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SOME THERMOCHEMICAL PROPERTIES OF THE SYSTEM VANADIUM–NITROGEN AND VANADIUM–CARBON–NITROGEN IN THE TEMPERATURE RANGE 1000–1550°C

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ABSTRACT

Thermochemical properties of vanadium nitride and carbonitride (δ-phases) have been studied in situ at 950–1550°C and nitrogen gas pressures of 9–760 mm Hg with the aid of thermoanalytical techniques. Thermogravimetric equilibrium measurements within the given temperature–nitrogen pressure range showed the δ-VN_x stoichiometry to vary, with $x =$ 0.792–0.964. Partial molar entropies and enthalpies were determined for δ-VN_x within the N content region of $x = 0.85$–0.96. Vanadium carbonitride displayed a wide homogeneity region with the following features: (a) the sum of N and C atomic fraction amounts per V atom ($x + y$ in VN_xC_y) was approximately constant at constant temperature, and (b) a temperature-dependent C content which limits the one-phase carbonitride region was found for the VN_xC_y [$y_{max} \approx 0.45$ (1000°C) and ≈ 0.68 (1200°C)]. Beyond these limits VN_xC_y coexisted with graphite.

INTRODUCTION

The existence of two vanadium nitrides has been finally established in the work of Hahn [1] by comprehensive X-ray diffraction measurements. In nitrogen-rich V–N alloys cubic VN_x [mononitride (δ-phase)] with $x = 1.00$–0.71 was identified. At lower N content an intermediate hexagonal nitride was found which was designated as V_2N_x (β-phase) with the phase boundaries corresponding to $x = 0.72$–0.86. Epelbaum and Ormont [2], studied the stoichiometry variations of the cubic δ-VN_x prepared by decomposition of ammonium vanadate at 600–1400°C. Their suggestion that the δ-phase structure may display not only nitrogen but also metal deficiency at high temperatures (V:N ratio 0.96:1–1.17:1) has, however, not been supported by any of the later works. The compositional variation in the δ-VN_x on the side of the N sublattice has been further corroborated by the work of Brauer

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and Schnell [3]. For this phase they give the homogeneity range of $VN_{0.72}$–$VN_{1.00}$ close to the values of Hahn. For the nitrogen-rich phase boundary of the β-phase (V_2N_x) they estimate the composition to be $V_2N_{0.98 \pm 0.02}$ (Hahn: 0.86). These authors [3] have also measured the nitrogen pressures of the δ–β- phase equilibrium. Assuming an essentially invariable composition for these phases they have determined the thermodynamic quantities for the reaction

$$\delta \rightleftharpoons \beta + N_2$$

Brauer and Schnell [4] have also investigated the system V–C–N. Their measurements involved treatment of vanadium carbide powders in nitrogen at 1100–1400°C. Two ternary carbonitrides were identified: the hexagonal β-phase [$V_2(C,N)$] and the cubic δ-phase [$V(C,N)$], which are isostructural with the corresponding V-carbides and V-nitrides. These phases were found to exist within wide single-phase and coexistence regions of composition. No significant variation of the phase boundaries with temperature could be observed. As has been demonstrated in previous works [5,6], the compositional variations of this type of interstitial compounds can be accurately determined as a function of temperature using in situ equilibrium thermogravimetric measurements under controlled atmospheric conditions.

The present work is concerned with the exploration of the homogeneity regions of the δ-VN_x and δ-VN_xC_y phases as a function of temperature, nitrogen pressure and the carbon content (for the carbonitride) using the technique of thermogravimetry. These phases are important as second phase precipitates in V-bearing steels. A knowledge of their stoichiometrical variation is essential for determining the distribution of N and C as (carbo)nitride precipitates and interstitial atoms in iron and steel.

EXPERIMENTAL

Materials

The vanadium powder used was from Alfa Products Ltd. Typical characteristics: purity, 99.7%; particle size, −325 mesh; main impurities (content in ppm), 100 Al, 340 C, 1000 Fe, 1000 Si.

Apparatus and experimental conditions

A microthermobalance (Mettler TA1) equipped with TG, DTG and DTA units was employed. The parameters characteristic of the runs were: sample weight 500–1000 mg; Al_2O_3 crucibles; TG–DTG–DTA sensitivity 5 ×

10^{-5} g–5, 10 mg min^{-1}–50, 100 μV; heating rates 8–15°C min^{-1}; gas flow rate 5–10 l h^{-1}.

Experimental procedure

Specimens were heated in the furnace of the thermobalance either in flowing purified (Ti getter) N_2 gas at atmospheric pressure or in static N_2 gas at 9–760 mm Hg. In the equilibrium meaurements the nitrogen uptake was recorded continuously as a weight gain (loss) at constant temperatures and N_2 pressures. Stabilized weight was taken as an indication that equilibrium was attained between the solid nitride phase and the gas phase. To control this the temperature was varied up and down around the equilibration value which caused the N content in the specimens to vary accordingly. After returning to the original temperature the TG curve (indicating the N content) also stabilized at the starting level.

Starting materials in the study of the V–C–N system were vanadium carbide phases. These phases were prepared by introduction of a predetermined amount of carbon into vanadium powder using a TG-controlled carburization in a methane–hydrogen atmosphere. The gas composition CH_4/H_2 was optimized to a ratio of 10:90 vol.% at 950°C. No spontaneous decomposition of CH_4 was observed although the ratio for the metastable equilibrium CH_4/H_2 is approximately 3:97 vol.% already at 900°C. Methane thus appears to be kinetically stable under these conditions which leads to a very high carbon activity (with respect to graphite) to the V metal. During the heating-up stage of carburization, hydrogen also dissolved in vanadium. However, it was then removed again as the carbon was taken up. No reabsorption was observed on cooling in the low temperature range where the solubility of H_2 in V is high [7].

RESULTS AND DISCUSSION

Nitride formation

The vanadium powder used starts to react with N_2 gas at about 350°C. The maximum reaction rate (DTG) is attained at 770°C (heating rate: 10°C min^{-1}). Nitridation at 1000°C leads to equilibrium after about 5 h. Identification (X-ray diffractometry) after cooling the specimen to room temperature shows the presence of a pure VN_x (δ-phase, cubic) with $x = 0.964$. Below 1000°C equilibrium is attained very slowly (950°C: ca. 20 h) and the composition varies only slightly (950°C: $x = 0.965$).

Stoichiometric nitride $VN_{1.00}$ thus could not be prepared at 1 atm N_2

pressure. This may be due to lowering the activity of V by the presence of impurities. However, the nitrogen activity in N_2 gas at 1 atm can also be too low to attain the composition corresponding to V:N = 1:1. The lower nitride phase (V_2N_x, hexagonal) appears in uncompletely nitrided samples. However, it cannot be prepared pure in N_2 gas at 1 atm pressure. After a partial nitridation, a homogenization temperature below ca. 450°C is required to avoid nitrogen uptake (leading to the formation of δ-phase). Pure V_2N_x phase can, however, be prepared by homogenization in argon, e.g., 900°C for 5 h, without any significant nitrogen loss.

The nitride formation is strongly exothermal. The enthalpy change (ΔH) for this thermal reaction was estimated from the DTA peak area with K_2SO_4 as a calibration substance. The weight gain corresponding to the thermal effect was related to the reaction according to

$$V(s) + 0.48\ N_2(g) \rightarrow VN_{0.96}(s)$$

and the ΔH value was found to be 63 ± 6 kcal mole^{-1} $VN_{0.96}$. This value is in good agreement with the calorimetrically determined enthalpy change of 60 kcal mole^{-1} VN [8] for the stoichiometric nitride (V:N = 1:1).

Equilibrium measurements

In the V–N system the measurements included equilibration of V powder specimens at 950–1550°C and nitrogen partial pressures of 9–760 mm Hg. Figure 1 shows the isobars obtained as a function of temperature (nitrogen content is given in atomic %). They are seen to be continuous within the region investigated and thus cover a one-solid phase region corresponding to δ-VN_x (mononitride). Within the range studied the stoichiometry of the δ-phase (x in VN_x) is seen to vary between 0.964 and 0.792. According to the data of Darken and Gurry [9] the equilibrium nitrogen pressure for the vanadium nitride given by the stoichiometric formula VN would be 1 atm (760 mm Hg) at ca. 1600°C. Extrapolation of the isobar at 760 mm Hg in Fig. 1 shows, however, that the VN_x composition will be highly nitrogen-deficient, corresponding to $VN_{0.82}$.

The isobars in fig. 1 have been used for the determination of relative partial molar free enthalpies (chemical potentials) of dissolution of 0.5 mole nitrogen gas in δ-VN_x at constant composition (x = const.). These enthalpies can be expressed as

$$\Delta\bar{G}_{N_2} = \bar{G}_{N_2} - \bar{G}^0_{N_2} = \tfrac{1}{2}RT \ln p_{N_2}$$

and correspond to a chemical equation of

$$aVN_x(s) + \tfrac{1}{2}N_2(g) \rightleftharpoons a\ VN_{x+1/a}(s)$$

where $a \gg 1$.

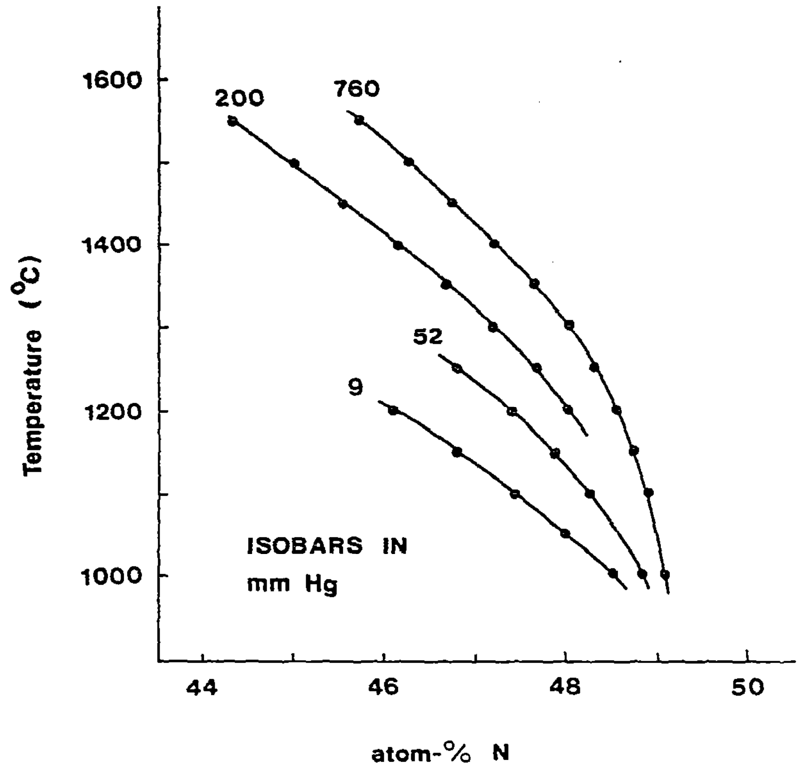

Fig. 1. Isobars for N_2 dissolution in δ-VN_x as a function of absolute temperature (N concentration in at. %).

With the aid of these values the relative partial molar enthalpies and entropies can be determined. Figure 2 shows $\Delta\bar{G}_{N_2}/T$ as a function of reciprocal temperature (in K) for constant compositions in the region 46.0–49.0 at. % nitrogen ($VN_x, x = 0.85$–0.96). As expected, linear relationships are obtained. Thus these lines may be extrapolated even below 1000°C when, for instance, it is desired to determine the stoichiometry of the δ-phase precipitated in iron at a given nitrogen activity.

The slopes of the lines in fig. 2 give the partial molar enthalpies (Δh_{N_2}). Corresponding entropies, Δs_{N_2}, are obtained from a graph of $\Delta\bar{G}_{N_2}$ vs. T (in K). Within the given region (46.0 — 49.0 at. % N) the following values have been obtained:

$\Delta h_{N_2} = -37000 \pm 1000$ cal mole^{-1} N

$\Delta s_{N_2} = -22 \pm 2$ cal mole^{-1} N K^{-1}

Kinetically, the equilibrium is attained rapidly above 1100°C. At a heating rate of 10°C min^{-1} some minutes were needed only for equilibration after

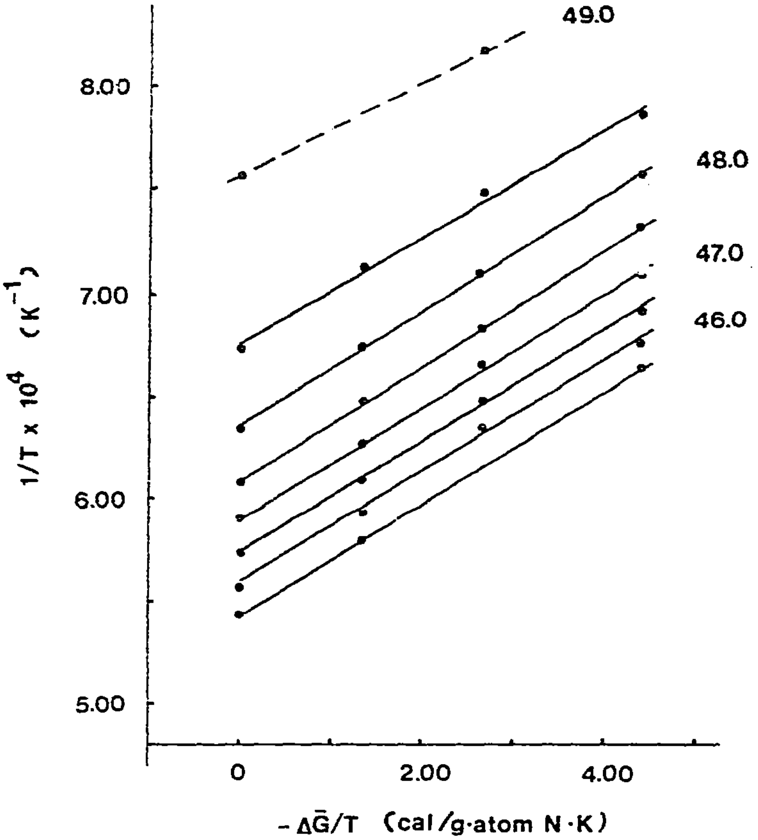

Fig. 2. Ratios $\Delta\bar{G}_{N_2}/T$ as functions of the reciprocal temperature for constant compositions in the phase region of δ-VN_x.

reaching constant temperature in the furnace. As a consequence of this, a considerable reabsorption of nitrogen occurred even on rapid cooling of the specimens. The N content could increase by 1–4 wt.%; thus the phases obtained after cooling were not representative of those at equilibrium.

In the V–N–C system the starting materials were carburized samples containing 21.8–44.8 at.% carbon. The specimens consisted of two phases, β-V_2C_x (hexagonal) and δ-VC_x (cubic, monocarbide). The specimen with the highest C content (corresponding to $VC_{0.812}$) was almost pure monocarbide.

Nitridation of the vanadium carbide phases prepared was carried out at 1000°C in N_2(g) at atmospheric pressure. The equilibration process occurred differently depending on the range of the total carbon content in the starting vanadium carbide samples. For the phases with the C content in the range $C:V = 0$–0.45, equilibrium was attained within 5–15 h. X-Ray diffractometry showed only one phase, the cubic (fcc) carbonitride. For the specimens with the C content corresponding to $C:V > 0.45$, the equilibration time was typically an order of magnitude longer. Thus, nitridation of a specimen with C:V = 0.81 required ca. 90 h for the attainment of equilibrium. The nitrogen amount taken up together with the initial carbon content gave a total non-metal amount corresponding to N + C = 1.34 per vanadium atom. X-Ray diffractometry showed the presence of vanadium carbonitride and graphite, thus indicating that a phase separation occurred. This suggests that the one-solid phase field of the δ-phase at 1000°C is limited to a certain C content. The value of this limiting C content corresponds, by extrapolation, to C:V = 0.452 (±0.003). At higher C concentrations the carbonitride appears to coexist with graphite and not with the carbide, as suggested by Brauer and Schnell [4].

Figure 3 shows schematically the stability regions for the appearing phases in the system V–C–N at 1000°C and the variation of C and N content per V atom in the one-phase region of VC_xN_y. At a constant nitrogen activity corresponding to $p_{N_2} = 1$ atm, the N content is seen to vary with a given C content so that their sum is nearly constant. However, this sum increases somewhat (0.964–0.983) with the decreasing N content, as shown in Table 1 (accuracy: ±0.003).

Figure 4 shows the stoichiometric variation of VC_xN_y at 1000 and 1200°C at $p_{N_2} = 1$ atm. The studies at 1200°C were carried out by TG-controlled nitridation of VC_x specimens prepared from V and C powders [10]. As seen

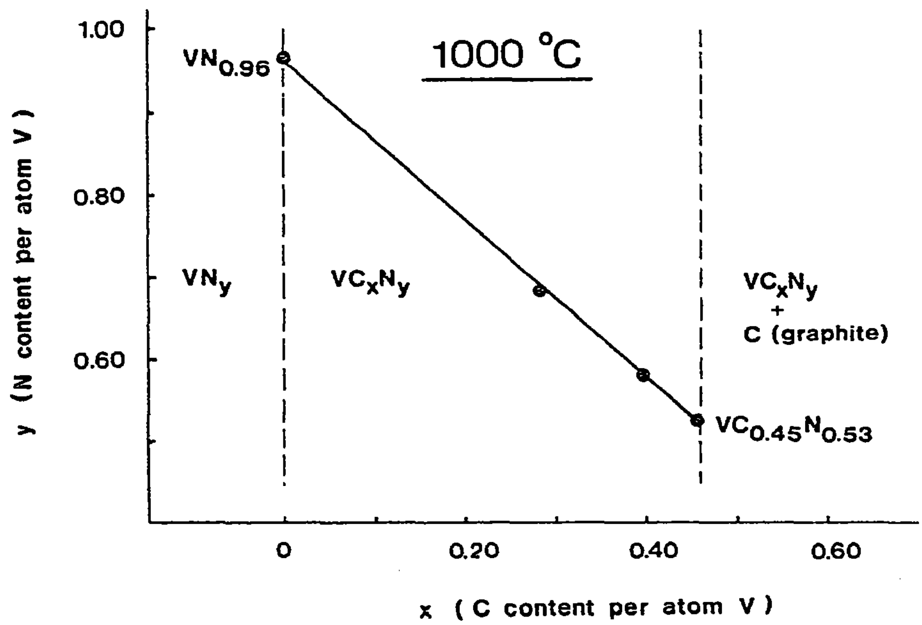

Fig. 3. Schematic plot of the stability regions for the appearing phases in the system V–N–C at 1000°C ($p_{N_2} = 1$ atm).

TABLE 1

Carbon and nitrogen content per V atom in δ-vanadium carbonitride at 1000°C and $p_{N_2} = 1$ atm

C	N	C+N
0	0.964	0.964
0.279	0.683	0.962
0.394	0.581	0.975
0.452	0.531	0.983

in Fig. 4 the limiting C content for the one-solid phase region of VN_xC_y is increased to C:V = 0.68. Thus, unlike previous findings [4], a significant variation of the phase boundary as well as of the stoichiometry appears to exist for the δ-VN_xC_y under the given conditions. As an implication of this, the vanadium carbonitride particles with a C content close to the limiting one, which may precipitate in steel at 1200°C, will give off carbon on cooling. This carbon may then dissolve in the metal matrix, thereby creating embrittled microzones around the particles. On the other hand, this embrittling effect may be diminished somewhat by a simultaneous dissolution of nitrogen (present in the metal matrix) in the carbonitride particles.

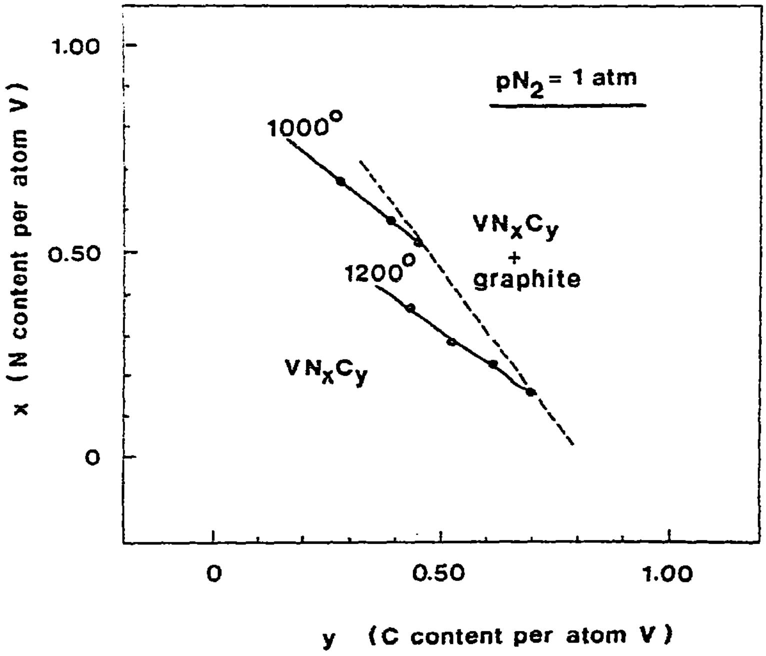

Fig. 4. Stoichiometric variation of VN_xC_y at 1000 and 1200°C ($p_{N_2} = 1$ atm).

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