Thermodynamic Investigation of Nonmetallic Inclusions in Steel (II)

(Behavior of Titanium-, Zirconium-, and Vanadium-Nitrides and Carbides; and their Effect on Austenite Grain Size of Steel)

By

Hiroshi Sawamura and Toshisada Mori

Department of Metallurgy

I. Introduction

The authors made a thermodynamic calculation in the previous report[1] concerning the equilibrium relation among the dissolved aluminum and silicon in steel and their precipitated nitrides; and the conditions under which nonmetallic inclusions are formed were discussed in connection with the austenite grain refining. In the present work the formation of titanium-, zirconium- and vanadium-nitrides and carbides and the conditions of these inclusions as grain growth inhibitors are discussed.

II. Chemical reactions of formation of the inclusions and the method of derivation of their free energy equations

The free energy equations for the formation of nitrides and carbides in steel were derived by the same method as described elsewhere[1]. Only the necessary equations are shown here and the assumptions used for deriving these equations are briefly explained in this section.
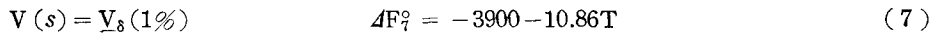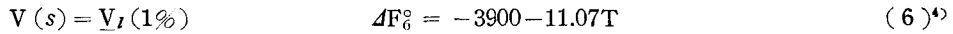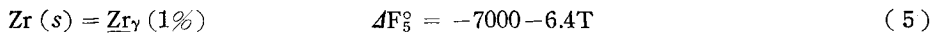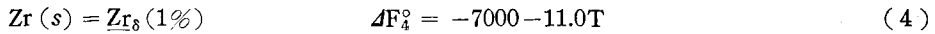
(A) Free energies of the solution of titanium, zirconium and vanadium in iron

In iron-titanium, iron-zirconium and iron-vanadium binary alloys, the melting point depressions of pure iron are $18°C$[2], $5°C$[3] and $2°C$[2] respectively for the addition of 1% of each element; and the following equations are derived by the values estimated by Chipman[4] and by the calculation from these equilibrium diagrams.[3,5,6,7,8,9,10,11]

$$\text{Ti}(s) = \underline{\text{Ti}}_l\,(1\%) \qquad \varDelta F_1^\circ = -7000 - 11.0T \qquad (1)^{[4]}$$

$$\text{Ti}(s) = \underline{\text{Ti}}_\delta\,(1\%) \qquad \varDelta F_2^\circ = -7000 - 7.1T \qquad (2)$$
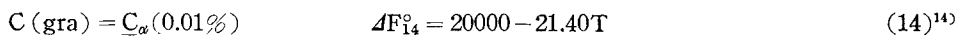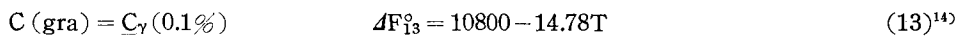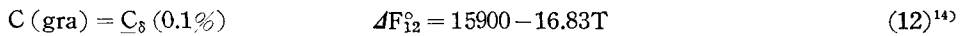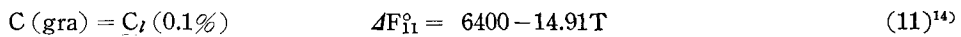
$$\text{Zr}(s) = \underline{\text{Zr}}_l\,(1\%) \qquad \varDelta F_3^\circ = -7000 - 12.2T \qquad (3)^{[4]}$$

$$Zr\ (s) = \underline{Zr}_\delta\ (1\%) \qquad \Delta F_4^\circ = -7000 - 11.0T \qquad (4)$$

$$Zr\ (s) = \underline{Zr}_\gamma\ (1\%) \qquad \Delta F_5^\circ = -7000 - 6.4T \qquad (5)$$

$$V\ (s) = \underline{V}_l\ (1\%) \qquad \Delta F_6^\circ = -3900 - 11.07T \qquad (6)^{4)}$$

$$V\ (s) = \underline{V}_\delta\ (1\%) \qquad \Delta F_7^\circ = -3900 - 10.86T \qquad (7)$$

The $\gamma + \alpha$ two phase equilibriums in both iron-titanium and iron-vanadium binary alloys are restricted in very narrow ranges and, therefore, the free energy changes of $\delta \rightleftarrows \gamma$ and $\gamma \rightleftarrows \alpha$ transformations are neglected in the authors' calculation.
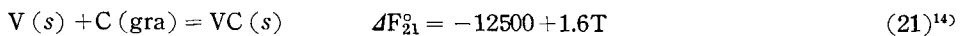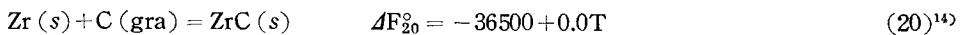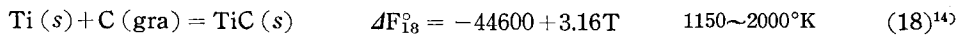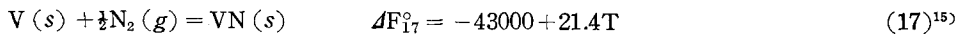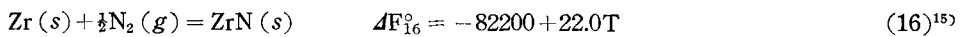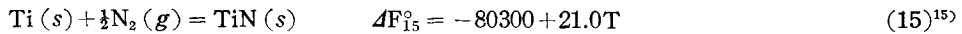
(B) Free energies of the solution of nitrogen and carbon in iron

The free energy equations needed for the authors' calculation are as follows:

$$\tfrac{1}{2}N_2\ (g) = \underline{N}_l\ (1\%) \qquad \Delta F_8^\circ = 2580 + 5.02T \qquad (8)^{4)}$$

$$\tfrac{1}{2}N_2\ (g) = \underline{N}_\gamma\ (1\%) \qquad \Delta F_9^\circ = 782 + 6.50T^* \qquad (9)^{1)}$$

$$\tfrac{1}{2}N_2\ (g) = \underline{N}_\alpha\ (1\%) \qquad \Delta F_{10}^\circ = 4880 + 8.00T^* \qquad (10)^{1)}$$

$$C\ (gra) = \underline{C}_l\ (0.1\%) \qquad \Delta F_{11}^\circ = 6400 - 14.91T \qquad (11)^{14)}$$

$$C\ (gra) = \underline{C}_\delta\ (0.1\%) \qquad \Delta F_{12}^\circ = 15900 - 16.83T \qquad (12)^{14)}$$

$$C\ (gra) = \underline{C}_\gamma\ (0.1\%) \qquad \Delta F_{13}^\circ = 10800 - 14.78T \qquad (13)^{14)}$$

$$C\ (gra) = \underline{C}_\alpha\ (0.01\%) \qquad \Delta F_{14}^\circ = 20000 - 21.40T \qquad (14)^{14)}$$
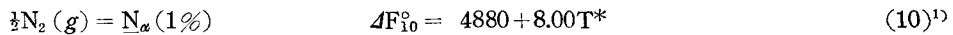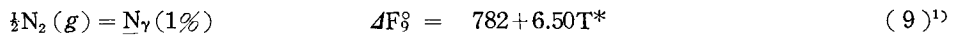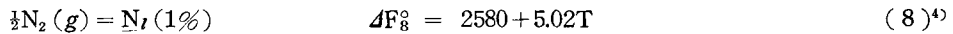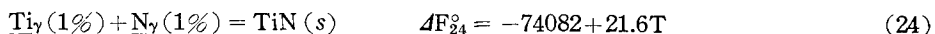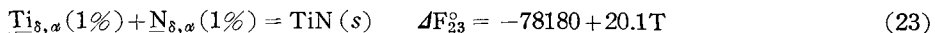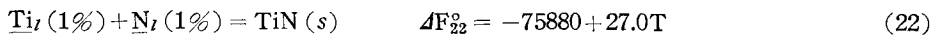
(C) Free energies of the formation of nitrides and carbides in steel

Standard free energy equations of the formation of nitrides and carbides are as follows:

$$Ti\ (s) + \tfrac{1}{2}N_2\ (g) = TiN\ (s) \qquad \Delta F_{15}^\circ = -80300 + 21.0T \qquad (15)^{15)}$$

$$Zr\ (s) + \tfrac{1}{2}N_2\ (g) = ZrN\ (s) \qquad \Delta F_{16}^\circ = -82200 + 22.0T \qquad (16)^{15)}$$

$$V\ (s) + \tfrac{1}{2}N_2\ (g) = VN\ (s) \qquad \Delta F_{17}^\circ = -43000 + 21.4T \qquad (17)^{15)}$$

$$Ti\ (s) + C\ (gra) = TiC\ (s) \qquad \Delta F_{18}^\circ = -44600 + 3.16T \quad 1150\sim2000°K \quad (18)^{14)}$$

$$\Delta F_{19}^\circ = -43750 + 2.41T \quad 298\sim1150°K \quad (19)^{14)}$$

$$Zr\ (s) + C\ (gra) = ZrC\ (s) \qquad \Delta F_{20}^\circ = -36500 + 0.0T \qquad (20)^{14)}$$

$$V\ (s) + C\ (gra) = VC\ (s) \qquad \Delta F_{21}^\circ = -12500 + 1.6T \qquad (21)^{14)}$$

Free energy equations of the formation of nitrides in iron can be derived by combining equations $(15) \sim (17)$ with $(1) \sim (10)$ and they are as follows:

$$\underline{Ti}_l\ (1\%) + \underline{N}_l\ (1\%) = TiN\ (s) \qquad \Delta F_{22}^\circ = -75880 + 27.0T \qquad (22)$$

$$\underline{Ti}_{\delta,\alpha}\ (1\%) + \underline{N}_{\delta,\alpha}\ (1\%) = TiN\ (s) \qquad \Delta F_{23}^\circ = -78180 + 20.1T \qquad (23)$$

$$\underline{Ti}_\gamma\ (1\%) + \underline{N}_\gamma\ (1\%) = TiN\ (s) \qquad \Delta F_{24}^\circ = -74082 + 21.6T \qquad (24)$$

---

* If the following equations, which have recently been reported, are used, a higher accuracy than in the case of equations (9) and (10) may be obtained:

$$\tfrac{1}{2}N_2(g) = \underline{N}_\gamma(1\%) \qquad \Delta F_9^\circ = -2060 + 8.944T \qquad (9)'^{\,12)}$$

$$\tfrac{1}{2}N_2(g) = \underline{N}_{\delta,\alpha}(1\%) \qquad \Delta F_{10}^\circ = 9060 + 3.637T \qquad (10)'^{\,12)}$$

$$\tfrac{1}{2}N_2(g) = \underline{N}_{\delta,\alpha}(1\%) \qquad \Delta F_{10}^\circ = 7200 + 4.615T \qquad (10)''^{\,13)}$$

$\underline{Zr}_l\,(1\%)+\underline{N}_l\,(1\%)=ZrN\,(s)$ $\varDelta F^\circ_{25}=-77780+29.2T$ (25)

$\underline{Zr}_\delta\,(1\%)+\underline{N}_\delta\,(1\%)=ZrN\,(s)$ $\varDelta F^\circ_{26}=-80080+25.0T$ (26)

$\underline{Zr}_\gamma\,(1\%)+\underline{N}_\gamma\,(1\%)=ZrN\,(s)$ $\varDelta F^\circ_{27}=-75982+21.9T$ (27)

$\underline{V}_l\,(1\%)+\underline{N}_l\,(1\%)=VN\,(s)$ $\varDelta F^\circ_{28}=-41680+27.5T$ (28)

$\underline{V}_{\delta,\alpha}\,(1\%)+\underline{N}_{\delta,\alpha}\,(1\%)=VN\,(s)$ $\varDelta F^\circ_{29}=-43980+24.3T$ (29)

$\underline{V}_\gamma\,(1\%)+\underline{N}_\gamma\,(1\%)=VN\,(s)$ $\varDelta F^\circ_{30}=-39882+25.8T$ (30)
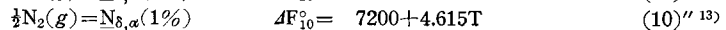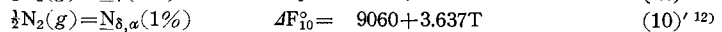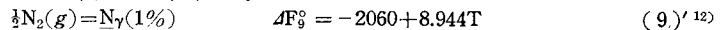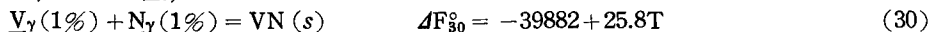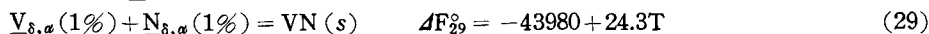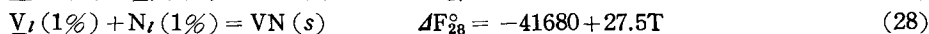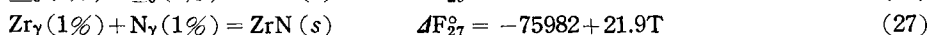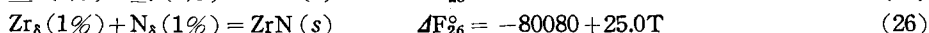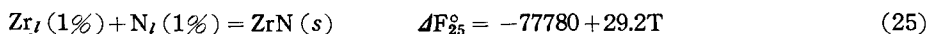
Free energy equations of the formation of carbides in iron can be calculated similarly by the combination of the foregoing equations and they are as follows:

$\underline{Ti}_l\,(1\%)+\underline{C}_l\,(0.1\%)=TiC\,(s)$ $\varDelta F^\circ_{31}=-44000+29.1T$ (31)

$\underline{Ti}_\delta\,(1\%)+\underline{C}_\delta\,(0.1\%)=TiC\,(s)$ $\varDelta F^\circ_{32}=-53500+27.1T$ (32)

$\underline{Ti}_\gamma\,(1\%)+\underline{C}_\gamma\,(0.1\%)=TiC\,(s)$ $\varDelta F^\circ_{33}=-48400+25.0T$ $1150\sim1765^\circ K$ (33)

                         $\varDelta F^\circ_{34}=-47550+24.3T$ $996\sim1150^\circ K$ (34)

$\underline{Ti}_\alpha\,(1\%)+\underline{C}_\alpha\,(0.01\%)=TiC\,(s)$ $\varDelta F^\circ_{35}=-56750+30.9T$ (35)

$\underline{Zr}_l\,(1\%)+\underline{C}_l\,(0.1\%)=ZrC\,(s)$ $\varDelta F^\circ_{36}=-35900+27.1T$ (36)

$\underline{Zr}_\delta\,(1\%)+\underline{C}_\delta\,(0.1\%)=ZrC\,(s)$ $\varDelta F^\circ_{37}=-45400+27.8T$ (37)

$\underline{Zr}_\gamma\,(1\%)+\underline{C}_\gamma\,(0.1\%)=ZrC\,(s)$ $\varDelta F^\circ_{38}=-40300+21.2T$ (38)

$\underline{V}_l\,(1\%)+\underline{C}_l\,(0.1\%)=VC\,(s)$ $\varDelta F^\circ_{39}=-15000+27.6T$ (39)

$\underline{V}_\delta\,(1\%)+\underline{C}_\delta\,(0.1\%)=VC\,(s)$ $\varDelta F^\circ_{40}=-24500+29.3T$ (40)

$\underline{V}_\gamma\,(1\%)+\underline{C}_\gamma\,(0.1\%)=VC\,(s)$ $\varDelta F^\circ_{41}=-19400+27.2T$ (41)

$\underline{V}_\alpha\,(1\%)+\underline{C}_\alpha\,(0.01\%)=VC\,(s)$ $\varDelta F^\circ_{42}=-28600+33.9T$ (42)
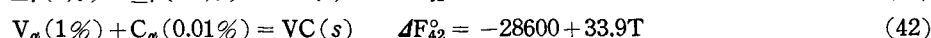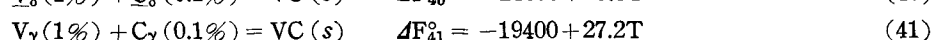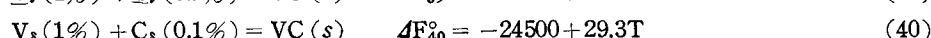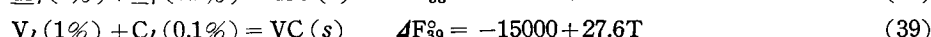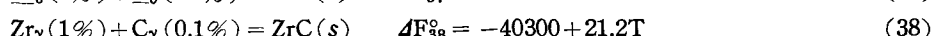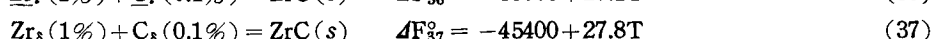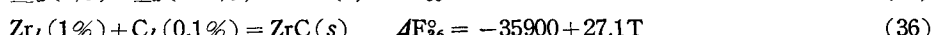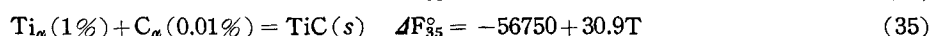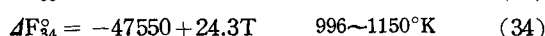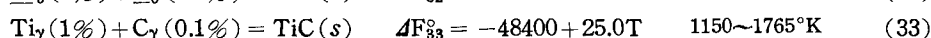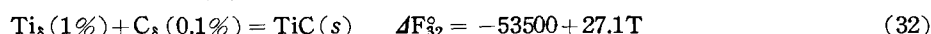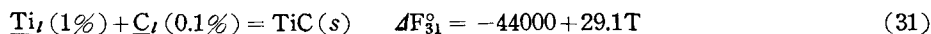
III. Formation of nitrides and carbides in molten and solidified steel

The same composition of steel as in the previous report was selected as an example in the present caculation. The content of carbon and nitrogen are 0.15% and 0.005% respectively. When a molten steel containing 0.15% carbon is slowly cooled, the ratio between the weight of δ (or α)-iron and that of liquid (or γ-iron) can be estimated from the iron-carbon equilibrium diagram[16] and this is shown in Table 1.

Discussion was made on the assumption that the existence of α-, γ-, δ-iron and melts was restricted in the range of temperature shown in Table 1.

Table 1. Equilibrium ratio between two phases in the range from 1534 to 723°C.

Temperature °C	Phase %		Phase %	
1534	δ	0	L	100
1529	δ	35	L	65
1520	δ	66	L	34
1500	δ	85	L	15
1492	δ	87.5	L	12.5
"	δ	37.5	γ	62.5
1484	δ	23	γ	77
1476	δ	0	γ	100
865	α	0	γ	100
850	α	17	γ	83
800	α	58	γ	42
723	α	81	γ	19
"	α	100	γ	0

(A) Formation of nitrides and carbides in molten steel

Titanium nitride is calculated to be formed by equation (18) in the range of temperature higher than 1492°C when the content of titanium is more than 0.063% in molten steel containing 0.005% nitrogen. When the molten steel contains 0.15% carbon, 0.1% titanium and 0.005% nitrogen, titanium nitride is also formed when the temperature becomes lower than 1529°C but not titanium carbide. When δ-iron crystallizes out from the molten steel, a large amount of δ-crystal is formed even by several degrees centigrade of temperature fall, because the slope of solidus line is sharp while that of liquidus line is more or less even. Titanium nitride may float up to the surface of molten steel, if there is no solid iron because the specific gravity of this nitride is smaller than that of the molten iron; but it may remain in the gaps of δ-dendrites which crystallize as the primary crystals before the formation of the nitrides. In the former case, the content of nitrogen in δ-iron decreases as the temperature falls and the calculation of the content of titanium nitride in δ-iron becomes very complex, and; therefore, the authors assumed to simplify the calculation that all the nitrides formed under 1529°C remain in the gaps of δ-dendrites and the distribution of nitrogen is homogeneous both in molten and solidified steel. Results of the calculation by equation (18) are shown in Table 2.

Zirconium nitride is formed in the molten steel containing more than 0.11% zirconium and 0.005% nitrogen, but zirconium carbide is not formed in the molten steel whose carbon content is less than 0.5%.

Both vanadium nitride and vanadium carbide are not formed in molten steel.

(B) Precipitation of nitrides and carbides in δ-iron

The content of titanium is calculated to be 0.0015% by equation (19) if the nitride is to be precipitated at the same time δ-iron is formed.

Table 2. Equilibrium content of $\underline{Ti}$, $\underline{N}$ and TiN in molten steel containing 0.15% C, 0.1% Ti and 0.005% N.

Temp. °C	$\underline{Ti}$ %	$\underline{N}$ %	TiN %
1529	0.1	0.005	0
1520	0.0983	0.00451	0.00217
1492	0.0944	0.00335	0.00729

Table 3. Equilibrium content of $\underline{Ti}$, $\underline{N}$ and TiN in δ-iron containing 0.15% C, 0.1% Ti and 0.005% N.

Temp. °C	$\underline{Ti}$ %	$\underline{N}$ %	TiN %
1529	0.0832	0.000097	0.02167
1520	0.0831	0.000068	0.02180
1492	0.0831	0.000062	0.02182
1484	0.0830	0.000054	0.02186

The equilibrium contents of titanium, nitrogen and titanium nitride in δ-iron containing 0.15% carbon, 0.1% titanium and 0.005% nitrogen are shown in Table 3.

The equilibrium contents of titanium, nitrogen and titanium nitride in the steel in the range of temperature from 1534 to 1492°C can be calculated, therefore, from

Table 1, 2 and 3 and they are shown in Fig. 1.

Zirconium nitride is calculated by equation (22) to be precipitated at the same time δ–iron is formed if the content of zirconium is more than 0.0119%, but zirconium carbide is not formed in δ–iron.

Both vanadium nitride and vanadium carbide are not precipitated in δ–iron.

(C) Precipitation of nitrides and carbides in γ– and α–iron

In γ–iron containing e.g. 0.15% carbon, 0.0015% titanium and 0.005% nitrogen, the nitride precipitation temperature is calculated to be 1370°C by equation (20), and, therefore, titanium nitride which is precipitated in δ–iron dissolves simultaneously with the disappearance of δ–iron and is formed again in γ–iron in the range of temperature lower than 1370°C. Calculation by equation (20) shows that all of the dissolved titanium practically changes into titanium nitride and, because 0.00456% of dissolved nitrogen still remains in austenite aluminum nitride or silicon nitride is precipitated if aluminum or silicon is contained together with these elements in the same steel. If the steel contains 0.03% aluminum, aluminum nitride begins to precipitate at 1000°C; the calculation of aluminum nitride precipitation can be made by the following equation:

$$\underline{Al}_\gamma\,(1\%)+\underline{N}_\gamma\,(1\%) = AlN\,(s) \qquad \varDelta F^\circ_{43} = -33855+8.92T\,. \tag{43)[17]}$$
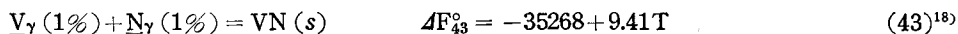
The temperature of titanium carbide precipitation in the steel containing 0.15% carbon and 0.0015% titanium can be calculated to be 1032°C by equation (33), but when 0.005% nitrogen is contained together, titanium carbide is not precipitated because practically all of the titanium changes into nitrides in the range of temperature higher than 1100°C. In the case of the steel which contains more dissolved titanium than the above mentioned example, e.g. in the steel containing 0.15% carbon, 0.1% titanium, 0.03% aluminum and 0.005% nitrogen, practically all of the nitrogen exists as nitrides in the range of temperature lower than 1300°C.

The temperature of carbide precipitation is found to be 1408°C by equation (32), but titanium carbide begins to precipitate at a lower temperature than 1408°C because of the preceding formation of nitride. The carbide precipitation temperature can be calculated by combining equation (20) and (33), and is found to be 1387°C. Aluminum nitride does not precipitate in this case. As the stability of titanium nitride and carbide is greater in ferrite than in austenite; and, both nitride and carbide, which have already precipitated in austenite, do not dissolve into ferrite in the range of temperature lower than 865°C. The above mentioned equilibrium relations among the dissolved elements and nitride or carbide are shown graphically in Figs. 1 and 2.

As for dissolved zirconium, zirconium nitride is precipitated together with the formation of δ–iron if 0.0119% zirconium and 0.005% nitrogen are contained in

steel because the nitride pre-
cipitation temperature is cal-
culated to be 1569°C by
equation (23). Since most of
the dissolved zirconium is
already changed into nitride
in the range of temperature
lower than 1100°C, aluminum
nitride begins to precipitate
together with zirconium ni-
tried at 966°C if 0.03%
aluminum is also contained.
Calculation by equation (38)
shows that zirconium carbide
is precipitated at 1108°C
if 0.0119% zirconium and
0.15% carbon are contained
in steel, but when 0.005%
nitrogen is contained together,
zirconium is precipitated as
nitride and, because most of
the dissolved zirconium is
consumed by nitrogen as
nitride, zirconium carbide is
not precipitated even if
0.15% carbon is contained
together.

Regarding the dissolved
vanadium, calculation by

Fig. 1. Relation between temperature and equilibrium
content of Al, C, Ti, N, TiN and TiC in steel contain-
ing 0.15% C, 0.1% Ti, 0.03% Al and 0.005% N.
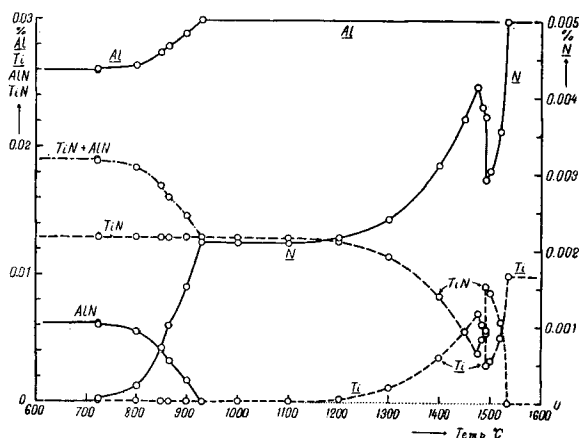
Fig. 2. Relation between temperature and equilibrium
content of Al, Ti, N, TiN and AlN in steel containing
0.15% C, 0.01% Ti, 0.03% Al and 0.005% N.

equation (26) shows that vanadium nitride is precipitated in the range of tempera-
ture lower than 825°C if 1% vanadium and 0.005% nitrogen are contained in steel,
but vanadium carbide is not precipitated in γ-iron. As far as the early thermodynamic
data are concerned, vanadium nitride can not be precipitated in austenite if the content
of vanadium in steel is not considerably great (e.g. 1%), but Shimose and Narita[18]
investigated very recently the equilibrium relation of vanadium nitride precipitation
in austenite and calculated the free energy equation as follows:

$$\underline{V}_\gamma \,(1\%) + \underline{N}_\gamma \,(1\%) = VN\,(s) \qquad \varDelta F^\circ_{43} = -35268 + 9.41\,T \qquad (43)^{[18]}$$

There are remarkable differences in the order of 13~25 kcal between these two

free energie calculated by equation (25) and (43) and the difference becomes greater in the higher temperature range. Free energy equations of the formation of vanadium nitrides were recalculated by using equation (43) as the calculation basis and are shown as follows:

$$V\ (s) + \tfrac{1}{2}N_2\ (g) = VN\ (s) \qquad \varDelta F^o_{44} = -38336 + 5.05T \qquad (44)$$

$$\underline{V}_l\ (1\%) + \underline{N}_l\ (1\%) = VN\ (s) \qquad \varDelta F^o_{45} = -37066 + 11.10T \qquad (45)$$

$$\underline{V}_{\delta, \alpha}\ (1\%) + \underline{N}_{\delta, \alpha}\ (1\%) = VN\ (s) \qquad \varDelta F^o_{46} = -39366 + 7.91T \qquad (46)$$
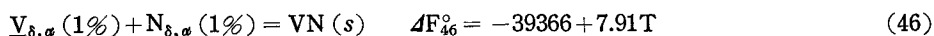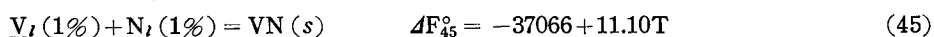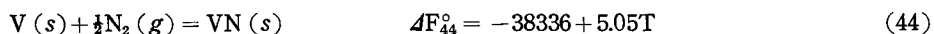
Calculation by equation (45) and (46) shows that vanadium nitride is formed in molten iron containing 0.15% carbon and 0.005% nitrogen in the range of temperature higher than 1492°C if the content of vanadium is higher than 1.37%, and is also precipitated in δ-iron together with the formation of δ-iron if the content of it is higher than 0.186%.

Vanadium nitride is precipitated in γ-iron containing 0.03% of vanadium and 0.005% nitrogen in the range of temperature lower than 1038°C and, therefore, vanadium nitride must be considered to be more stable than aluminum nitride because the precipitation temperature of the latter is 1009°C in γ-iron containing 0.03% aluminum and the same content of nitrogen as above.

IV. Discussion

The present calculation was made concerning the formation of TiN, ZrN, VN, AlN, TiC, ZrC and VC. Among these nitrides and carbides, the existence of AlN[19], VN[18)20)], TiN[21)22)], TiC[21)22)] in steel are affirmed. It is also recognized[23] that ZrN and ZrC show quite similar trends as TiN and TiC, but their existence in steel by X-ray or chemical analysis seems to be still unascertained although they are reported to have been found crystallographically or microscopically in steel as nonmetallic inclusions[18]. Both TiN and TiC[21)22)], and ZrN and ZrC[23] have mutual solubility and are ascertained to form one stable phase; however, the authors assumed that these nitrides and carbides exist as pure stoichiometric compounds because the free energy changes of the mixing of these compounds are unknown. The rate of reaction to form one homogeneous phase is considerably small because the melting point of these compounds are very high and; therefore, the above assumption is considered not to cause any serious error.

As for vanadium nitride, the precipitation of VN is recognized[18] but V_2N is not yet found in steel, although there is a recent report[24] concerning the investigation of vanadium-nitrogen equilibrium diagram which admitted the existence of V_2N. Wever, Rose and Eggers[25] investigated iron-vanadium-carbon ternary equilibrium diagram and showed several sectional equilibrium diagrams where the content of vanadium varies from 0.5 to 5%. According to their results V_4C_3 is precipitated at c.a. 800°C

in austenite containing 0.5% vanadium and 0.35% carbon, and also at c.a. 860°C in austenite containing 1.5% vanadium and more than 0.3% carbon. If the content of vanadium increases, V_4C_3 begins to be precipitated in a higher temperature range. V_4C_3 is precipitated at c.a. 925°C in ferrite containing 0.5% vanadium and the precipitation temperature becomes higher as the content of vanadium increases. Craft and Lamont[26] examined by X-ray analysis the formation of V_4C_3 in the heat treated Cr-V steels and ascertained the existence of this compound. Their electron-microphotograph shows that the particles of V_4C_3 are very finely dispersed in iron matrix compared with the precipitated particles such as Cr_7C_3 and Fe_3C. Ooya and Oosawa[27], on the other hand, reported the formation of the compound 'V$_5$C', while Rostoker and Yamamoto[28] stated that it was not V_5C but V_2C, and the compound which was formed in the range between V and VC was V_2C only and not V_4C_3.

Maurer, Döring and Palewka[29] reported that V_4C_3 consisted one phase with VC. It is, thus, very difficult to determine which of these reports is correct, but it may safely be said that either V_4C_3 or V_2C exists in the range between V and VC. In iron-vanadium-carbon ternary alloys containing small amount of carbon and vanadium, therefore, the precipitated compound may not be VC but V_4C_3 or V_2C. In view of the report by Craft and Lamont that extremely fine particles of vanadium carbides were formed in steel containing 1% vanadium and 0.25% carbon, vanadium carbide was considered to be effective to grain size refining but the authors could not calculate the equilibrium relation among vanadium, carbon and vanadium carbide because the free energy equation was unknown.* It is also known that V_4C_3 does not form double carbide with Fe_3C. The authors made thermodynamic calculation with respect to the formation of VC and the result showed that VC did not form in steel. This is very natural from the reason mentioned above.

Let us consider now the grain size refining or grain growth inhibition by these nitrides or carbides. As already stated in the previous report, the content and the size of these inclusions greatly influence the grain size refining of austenite. The inclusions are not effective for the grain size refining of austenite unless they are smaller than a certain critical size. As the inclusions formed in molten steel are easier to move and coagulate than those in solid steel, these large inclusions may not be very effective as grain growth inhibitors. This tendency is recognized experimentally regarding alumina inclusions[31] which forms in molten steel. In view of the above reason, nitrides or carbides which are formed in molten steel is likely to have the tendency to coagulate into large inclusions; therefore, great effect for grain refining

---

* The free energy equation for the reaction $4\underline{V}_\gamma + 3\underline{C}_\gamma = V_4C_3(s)$ was very recently reported by Bungardt, Kind and Oelsen[30]. Their data shows that V_4C_3 is precipitated in austenite and is considered to be effective for grain size refining.

by these inclusions cannot be expected. If the content of titanium or zirconium in steel is high, titanium or zirconium carbide is precipitated in solid steel as shown in Fig. 1. The precipitated carbides will be effective for grain size refining if they are fiinely dispersed in steel and, moreover, austenite grain growth will be inhibited up to a higher temperature range by these inclusions than by aluminum nitride because they are not soluble into austenite until a high temperature is reached. The grain size refining can be, therefore, expected by titanium or zirconium nitrides when the content of titanium or zirconium is low (e.g. $<0.01\%$ titanium or $<0.1\%$ zirconium) in steel containing c.a. 0.005% nitrogen (Fig. 1); while it can be expected by titanium or zirconium carbides when their contents are high (e.g. 0.1% titanium or 1% zirconium). Though aluminum nitride is precipitated together with titanium nitrides in a steel having a chemical composition of 0.15% carbon, 0.01% titanium, 0.03% aluminum and 0.005% nitrogen (Fig. 2), but the latter may be more effective than the former because titanium nitrides are more stable in high temperature range than aluminum nitride which are soluble into austenite at the forging or rolling temperature.

As for the behavior of vanadium in steel, vanadium nitride is precipitated in the range of temperature lower than 825°C according to the early thermodynamic data. Vanadium is, therefore, effective in the same order as silicon, while it is more effective than aluminum according to the data by Snimose and Narita[18]. Turkdogan, Ignatowicz and Pearson[32] have recently investigated the effect of vanadium on the solubility of nitrogen in α-iron; and their results indicate that up to 0.051% vanadium has no influence on the solubility of nitrogen in α-iron. There are no indication of the formation of a vanadium nitride phase at nitrogen potentials below those of iron nitride, Fe_4N. This is extremely contradictory to the data by Shimose and Narita because the stability of vanadium nitride is greater in α-iron than in γ-iron. Further experiments, therefore, are needed to confirm the effect of vanadium nitride.

Judging from the affinity of these elements to oxygen, or in view of the recovery of these elements in molten steel, vanadium and titanium are more stable than zirconium and aluminum, but which of these is the most effective for grain size refining must be determined by experiments.

The free energy equations used in the present calculation are shown in Fig. 3 together with those in the previous report. The numbers attached to the lines in the figure represent the reactions shown under the figure. Explanation of Fig. 3 is found in the previous report.

The authors neglected the change of activity coefficient by the effect of the 3rd and 4th elements, etc. in multicomponent alloys, i.e. interaction coefficients were assumed to be unity. The precipitation temperatures of these nitrides and carbides
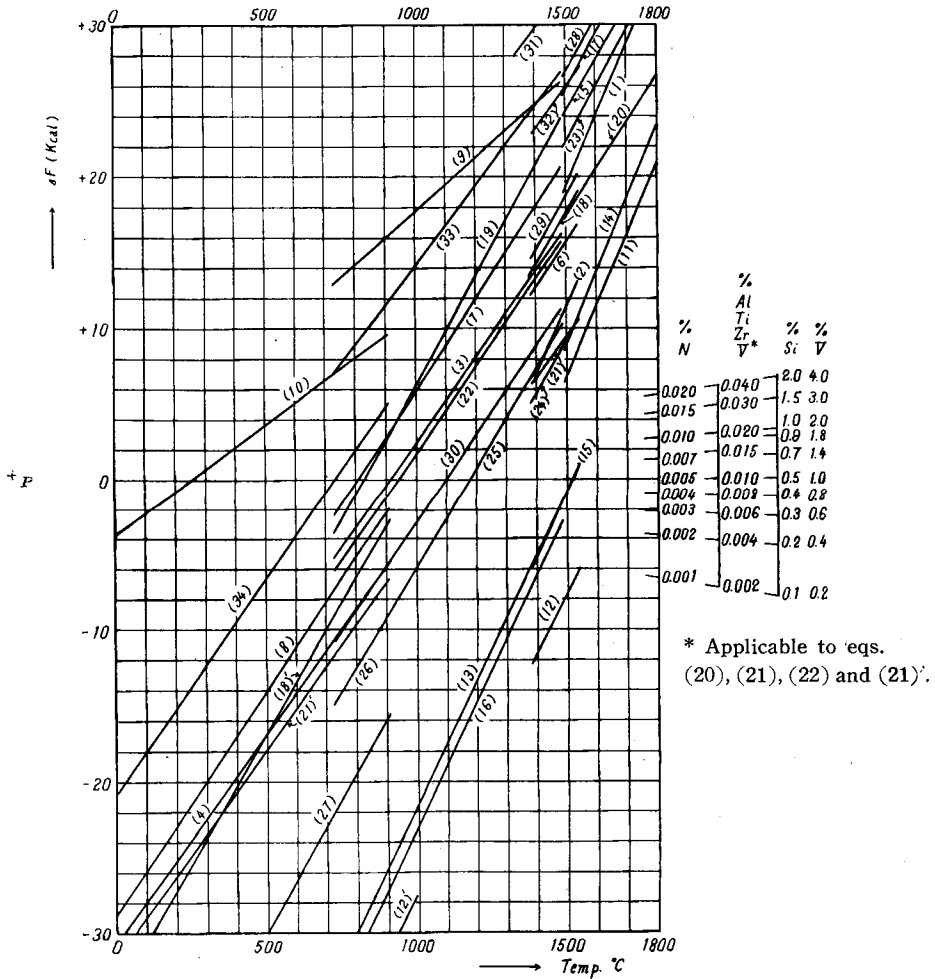
Fig. 3.   The free energy of formation of nitrides and carbides as a function of temperature.

No.	Reaction	No.	Reaction
1	$\underline{Al}_l$ (0.01%)$+\underline{N}_l$ (0.005%) = AlN	19	$\underline{V}_\gamma$ (1%)$+\underline{N}_\gamma$ (0.005%) = VN
2	$\underline{Al}_\delta$ (0.01%)$+\underline{N}_\delta$ (0.005%) = AlN	18′	$\underline{V}_\alpha$ (1%)$+\underline{N}_\alpha$ (0.005%) = VN
3	$\underline{Al}_\gamma$ (0.01%)$+\underline{N}_\gamma$ (0.005%) = AlN	20	$\underline{V}_l$ (0.01%)$+\underline{N}_l$ (0.005%) = VN
4	$\underline{Al}_\alpha$ (0.01%)$+\underline{N}_\alpha$ (0.005%) = AlN	21	$\underline{V}_\delta$ (0.01%)$+\underline{N}_\delta$ (0.005%) = VN
5	$\frac{3}{4}\underline{Si}_l$ (0.5%)$+\underline{N}_l$ (0.005%) = $\frac{1}{4}Si_3N_4$	22	$\underline{V}_\gamma$ (0.01%)$+\underline{N}_\gamma$ (0.005%) = VN
6	$\frac{3}{4}\underline{Si}_\delta$ (0.5%)$+\underline{N}_\delta$ (0.005%) = $\frac{1}{4}Si_3N_4$	21′	$\underline{V}_\alpha$ (0.01%)$+\underline{N}_\alpha$ (0.005%) = VN
7	$\frac{3}{4}\underline{Si}_\gamma$ (0.5%)$+\underline{N}_\gamma$ (0.005%) = $\frac{1}{4}Si_3N_4$	23	$\underline{Ti}_l$ (0.01%)$+\underline{C}_l$ (0.15%) = TiC
8	$\frac{3}{4}\underline{Si}_\alpha$ (0.5%)$+\underline{N}_\alpha$ (0.005%) = $\frac{1}{4}Si_3N_4$	24	$\underline{Ti}_\delta$ (0.01%)$+\underline{C}_\delta$ (0.15%) = TiC
9	$4Fe+\underline{N}_\gamma$ (0.005%) = Fe_4N	25	$\underline{Ti}_\gamma$ (0.01%)$+\underline{C}_\gamma$ (0.15%) = TiC
10	$4Fe+\underline{N}_\alpha$ (0.005%) = Fe_4N	26	$\underline{Ti}_\gamma$ (0.01%)$+\underline{C}_\gamma$ (0.15%) = TiC
11	$\underline{Ti}_l$ (0.01%)$+\underline{N}_l$ (0.005%) = TiN	27	$\underline{Ti}_\alpha$ (0.01%)$+\underline{C}_\alpha$ (0.15%) = TiC
12	$\underline{Ti}_\delta$ (0.01%)$+\underline{N}_\delta$ (0.005%) = TiN	28	$\underline{Zr}_l$ (0.01%)$+\underline{C}_l$ (0.15%) = ZrC
13	$\underline{Ti}_\gamma$ (0.01%)$+\underline{N}_\gamma$ (0.005%) = TiN	29	$\underline{Zr}_\delta$ (0.01%)$+\underline{C}_\delta$ (0.15%) = ZrC
12′	$\underline{Ti}_\alpha$ (0.01%)$+\underline{N}_\alpha$ (0.005%) = TiN	30	$\underline{Zr}_\gamma$ (0.01%)$+\underline{C}_\gamma$ (0.15%) = ZrC
14	$\underline{Zr}_l$ (0.01%)$+\underline{N}_l$ (0.005%) = ZrN	31	$\underline{V}_l$ (1%)$+\underline{C}_l$ (0.15%) = VC
15	$\underline{Zr}_\delta$ (0.01%)$+\underline{N}_\delta$ (0.005%) = ZrN	32	$\underline{V}_\delta$ (1%)$+\underline{C}_\delta$ (0.15%) = VC
16	$\underline{Zr}_\gamma$ (0.01%)$+\underline{N}_\gamma$ (0.005%) = ZrN	33	$\underline{V}_\gamma$ (1%)$+\underline{C}_\gamma$ (0.15%) = VC
17	$\underline{V}_l$ (1%)$+\underline{N}_l$ (0.005%) = VN	34	$\underline{V}_\alpha$ (1%)$+\underline{C}_\alpha$ (0.15%) = VC
18	$\underline{V}_\delta$ (1%)$+\underline{N}_\delta$ (0.005%) = VN		

in both molten and solid steel should be lowered by the decrease in activity coefficients because the interaction coefficients such as $f_C^{(Ti)}$, $f_C^{(Zr)}$, $f_N^{(Ti)}$ and $f_N^{(Zr)}$ can well be considered to be less than unity but their numerical values are unknown at present.

V. Summary

Thermodynamic calculation of the formation of titanium, zirconium and vanadium nitrides and carbides in steel was made, and the relations between austenite grain size and conditions of the formation of these inclusions were discussed.

Acknowledgment

References

1) H. Sawamura and T. Mori: Memoirs of the Faculty of Engineering, Kyoto University. Vol. XVIII (1956), No. 4, 378.
2) 'Basic Open Hearth Steelmaking' (1951), 632.
3) R. Vogel and W. Tonn: Arch. Eisenhüttenw., 5 (1932/33), 387.
4) 2), 638.
5) H. Witte and H. Walbaum: Z. Metallkunde, 30 (1938), 100.
6) W. P. Roe and W. P. Fishel: Trans. Am. Soc. Metals, 44 (1952), 1030.
7) W. R. Lucas and W. P. Fishel: ibid., 46 (1954), 277.
8) S. Ooya: Kinzoku no Kenkyu, 5 (1928), 349.
9) F. Wever and W. Jellinghaus: Mitt. Kais-Wilh. Inst. Eisenf., 12 (1930), 317, Stahl und Eisen, 50 (1930), 1788.
10) R. Vogel and E. Martin: Arch. Eisenhüttenw., 4 (1931), 487.
11) E. Mauer: Stahl und Eisen, 45 (1925), 1629.
12) N. S. Corney and E. T. Turkdogan: J. Iron and Steel Inst., 180 (1955), 344.
13) J. D. Fast and M. B. Verrijp: ibid., 337.
14) F. D. Richardson: ibid., 175 (1953), 33.
15) 2), 573.
16) 'Metals Handbook' (1948), 1181.
17) L. S. Darken, R. P. Smith and E. W. Filer: J. Metals, 3 (1951), 1175.
18) T. Shimose and K. Narita: Investigation Report No. 893 (1955), Feb. Kobe Steel Works Co. Ltd.
19) H. F. Beeghly: Anal. Chemistry, 21 (1949), 1913.
20) A. M. Portevin and R. Castro: J. Iron and Steel Inst., 135 (1937), No. I, 223 p.
21) C. Agte: Dissertation, Technische Hochschule, Berlin (1931), 38.
22) W. Hume-Rothery, G. V. Raynor and A. T. Little: J. Iron and Steel Inst., 145 (1942), 129.
23) C. E. Ransley and H. P. Rooksby: In discussion of reference 22.
24) H. Hahn: Zeit. anorg. chem., 258 (1949), Feb. 58.
25) F. Wever, A. Rose and E. Eggers: Mitt. Kais-Wilh. Inst. Eisenfg., 18 (1936), 239.
26) W. Craft and J. L. Lamont: J. Metals, 2 (1950), 561.
27) S. Ooya and A. Oosawa: Science Report Tohoku Univ., 19 (1930), 95.
28) W. Rostoker and A. Yamamoto: Trans. Am. Soc. Metals, 46 (1954), 1136.
29) E. Maurer, J. Doring and W. Palewka: Arch. Eisenhüttenw., 13 (1940), 337.

30) K. Bungardt, K. Kind and W. Oelsen: ibid., 27 (1956), Jan. 61.
31) Z. Takao, T. Noda, K. Kunii and H. Takada: Tetsu to Hagane, 40 (1954), 216.
32) E. T. Turkdogan, S. Ignatowicz and J. Pearson: J. Iron and Steel Inst. 181 (1955), 227.