A Thermodynamic Study of $CaCN_2$

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ABSTRACT

The equilibrium nitrogen pressures for the following reaction have been measured at temperatures between 1123 K and 1303 K:

$$<CaCN_2> + <C> = <CaC_2> + (N_2)$$

The equilibrium nitrogen partial pressures above the mixture of $<CaCN_2>$ + $<C>$ = $<CaC_2>$ could be expressed as

$$\log (P_{N_2} / \text{Pa}) = -3660 / (T/\text{K}) + 6.98$$

at temperatures between 1123 and 1303 K.

INTRODUCTION

The nitrogen case-hardening process, which is termed nitriding, consists of subjecting a machined and heat-treated part of steel to the action of a nitrogenous medium, commonly a gaseous ammonia-hydrogen mixture, at temperatures about 700 to 850 K. Almost any quenched and tempered steel may be nitrided with little or no distortion of change in surface finish. Nitride cases are normally shallow and very hard with surface hardness greater than 700 Vickers.

Chromium and aluminum are desirable in steels for nitriding. This is attributed to a relatively strong chemical affinity between these elements and nitrogen. Figure 1 shows the standard Gibbs energy of formation of nitride:

$$(2y/x)\ <M> + (N_2) = (2y)\ <M_xN_y> \qquad (1)$$

$$\Delta G^o_f <M_xN_y> = R\,T\,\ln P_{N_2} \qquad (2)$$

In equations (1) and (2) the Kubaschewski-Alcock notation /1/ is used and R, T and P_{N_2} have normal meanings. Curves 1, 2, 3 and 4 in Figure 1 correspond to M = H, Fe, Cr and Al, respectively /1,2/. About 1 per cent of aluminum, for example, will produce a very high surface hardness of about 1200 Vickers compared with the 700 Vickers in steels not containing this element /3/. Alloy steels containing Cr and Al, which are especially adapted to nitriding, have been developed.

The outer layer of a conventionally nitrided steel contains a shallow but very brittle "white layer" consisting of iron and other nitride. High nitrogen potentials of an ammonia-hydrogen gas mixture would be responsible for the formation of white layer. Where

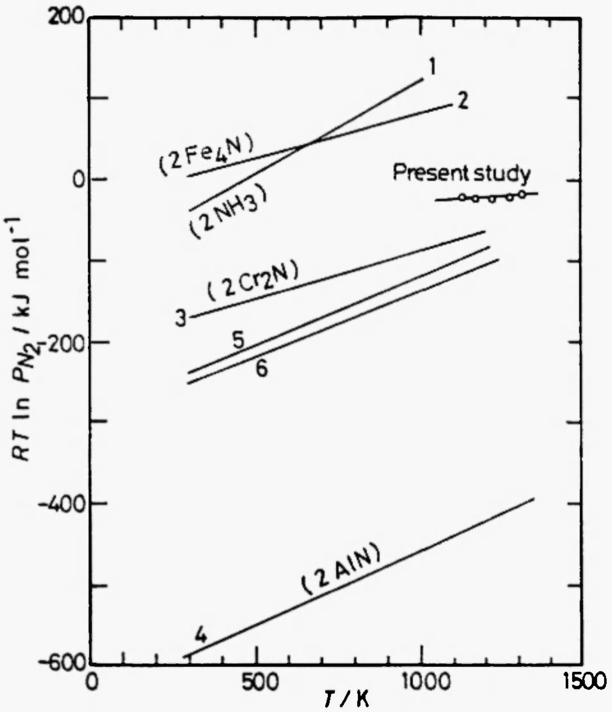

Fig. 1: The standard Gibbs energy of formation of nitride; (2y/x) <M> + (N_2) = (2y) $<M_xN_y>$.
Curve 1, 3 (H_2) + (N_2) = 2 (NH_3).
Curve 2, 8 <Fe> + $N_2)$ = 2 $<Fe_4N>$.
Curve 3, 4 <Cr> + (N_2) = 2 $<Cr_2N>$.
Curve 4, 2 Al + (N_2) = 2 <AlN>.
Curves 5 and 6 represent, respectively, the Gibbs energy change for reaction (3), $<CaC_2>$ + (N_2) = $<CaCN_2>$ + <C>, $\Delta G^o(3, Barin)$ and $\Delta G^o(3, Fujita\ et\ al)$, respectively. Open circles show the present data, $\Delta G^o(3, Present\ study)$.

specification or performance requirements will not permit the presence of such a white layer, the layer has to be removed by costly finish grinding or pickling operations. To minimize the formation of white layer, the authors conceived the use of $CaCN_2$ /4/ instead of NH_3 + H_2 gas mixture. During a course of studies directed towards developing such a nitriding process, it became necessary to know the equilibrium nitrogen partial pressures of reaction:

$$<CaC_2> + (N_2) = <CaCN_2> + <C> \qquad (3)$$

$$\Delta G^o(3) = R\,T \ln P_{N_2} \qquad (4)$$

Reaction (3) is known as "nitrogen fixation". Production of $CaCN_2$ is normally based upon this reaction: CaC_2 is heated in a stream of nitrogen at temperatures between 1173 and 1373 K. The reaction product is termed "nitrolime", which is normally used as a fertilizer. Typical chemistry of nitrolime is 20 wt% C, 18 wt% CaO, and 62 wt% $CaCN_2$ /5/.

Values of $\Delta G^o(3)$ can be derived through

$$\Delta G^o(3) = G<CaCN_2> + G<C> - G<CaC_2> - G(N_2) \qquad (5)$$

where $G<CaCN_2>$, $G<C>$, $G<CaC_2>$ and $G(N_2)$ are the Gibbs energies of $<CaCN_2>$, <C>, $<CaC_2>$ and (N_2), respectively, Values for $G<CaCN_2>$, $G<C>$, $G<CaC_2>$ and $G(N_2)$ are given in the compilation of Barin /6/. Curve 5 represents values of $\Delta G^o(3, Barin)$:

Table 1

The equilibrium nitrogen partial pressure for the reaction, $<CaC_2>$ + (N_2) = $<CaCN_2>$ + <C>

T/K	P_{N_2} /Pa	P_{N_2} /atm	$\Delta G^o(3, Present\ study)$ /J mol⁻¹
1,123	5,300	5.23×10^{-2}	-27,550
1,173	8,100	7.99×10^{-2}	-24,630
1,223	8,500	8.39×10^{2}	-25,200
1,273	12,000	11.84×10^{2}	-22,570
1,303	17,000	16.78×10^{-2}	-19,330

$$\Delta G^o(3, Barin) = G\langle CaCN_2, Barin\rangle + G\langle C, Barin\rangle - G\langle CaC_2, Barin\rangle - G(N_2, Barin) \quad (6)$$

However, values of $G\langle CaCN_2, Barin\rangle$ are based upon theoretical estimation rather than experimental determinations. It is not known, at the time of this writing, how the $G\langle CaCN_2, Barin\rangle$ values were estimated.

By using a manner reported by Latimar /7/, and adapting standard enthalpy of formation of $CaCN_2$ at 298 K, i.e., $H\langle CaCN_2, 298K\rangle = -351$ kJ mol^{-1} /6/, Fujita *et al.* /4/ estimated $G\langle CaCN_2\rangle$ as

$$G\langle CaCN_2, Fujita\ et\ al\rangle / J\ mol^{-1} = -372{,}860 + 73.2\,(T/K) - (T/K)\,\{73.2 \ln(T/K) - 308\} \quad (7)$$

Curve 6 represents ΔG^o (3, *Fujita et al*):

$$\Delta G^o(3, Fujita\ et\ al) = G\langle CaCN_2, Fujita\ et\ al\rangle + G\langle C, Barin\rangle - G\langle CaC_2, Barin\rangle - G(N_2, Barin) \quad (8)$$

Because of lack of experimental data, it was decided to measure directly nitrogen pressure of reaction (3) to determine $\Delta G^o(3)$.

EXPERIMENTAL ASPECTS

Calcium cyanamide was prepared *via* reaction (3). Namely, reagent-grade calcium carbide was contained in an alumina crucible and heated at 1273 K in a stream of nitrogen for 5 to 10 days. X-ray diffraction analysis made on calcium cyanamide thus obtained detected CaC_2 and CaO as major impurities.

Calcium carbide was, in turn, prepared by the decomposition of nitrolime at 1273 K

$$\langle CaCN_2\rangle + \langle C\rangle = CaC_2\rangle + (N_2) \quad (9)$$

Nitrolime mixed with an excess amount of graphite powder, contained in a graphite crucible, was heated at 1373 K in vacuum for 3 days. Calcium oxide and graphite were major impurities in the calcium carbide thus obtained, as detected by X-ray diffraction.

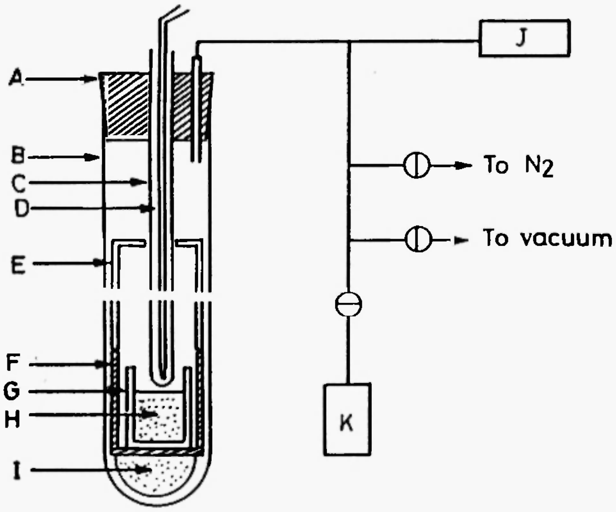

Fig. 2: Experimental set-up: (A) rubber stopper, (B) transparent silica tube, (C) alumina thermocouple sheath, (D) Pt-PtRh13 thermocouple, (E) alumina radiation shield, (F) alumina protection crucible, (G) graphite crucible, (H) mixture of $\langle CaCN_2\rangle + \langle CaC_2\rangle + \langle C\rangle$, (I) alumina pedestal, (J) gas reservoir, and (K) vacuum pump.

Reaction pressures were measured in the apparatus shown in Figure 2. A graphite crucible of 25 mm o.d., 20 mm i.d. and 50 mm height was charged with an equimolar mixture of $\langle CaCN_2\rangle + CaC_2\rangle + \langle C\rangle$ within a SiC resistance furnace equipped with a transparent silica tube of 42 mm o.d., 38 mm i.d. and 600 mm in length. The graphite crucible was contained in an alumina crucible in order to avoid reaction between silica and graphite: $\langle SiO_2\rangle + 3\langle C\rangle = \langle SiC\rangle + 2(CO)$.

The furnace tube with the charged crucible was first evacuated continuously at 500 K for 8 hours to remove moisture, and subsequently nitrogen was admitted from a cylinder. The gas purification train for nitrogen consisted of silica gel, magnesium perchlorate and phosphorous pentoxide and magnesium chips kept at 873 K. All the measurements were conducted at temperatures between 1123 and 1303 K. Temperatures were measured with a Pt-PtRh13 thermocouple placed 5 mm from the mixture, and controlled to within ±1 K, by using a PID-type temperature regulator and a control thermocouple.

An electronic manometer was used to measure nitrogen pressures. At a fixed temperature, equilibrium was obtained after 3 to 10 days, depending upon temperature. Particular difficulties were experienced due to leaks in reaction tubes. Fused silica tubes proved satisfactory. However, life was comparatively short. Failure was normally due to the development of fine cracks and leakage near the reaction zone. Thus in order to make sure that the nitrogen pressures determined were not affected by such leakage the nitrogen pressures were adjusted to reach equilibrium from both the high- and low-pressure directions. Such precautions would also be required to prevent the results from being affected by any side reactions.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 3 shows that the effect of temperature on the equilibrium nitrogen pressure can be represented by a linear relationship with a correlation factor (r^2) of 0.93:

$$\log (P_{N_2} / \mathrm{Pa}) = - 3660 / (T/\mathrm{K}) + 6.98 \qquad (10)$$

By combining equations (4) and (5) one obtains

$$\Delta G^{o}(3,\ \textit{Present study}) / \mathrm{J\ mol^{-1}} = -70{,}000 + 37.8\,(T/\mathrm{K}) \pm 1{,}400 \qquad (11)$$

The assigned uncertainty, ±1,400 J mol^{-1}, is due to the maximum deviation of the experimental data from the regression equation (10). The values of ΔG^{o}*(3, Present study)* are expressed by open circles in Figure 1. As shown in this diagram, ΔG^{o}*(3, Present study)* differs significantly from ΔG^{o}*(3, Barin)* and ΔG^{o}*(3, Fujita et al).*

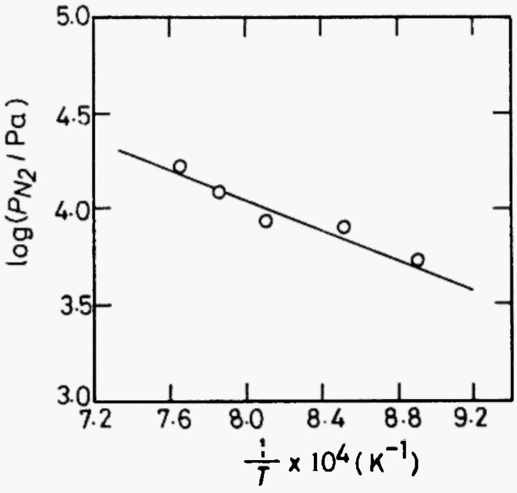

Fig. 3: Relation between log (P_{N_2} / Pa) and 1 / (T/K) for reaction $\langle CaC_2\rangle + (N_2) = \langle CaCN_2\rangle + \langle C\rangle$.

In Figure 1, the present data can also be compared with the available thermochemical data for the standard Gibbs energies of formation of nitride, $\Delta G^{o}_{f}\ \langle M_xN_y\rangle$. Reaction (1) is that one gas molecule is consumed during the reaction, and this would be mainly responsible for entropy change /2/. As long as both element and nitride are condensed phases, the 2nd-law entropy for the formation of nitride would have almost the same values of about –200 J mol^{-1} K^{-1}; see the slopes of curves 2, 3 and 4 in Figure 1.

Reaction (3) also corresponds to consumption of one gas molecule. Nevertheless, the 2nd-law entropy of -37.8 J mol^{-1} K^{-1} obtained in this study is much greater than expected values of about -200 J mol^{-1} K^{-1}. This would presumably be due to the limited temperature range investigated: see the open circles in Figure 1. It should be stated that extrapolation of ΔG^{o}*(3, Present study)* to lower or higher temperatures is questionable.

By combining ΔG^{o}*(3, Present study)* with the standard Gibbs energy of formation of CaC$_2$, $\Delta G^{o}_{f}\langle CaC_2\rangle$, the standard Gibbs energy of formation of CaCN$_2$, $\Delta G^{o}_{f}\langle CaCN_2\rangle$ can be derived:

$$\{Ca\} + \langle C\rangle + (N_2) = \langle CaCN_2\rangle \qquad (12)$$

$$\Delta G^{o}_{f}\langle CaCN_2\rangle = \Delta G^{o}(3,\ \textit{Present study}) + \Delta G^{o}_{f}\langle CaC_2\rangle \qquad (13)$$

Values for $\Delta G^{o}_{f}\langle CaC_2\rangle$ are from Kubaschewskii and Alcock /1/ and Ono *et al.* /8/. Such literature data, however, involve considerable discrepancy as given below:

$$\Delta G^{o}_{f}\langle CaC_2,\ K\ \$\ A\rangle / \mathrm{J\ mol^{-1}} = -57300 - 28.5\,(T/\mathrm{K}) \qquad (14)$$

$$\Delta G^{o}_{f}\langle CaC_2,\ \textit{Ono et al}\rangle / \mathrm{J\ mol^{-1}} = -90100 - 11.0\,(T/\mathrm{K}) \qquad (15)$$

Obviously, values for $\Delta G^{o}_{f}\langle CaCN_2\rangle$ depend very significantly upon the literature data for $\Delta G^{o}_{f}\langle CaC_2\rangle$. Further discussion on $\Delta G^{o}_{f}\langle CaCN_2\rangle$ will not be made in this paper.

REFERENCES

1. O. Kubaschewski and C.B. Alcock, *Metallurgical Thermochemistry*, 5th edition, Pergamon Press, Oxford, U.K., 1979.
2. T. Rosenqvist, *Principle of Extractive Metallurgy*, McGraw-Hill Inc., New York, 1974.
3. W.T. Lankford, N.L. Samways, R.F. Craven and H.E. McGannon (Eds.), *The Making, Shaping and Treating of Steel*, 10th edition, Association of Iron and Steel Engineers, Pittsburgh, Pa, U.S.A., 1985.
4. H. Fujita, O. Kudo, M. Furuya, M. Iwase and M. Tokizane, *Heat Treatment* (*Netsu Shori*), **35**, 349 (1996) [in Japanese].
5. S. Nagakura, H. Izawa, H. Ezawa, S. Iwamuara, H. Saho and R. Kubo (Eds.), *Rikagaku-jiten*, 5th edition, Iwanami-shoten, Tokyo, Japan, 1998.
6. I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1989.
7. W.M. Latimer, *J. Amer. Chem. Soc.*, **73**, 1480 (1951).
8. H. Ono, A. Kobayashi, F. Tsukihashi and N. Sano, *Met. Trans.*, **23B**, 313 (1992).