phase.

to the transition temperature at $p = p_0$. However, at $T'_0 < T_0$, as can be seen in Fig. 16(b), since $G_\alpha(T'_0) < G_\beta(T'_0)$, then $\alpha$-phase is more stable than $\beta$- at this temperature. On the other hand, $\beta$-phase is stable at $T''_0 > T'_0$.

As shown in Fig. 3-5(a), $G_\alpha$ and $G_\beta$ are comparable to each other at $T_0$, then both $\alpha$- and $\beta$-phase can coexist in the system. The latent heat $\Delta H$ and the entropy $\Delta S$ in the transition is

$$\Delta H = H_\beta - H_\alpha$$  \hspace{1cm} (4) \\
$$\Delta S = S_\beta - S_\alpha$$  \hspace{1cm} (5)

At the transition point $(p_0, T_0)$, since $G_\alpha = G_\beta$, then

$$\Delta H = T \Delta S$$  \hspace{1cm} (6)

Fig. 17 shows $G$-$T$ curve derived from the intercept of the minimum $G_\alpha$ and $G_\beta$ at various $T$. $G_\alpha$ and $G_\beta$ cross each other at $T_0$, and then $\alpha$-phase is stable at $T \leq T_0$, while $\beta$-phase is stable at $T \geq T_0$. Additionally, from the slopes of $\partial G_\alpha / \partial T (\approx -S_\alpha)$ and $\partial G_\beta / \partial T (\approx -S_\beta)$, it is clear that $S_\beta$ is larger than $S_\alpha$ at $T_0$.

3.5 Free energy and phase diagram

Consider a binary alloy consisted of A and B atoms with the total amount of molar $N$, and define the
molar fraction of A and B as $x$ and $1-x$, respectively. In this system, you can see two-phase separation at ① and ② with the molar of $N_1$ with the fraction of $x_1$ and $N_2$ with $x_2$, respectively, then

$$N = N_1 + N_2, \quad N x = N_1 x_1 + N_2 x_2$$

(7)

then

$$N_1 = \frac{N(x_2 - x)}{x_2 - x_1}, \quad N_2 = \frac{N(x - x_1)}{x_2 - x_1}$$

(8)

In other words, the ratio of $N_1$ to $N_2$ is defined as $(x_2 - x) / (x - x_1)$, which is called a "lever law". From eq. (8), the total amount of the free energy with two kinds of precipitate with the molar fraction of $x_1$ and $x_2$ is

$$N_1 F(x_1) + N_2 F(x_2) = NF(x_1) + N \left[ F(x_2) - F(x_1) \right] \frac{x - x_1}{x_2 - x_1}$$

(9)

corresponding to $F(x)$ at the point ③ on the straight line combining with ① and ② as shown in Fig. 18(a). Since $F(③) > F(④)$, then two-phase separation does not occur in this system. Now, we represent the free energy in the liquid and the solid phase with round and square brackets as $[F]$ and $\{F\}$, respectively. From Fig. 3-7(a), the relationship between $[F]$ and $\{F\}$ leads to Fig. 3-8(a)-(c) at various temperatures, and then the phase diagram is given in Fig. 19(d).

![Fig. 18 Free energy and two-phase separation as a function of $x$.](image)

On the other hand, since $F(③) < F(④)$ in Fig. 18(b), then the two-phase separation does occur here. This type of variation of the free energy shown in Fig. 20(a) is often detected in Cu-Ag system. In this system, since $(F) > [F]$ as shown in Fig. 20(b), then only the solid state is detected, while separating into two kinds of solid precipitates with Ag concentrations of $\theta_1$ and $\theta_3$. At higher temperature $T'$, two kinds of a liquid and solid coexistence state is detected at different concentrations between $\theta_1', \theta_3'$ and $\theta_3' \theta_2'$ in Fig. 20(c).

![Fig. 19(a)-(c) Free energy as a function of $x$ at various temperatures, and (d) phase diagram fabricated in this system.](image)
3. Thermodynamics in a phase diagram

3.6 Fabrication of a phase diagram by calculating atomic interactions

Consider a phase diagram from a little more microscopic viewpoint. According to eq. (1), $E$ and $S$ should be calculated separately. Statistically, in calculating the entropy $S$ in an alloy consisted of A and B atoms, we consider the mixing entropy as follows

$$S = -k_B N \left[ x \ln x + (1-x) \ln(1-x) \right]$$

On the other hand, in calculating the internal energy $E$ from the interaction between atoms, we just take into account of the nearest neighbors and calculate as follows

$$E = n_{AA} \nu_{AA} + n_{AB} \nu_{AB} + n_{BB} \nu_{BB}$$

where $\nu_{AA}$, $\nu_{BB}$ and $\nu_{AB}$ corresponds to the interaction energy between A-A, B-B and A-B pair, respectively. Supposing the number of the nearest neighbor atom is $z$, corresponding to the coordination number of A or B atom, the number of each pair is then estimated as follows;

$$n_{AA} = \frac{1}{2} zN x^2$$

$$n_{AB} = zNx(1-x)$$

$$n_{BB} = \frac{1}{2} zN(1-x)^2$$

From eq. (12), eq. (11) is estimated as follows;

$$E = \frac{1}{2} zN \nu_{AA} x^2 + zN x(1-x) \nu_{AB} + \frac{1}{2} zN \nu_{BB} (1-x)^2$$

The difference in the interaction energy between homogeneous and heterogeneous atoms is

$$\Lambda = zN \left( \nu_{AB} - \frac{\nu_{AA} + \nu_{BB}}{2} \right)$$

The sublimation energy $Q_A$ for a metal consisted of only A atom corresponds to that required to break apart
A-A bonding, then

\[-Q_A = \frac{1}{2} z N \nu_{AA}\]

\[-Q_B = \frac{1}{2} z N \nu_{BB}\]  

(15)

From (3-13) and (3-15),

\[E = -[Q_A]x - [Q_B]x(1-x) + [\Lambda]x(1-x)\]  

(16)

\[E = -(Q_A) x - (Q_B) x(1-x) + (\Lambda) x(1-x)\]  

(17)

The latent heat \(L_A\) and \(L_B\) is defined as

\[L_A = [Q_A] - (Q_A)\]

\[L_B = [Q_B] - (Q_B)\]  

(18)

The difference in the entropy at the melting point is empirically estimated as

\([S] - [S] = L / T_m \approx R\]  

(19)

From (3-17) and erasing \((Q_A)\) and \((Q_B)\), (3-19) is then

\[E = -[Q_A] x - [Q_B] x(1-x) + L_A x + L_B (1-x) + (\Lambda) x(1-x)\]  

(20)

\[F = [\Lambda] x(1-x) + RT (x \ln x + (1-x) \ln(1-x)) - [Q_A] x - [Q_B] x(1-x)\]  

(21)

\[(F) = L_A x + L_B (1-x) + (\Lambda) x(1-x) + RT (x \ln x + (1-x) \ln(1-x)) - RT - [Q_A] x - [Q_B] x(1-x)\]  

(22)

When an appropriate value is given to the parameters \([\Lambda]\), \((\Lambda)\), \(L_A\) and \(L_B\), both \([E]\) and \((F)\) is estimated as a function of \(x\) with various \(RT\) values, and the results are shown in Fig. 20(b)-(d). From these figures, a phase diagram in this system is given in Fig. 20(a).

3.7 Phases of the iron-carbon system

Steels, which are primarily alloys of iron and carbon, offer illustrations of the majority of reactions and microstructures available to engineers for adjusting material properties. The iron-carbon alloys are among the prominent structural materials.

The versatility of the steels as engineering materials is evidenced by the many kinds of steel that are manufactured. At one extreme are the soft steels used for deep-drawing applications such as automobile fenders and stove panels. At the other extreme are the hard and tough steels used for gears and blades. Some steels must have abnormally high resistance to corrosion. Steels for such electrical purposes as...
transformer sheets must have special magnetic characteristics so that they may be magnetized and
demagnetized many times each second with low power losses. Other steels must be completely
nonmagnetic, for such applications as wrist watches and minesweepers. Phase diagrams can be used to
help explain each characteristic described above.

Pure iron changes its crystal structure twice before it melts. Iron changes from bcc to fcc at 912 °C
with increasing the temperature. This change is reversed at 1394 °C to form the bcc structure again. The
bcc polymorph then remains stable until iron melts at 1538 °C.

3.7.1 Ferrite (α-iron)

The structural modification for pure iron at room temperature is called either “ferrite” or “α-iron”.
Ferrite is quite soft and ductile; in the purity that is encountered commercially, its tensile strength is less
than 310 MPa. It is a ferromagnetic material at room temperatures under 770 °C. The density of ferrite
is 7.88 g/cm³.

Since a ferrite has a bcc structure, the spaces between atoms are small and pronouncedly ablate and
cannot readily accommodate even a small spherical carbon atom. Therefore, solubility of carbon in ferrite
is very low, less than 0.1 at%. The carbon atom is too small for substitutional solid solution in ferrite, and
too large for extensive interstitial solid solution.

3.7.2 Austenite (γ-iron)

The face-centered modification of iron is called “austenite”, or “γ-iron”. It is the stable form of pure
iron at temperature between 912 °C and 1394 °C. Making a direct comparison between the mechanical
properties of austenite and ferrite is difficult because they must compared at different temperatures.
However, at its stable temperatures, austenite is soft and ductile and consequently is well suited to
fabrication processes. Most steel forging and rolling operations are preformed at 1100 °C or above, when
the iron is fcc. Austenite is not ferromagnetic at any temperature.

The fcc structure of iron has larger interatomic spacings than does ferrite. Even so, the holes are
barely large enough to crowd the carbon atoms into interstices, and this crowding introduces strains into
the structure. As a result, not all the holes can be filled at any one time, ~6 wt% at 912 °C. The maximum
solubility is only 2.11 wt% carbon. By definition, steels contain less than 1.2 wt% carbon; thus steels may
have their carbon completely dissolved in austenite at high temperatures.
3.7.3 δ-iron

Above 1394 °C, austenite is no longer the most stable form of iron, since the crystal structure changes back to a bcc phase called “δ-iron”. δ-iron is the same structure as α-iron except for its temperature range, and so it is commonly called δ-ferrite. The solubility of carbon in δ-ferrite is small, but it is measurably larger than that in α-ferrite, because of the higher temperature.

![Fig. 22 Crystal structure of α- and γ-iron with carbon atoms](image)

Although there is a more efficient iron packing factor in the fcc γ-, 0.74, than in the bcc α-, 0.68, the interstices within γ- are larger. As a result, the carbon atoms are less crowded in the γ- than in the α-. This permits a higher solubility in the fcc structure.

3.7.4 Iron carbide

In iron-carbon alloys, carbon in excess of the solubility limit must form a second phase, which is most commonly iron carbide, or cementite. Iron carbide has the chemical composition of Fe₃C. This does not mean that iron carbide forms discrete molecules of Fe₃C; it simply means that the crystal lattice contains iron and carbon atoms in a three-to-one ratio. Fe₃C has an orthorhombic unit cell with 12 iron atoms and 4 carbon atoms and thus has a carbon content of 6.7 wt%. Its density is 7.6 g/cm³.

As compared with austenite and ferrite, cementite is very hard. The presence of iron carbide with ferrite in steel greatly increases the strength of the steel. However, because pure iron carbide is nonductile, it cannot adjust to stress concentrations; therefore, it is relatively weak by itself.

3.8 Fe-Fe₃C phase diagram

Fig. 23 shows the phase diagram between iron and iron carbide, Fe₃C. This phase diagram is the basis for the heat-treating of the majority of our steels.

If you cover the 0-1 wt% carbon region in Fig. 23 by your hand, you can see a close resemblance to previous phase diagrams. The eutectic composition is at 4.3 wt% carbon; the eutectic temperature is 1148 °C. Cast irons are based on this eutectic region, since they typically contain 2-3.5 wt% carbon. They have relatively low melting points with certain desirable processing and mold-filling characteristics. The iron-rich γ can dissolve up to 2.1 wt% carbon. As discussed in the last section, the carbon atoms...
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3.9 The eutectoid reaction

In Fig. 24, a comparison is conducted between the addition of carbon to austenite and that of common salt to water. In each case, the addition of the solute lowers the stable temperature range of the solution. These two examples differ in only one respect; in the ice-salt system, a “liquid solution” exists above the eutectic temperature; in iron-carbon system, a “solid solution” exists, so that a true eutectic reaction does not occur upon cooling. However, because of the analogy of this reaction to the eutectic reaction, it is called eutectoid, or eutectic-like.

Eutectic: $L \xrightarrow{\text{Cooling}} S_1 + S_3$  \hspace{1cm} (23)

Eutectoid: $S_2 \xrightarrow{\text{Cooling}} 2S_1 + S_3$  \hspace{1cm} (24)

The eutectoid temperature for iron-carbon alloys is 727 °C. The corresponding eutectoid composition is approximately 0.8 wt% carbon. The specific eutectoid reaction for Fe-C is

$$\gamma(0.77 \text{ wt\% C)} \xrightarrow{727^\circ \text{C}} \alpha(0.02 \text{ wt\% C}) + Fe_3C(6.7 \text{ wt\% C})$$

(25)

Fig. 24 Eutectic and eutectoid-like (eutectoid) region of phase diagrams.

Fig. 25 shows the eutectoid region in greater detail than does Fig. 23.
3.10 Austenite decomposition

During the cooling, the Fe-Fe₃C eutectoid reaction involves the simultaneous formation of ferrite α and carbide, C, from the decomposition of austenite γ of eutectoid composition:

\[ \gamma(-0.8 \text{ wt}\% \text{ C}) \rightarrow \alpha + \text{carbide} \]  

(26)

Nearly 12 wt% carbide and more than 88 wt% ferrite are in the resulting mixture. Since the carbide and ferrite form simultaneously, they are intimately mixed. Characteristically, the mixture is “lamellar”; i.e. it is composed of alternate layers of ferrite and carbide. The resulting microstructure, called “pearlite”, is very important in iron and steel technology, because it may be formed in almost all steels by suitable heat treatments.

Pearlite is a lamellar mixture of ferrite and carbide, formed by decomposing austenite of eutectoid composition. This distinction is important, since mixtures of ferrite and carbide may be formed by other reactions as well. However, the microstructure resulting from other reactions will not be lamellar and consequently the properties of such mixtures will be different.

Since pearlite comes from austenite of eutectoid composition, the amount of pearlite present is equal to that of austenite transformed. We can determine this amount by calculating the fraction of γ just above the eutectoid temperature.
Fig. 26 Surface morphology of Pearlite (∗2,500). This microstructure is a lamellar mixture of ferrite (lighter matrix) and carbide (darker). Pearlite forms from austenite of eutectoid composition. Therefore, the amount and composition of pearlite is the same as that of eutectoid austenite.