

Thermodynamic Investigation of Nonmetallic Inclusions in Steel (I)

(Behavior of Aluminum-, Silicon- and Iron-Nitrides and their
Effect on Austenite Grain Size of Steel)

By

Hiroshi SAWAMURA and Toshisada MORI

Department of Metallurgy

(Received August 15, 1956)

I. Introduction

The solid nonmetallic inclusions are present to some extent in all commercial steels and from the point of view of origin, they fall naturally into two classes: (1) those occurring as a result of reactions which take place in the body of molten or solidifying metal and (2) those resulting from mechanical incorporation of refractories or other materials with which molten steel comes into contact. The inclusions of the former class are by far the more numerous and are called the indigenous inclusions. Those of the latter are by their very nature sporadic in occurrence and are called the exogenous inclusions. The present investigation was carried out for the purpose of studying the change of content and the state of nonmetallic inclusions in steel which influence on the mechanical properties of steel especially on its austenite grain size; therefore, only the indigenous inclusions were taken into consideration as the object of the present study.

Nonmetallic inclusions are known to have serious effect on austenite grain size, and various hypotheses have been reported concerning the mechanism of austenite grain refining or that of grain growth inhibition. Though these hypotheses can be roughly divided into four different kinds, i.e. alumina hypothesis¹⁾, residual aluminum hypothesis²⁾, aluminum-nitride hypothesis³⁾, and sulphide hypothesis⁴⁾, aluminum-nitride hypothesis is most generally accepted at present.

In the present study the behavior of aluminum-nitride (AlN), silicon-nitride (Si_3N_4) and iron-nitride (Fe_4N) were thermodynamically investigated, and the standard free energy equations of the formation of these nitrides as the function of temperature were derived both from the references already reported and from equilibrium diagrams, the method of which is explained in the following section.

II. Chemical reactions of the formation of nonmetallic inclusions and the method of calculation of free energy equations

The free energy F of a binary solution composed of any two elements A and B is given by

$$F = n_A F_A + n_B F_B + F^M \quad (1)$$

where n_A and n_B are the number of moles of A and B, F_A and F_B are molar free energy of A and B, and F^M is the relative integral free energy caused by mixing.

If A and B have no mutual solubility and the system is composed of the mechanical mixture of A and B, then

$$F^M = 0.$$

But, if the system is a solution, then

$$F^M < 0.$$

Now, F^M is given by the following equation

$$F^M = H^M - T S^M \quad (2)$$

where H^M is the relative integral enthalpy caused by mixing, S^M is the relative integral entropy and T is absolute temperature ($^{\circ}\text{K}$) under consideration. If the change of volume caused by mixing is negligibly small, then the relative integral enthalpy is equal to the change of internal energy which is equal to the difference of the interaction energy between atoms. The difference of the interaction energy $\Delta\epsilon$ by the formation of unit A-B bond is expressed by

$$\Delta\epsilon = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2 \quad (3)^5$$

where ϵ_{AB} , ϵ_{AA} and ϵ_{BB} are respectively the bonding energy between the atoms A-B, A-A and B-B. If the atoms of the solution is assumed to be randomly distributed, the probability for A having B as its neighbour or B having A as its neighbour on a given pair of sites is equal to $2n_A n_B / (n_A + n_B)^2$. Among the P bonds in one mole, the total number of bonds between unlike atoms is therefore $2 \frac{n_A n_B}{(n_A + n_B)^2} P$.

The total heat of mixing H^M is therefore given as follows:

$$\begin{aligned} H^M &= -2 \frac{n_A n_B}{(n_A + n_B)^2} (n_A + n_B) P \cdot \Delta\epsilon \\ &= - \frac{n_A n_B}{n_A + n_B} k \Delta\epsilon \end{aligned} \quad (4)^6$$

where k is equal to $2P$ and is constant as far as A and B are concerned. The negative sign indicates that the transition from the gaseous state to the condensed state results in a decrease of energy. Thus, the values of individual bonding energy ϵ_{AA} , ϵ_{BB} and ϵ_{AB} are positive.

The relative integral entropy S^M of the above mentioned solution is given as follows :

$$S^M = -R \left(n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_B}{n_A + n_B} \right) \quad (5)'$$

where R is gas constant. Substituting equation (4) and (5) into (2), we have

$$F^M = - \frac{n_A n_B}{n_A + n_B} k \Delta \epsilon + RT \left(n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_B}{n_A + n_B} \right). \quad (6)$$

Substituting equation (6) into (1), we get

$$F = n_A F_A + n_B F_B - \frac{n_A n_B}{n_A + n_B} k \Delta \epsilon + RT \left(n_A \ln \frac{n_A}{n_A + n_B} + n_B \ln \frac{n_B}{n_A + n_B} \right). \quad (7)$$

Partial differentiation of F by n_A gives

$$\mu_A \equiv \left(\frac{\partial F}{\partial n_A} \right)_{n_B} = F_A - (1-x)^2 k \Delta \epsilon + RT \ln x \quad (8)$$

where x is the molar fraction of A, i.e.

$$x = n_A / (n_A + n_B). \quad (9)$$

The relation between molar fraction x and weight percentage $a\%$ is expressed as follows :

$$x = \frac{(a\%)/M_A}{(a\%)/M_A + \{100 - (a\%)\}/M_B} \quad (10)$$

where M_A and M_B are molecular weight of A and B.

If $(a\%) \ll 100$,

then
$$x \approx \frac{M_B}{100M_A} (a\%). \quad (11)$$

Substituting equation (11) into (8) and rearranging, we obtain

$$\mu_A = F_A - \left\{ 1 - \frac{M_B}{100M_A} (a\%) \right\}^2 k \Delta \epsilon + TR \ln \frac{M_B}{100M_A} + RT \ln (a\%). \quad (12)$$

If $\frac{M_B}{100M_A} (a\%) \ll 1$,

then
$$\mu_A = F_A - k \Delta \epsilon + RT \ln \frac{M_B}{100M_A} + RT \ln (a\%). \quad (13)$$

If the partial molar free energy of A of a solution containing 'a' weight percentage is expressed by $\mu_A(a\%)$, then equation (13) is expressed as follows :

$$\mu_A(a\%) - F_A = -k \Delta \epsilon + RT \ln \frac{M_B}{100M_A} + RT \ln (a\%). \quad (13)'$$

When the concentration of A changes only within small range in the solution,

$\Delta\epsilon$ may be considered as a constant. In such a condition, equation (13)' becomes

$$\mu_A(a\%) - F_A = \Delta H + RT \ln \frac{M_B}{100M_A} + RT \ln (a\%) \quad (14)$$

where ΔH is equal to $-k\Delta\epsilon$ and is a constant.

If the concentration of A is (b%), equation (14) becomes

$$\mu_A(b\%) - F_A = \Delta H + RT \ln \frac{M_B}{100M_A} + RT \ln (b\%). \quad (14)'$$

Subtracting equation (14) from (14)' gives

$$\mu_A(a\%) - \mu_A(b\%) = 4.575T \log \frac{(a\%)}{(b\%)}. \quad (15)$$

If b is unity, then

$$\mu_A(a\%) - \mu_A(1\%) = 4.575T \log (a\%). \quad (16)$$

Equation (14) is also valid in a solid solution.

If the state of a solution under consideration is expressed by adding a suffix 'l' (liquid) or 's' (solid), equation (13) becomes

$$A_{(s)} = \underline{A}(a\%)_{(s)}:$$

$$\mu_A(a\%)_{(s)} - F_{A(s)} = -k\Delta\epsilon_{(s)} + RT \ln \frac{M_B}{100M_A} + RT \ln (a\%) \quad (17)$$

$$A_{(l)} = \underline{A}(a\%)_{(l)}:$$

$$\mu_A(a\%)_{(l)} - F_{A(l)} = -k\Delta\epsilon_{(l)} + RT \ln \frac{M_B}{100M_A} + RT \ln (a\%). \quad (17)'$$

When one mole of pure A melts at $T^\circ\text{K}$, the change of free energy ΔF_f caused by the fusion is expressed as follows:

$$A_{(s)} = A_{(l)}: \Delta F_f = F_{A(l)} - F_{A(s)} = \Delta H_f - T\Delta S_f \quad (18)$$

where ΔH_f and ΔS_f are the heat of fusion and the change of its entropy caused by the phase change at $T^\circ\text{K}$. Subtracting equation (18) from (17), we have

$$A_{(l)} = \underline{A}(a\%)_{(s)}:$$

$$\begin{aligned} \mu_A(a\%)_{(s)} - F_{A(l)} &= -k\Delta\epsilon_{(s)} - \Delta H_f + RT \ln \frac{M_B}{100M_A} \\ &+ T\Delta S_f + RT \ln (a\%). \end{aligned} \quad (19)$$

Fig. 1 shows part of a binary equilibrium diagram where T_0 is the melting point of B, and the lines $\overline{T_0a}$ and $\overline{T_0b}$ are liquidus and solidus lines respectively. When a liquid solution containing $x\%$ of A is slowly cooled down to the temperature $T_1^\circ\text{K}$ and then kept at that

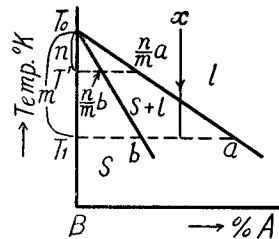


Fig. 1. Part of B-A equilibrium diagram.

temperature, the liquid 'a' and solid 'b' are in equilibrium and the equilibrium relation is expressed as follows:

$$\mu_A(a\%)_{(l)} = \mu_A(b\%)_{(s)}. \quad (20)$$

From equations (17)', (19) and (20):

$$\begin{aligned} & -k\Delta\varepsilon_{(l)} + RT_1 \ln \frac{M_B}{100M_A} + RT_1 \ln (a\%) \\ & = -k\Delta\varepsilon_{(s)} - \Delta H_f + RT_1 \ln \frac{M_B}{100M_A} + T_1\Delta S_f + RT_1 \ln (b\%). \end{aligned} \quad (21)$$

It is obvious that the 1st and 2nd terms on the left side of equation (21) are equal to the relative partial free energy in the change $A_{(l)} = \underline{A}(1\%)_{(l)}$, and therefore these terms can be generally written as $\Delta H - T\Delta S$, while the 1st to 4th terms on the right side are the relative partial free energy in the change $A_{(s)} = \underline{A}(1\%)_{(s)}$, and therefore these can also be written as $\Delta H' - T\Delta S'$. Thus equation (21) can generally be written as follows:

$$\Delta H - T_1\Delta S + RT_1 \ln (a\%) = \Delta H' - T_1\Delta S' + RT_1 \ln (b\%). \quad (22)$$

If the solution under consideration is a dilute solution of A and the difference of T_0 and T_1 is very small, then both liquidus and solidus lines can be assumed as straight lines. At any temperature T' °K within the range of from T_1 to T_0 °K, the equilibrium concentrations of liquid and solid solution are $(n/m)a\%$ and $(n/m)b\%$, where m and n are taken as follows:

$$\begin{aligned} & \frac{T_0 - T'}{T_0 - T_1} = \frac{n}{m} \\ \text{or} \quad & T' = \frac{m-n}{m}T_0 + \frac{n}{m}T_1. \end{aligned} \quad (23)$$

Similar relation as equation (22) is valid in the equilibrium state at T' °K, i.e.

$$\begin{aligned} & \Delta H - \left(\frac{m-n}{m}T_0 + \frac{n}{m}T_1\right)\Delta S + R\left(\frac{m-n}{m}T_0 + \frac{n}{m}T_1\right) \ln \left(\frac{n}{m}a\%\right) \\ & = \Delta H' - \left(\frac{m-n}{m}T_0 + \frac{n}{m}T_1\right)\Delta S' + R\left(\frac{m-n}{m}T_0 + \frac{n}{m}T_1\right) \ln \left(\frac{n}{m}b\%\right). \end{aligned} \quad (24)$$

Subtracting equation (24) from (22) and rearranging, we obtain

$$\begin{aligned} & \Delta S' = \Delta S - R \ln \frac{(a\%)}{(b\%)} \\ & = \Delta S - 4.575 \log \frac{(a\%)}{(b\%)}. \end{aligned} \quad (25)$$

Subtracting equation (25) from (22) gives

$$\Delta H = \Delta H'. \quad (26)$$

The relations of equations (25) and (26) are adequate not only in the equilibrium between liquid and solid but also between two solids.

The relative partial free energy in the change $A_{(L)} = A(1\%)_{(S)}$ is thus calculated in view of the atomic state, while quite the same results can be derived from the following thermodynamic relations

$$\mu_A(a\%)_{(L)} - \mu_A(1\%)_{(L)} = RT \ln(a\%) \quad (27)$$

$$\mu_A(b\%)_{(S)} - \mu_A(1\%)_{(S)} = RT \ln(b\%) \quad (27)'$$

Details of the method are omitted here.

Supposing that the element B in Fig. 1 is iron, the melting temperature T_0 is then 1812°K and the heat of fusion ΔH_f of iron at that temperature is 3670 cal/mole. Therefore, the following equation is derived by the adequate modification of van't Hoff equation.

$$\Delta T = \frac{1000(a\% - b\%)}{M_A} \quad (38)^{8)}$$

where

$$\Delta T = T_0 - T_1.$$

The melting point depression of pure iron caused by the addition of 1% silicon is 12°C; therefore, the concentration of silicon of δ -iron in equilibrium with the liquid solution containing 1% silicon is calculated as follows:

$$12 = \frac{1000(1 - b\%)}{28.06}$$

$$b = 0.66. \quad (29)$$

The liquidus and solidus lines of iron-silicon binary solution can be regarded as straight lines within the range of less than 1% silicon concentration.

The relative partial free energy of the solution of silicon in liquid iron is given as follows:

$$\text{Si}(l) = \underline{\text{Si}}_l(1\%) \quad \Delta F^\circ = -29000 - 0.30T. \quad (30)^{9)}$$

Therefore, the relative partial free energy of solution of the silicon in δ -iron can be calculated as follows:

$$\text{Si}(l) = \underline{\text{Si}}_\delta(1\%) \quad \Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = 0.30 - 4.575 \log \frac{1}{0.66}$$

$$= -0.53$$

$$\Delta H^\circ = -29000$$

$$\Delta F^\circ = -29000 + 0.53T. \quad (31)$$

Many data have been reported concerning $\gamma = \alpha(\delta)$ phase transformation in the iron-silicon binary system, and by summerizing the data reported by F. Wever and

P. Gianti¹⁰), H. Esser and P. Oberhoffer¹¹), C. Kreutzer¹²), R. Ruer and R. Klesper¹³), and M. Hansen¹⁴), the figure of the loop in the vicinity of A_3 and A_4 points can be drawn as shown in Fig. 2 where the solubility lines may be regarded as straight lines within the range of less than 0.5% concentration of silicon.

From the values shown in the figure, the relative partial free energy of the solution of silicon in austenite and ferrite can be calculated as follows:

$$\text{Si}(l) = \underline{\text{Si}}_{\gamma}(1\%) \quad \Delta F^{\circ} = -29000 + 1.54T \quad (32)$$

$$\text{Si}(l) = \underline{\text{Si}}_{\alpha}(1\%) \quad \Delta F^{\circ} = -29000 + 0.77T. \quad (33)$$

Similar consideration can be applied to the iron-aluminum binary solution. Equilibrium diagram of the iron-aluminum binary system has been investigated by A.G.C. Gwyer and H.W.L. Phillips¹⁵), N. Kurnakov, G. Vrazov and A. Grigoriev¹⁶), F. Wever and A. Müller¹⁷), M. Isawa and T. Murakami¹⁸), and M. Hansen¹⁴). According to the results they obtained the melting point depression of pure iron is 3°C¹⁸) by the addition of 1% aluminum. The concentration of aluminum in δ -iron in equilibrium with the liquid solution containing 1% aluminum can be, therefore, calculated to be 0.92%.

The relative partial free energy of the solution of aluminum in liquid iron is given as follows:

$$\text{Al}(l) = \underline{\text{Al}}_l(1\%) \quad \Delta F^{\circ} = -11700 - 7.7T. \quad (34)^{9)}$$

Therefore, the relative partial free energy of the solution of aluminum in δ -iron can be calculated by equation (25) and (26) as follows:

$$\text{Al}(l) = \underline{\text{Al}}_{\delta}(1\%) \quad \Delta F^{\circ} = -11700 - 7.53T. \quad (35)$$

The figure of γ -loop in the iron-aluminum binary system has not been clearly determined and, therefore, the free energy equation for the change of γ - δ phase transformation was calculated by the following method.

Standard free energy of the formation of aluminum-nitride and the relative partial free energy of the solution of gaseous nitrogen in γ -iron are given as follows:

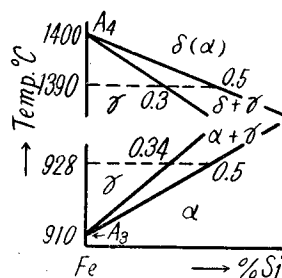
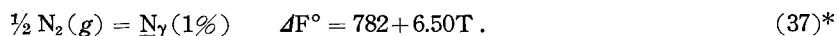
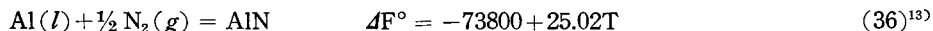


Fig. 2. Part of γ -loop of Fe-Si diagram at A_3 and A_4 point.

* Equation (37) was derived by the method described later. Experimental equation has recently been reported by N. S. Corney and E. T. Turkdogan²²).

Subtracting equation (37) from (36) gives

$$\text{Al}(l) + \underline{\text{N}}_{\gamma}(1\%) = \text{AlN} \quad \Delta F^{\circ} = -74582 + 18.52T. \quad (38)$$

Supposing that the relative partial free energy of the solution of aluminum in γ -iron is given as follows:

$$\text{Al}(l) = \underline{\text{Al}}_{\gamma}(1\%) \quad \Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}, \quad (39)$$

then, subtracting equation (39) from (38) gives

$$\underline{\text{Al}}_{\gamma}(1\%) + \underline{\text{N}}_{\gamma}(1\%) = \text{AlN} \quad \Delta F^{\circ} = (-74582 - \Delta H^{\circ}) + (18.52 + \Delta S^{\circ})T. \quad (40)$$

L. S. Darken, R. P. Smith and E. W. Filer²⁰⁾ and T. Shimose and K. Narita²¹⁾ investigated the equilibrium relation of aluminum and nitrogen dissolved in γ -iron and experimentally determined the following equations:

$$\text{Darken, Smith and Filer:} \quad \log [\text{Al}][\text{N}] = -\frac{7400}{T} + 1.95 \quad (41)$$

$$\text{AlN} = \underline{\text{Al}}_{\gamma}(1\%) + \underline{\text{N}}_{\gamma}(1\%) \quad \Delta F^{\circ} = 33855 - 8.92T \quad (42)$$

$$\text{Shimose and Narita:} \quad \log [\text{Al}][\text{N}] = -\frac{7184}{T} + 1.79 \quad (43)$$

$$\text{AlN} = \underline{\text{Al}}_{\gamma}(1\%) + \underline{\text{N}}_{\gamma}(1\%) \quad \Delta F^{\circ} = 32867 - 8.19T. \quad (44)$$

Although these two equations are in good agreement with each other, the former was used in the authors' calculation.

As the equation (40) and (42) are identically equal (though the sign is opposite), ΔH° and ΔS° can be calculated easily by comparing these two equations. Equation (39) is therefore given as follows:

$$\text{Al}(l) = \underline{\text{Al}}_{\gamma}(1\%) \quad \Delta F^{\circ} = -40727 + 9.60T. \quad (45)$$

There is no experimental datum, as far as we know, concerning the relative partial free energy of the solution of aluminum in α -iron, and, therefore, the following equation is roughly calculated, as shown in Fig. 3, by assuming that the solubility of aluminum in γ -iron is ca. 0.42% in equilibrium with α -iron containing 0.5% aluminum:

$$\text{Al}(l) = \underline{\text{Al}}_{\alpha}(1\%) \quad \Delta F^{\circ} = -40727 + 9.3T. \quad (46)$$

The data reported by V. G. Paranjpe, M. Cohen, M. Bever and C. F. Floe²³⁾ concerning the iron-nitrogen binary system and those by L. J. Dijkstra²⁴⁾ concerning the solubility of nitrogen in α -iron can be regarded most reliable, but the experimental data in the range higher than 700°C cannot be found as far as we know. The relative partial free energy of the solution of gaseous nitrogen in γ -iron is calculated, therefore, by extrapolation of

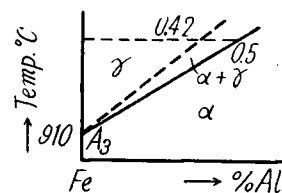


Fig. 3. Part of γ -loop of Fe-Al diagram at A_3 point.

the data experimentally determined by Paranjpe et alii. Solubility of nitrogen in α - and γ -iron is shown in Table 1.

The relative partial free energy of the solution of gaseous nitrogen expressed in 0.01% standard in α -iron is

$$\frac{1}{2}N_2(g) = N_\alpha(0.01\%) \quad \Delta F^\circ = 4880 - 1.15T. \quad (47)^{19)}$$

The free energy change of dissolved nitrogen from the concentration of 0.01% to that of 1% can be calculated by equation (16) as follows:

$$N_\alpha(0.01\%) = N_\alpha(1\%) \quad \Delta F^\circ = 4.575T \log \frac{1}{0.01}. \quad (48)$$

Adding equation (47) to (48) gives

$$\frac{1}{2}N_2(g) = N_\alpha(1\%) \quad \Delta F^\circ = 4880 + 8.00T. \quad (49)$$

Supposing that the relative partial free energy of the solution of nitrogen in γ -iron is given as follows:

$$\frac{1}{2}N_2(g) = N_\gamma(1\%) \quad \Delta F^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (50)$$

and if the equilibrium constant is expressed by K_γ , the following equation is obtained.

$$\log K_\gamma = \log \frac{[N]_\gamma}{p_{N_2}^{1/2}} = -\frac{\Delta H^\circ}{4.575T} + \frac{\Delta S^\circ}{4.575}. \quad (51)$$

Equation (49) gives

$$\log K_\alpha = \log \frac{[N]_\alpha}{p_{N_2}^{1/2}} = -\frac{1066.7}{T} - 1.75 \quad (52)$$

where K_α is the equilibrium constant for the reaction expressed by equation (49).

In ($\alpha + \gamma$) two phase range, the nitrogen pressure in equation (51) and (52) is the same and, therefore, subtracting equation (52) from (51) gives

$$\log K_\gamma = \log [N]_\gamma - \log [N]_\alpha + \log K_\alpha. \quad (53)$$

Calculation of equation (53) from the data in Table 1 and by the value of equation (52) gives

$$\log K_\gamma = -\frac{171}{T} - 1.42 \quad (54)$$

$$\therefore \frac{1}{2}N_2(g) = N_\gamma(1\%) \quad \Delta F^\circ = 782 + 6.50T. \quad (55)$$

Equation (37) is identically equal to equation (55) and was thus obtained.

Solubility of nitrogen in austenite in equilibrium with iron-nitride (Fe_4N) is shown in Table 2.²³⁾

Table 1. Solubility of nitrogen in α - and γ -iron.

Temp. °C	% N	
	α -iron	γ -iron
877	0.008†	0.10†
800	0.034†	0.50†
700	0.069*	1.19†
675	0.073†	1.40*
650	0.086*	1.64*
590	0.10*	2.35*

* Observed † Estimated

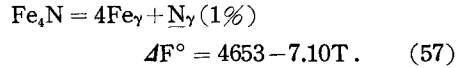
Table 2. Solubility of nitrogen in austenite in equilibrium with iron-nitride (Fe₄N).

Temp. °C	% N
650	2.80
625	2.64
590	2.35

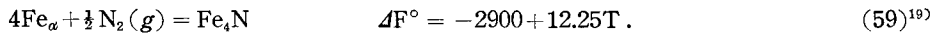
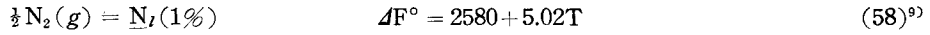
These results are expressed by

$$\log [N]_{\gamma} = -\frac{1017}{T} + 1.55, \quad (56)$$

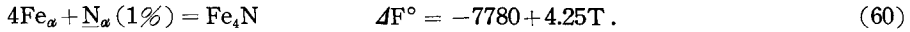
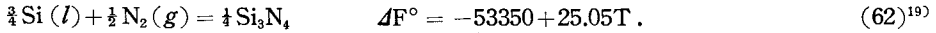
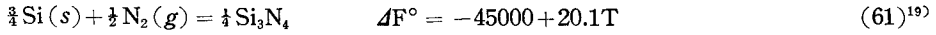
and the precipitation reaction of nitride in austenite is given as follows:



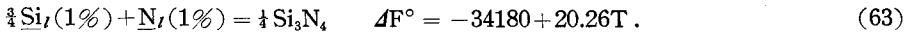
The relative partial free energy of the solution of nitrogen in liquid iron and the standard free energy of the formation of iron-nitride are given by



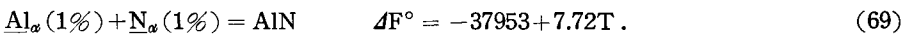
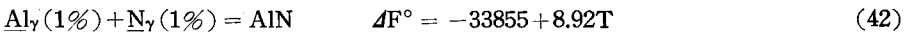
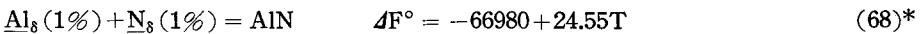
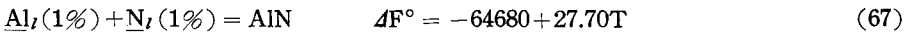
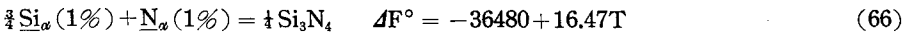
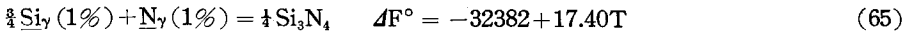
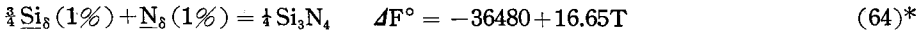
Subtracting equation (49) from (59) gives


 Standard free energy equations of the formation of silicon-nitride (Si₃N₄) are given by


Equation (30), (58) and (62) give



The following equations are derived in the same way:



These equations were used for the calculation of nitride precipitation in iron which are explained in the later section.

 L. S. Darken et al.'s data²⁰⁾ indicate that the value of the equilibrium constant of the equation (42) scarcely changes in the range of composition $C < 0.2\%$,

* Equation (64) and (68) are calculated by assuming that equation (49) is adequate in δ -iron.

$\text{Si} < 0.5\%$ and $\text{Mn} < 1.5\%$. The interaction coefficient $f_{\text{Al}}^{(\text{N})}$ can well be considered to be unity if the content of nitrogen is very small (0.005%). The interaction coefficient $f_{\text{N}}^{(\text{Al})}$ can, therefore, be considered to be nearly equal to unity, when the content of aluminum is less than 0.03%. From the above reasons the authors assumed that all of the interaction coefficients in equations (67)~(69) are nearly equal to unity. J. Chipman²⁵⁾ calculated the interaction coefficient $f_{\text{N}}^{(\text{Si})}$ at 1630°C as follows:

$$\log f^{(\text{Si})} = -0.038 [\% \text{Si}]. \quad (70)$$

Therefore $f_{\text{N}}^{(\text{Si})} = 0.96$

if the content of silicon is 0.5%. $f_{\text{N}}^{(\text{Si})}$ may be reduced in solid iron*, but these were assumed to be unity in the authors' calculation in equations (63)~(66).

III. Precipitation of nitrides in liquid and solid iron

Silicon and aluminum killed low carbon steel was taken as an example for the calculation of nitride precipitation, the chemical composition of which is selected as follows:

	C	Si	Mn	Metallic Al	Total N
%	0.15	0.15	< 1.5	0.03	0.005

Metallic aluminum means the difference of the content of aluminum between total aluminum and alumina type aluminum. Alumina contained in steel is very stable and was assumed, therefore, not to show any appreciable change in its amount throughout the whole temperature range under consideration. The content of total nitrogen was fixed so as to contain an average value in the open hearth steel.

Now, aluminum-nitride (AlN), silicon-nitride (Si_3N_4), manganese-nitride (Mn_3N_2) and iron-nitride (Fe_4N) are to be considered as the precipitates in the above mentioned steel. Among these nitrides the presence of aluminum-nitride in steel is recognized by chemical analysis²⁶⁾, micro- and electron-micro-photograph²⁷⁾, and the precipitation of silicon-nitride is also presumed by X-ray analysis²⁸⁾. As for iron-nitride, $\text{Fe}_8\text{N}^{29)}$ precipitates as a metastable phase³⁰⁾ by a low temperature annealing (e.g. 200~250°C) before the precipitation of Fe_4N . Fe_8N is not shown in iron-nitrogen equilibrium diagram and thermodynamic datum is unknown** at present and, therefore, there is no method of calculation for the precipitation of Fe_8N . But the thermodynamic data

* When a steel contains 0.58% silicon, the equilibrium content of dissolved nitrogen under one atmospheric nitrogen gas slightly decreases. This is contradictory to the results in liquid iron obtained by J. Chipman²⁵⁾. But Darken et al²⁰⁾ suggest that higher silicon steels will show higher nitrogen solubility than pure iron.

** Free energy equation for the reaction ' $\text{Fe}_8\text{N}' = 8\text{Fe}_\alpha + \text{N}_\alpha (1\%)$ ' was recently reported by J. D. Fast and M. B. Verrijp³¹⁾.

of Fe_4N are known as already stated, therefore, we could calculate solely the amount of Fe_4N . Although the temperature function of standard free energy of the formation of manganese-nitride is unknown as yet, the free energy at room temperature was determined to be as follows:



Since this value is higher than that of silicon-nitride, there may be no serious error in assuming that the precipitation of manganese-nitride does not occur when small amount of aluminum or silicon is present together with manganese so long as there is no great difference between the constants of manganese and silicon. But manganese resembles iron both physically and chemically and, therefore, the precipitation of manganese-nitride may occur in a low temperature range (probably lower than several hundred degree centigrade) if the steel contains manganese, nitrogen and a trace of aluminum or silicon. J. D. Fast³²⁾, for example, stated that age-hardening was observed in a pure iron containing 0.02% nitrogen in a low temperature range but it could not be recognized in the same steel when 0.5% manganese was added together, and these facts were probably due to the precipitation of manganese-nitride in a higher temperature before the formation of iron-nitride.

Concerning the stability of these nitrides, aluminum-nitride is most stable and silicon-nitride is more stable than iron-nitride. The authors performed, therefore, the calculation of the nitride precipitation in order of their stability.

(1) Precipitation of aluminum-nitride in liquid and solid iron containing aluminum and nitrogen.

When 0.03% aluminum and 0.005% nitrogen are contained in a steel, the free energy change ΔF can be calculated as follows:

$$\underline{\text{Al}}_l(1\%) + \underline{\text{N}}_l(1\%) = \text{AlN} \quad \Delta F^\circ = -64680 + 27.70T \quad (67)$$

$$\underline{\text{Al}}_l(1\%) = \underline{\text{Al}}_l(0.03\%) \quad \Delta F = 4.575T \log 0.03$$

$$\underline{\text{N}}_l(1\%) = \underline{\text{N}}_l(0.005\%) \quad \Delta F = 4.575T \log 0.005$$

$$\underline{\text{Al}}_l(0.03\%) + \underline{\text{N}}_l(0.005\%) = \text{AlN}$$

$$\Delta F = -64680 + 27.70T - 4.575T (\log 0.03 + \log 0.005).$$

$$\text{At } T = 1539^\circ\text{C} (1812^\circ\text{K}), \quad \Delta F = 17204 > 0.$$

Therefore the precipitation of aluminum-nitride does not occur in liquid iron.

In the same way, we can calculate from equation (68) that the nitride precipitation does not occur either in δ -iron.

The following equation is obtained from equation (42) in γ -iron.

$$\underline{\text{Al}}_\gamma(0.03\%) + \underline{\text{N}}_\gamma(0.005\%) = \text{AlN} \quad \Delta F = -33855 + 26.41T.$$

$$\text{At } T = 1009^\circ\text{C} (1282^\circ\text{K}), \quad \Delta F = 0.$$

Therefore aluminum-nitride precipitates in γ -iron at the temperature lower than 1009°C. L. S. Darken et al.'s experiments²⁰⁾ were performed in the temperature range of only from 930 to 1350°C, and in these conditions the activity coefficients of aluminum and nitrogen can be assumed to be constant. But when the steel containing 0.15% carbon is slowly cooled, ferrite crystallizes out at about 865°C and austenite increases its carbon content along A_3 line which may influence the activity coefficient of aluminum and nitrogen. The reliability of equation (41) is, therefore, unknown when the content of carbon increases to more than 0.2% and when the equilibrium temperature is lower than 930°C. Nevertheless, the following calculation was made with the assumption that equation (41) is adequate all through the temperature concerned.

If the equilibrium among aluminum and nitrogen dissolved in γ -iron and aluminum-nitride is attained, the following equation is derived from equation (41).

$$\log (0.03-x)\left(0.005-\frac{14}{27}x\right) = -\frac{7400}{T} + 1.95 \quad (41)'$$

where x is the weight percent aluminum of aluminum-nitride and $\frac{14}{27}x$ is, therefore, that of nitride nitrogen. The solubility of aluminum-nitride in the state of molecule in austenite is assumed to be zero. This assumption is applied to all the cases of nitride formation. Table 3 can be obtained from the calculation of equation (41)'.

Equation (69)' as shown below can be derived from equation (69) concerning the equilibrium in α -iron, and Table 4 is obtained by calculating equation (69)'.

$$\log [Al][N] = -\frac{8295.7}{T} + 1.69 \quad (69)'$$

Table 3. Equilibrium content of Al, N and AlN in austenite.

Temp. °C	<u>Al</u> %	<u>N</u> %	AlN %
≥ 1009	0.03	0.005	0
1000	0.0294	0.0047	0.00091
900	0.0238	0.0018	0.00936
865	0.0228	0.0012 ₆	0.0110
850	0.0224	0.0010	0.0116
800	0.0214	0.0005 ₄	0.0131
∇ 730	0.0204	0	0.0146

Table 4. Equilibrium content of Al, N and AlN in ferrite.

Temp. °C	<u>Al</u> %	<u>N</u> %	AlN %
910	0.02073	0.00020	0.01408
865	0.02059 ₁	0.00012 ₁	0.01429
850	0.02054 ₆	0.00009 ₈	0.01436
800	0.02044 ₁	0.00004 ₄	0.01452
730	0.02038	0.00001 ₂	0.0146

It may well be considered from Table 4 that nitrogen in α -iron practically exists as nitride. The ratio between the weight of ferrite and that of austenite of a steel containing 0.15% carbon in the range of temperature from A_1 to A_3 can be estimated from the iron-carbon equilibrium diagram³³⁾ and is shown in Table 5.

Table 5. Equilibrium content of ferrite and austenite in the range from A_1 to A_3 point.

Temp. °C	Ferrite %	Austenite %	C % in austenite
865	0	100	0.15
850	17	83	0.18
845	25	75	0.20
830	31	69	0.25
800	58	42	0.36
777	68	32	0.47
750	76	24	0.62
730	80	20	0.75
723	{ 81 100	{ 19 0	0.80

The equilibrium relation among aluminum, nitrogen in iron and aluminum-nitride, therefore, can be calculated from Table 3, 4 and 5, and is shown in Table 6 and Fig. 4.

Table 6. Equilibrium content of Al, N and AlN in the range from A_1 to A_3 point.

Temp. °C	Al %	N %	AlN %
865	0.0228	0.00126	0.0110
850	0.0220 ₈	0.00084 ₇	0.0120 ₇
800	0.0208 ₄	0.00025 ₂	0.0139 ₂
≤730	0.0204	0	0.0146

(2) Precipitation of silicon-nitride in liquid and solid iron containing silicon and nitrogen.

When 0.5% silicon and 0.005% nitrogen are contained in a steel, the free energy changes of the formation of silicon-nitride in liquid and solid iron can be calculated by equations (63), (64), (65) and (66).

Calculation showed that silicon-nitride cannot be precipitated in liquid and δ -iron but it can be pre-

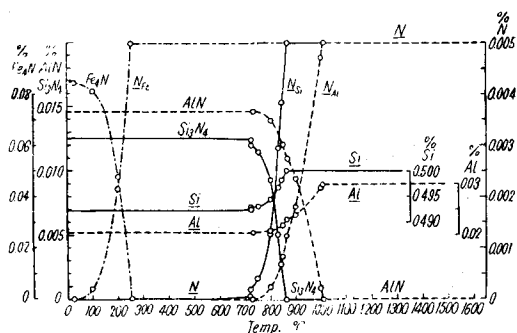


Fig. 4. Equilibrium content of Al (or Si), N and AlN (or Si_3N_4) in steel containing 0.5% C, 0.005% N and 0.03% Al (or 0.5% Si), and that of Fe_4N and N in steel containing 0.005% N.

precipitated in γ -iron when the temperature becomes lower than 845°C. Equation (65) can be written as follows:

$$\log [\text{Si}]^{3/4}[\text{N}] = -\frac{7078}{T} + 3.80, \quad (65)'$$

which can be modified as:

$$\frac{3}{4} \log (0.5 - x) + \log (0.005 - 0.6656x) = -\frac{7078}{T} + 3.80 \quad (71)$$

where x is the weight percent silicon of silicon-nitride and $0.6656x$ is that of nitride nitrogen.

In the same way, we can derive from equation (66)

$$\log [\text{Si}]^{3/4}[\text{N}] = -\frac{7973.8}{T} + 3.60, \quad (66)'$$

and can calculate the equilibrium content of silicon, nitrogen in α -iron and silicon-nitride.

Combining these results with the value shown in Table 5, we obtain the equilibrium content of silicon, nitrogen and silicon-nitride in a steel containing 0.15% carbon, 0.5% silicon and 0.005% nitrogen which is shown in Table 7 and in Fig. 4.

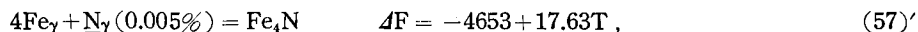
Table 7. Equilibrium content of Si, N and Si_3N_4 in the range from A_1 to A_3 point.

Temp. °C	Si %	N %	Si_3N_4 %
865	0.5	0.005	0
845	0.49831	0.003875	0.002816
830	0.49692	0.002949	0.005133
800	0.49443	0.001286	0.009294
750	0.49308	0.000396 ₄	0.011520
723*	{(0.49281) 0.49259}	{(0.000214 ₇) 0.000067 ₂ }	{(0.011975) 0.012344}

* The equilibrium values at 723°C in parenthesis change to the values written below.

(3) Precipitation of iron-nitride in solid iron.

When a steel contains only 0.005% of nitrogen, the free energy change of formation of iron-nitride in γ -iron is derived from equation (57) as follows:



and as the free energy difference ΔF of the formation of iron-nitride is positive in γ -iron, iron-nitride does not precipitate in this phase.

The pure compound of iron-nitride (Fe_4N) transforms to ϵ -phase at 680°C and as the solubility of the solid solution ϵ to γ -iron is also great, no iron-nitride other than

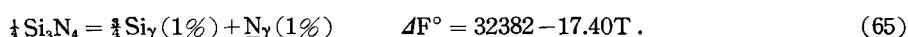
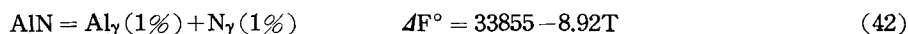
Fe₄N precipitates in γ -iron. On the other hand, free energy difference of the formation of iron-nitride in α -iron can be derived from equation (60) as follows:

$$\log [N] = -\frac{1700.6}{T} + 0.93. \quad (60)'$$

Calculation by equation (60)' shows that iron-nitride precipitates in the temperature range of lower than 253°C. But it will require a long time to precipitate iron-nitride without any cold deformation because this temperature is comparatively low. If the steel is heated to 150~200°C and is kept at these temperature for a long time, the precipitation of iron-nitride occurs and precipitation hardening may be recognized. We can calculate the equilibrium content of iron-nitride from equation (60)' and it is shown in Fig. 4.

(4) Equilibrium relation among aluminum, silicon, nitrogen and their nitrides in γ and α -iron.

As already shown in the section II, the free energy changes of the formation of aluminum- and silicon-nitride are expressed as follows:



Subtracting equation (42) from (65) gives



Equation (42), (65) and (72) can be written as follows:

$$\log K_1 = \log [\text{Al}][\text{N}] = -\frac{7400}{T} + 1.95 \quad (41)$$

$$\log K_2 = \log [\text{Si}]^{3/4}[\text{N}] = -\frac{7078}{T} + 3.80 \quad (65)'$$

$$\log K_3 = \log \frac{[\text{Si}]^{3/4}}{[\text{Al}]} = \frac{322}{T} + 1.85. \quad (72)'$$

If both equation (41) and (65)' are in an equilibrium state, equation (72)' is simultaneously in equilibrium. In the case of a steel containing 0.03% aluminum, 0.5% silicon and 0.005% nitrogen, aluminum-nitride begins to precipitate at a temperature lower than 1009°C as shown in Table 3, but the content of solid solution nitrogen, which is determined by equation (41), does not satisfy equation (65)' at any temperature in which the concentration of silicon is 0.5%, and therefore silicon-nitride precipitation does not occur in this case.

Similar consideration can be applied in the equilibrium in α -iron. The equations used in this case are as follows:

$$\text{AlN} = \underline{\text{Al}}_{\alpha}(1\%) + \underline{\text{N}}_{\alpha}(1\%) \quad \Delta F^{\circ} = 37953 - 7.72T \quad (69)$$

$$\frac{1}{4}\text{Si}_3\text{N}_4 = \frac{1}{4}\underline{\text{Si}}_{\alpha}(1\%) + \underline{\text{N}}_{\alpha}(1\%) \quad \Delta F^{\circ} = 36480 - 16.47T \quad (66)$$

$$\underline{\text{Al}}_{\alpha}(1\%) + \frac{1}{4}\text{Si}_3\text{N}_4 = \frac{1}{4}\underline{\text{Si}}_{\alpha}(1\%) + \text{AlN} \quad \Delta F^{\circ} = -1473 - 8.75T \quad (73)$$

$$\log K_1' = \log [\text{Al}][\text{N}] = -\frac{8295.7}{T} + 1.69 \quad (69)'$$

$$\log K_2' = \log [\text{Si}]^{3/4}[\text{N}] = -\frac{7973.7}{T} + 3.60 \quad (66)'$$

$$\log K_3' = \log \frac{[\text{Si}]^{3/4}}{[\text{Al}]} = \frac{322}{T} + 1.91 \quad (73)'$$

In the case of a steel having the same composition as mentioned above, the nitride precipitated in α -iron is not silicon-nitride but aluminum-nitride. We are able to know from these calculations that the precipitation of nitride in these two cases is quite the same as in the steel containing 0.03% aluminum and 0.005% nitrogen, and 0.5% silicon is indifferent to the precipitation reaction.

If the content of aluminum becomes lower or that of silicon becomes higher than the values mentioned above, both aluminum- and silicon-nitride precipitate simultaneously and the equilibrium relation becomes comparatively complex. Let us consider, for example, the steelmaking condition in which the addition of aluminum is small and the concentration of metallic aluminum becomes 0.01% while those of silicon and nitrogen in the steel remain constant. Aluminum- and silicon-nitride co-exist in this case in γ -iron at lower than 777°C, and the similar equilibrium relation exists also in α -iron. The equilibrium content of a steel containing 0.15% carbon, 0.01% aluminum, 0.5% silicon and 0.005% nitrogen is shown as an example in Fig. 5.

The precipitation of iron-nitride does not occur, of course, if aluminum and (or) silicon of a similar quantity are (is) contained in a steel.

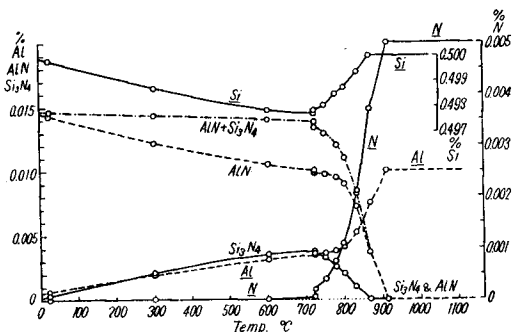


Fig. 5. Equilibrium content of Al, Si, N, AlN and Si_3N_4 in steel containing 0.15% C, 0.01% Al, 0.5% Si and 0.005% N.

IV. Discussion

According to the definition by F. E. Burke and D. Turnbull³⁴⁾, recrystallization and grain growth of metals are generally classified into three processes, i.e. "primary recrystallization," "secondary recrystallization," and "grain growth." The phenomenon that a fine grained steel shows an abrupt grain coarsening at a coarsening temperature belongs to the secondary recrystallization and the phenomenon in which the

once coarsened grains (whose grain size number is No. 1 or 2) show the gradual growth³⁵⁾ by keeping the heating temperature further or by heating further to a higher temperature is called the normal grain growth. The phenomenon of secondary recrystallization at a fixed temperature is expressed by a function of nucleation frequency \dot{N} and linear rate of growth G .

Although the influence of various factors upon \dot{N} and G have been reported by many investigators, the mechanism of grain growth remains still uncertain. Nevertheless, the fact that the secondary recrystallization is strongly inhibited by very finely dispersed inclusions has been shown in many reports³⁶⁾. If we consider the relation between these nitrides and grain coarsening by the results of our calculation shown in the preceding paragraph, we can readily know that aluminum-nitride is a strong grain growth inhibitor and silicon-nitride has a similar function though not so strong as the former, because both aluminum- and silicon-nitride change their content according to the change of temperature and we can assume that the grain growth begins when the content of nitrides decreases to a certain small quantity. Moreover, we can easily explain that the grain coarsening temperature of an aluminum killed steel is higher than that of the silicon killed steel³⁷⁾, because silicon-nitride dissolves into γ -iron at a temperature lower than the temperature in which aluminum-nitride dissolves. If the content of aluminum, silicon and nitrogen in a steel increases, the precipitation temperature of nitrides moves to a higher temperature range and the quantity of nitrides formed at any temperature becomes much more than before. If we aim to get the same order of effect by silicon instead of 0.03% aluminum in a steel, the content of silicon can be calculated from equation (65)' to be 5.8% and the value is too high to be added into common steels because the content of silicon is limited by mechanical properties, castability of steel ingot, etc. We cannot, therefore, get a silicon killed steel of as fine grain as an aluminum killed steel at high temperatures.

H. F. Beeghly²⁶⁾ showed the change of aluminum-nitride nitrogen in low carbon steels (Fig. 6) which were hot rolled and air cooled followed by water quenching after keeping it for 1 hr. at various temperatures. The trend of the change of nitride nitrogen in austenite is in good agreement with the curves shown in Fig. 4 and 5. Fig. 6 shows that the content of aluminum-nitride is very low in the range of temperature lower than 400°C and it increases suddenly at ca. 675°C. As these specimens were air cooled from the rolling temperature, the equilibrium state among aluminum, nitrogen and aluminum-nitride was not attained and after the reaction velocity became great enough to reach equilibrium, the precipitation of aluminum-nitride had occurred. The temperature at which the reaction velocity of nitride precipitation becomes great must roughly agree with the temperature in which the diffusion velocity of nitrogen

atom becomes great. This temperature is ca. $400^{\circ}\text{C}^{38)}$ * and it shows a good agreement with the results shown in Fig. 6.

Let us now consider the austenite grain size of a steel ingot. When molten steel is cast into an ingot mould, the steel should not contain any nitride if the equilibrium condition among aluminum, silicon and nitrogen is attained. Consequently, the austenite grains produced during cooling from molten state must be independent of nitrides, but when

the steel is cooled down to room temperature or to the temperature at least below A_1 point, nitride precipitates in the steel and if the steel is reheated to austenite range, the austenite grains produced during A_1 and A_3 transformation must be influenced by the nitride already precipitated and their growth will be inhibited by these nitrides. Therefore, these grain size formed during the transformation must be fine and different from these produced while the ingot is being cooled from molten state.

When fine grained steel is desired to be obtained, it is better to cool the steel down to room temperature and reheat it to the rolling or forging temperature. The rolling temperature should be as low as possible so as not to dissolve nitrides. In manufacturing HSB-Stahl^{3b)}, the maximum rolling temperature is controlled not to exceed 1000°C . One of the aims of this process is at least to get a fine grained steel by inhibiting the dissolution of aluminum-nitride. According to the results obtained by K. Born and W. Koch^{3b)} and W. C. Leslie, R. L. Rickett, C. L. Dotson and C. S. Walton²⁷⁾, it requires a long time to reach equilibrium among aluminum, nitrogen and aluminum-nitride. But the time during which the steel is heated over 1000°C and maintained must be as short as possible if the fine grained steel is desired; and also, it is better to reheat the steel after it is cooled down to below A_1 temperature if the steel is heated, e.g. over 1200°C , for a long time and almost all the nitrides is dissolved.

Concerning the size of nonmetallic inclusions, it is necessary, as mentioned before, that the inclusions must be smaller than a certain critical size in order to be effective for inhibition of grain coarsening. Inclusions such as those produced in molten iron which do not change their content in both austenite and ferrite may not show any

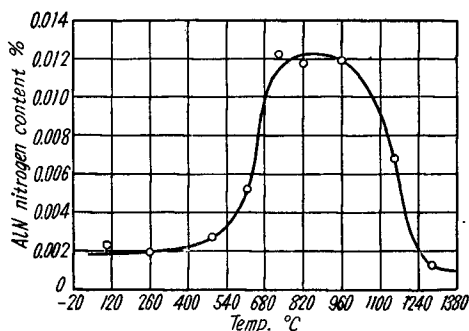


Fig. 6. Aluminum nitride nitrogen content of ester-halogen residues from steel heated for 1h at different temperatures. (H. F. Beeghly)

* The diffusion constant of nitrogen in iron attains the order of 10^{-7} cm^2/sec . at 400°C and nitriding of steel becomes practically capable at this temperature.

change in their number and size even by heat treatment, and even if they change their size, they will have a tendency to coagulate with each other to form larger particles and decrease their number. Alumina can be considered one of them. Therefore, assuming that alumina is effective as a grain growth inhibitor, only those very finely dispersed may be effective and those coagulated into large particles may have less effective inhibiting or refining action.

On the other hand, concerning the inclusions whose content changes by heat treatment, e.g. aluminum- and silicon-nitride, it will be possible to control their size and number by changing their heating velocity of heating temperature.

It is quite proper to consider such inclusions as these as very effective inhibitors. Coagulation may occur even in these nitrides and, therefore, there may be an upper limit of the content to be effective as grain growth inhibitors but the limit is not yet clear at present. There may also be a lower limit for the inclusions to be effective inhibitors and the lower limit was determined to be 0.010% of aluminum-nitride by K. Born and W. Koch^{3b)} or 0.008% by Z. Takao, T. Noda, K. Kunii and H. Takada^{3c)}.

When a steel contains aluminum-nitride of this order of quantity, the austenite grain size remains to be as fine as No. 9 in the number of ASTM grain size chart even if the steel is heated to 925°C for several hours.

To facilitate understanding, the free energy change of the formation of nitrides are shown as functions of temperature in Fig. 7 where the content of aluminum, silicon and nitrogen were selected as follows :

	Al	Si	N
%	0.01 or 0.03	0.5	0.005.

If the lines lie above the horizontal line of $\Delta F = 0$, nitride does not precipitate and aluminum, silicon and nitrogen are all in the state of solid (or liquid) solution in iron; and if the lines lie below the horizontal line, nitrides precipitate and its tendency is more conspicuous when the line is located lower. The intersecting point of ΔF line and the horizontal line shows, therefore, the temperature of nitride precipitation.

If we desire to know the temperature of nitride precipitation when the content of nitrogen varies, we can know the temperature easily by the following method. For example, in the case of a steel containing 0.01% aluminum and 0.020% nitrogen, combine the point of 0.020% nitrogen in the right side ordinate and the point P of 0°K on the extrapolating line of abscissa by a transparent scale or a string. The reading at the intersecting point on the scale line and the line "F" will be approximately 1035°C.

This temperature corresponds to that of aluminum-nitride precipitation. If we

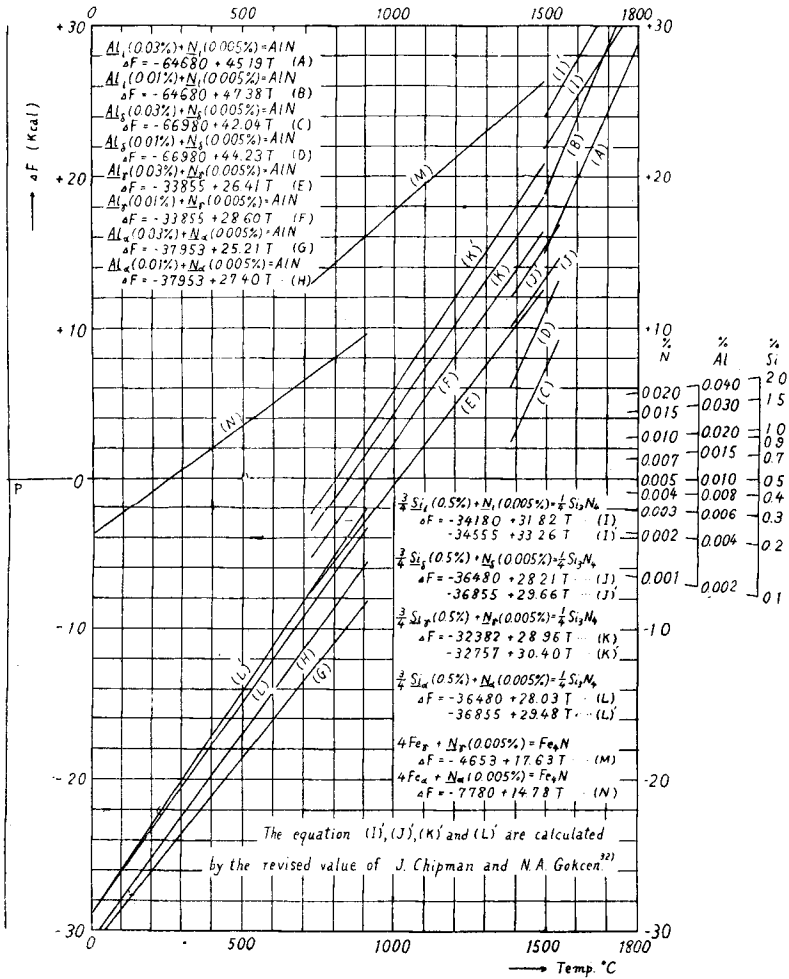


Fig. 7. The free energy of formation of nitrides and carbides as a function of temperature.

wish to know the nitride precipitation temperature when the content of aluminum or silicon varies, we can know the temperature easily by combining the point of required content of aluminum or silicon in the right side ordinate and the point P, and by the same method just described.

V. Summary

1. When aluminum, silicon and nitrogen are contained in a steel, the free energy changes of the formation of nitrides were calculated mainly from the equilibrium diagrams.

2. The equilibrium reactions of precipitation of aluminum-, silicon- and iron-

nitride were calculated in the whole range from molten state to the solid at room temperature by assuming that the composition of the steel was as follows :

	C	Al	Si	N	Mn
%	0.15	0.01 or 0.13	0.5	0.005	<1.5.

3. Results of calculation concerning aluminum-nitride agree with the experimental results reported by several authorities.

4. Silicon-nitride (Si_3N_4) may also precipitates in steel and may act as grain growth inhibitor but not so effective as aluminum-nitride.

5. Some considerations were made concerning the conditions of inclusions which inhibited austenite grain growth of steel.

Appendix

For the relative partial free energy of the solution of silicon in iron, the following equation given by J. Chipman⁹⁾ was used in the authors' thermodynamic calculation ;

$$\text{Si}(I) = \underline{\text{Si}}_I(1\%) \quad \Delta F^\circ = -29000 - 0.30T \quad (30)$$

J. Chipman and N. A. Gokcen³⁹⁾ revised this equation as follows ;

$$\Delta F^\circ = -28500 - 2.23T. \quad (74)$$

The authors recalculated, therefore, the free energy equations concerning the equilibrium of silicon-nitride precipitation. Recalculation by the revised equation showed that silicon-nitride does not precipitate in austenite when the steel contains 0.01% aluminum, 0.5% silicon and 0.005% nitrogen, but if the steel contains 1% silicon and the same contents of aluminum and nitrogen as above, silicon-nitride precipitates as shown in Fig. 8 and the equilibrium relation between between aluminum- and silicon-nitride is quite similar to the relation in Fig. 5.

This means that the stability of silicon dissolved in iron calculated by the revised value is greater than that by the former equation and the precipitation of silicon-nitride becomes so much difficult. If this revised value is more accurate than the former value, silicon-nitride will not precipitate in most aluminum killed steels containing

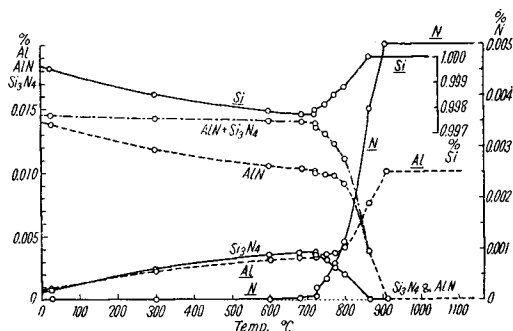


Fig. 8. Equilibrium content of Al, Si, N, AlN and Si_3N_4 in steel containing 0.15% C, 0.01% Al, 1.0% Si and 0.005% N calculated by using J. Chipman and N. A. Gokcen's revised equation.

less than 1% of silicon.

In the discussion of the report by J. Chipman et al., E. T. Turkdogan⁴⁰⁾ gave, on the other hand, a different method for the treatment of Chipman's data and calculated the relative partial free energy of the same reaction as follows:

$$\text{Si}(l) = \text{Si}_l(1\%) \quad \Delta F^\circ = -28500 - 0.77T. \quad (75)$$

In deriving equation (75), he took into account the change of activity coefficient of silicon not only by silicon itself but by oxygen. The value of the free energy calculated by equation (75) is much closer to that calculated by equation (30) than by equation (74).

Further experiments are felt necessary to determine which of these three equations has the highest accuracy, and the authors cannot decide either until further investigation which of these two results shown in Fig. 5 and 8 conforms better to the experimental results.

References

- 1) (a) G. Derge, A. R. Kommel and R. F. Mehl: *Trans. Am. Soc. Metals*, 26 (1938), 153.
(b) A. Hultgren: *Jernkontorets Annaler*, 119 (1935), 169.
(c) A. Hultgren: In the discussion of T. Swinden and G. R. Bolsover; *J. Iron and Steel Inst.*, 134 (1936), 457.
- 2) (a) H. W. McQuaid: *Trans. Am. Soc. Metals*, 23 (1935), 797.
(b) T. Swinden and G. R. Bolsover: Ref. 1) (c).
- 3) (a) E. Houdrement and H. Schröder: *Arch. Eisenhüttenw.*, 12 (1938/39), 393.
(b) K. Born and W. Koch: *Stahl und Eisen*, 72 (1952), 1268.
(c) Z. Takao, T. Noda, K. Kunii and H. Takada: *Tetsu to Hagane*, 40 (1954), 216.
- 4) J. W. Halley: *Trans. Am. Inst. Min. Met. Engr.*, 167 (1946), 224.
- 5) C. Wagner: *Thermodynamics of alloys*, (1952), 32.
- 6) *Ibid.* 35.
- 7) *Ibid.* 34.
- 8) *Basic Open Hearth Steelmaking*, (1951), 631.
- 9) *Ibid.* 638.
- 10) F. Wever and P. Giani: *Mitt. Kais. Wilh.-Inst. Eisenf.*, 7 (1925), 59.
- 11) H. Esser and P. Oberhoffer: *Ber. Ver. dtsh. Eisenhüttenleute Werkstoffausschuss*, Ber. Nr. 69 (1925).
- 12) C. Kreutzer: *Zeit. Physik*, 48 (1928), 558.
- 13) R. Ruer and R. Klesper: *Ferrum*, 11 (1913/14), 259.
- 14) M. Hansen: *Der Aufbau der Zweistofflegierungen*, (1936), 734.
- 15) A. G. C. Gwyer and H. W. L. Phillips: *J. Inst. Metals*, 38 (1927), 35.
- 16) N. Kurnakov, G. Vrazov and A. Grigoriev: *Izvest Inst. Fiz-Khim Anal.*, 1 (1919), 9.
- 17) F. Wever and A. Müller: *Mitt. Kais. Wilh.-Inst. Eisenf.*, 11 (1929), 220.
- 18) M. Isawa and T. Murakami: *Kinzoku no Kenkyu*, 4 (1927), 467.
- 19) J. Pearson and U. J. C. Ende: *J. Iron and Steel Inst.*, 175 (1953), 52.
- 20) L. S. Darken, R. P. Smith and E. W. Filer: *J. Metals*, 3 (1951), 1175.
- 21) T. Shimose and K. Narita: *Tetsu to Hagane*, 40 (1954), 242.
- 22) N. S. Corney and E. T. Turkdogan: *J. Iron and Steel Inst.*, 180 (1955), 344.
- 23) V. G. Paranjpe, M. Cohen, M. B. Bever and C. F. Floe: *J. Metals*, 2 (1950), 261.

- 24) L. S. Dijkstra : *J. Metals*, 1 (1949), 252.
- 25) J. Chipman : *J. Iron and Steel Inst.*, 180 (1955), 97.
- 26) H. F. Beeghly : *Anal. Chem.*, 21 (1949), 1513.
- 27) W. C. Leslie, R. L. Rickett, C. L. Dotson and C. S. Walton : *Trans. Am. Soc. Metals*, 46 (1954), 1470.
- 28) W. C. Leslie, K. G. Carroll and R. M. Fisher : *J. Metals*, 4 (1952), 204.
- 29) K. H. Jack : *Acta Crystallogr.*, 3 (1950), 392.
- 30) B. E. Hopkins and H. R. Tipler : *J. Iron and Steel Inst.*, 177 (1954), 110.
- 31) J. D. Fast and M. B. Verrijp : *J. Iron and Steel Inst.*, 180 (1955), 337.
- 32) J. D. Fast : *Stahl und Eisen*, 73 (1953), 1484.
- 33) *Metals Handbook* (1948), 1181.
- 34) F. E. Burke and D. Turnbull : *Progress in Metal Physics*, 4 (1952), vol. 3 220/292.
- 35) O. O. Miller : *Trans. Am. Soc. Metals*, 43 (1951), 260.
- 36) (a) C. H. Herty, Jr., D. L. McBride and S. O. Hough : *Mining and Met. Investigations, Carnegie Inst. Tech. Mining Met. Advisory Board, Coöp. Bull.*, 65 (1934), 46.
(b) K. Kovraiskie : *Teoriya Prakt. Met.*, 5 (1937), 72.
(c) G. Derge, A. R. Kommel and R. F. Mehl : *Ref. 1* (a).
(d) P. A. Beck, M. L. Holzworth and P. R. Sperry : *J. Metals*, 1 (1949), 163.
(e) Z. Jeffries and R. S. Archer : *The Science of Metals* (1924), 95.
(f) J. E. Burke : *J. Metals*, 2 (1950), 1324.
- 37) H. Buchholtz : *Stahl und Eisen*, 16 (1939), 331.
- 38) J. D. Fast and M. B. Verrijp : *J. Iron and Steel Inst.*, 176 (1954), 24.
- 39) J. Chipman and N. A. Gokcen : *J. Metals*, 5 (1953), 1017.
- 40) E. T. Turkudogan : In the discussion of J. Chipman and N. A. Gokcen ; *Ibid.*, 6 (1954), 1296.