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NITRIDE PRECIPITATION IN A POWDERED IRON ALLOY STUDIED BY THERMOANALYTICAL METHODS

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ABSTRACT

Precipitation of nitrides ($MnSiN_2$, δ-VN_x) is studied in a powdered iron alloy (7.9 w/o Mn, 9.3 w/o Si, 1.2 w/o V, 0.03 ± 0.01 w/o N) of typical particle size 20 μm, by thermoanalytical techniques (TG, DTG, DTA). Equilibrium measurements are carried out at 900—1100°C in the N_2 pressure range 50—760 mm Hg. The nitride precipitates formed are isolated from the alloy matrix by a copper—ammonia separation method The equilibration studies provide thermodynamic data which characterize the solubility of $MnSiN_2(s)$ in the alloy used.

INTRODUCTION

The mechanical properties of steels are affected profoundly by the distribution of nitrogen as an interstitial solution and by (carbo)nitride precipitates. Investigation of the conditions leading to precipitation of nitride or carbonitride particles frequently involves constant-temperature ageing of steel specimens to which N has been introduced in the early stages of the manufacturing process. Another method is to treat the steel specimens in a nitriding atmosphere (NH_3/H_2, N_2/H_2). Below 1000°C the diffusivity of the interstitial nitrogen formed is considerably higher than that of most solute, nitride-forming elements [1]. When using NH_3/H_2 mixtures under proper reaction conditions the activity of nitrogen is very high at the metal surface. This leads to a considerable diffusion potential for the N atoms. The nitrogen consumed during the nitride precipitation is then replenished rapidly ("constant activity ageing") [2,3]. The rate-determining step for the precipitation is diffusion of the solute atoms.

When nitrogen gas (with H_2) is used at nearly atmospheric pressure, the N activity is substantially lower and the rate of N uptake, as well as that of precipitation, is in general rather sluggish [4].

Nitriding procedures usually involve treatment of the sample in the form of bars, sheets, etc., in conventional furnaces. The equilibration times required are often of the magnitude of 50—500 h because the time necessary to attain equilibrium is not known. Sample surfaces are thus subject to oxidation. Small oxidant impurities (O_2, $H_2O(g)$), which are frequently present in nitriding gases, may affect the rate of N uptake [5]. Even the formation of relatively thin oxide films can severely limit or even prevent the absorption of nitrogen [6].

The technique of thermogravimetry (TG) has been found useful in studying the N solubility in iron alloys [7,8]. The nitrogen uptake is recorded continuously as a weight gain on a thermobalance. The stabilized weight of the specimen may then be taken as an indication of equilibrium. The time of nitridation can thus be limited to that necessary for equilibration. This technique has been applied in studying the precipitation of $MnSiN_2$ in an Mn—Si—Fe alloy, in a 2% NH_3/H_2 atmosphere. For thin sheet specimens (0.15 mm) equilibrium was attained in 40—70 h at 700—760°C. The thermogravimetrically determined amount of N taken up agreed well with that found by atomic absorption analysis.

The above equilibration times were still too long from the point of view of oxidation. Nitridation of the same specimens in N_2 + 5% H_2 resulted in preferential oxidation of Mn and Si, leading to a small but significant reduction of the content of these elements in the alloy. An oxidized layer ($MnSiO_3$), which hindered the uptake of nitrogen, was formed on the surface.

If, instead, powdered alloys are used, the surface for N uptake is increased by many orders of magnitude and the equilibration time may be decreased. In consequence, the detrimental effect of oxygen in the nitriding atmosphere will be substantially reduced.

The present investigation extended the application of thermoanalytical methods (TG, DTG, DTA) to the in-situ study of the process of nitridation of a selected powdered iron alloy (Mn—Si—V—Fe). The aim was to investigate the equilibrium precipitation of nitrides at various temperatures and nitrogen partial pressures. The phases formed were identified by XRD, IR spectroscopy and thermal analysis in an oxidizing atmosphere. Two selected nitrided powders were also investigated with an ion microprobe (CAMECA).

EXPERIMENTAL

The alloy used was prepared and analyzed by Surahammars Bruk AB, Sweden. It was vacuum-melted using electrolytical iron with Mn, Si and V. After quenching in water it consisted of large brittle grains and lumps. These were transformed to a powder of typical particle size 200 μm by crushing in a diamond mortar and sieving. The powder was then milled in a vibration mill for ca. 5 h to a final particle size of 20 μm. Prolonged milling ($\approx$20 h) resulted in finer particles but the powder was contaminated ($\approx$0.2 w/o) by material from the mill walls (hard plastic). Analysis of the alloy after milling gave the following values (in wt.%): Si 9.3, Mn 7.9, V 1.2 and N 0.03 ± 0.01.

The thermoanalytical studies were done with a Mettler TA1 universal micro-thermobalance, and nitridation carried out at 25—1100°C in nitrogen gas at a partial pressure P_{N_2} of 50—760 mm Hg. In the thermoanalytical runs in N_2 (or Ar) at atmospheric pressure the alloy samples (2 g; typical particle sizes 20 μm, 200 μm) were heated at 10—15°C min^{-1} and TG, DTG and/or

DTA curves were recorded as functions of time and/or temperature.

In the equilibration measurements at various constant nitrogen pressures the specimens were nitrided in N_2 gas at 1 atm. After cooling to room temperature the N_2 pressure was adjusted to a selected lower value and the nitrogen loss was measured thermogravimetrically at constant temperatures in the range 930—1100°C. Stabilization of weight was taken as an indication of equilibrium between the alloy samples and the N_2 gas phase. The reproducibility was checked for four specimens at 1000°C and 1 atm N_2 pressure. The difference between the maximum and minimum N content measured corresponded to 2%.

The other experimental parameters in these measurements were as already reported [9].

RESULTS AND DISCUSSION

The initial stage of the process of nitridation (N_2 gas at 1 atm) of the alloy powder (particle size 20 μm) up to 1030°C at a heating rate of 10°C min^{-1} is illustrated by the thermogram in Fig. 1. As indicated by the DTG curve, nitrogen uptake began at about 840°C and was rapid enough to give an exothermal DTA peak (sensitivity 100 μV). Stabilization of weight was attained within 3 h at 1030°C. By increasing (or decreasing) the temperature to various constant values, nitrogen was given off (or taken up) until a new stabilized weight was attained. On returning to the initial constant temperature the amount of nitrogen taken up was equal to the initial value. Thus, equilibrium could be attained from both sides and no hysteresis effects such as those observed [10] for the metastable precipitation of δ-VN_x were observed, within experimental error.

Even for rapid cooling of the nitrided alloy powder from above 1000°C in

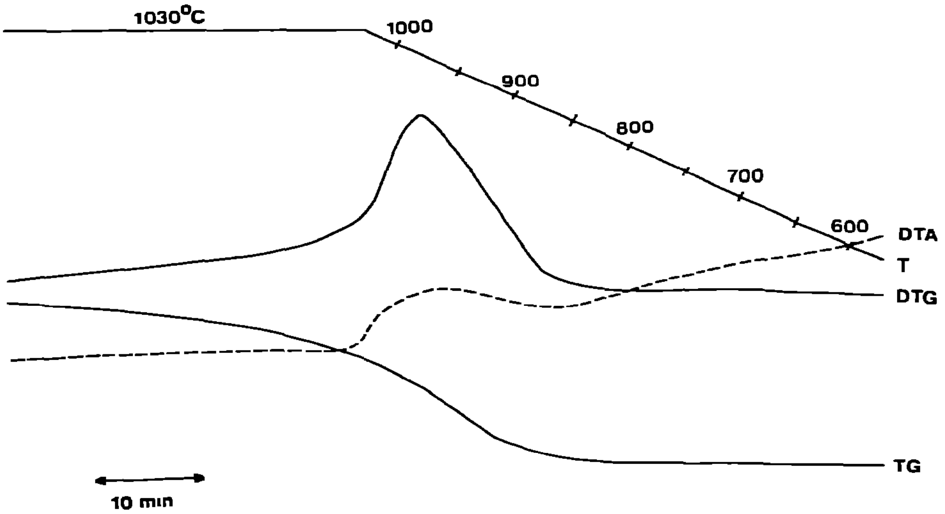


Fig. 1. Nitridation of the alloy powder (particle size 20 μm) to 1030°C at a rate of 10°C min^{-1} in N_2 gas at 1 atm (0.1 MPa).

the N_2 gas atmosphere, substantial amounts of N were re-absorbed. The thermogravimetric technique made it possible to record these amounts and determine, with sufficient accuracy, the true N amounts corresponding to the equilibration temperatures used. On heating (10°C min^{-1}) the alloy powder, nitrided to equilibrium at 1000°C, in Ar the nitrogen could be driven off within 6 h at 1000°C.

When using powders of typical particle size 200 μm, attainment of equilibrium in the N_2 gas required, as expected, significantly longer times, i.e. 15—20 h at 1000°C. Similarly, about 25 h were needed to remove nitrogen in Ar at 1000°C. Therefore, in the ensuing equilibration runs only the 20-μm alloy powders were used. This particle size was still expected to be large enough for the thermodynamic properties of the powdered alloy to be representative of the alloy in bulk.

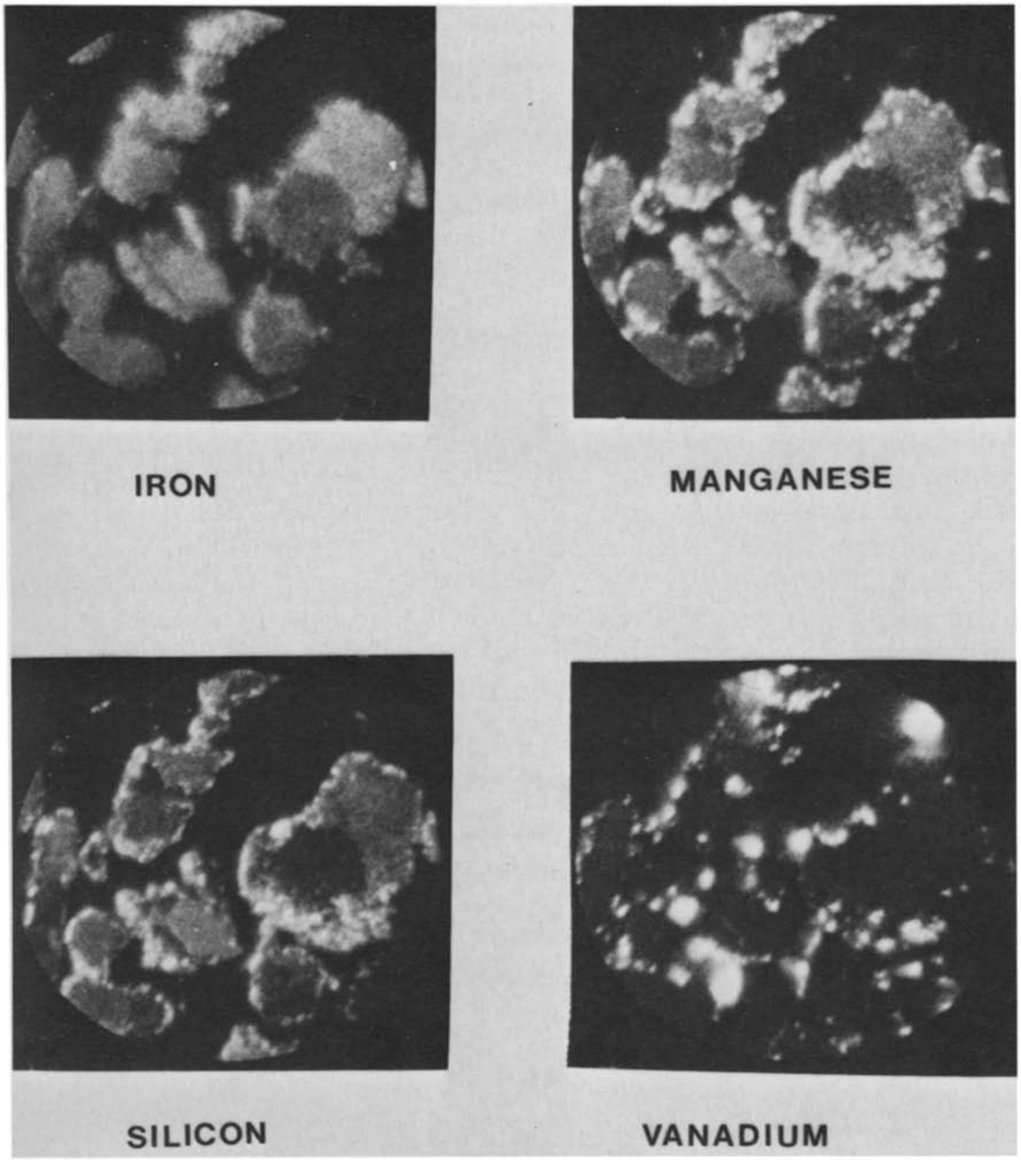
The X-ray diffraction patterns of the nitrided alloy powders showed the presence of α-Fe and orthorhombic $MnSiN_2$. Weak reflexions due to the cubic V mononitride (δ-VN_x) could also be occasionally identified.

Two powder samples, equilibrated at 900°C and 1030°C in N_2 gas, were cast into a hard epoxy resin, wet-ground and polished (diamond paste). This simple technique gave, with the aid of microscopic techniques, a cross-sectional view and a means of determining the size distribution of the alloy particles as well as the nitride precipitates within these particles.

Figure 2 shows the surface images (diameter ≈200 μm) produced by mass-analyzing the secondary ions obtained by oxygen ion bombardment of the surface of the sample nitrided to equilibrium at 1030°C. That analysis was made for Fe, Mn, Si and V. The Fe image shows the appearance of alloy particles. In the image obtained for Mn and Si more intense signals (white spots) are seen at the same locations in the particles. These are due to the enrichment of Mn and Si as $MnSiN_2$. The nitride appears to be precipitated mainly in the subsurface region of the alloy particles. There is also a relatively uniform background signal from the matrix showing the contour of the alloy particles to be similar to that of Fe. This indicates the presence of Mn and Si in solid solution in the Fe matrix. For Mn, which is deficient because of $MnSiN_2$ formation, the background image from the matrix is completely absent for the sample nitrided at 900°C (not shown in the figure), at which temperature virtually all Mn was precipitated as the nitride.

In the image for V the intense spots are concentrated at the subsurface region of the particles and show that the vanadium present occurs predominantly as a nitride precipitate.

The nitride phases precipitated in various equilibration runs (900—1050°C, 760 mm Hg N_2 pressure) were isolated from the alloy matrix using the previously reported copper—ammonia method [11]. Saturated aqueous copper sulphate solution was used to dissolve the matrix. The copper metal precipitated and the nitride residue were separated and treated as previously described. The estimated particle size (optical microscope, ion microprobe) of the residue was of the magnitude of 1 μm or less. The X-ray diffraction pattern was dominated by reflexions due to orthorhombic $MnSiN_2$. The reflexions corresponding to δ-VN_x (mononitride) could also be clearly identified. No further compounds indicative of interaction between these



IRON

MANGANESE

SILICON

VANADIUM

Fig. 2. Surface images of the alloy particles (equilibrated at 1030°C in $N_2(g)$) analyzed with an ion microprobe (CAMECA) for Fe, Mn, Si and V.

nitrides and the reagents used during the isolation (aqueous solution of $CuSO_4$, ammonia and 10 M $(NH_4)_2S_2O_8$ solution) could be observed.

The lattice constant for the δ-VN_x isolated was 4.13 Å. Interpolation of the values of lattice constants given by Hahn [12] as a function of the N content of this nitride corresponded to a stoichiometry with $x \approx 0.96$.

Thermal analysis (TG, DTG, DTA) of the residues was carried out in air up to 1000°C (10°C min^{-1}). No attempt was made to determine $MnSiN_2$ and δ-VN_x selectively since the thermal processes observed were dominated by the oxidation of $MnSiN_2$ in the range 390—920°C. Nevertheless, manganese silicon nitride could again be identified by DTA. As in the cases where this nitride was isolated from compact nitrided steel samples [8] or prepared synthetically from pure Mn and Si powders [13], a sharp reproducible DTA peak was observed at 850°C indicating the presence of $MnSiN_2$.

The results of analysis (thermal, ion microprobe, XRD, IR spectra) indicate that the nitrogen taken up by the powder alloy in the equilibration runs occurs mainly as the nitride precipitates identified, $MnSiN_2$ and δ-VN_x (mononitride). Precipitation of silicon nitride is also conceivable at a decreased Mn activity under the given conditions [3,4] but this could not be detected by any of the analytical methods used. The amount of N taken up in solid solution in the alloy was considered to be negligible compared to that precipitated. Moreover, since silicon was always present in excess in the solid solution during $MnSiN_2$ precipitation, this alloy was expected to retain its α-Fe structure over the whole experimental range. The solubility of N in this structure is of the order of 10^{-2} w/o.

Because of excess Si in the alloy, for formation of $MnSiN_2$ it is relevant to determine the amount of N precipitated as nitrides according to the Mn (and V) contents of the alloy. The maximal amount of N in the alloy as these nitride precipitates was calculated to be 4.3 wt.%. Of this amount, the precipitation of δ-VN_x will consume 0.3 wt.% N since only half a mole of N is taken up per mole of V. Consequently, variation of the δ-VN_x solubility will be confined to a range which is one order of magnitude lower compared to that for $MnSiN_2$. Most of the variations will thus be due to the solubility of $MnSiN_2$. Figure 3 shows the equilibrium amount of nitrogen taken up at different N_2 pressures at constant temperatures of 930, 960 and 1000°C. Since the relative amounts of Mn and V precipitated as nitrides are not known, the nitrogen taken up is expressed cumulatively in wt.% of alloy. Similarly Figure 4 shows the variation of amount of nitrogen taken up at various equilibration temperatures under isobaric conditions (50—760 mm

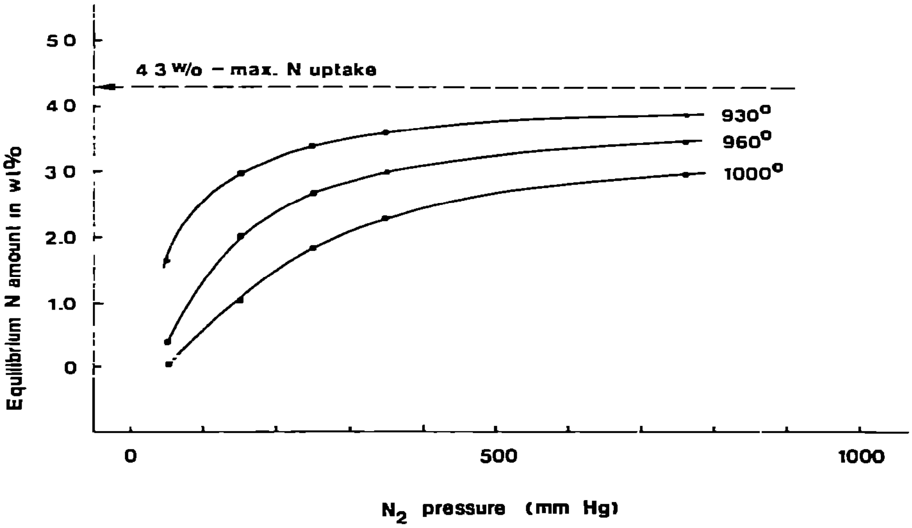


Fig. 3. Equilibrium amount of nitrogen (in wt.% of alloy) taken up at 930, 960 and 1000°C as function of nitrogen pressure (mm Hg).

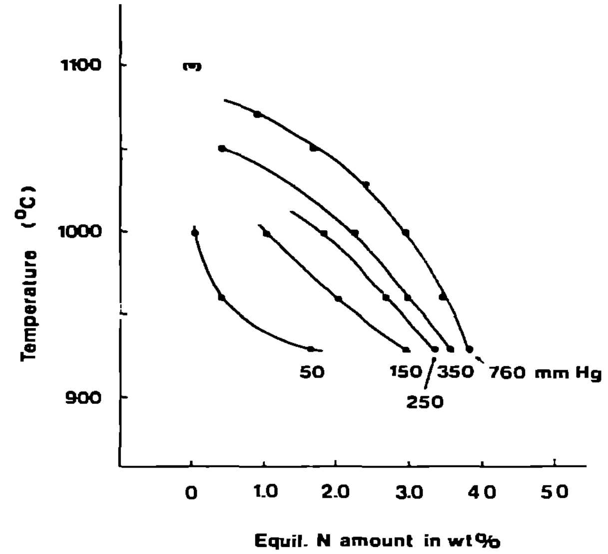


Fig. 4. Equilibrium amount of nitrogen (in wt.% of alloy) taken up at various constant nitrogen pressures in the range 50—760 mm Hg as function of temperature.

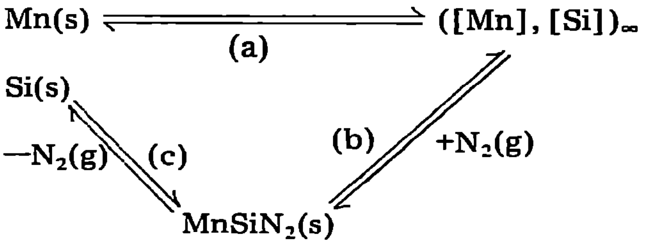
Hg N_2 pressure). As already mentioned the solubility variation of N as δ-VN_x is observable only within the nitrogen concentration range 0—0.3 wt.%. Figures 3 and 4 thus illustrate the isothermal and isobaric solubility, respectively, for $MnSiN_2$ in this alloy.

The measurements made at 760 mm Hg N_2 pressure (Fig. 4) show that essentially all the nitrogen precipitated at 1070°C (the last experimental point on the isobaric curve) has been driven off at 1100°C. This indicates that the nitrides precipitated (δ-VN_x, $MnSiN_2$) are dissolved completely above this temperature. Below 1100°C the variation of the δ-VN_x solubility is limited to a small range. It may be assumed, as a first approximation, that this variation will, at least within a limited solubility range, have only a minor and negligible effect on the solubility variations of $MnSiN_2$. The measurements represented in Figs. 3 and 4 can then be used to determine the thermodynamic quantities characteristic of the solubility of $MnSiN_2$ in the alloy used.

For the precipitation of $MnSiN_2$ only, these quantities are the partial molar enthalpies, free enthalpies and entropies related to the dissolution (or precipitation) of 1 mole of $MnSiN_2$ in an, by definition, infinite amount of the alloy of a certain fixed composition. The equilibrium chemical equation for this is

$$[\mathrm{Mn}] + [\mathrm{Si}]\ (\text{in alloy}) + N_2(g) \rightleftharpoons MnSiN_2(s) \qquad (1)$$

where the brackets indicate that Mn and Si are present in solid solution. These quantities are, of course, also related to those of formation of the pure solid $MnSiN_2$. This may be illustrated using a hypothetical thermodynamic cycle according to the following scheme (at constant temperature and pressure)



Starting, for instance, clockwise with 1 mole of Mn(s) and 1 mole of Si(s), these elements are dissolved in a comparatively very large amount of Mn—Si alloy of fixed composition (step (a)). The next step (b) involves an equilibrium reaction of this alloy with 1 mole of N_2(g) to give 1 mole of $MnSiN_2$(s) precipitate. In step (c) $MnSiN_2$(s) is decomposed into the starting materials and N_2(g), and the system returns to its initial state. Then, for example, the sum of the enthalpy changes during these steps is zero, i.e. $\Delta\bar{H}_a + \Delta\bar{H}_b + \Delta H_c = 0$, where the bars over the ΔH values for the steps (a) and (b) indicate that they are partial molar quantities, related to a solid solution of certain fixed composition. The quantities which may be determined in the present case are those corresponding to step (b).

The absorbed equilibrium amounts of N given in Figs. 3 and 4 in wt.% of the alloy are, of course, inversely proportional to the equilibrium amounts of the nitride-forming constituents in solid solution — small amounts of N taken up correspond to large amounts of Mn, Si (and V) left in solution (in equilibrium with the nitride precipitates and N_2(g) at a given pressure) and vice versa. For an essentially stoichiometric compound such as $MnSiN_2$ [14] the constant amount of N absorbed thus corresponds to a constant amount of Mn and Si in solid solution.

Figure 5 shows a plot of partial molar free enthalpies ($\Delta\bar{G}_c$) as a function of absolute temperature (T) for constant equilibrium contents (c) of N precipitated in the range 0.5—3.5 wt.% (w/o). The $\Delta\bar{G}_c$ values were calculated using the relationship

$$\Delta\bar{G}_c = \bar{G}_c - G_c^0 = -RT \ln P_{N_2} \qquad (2)$$

for reaction (1). The reference state (corresponding to the value of G_c^0) is N_2(g) at 1 atm (0.1 MPa) pressure and a solid solution of Mn, Si (and V) in Fe of given fixed composition. The $\Delta\bar{G}_c$ values thus give the changes in partial molar free enthalpy occurring when 1 mole of $MnSiN_2$(s) is precipitated (or dissolved) in the alloy of given fixed composition.

As seen in Fig. 5, the $\Delta\bar{G}_c$—T relationships may be reasonably represented by straight lines. The slopes of these lines give the corresponding partial molar entropies ($\Delta\bar{S}_c$). Similarly, the slopes in the plot of $\Delta\bar{G}_c/T$ values against the reciprocal of absolute temperature ($1/T$) (Fig. 6) yield the partial molar enthalpies ($\Delta\bar{H}_c$). These plots also suggest that the approximation made was fairly justifiable. Thus, this shows that the solubility variation of $MnSiN_2$ can be characterized satisfactorily, even in the presence of a limited amount of another nitride (δ-VN_x).

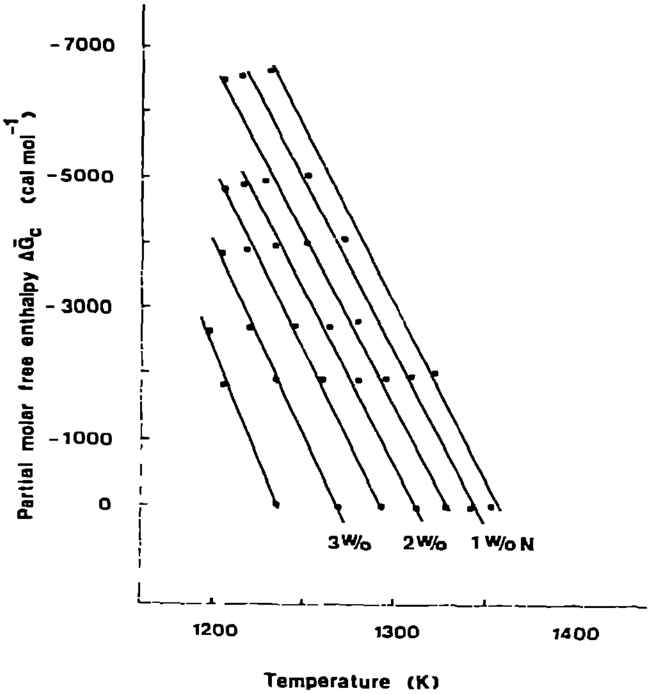


Fig. 5. Partial molar free enthalpy ($\Delta\bar{G}_c$) as function of absolute temperature (T) at constant content of nitrogen precipitated (in w/o).

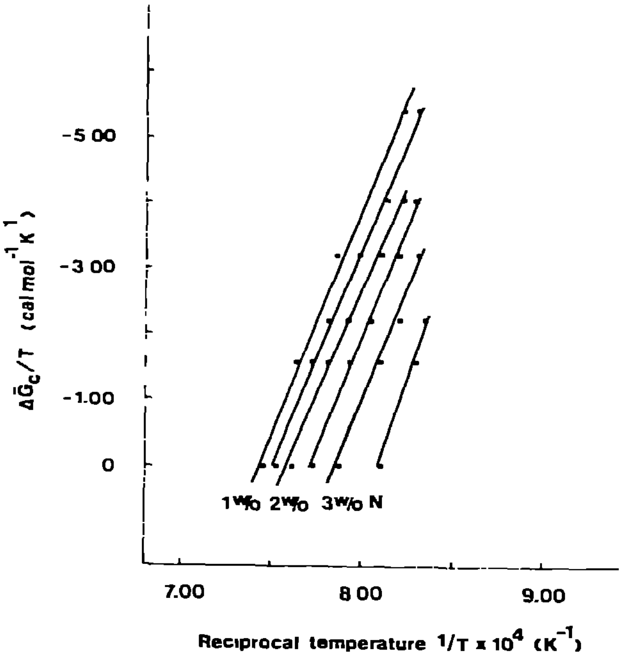


Fig 6. Ratio $\Delta\bar{G}_c/T$ as function of the reciprocal of absolute temperature ($1/T$) at constant content of nitrogen precipitated (in w/o).

Figure 7 shows the values of $\Delta\overline{H}_c$ and $\Delta\overline{S}_c$ determined from Figs. 5 and 6 as a function of the amounts of N precipitated (inversely proportional to the contents of Mn, Si (or V) remaining in solution). Above about 2.5 w/o N these values are statistically very uncertain. Moreover, as the Mn content in this alloy decreases it may eventually approach the same magnitude as that of V. The variation of these values above 2.5 w/o N can thus scarcely be interpreted unequivocally except in terms of $MnSiN_2$ precipitation.

Within the range of 0.5 to about 2.5 w/o N (the concentration region corresponding to a large fraction of Mn, Si (or V) in solid solution) the $\Delta\overline{H}_c$ values are seen to be essentially independent of the content of the nitride-forming constituents in this alloy, while $\Delta\overline{S}_c$ values increase slightly. Knowledge of these values makes it possible to express the isobaric and isothermal $MnSiN_2$ solubility variations as in Figs. 3 and 4. For the different stages of precipitation the "critical" temperatures (T_p) above which essentially no $MnSiN_2$ will be precipitated at a given N_2 pressure and alloy composition may be calculated. The $\Delta\overline{H}_c$ and $\Delta\overline{S}_c$ values in the region below about 1 w/o N (where the amount of the nitrides precipitated is essentially zero) are found to be $\Delta\overline{H}_c = 68000 \pm 1000$ cal mole^{-1}, $\Delta\overline{S}_c = 52 \pm 1$ cal mole^{-1} deg^{-1}. Then, for instance, the T_p value corresponding to equilibrium between this alloy and $N_2(g)$ at 1 atm (760 mm Hg) can be obtained from the usual thermodynamic relationships

$$\Delta\overline{G}_c = RT_p \ln P_{N_2} = \Delta\overline{H}_c - T_p\Delta\overline{S}_c = 0 \tag{3}$$

as 1035 ± 45°C.

The isobar at 1 atm N_2 pressure (760 mm Hg) in Fig. 4 is seen to approach zero nitrogen content at 1070—1080°C. The agreement between these values may be considered as excellent in view of the simultaneous presence of δ-VN_x in this alloy, which necessarily leads to a certain increase in the T_p value observed. The T_p values at 1 atm N_2 pressure are determined only by

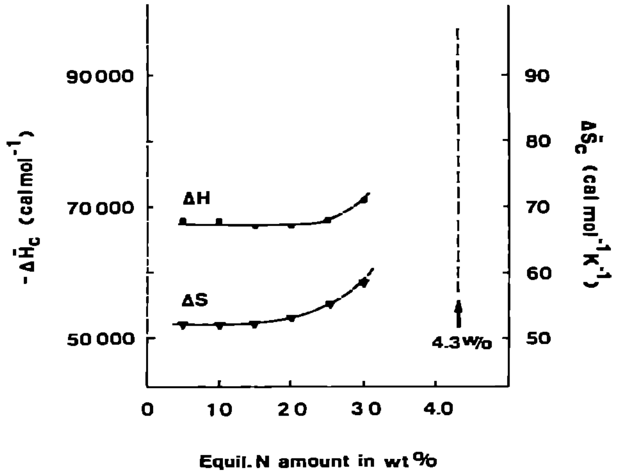


Fig. 7. Partial molar enthalpy ($\Delta\overline{H}_c$) and entropy ($\Delta\overline{S}_c$) as function of amount of nitrogen precipitated (in w/o).

the ratio $\Delta\overline{H}_c/\Delta\overline{S}_c$ (eqn. 3). These values, of course, decrease with increasing N content (Fig. 4) — that is decreasing contents (activities) of nitride-forming constituents. The ratio $\Delta\overline{H}_c/\Delta\overline{S}_c$ must thus also decrease and the increasing value of $\Delta\overline{S}_c$ as a function of N content (Fig. 7) is consistent with this requirement. The statistical uncertainty in the $\Delta\overline{S}_c$ and $\Delta\overline{H}_c$ values does not, however, permit the T_p values to be calculated with sufficient accuracy.

Mortimer and Svedung [15] have, from their studies of $MnSiN_2$ solubility in α-Fe, determined the free enthalpy of formation (ΔG_f) for pure $MnSiN_2$(s) (660—850°C) to be ΔG_f (= $\Delta H_f - T\Delta S_f$) = $-$ 86.100 + 34.0 T (cal mole^{-1}) with β-Mn, Si(s) and N_2(g) at 1 atm (0.1 MPa) as the reference state. Consideration of the thermodynamic cycle shown earlier indicates that the $\Delta\overline{H}_c$ and $\Delta\overline{S}_c$ values given above are at least qualitatively compatible with those of Mortimer and Svedung.

As might be expected, the $\Delta\overline{H}_c$ value is less negative than ΔH_f since the enthalpy change accompanying the dissolution of Mn and Si in the alloy is very likely to be negative. On the other hand, the entropy change corresponding to the decomposition of $MnSiN_2$(s) (ΔS_f) is positive, that of the dissolution of Mn and Si in the alloy may also be anticipated to be positive, and, therefore, $\Delta S_f < \Delta\overline{S}_c$.

CONCLUSIONS

It has been demonstrated that thermoanalytical methods can be very helpful in the field of equilibrium metallurgical measurements. Specifically the present study illustrates the possibility of determining certain thermodynamic parameters characteristic of the nitride precipitation in a given alloy without any need for explicit knowledge of the free enthalpy of formation of the nitride precipitated or the activities of the nitride-forming constituents in the alloy.

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