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A THERMOANALYTICAL INVESTIGATION OF LOWER MANGANESE NITRIDE PHASES

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ABSTRACT

The processes of formation and some thermochemical and equilibrium properties for the ε-phase ($\approx Mn_4N$) and the ζ-phase ($\approx Mn_5N_2$–Mn_2N) have been investigated. Thermochemical analysis of these phases was made in both oxidizing and inert atmospheres. The investigations were made using TG, DTG and DTA techniques in the temperature range 25–1030 °C.

INTRODUCTION

In the Mn–N system the two lowest nitride phases are known[1-3] to be the ε-phase and the ζ-phase. Below 400 °C the ε-phase has a narrow homogeneity range and is denoted by an ideal formula Mn_4N. The ζ-phase is found[4] to have a broader homogeneity range below 400 °C. Its limiting compositions approximately correspond to Mn_5N_2 and Mn_2N. Recent equilibrium measurements[5-7] combined with high temperature XRD indicate that: (1) the ε-phase decomposes to the ζ-phase at 882 °C and 18.6 at.% N, (2) a N-poor ζ′-phase may be distinguished as well as the established ζ-phase, (3) these phases have a broad homogeneity range above 900 °C, and (4) a second order phase transition $\zeta \rightleftarrows \zeta'$ takes place. The process of formation of ε and ζ has been dealt with in some investigations[8-10] where the N_2 uptake by Mn is studied at various temperatures, times and metal grain sizes. However, these have given inconsistent information, particularly concerning the N content in Mn as a function of temperature and P_{N_2}.

The preparation of the two phases is thus frequently performed on an empirical basis, e.g. by treating Mn metal of a certain granulation by N_2 gas or NH_3–H_2 mixtures at selected temperatures and times[11-14]. The purpose of this work has been to investigate, using the techniques of TG, DTG and DTA, the process of formation of these phases and to find definite possibilities of their preparation at $P_{N_2} = 1$ atm and lower.

Another aim of the investigation has been to determine the thermochemical properties of these phases in oxidizing and inert atmospheres for identification purposes.

The Mn–N phases are used as additives in commercial steels. Also, these nitride phases can also be precipitated in steels, i.e. during hardening processes. Knowledge of their thermochemical properties is thus of considerable importance, e.g. for identification of second phase residues by the TG–DTA technique.

EXPERIMENTAL

A microthermobalance (Mettler TA1)[15] equipped with DTA and DTG units was employed. The experimental parameters used were as follows: crucibles of s-platinum and/or sintered alumina; TG–DTG–DTA sensitivity: 5×10^{-5} g–10 mg min^{-1}–50, 100 μV; Pt–Rh thermocouples; temperature control: ±1.5°C; gases used: air, AR (SR), N_2(SR); gas flow: approximately 5 l h^{-1}.

In studying the formation of the nitride phases, the Mn metal powder (99.9%, granulation: 1–15 μ, 700–1000 mg) was nitrided in N_2 (g) at heating (cooling) rates 4–15°C min^{-1} in the range 25–1050°C and also at some selected constant temperatures. A series of equilibrium measurements was performed[6, 7] at various constant temperatures (600–1030°C) and at P_{N_2} in the range 3.5–750 mm Hg. The nitride phases were prepared by using the results of these measurements and by the TG-controlled nitridation of Mn.

In the oxidation studies the nitride samples (10–20 mg) were treated in air at heating rates 2–10°C min^{-1} in the range 25–1000°C. In the inert atmosphere (Ar) the nitride samples (200–300 mg) were heated at 10–15°C min^{-1} up to 1050°C and at 1000°C for approximately 10 h. The thermal reactions were evaluated by means of the recorded TG, DTG and DTA curves together with X-ray diffractometry. The enthalpy of reactions (ΔH) was estimated with the aid of the DTA peak areas. K_2SO_4 or $BaCO_3$ were used as the thermoactive reference substances. They were chosen so as not to interfere with the thermal effects of the samples. The mean value of at least three endothermal peak areas recorded in one run has been used. The mean deviation was approximately 5% for these references. Corrections for the enthalpy variations with temperature were made according to ref. 16 (eqn. 1).

RESULTS

Formation of the nitride phases

Figure 1 shows a thermogram obtained after nitriding the Mn powder in N_2(g) at atmospheric pressure. The nitriding process was carried out in three steps.

(1) In the range 25–870°C the heating rate was 10°C min^{-1}. The nitrogen uptake (TG curve) is seen to occur up to approximately 845°C. Above this temperature N was driven off at this heating rate.

(2) The temperature was decreased (10°C min^{-1}) to 600°C and more nitrogen was then taken up by the specimen.

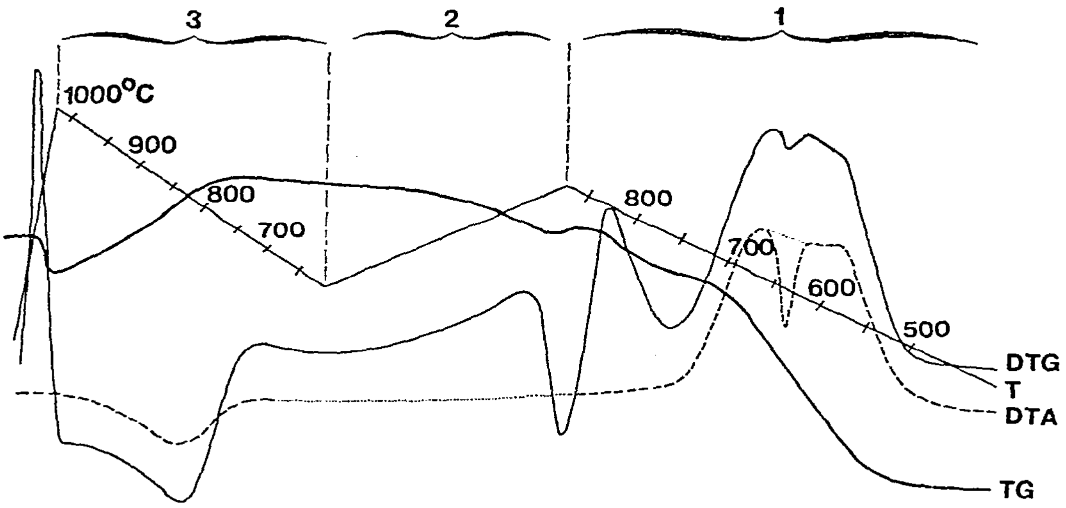

Fig. 1. Nitriding of Mn powder to 1030°C at $P_{N_2} = 1$ atm.

(3) The sample was heated at 15°C min^{-1} in the range 600–1030°C. The specimen started to give off nitrogen after reaching approximately 740°C.

At 1030°C the run was interrupted and the specimen was allowed to cool down to 25°C. Despite the rapid cooling it may be seen that a large amount of N was taken up at temperatures down to approximately 650°C. In step (1) the DTA curve shows an exothermal peak in the range 470–780°C. The weight gain in this temperature region corresponds to the formation of the ε-phase. The molar ratio of Mn was found to be 4 to 0.97–0.99.

In the range 605–665°C an endothermal peak appears to be superimposed on the exothermal one. The DTG curve indicates a decreased rate of N uptake in the temperature region of this peak. An endothermal DTA peak is obtained in step (3) between 735 and 960°C. The N content of the specimen at 960°C corresponded to approximately 20.3 at.%.

At heating rates 8–15°C min^{-1} step (1) had a similar appearance on the thermograms, the superimposed endothermal process begins at 605 ± 3°C. The amount of N taken up by the specimen in reaching this temperature varied with heating rate: 6.8, 9.9 and 11.2 at.% at 15, 10 and 8°C min^{-1}, respectively.

X-ray examination of the specimen with the N content lower than 20 at.% showed the presence of ε-phase and α-Mn. Above 20 at.% reflections due to the ζ-phase appeared.

The reaction enthalpies have been estimated with the aid of the known transition heats of K_2SO_4 and $BaCO_3$. In step (1) the DTA base line has been approximated over the region of the endothermal peak (Fig. 1). The exothermal peak is related to the reaction

$$4Mn(s) + 1/2N_2(g) \rightarrow Mn_4N(s)$$

The ΔH value is -27 ± 2 kcal mole^{-1} Mn_4N at heating rates of 8 and 10°C min^{-1}. The enthalpy value corresponding to the endothermal peak at 605°C was found to

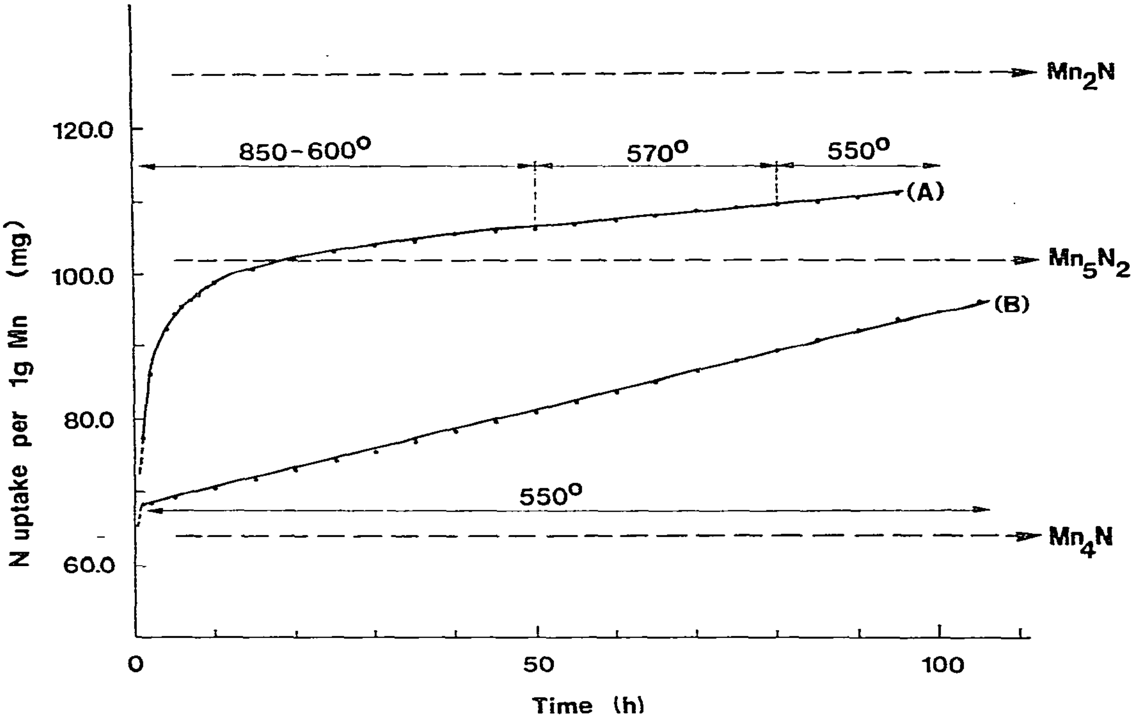

Fig. 2. Nitrogen uptake per 1 g Mn powder at (A) gradually decreased constant temperatures (750–550 °C) and (B) 550 °C.

be 0.44 ± 0.01 kcal and 0.40 ± 0.01 kcal mole^{-1} of the total amount of Mn, at 10 and 8 °C min^{-1}, respectively. In step (3) the endothermal release of N occurred in the region of the ζ-phase[7]. Only the section of the DTA peak corresponding to the weight change in the reaction $Mn_5N_2(s) \rightarrow 5/4Mn_4N(s) + 3/8N_2(g)$ was considered. The ΔH value was 7.5 ± 1.5 kcal mole^{-1} Mn_5N_2 at 15 °C min^{-1}.

Figure 2 shows the weight gain of 1 g Mn powder as a function of time in $N_2(g)$. The weight curve (A) was obtained by holding the specimen successively at the temperatures which produced the highest rates of N uptake. These temperatures are indicated in the Fig. 2. The weight curve (B) resulted when heating the Mn powder continuously at 10 °C min^{-1} to 750 °C, then cooling and holding the specimen at 550 °C. The N uptake is seen to be a linear function of time at this constant temperature. The amounts of N corresponding to the stoichiometric compositions Mn_4N, Mn_5N_2 and Mn_2N are indicated by the dotted lines. The weight curve (A) is shown to approach the ζ-phase region after approximately 20 h. This should be compared to about 130 h for the weight curve (B) at 550 °C.

Figure 3 shows the equilibrium amounts of N (in at.%) as a function of temperature at some selected P_{N_2} (750, 208 and 47 mm Hg). The compositions corresponding to Mn_4N and Mn_5N_2 are also indicated. The isobar at 750 mm Hg is shown to decrease linearly with increasing N content (at.%). The variation of the isobaric solubility of N in the ε-phase is seen to be only slight up to approximately 800 °C. Further details concerning these measurements are given elsewhere[6].

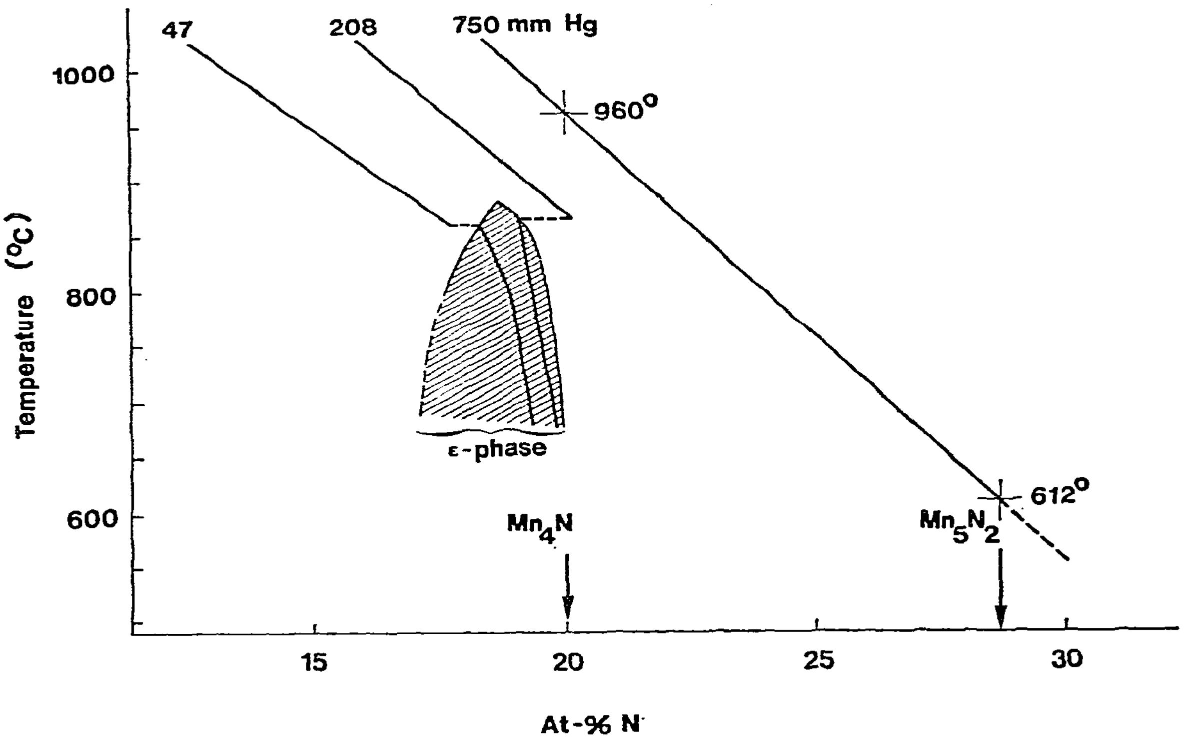

Fig. 3. Equilibrium N content (at. %) in Mn as a function of temperature at 47, 208 and 750 mm Hg N pressure.

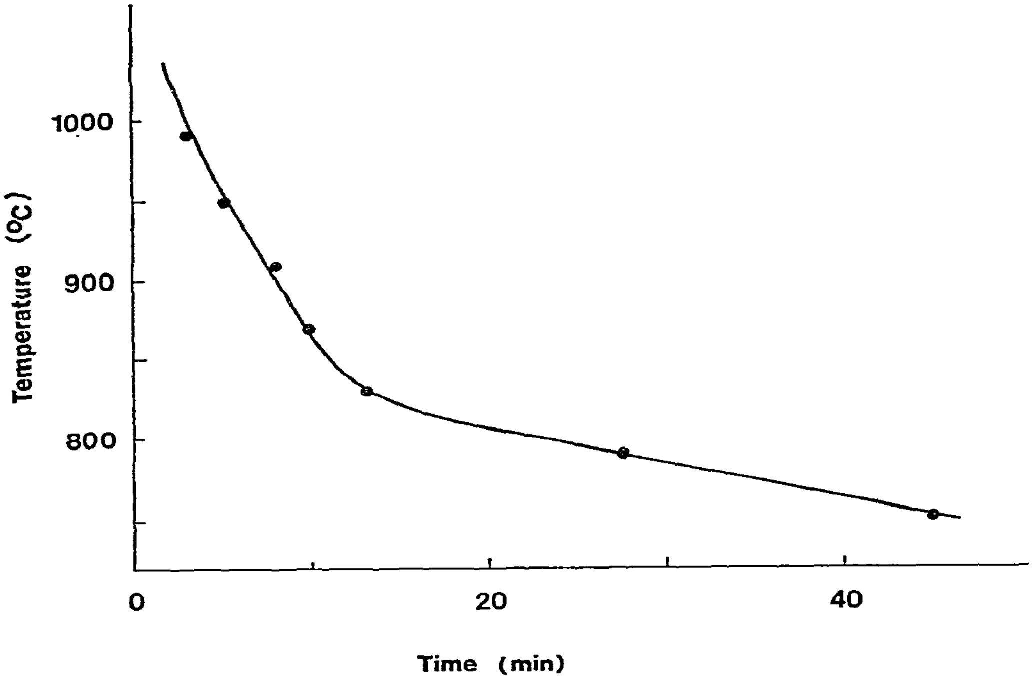

Fig. 4. Times required to attain equilibrium after increasing the temperature (15 °C min^{-1}) between two consecutive values, as a function of temperature at 750 mm Hg N pressure.

In performing these equilibration runs the times required to attain equilibrium varied, as expected, with temperature. Figure 4 shows these times observed at 750 mm Hg N pressure as a function of the equilibration temperatures. The temperature was increased by 40°C at 15°C min^{-1} between the consecutive equilibration values. Above approximately 830°C the largest part of the weight loss occurred during the increase of temperature. Below this temperature the equilibration time was considerably dependent on the equilibration temperature.

Preparation of the single nitride phases

(1) The ε- and ζ-phases of stoichiometric composition may be prepared with the aid of the isobar at 750 mm Hg N pressure (Fig. 3). As indicated the N content corresponding to Mn_4N and Mn_5N_2 is obtained by equilibration at 960 and 612°C, respectively. The specimens are then cooled rapidly below approximately 500°C in order to prevent an excessive uptake of N. This uptake may be considerable at high temperatures and small Mn grain sizes (see Fig. 1).

Extrapolation of this isobar below 600°C in the ζ-phase region suggests that Mn_2N can be obtained at 427°C. The rate of N uptake below 500°C, however, appears to be extremely low at 750 mm Hg. Several hundred hours seem to be necessary for the attainment of equilibrium for the Mn grain size used.

(2) At P_{N_2} in the range 50–200 mm Hg and equilibration temperatures lower than approximately 800°C the ε-phase may be prepared with the N content of approximately 19–20 at. % (Fig. 3).

(3) Phases with the stoichiometric compositions Mn_4N and Mn_5N_2 can, of course, be prepared in $N_2(g)$ by the TG-controlled introduction of N into Mn powder. The specimen may then be heated, e.g. for 1 h at 500°C in an inert atmosphere to remove possible N concentration gradients within the grains.

According to these methods (preferably (3)) the stoichiometric phases (Mn_4N, Mn_5N_2) have been prepared. Their X-ray patterns were in accordance with those given in the ASTM card index.

Thermal analysis in air

The specimens were oxidized preferentially at heating rates of 4–8°C min^{-1}. The appearance of the thermograms for Mn_4N and Mn_5N_2 was very similar. Figure 5 shows a typical thermogram for Mn_4N (4°C min^{-1}; 100 μV; 10 mg min^{-1}). The thermal reactions could be interpreted with the aid of X-ray analysis and thermogravimetrical calculations in the following way. The exothermal reaction appearing in the range ca. 340–750°C on this thermogram corresponds to a complete oxidation of Mn_4N according to

$$Mn_4N + 3O_2 \rightarrow 2Mn_2O_3 + 1/2N_2.$$

The endothermal reaction (ca. 900–980°C, 10°C min^{-1}) is that of the decomposition of Mn_2O_3 to Mn_3O_4. As indicated, Mn_3O_4 can be re-oxidized (ca. 2 h at 750°C) and the decomposition can be reproduced. The temperature of departure of the DTA

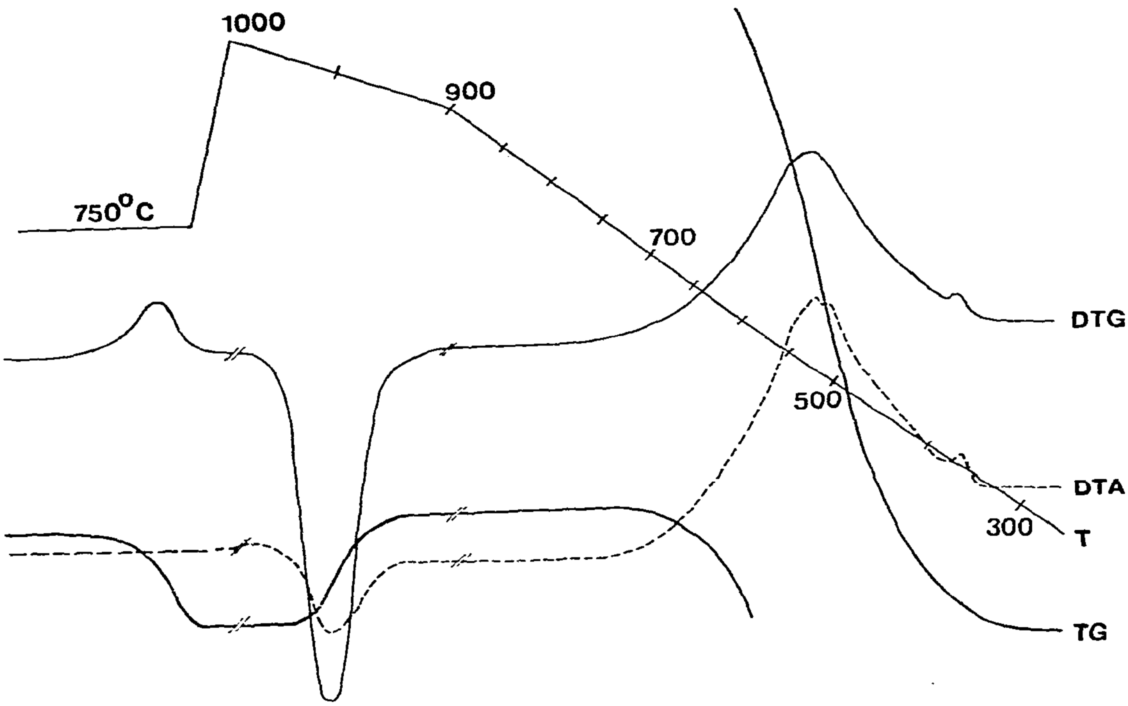

Fig. 5. Oxidation of Mn_4N in air up to 1000 °C at 4 °C min^{-1}.

curve from the base line for the oxidation reaction was found to be 325 ± 5 °C (6–8 °C min^{-1}) and 340 ± 5 °C (4 °C min^{-1}) for Mn_4N and 340 ± 5 °C (6–8 °C min^{-1}) for Mn_5N_2. As expected, it was somewhat higher at a lower heating rate (Mn_4N). The temperature of maximum reaction rate, as indicated by the DTG curve, appeared to coincide with that of the DTA curve for this reaction. The values of this temperature were essentially independent of the heating rates employed. They corresponded to 517 ± 3 °C and 525 ± 5 °C for Mn_4N and Mn_5N_2, respectively. The reaction enthalpies were preferably estimated using the corrected value[16] of the decomposition enthalpy of Mn_2O_3 to Mn_3O_4. As indicated in Fig. 5, these decompositions could be reproduced to obtain a statistically satisfying calibration value. The enthalpies of oxidation to Mn_2O_3 were found to be −403 ± 15 kcal mole^{-1} Mn_4N and −489 ± 15 kcal mole^{-1} Mn_5N_2.

Thermal analysis in argon

Initiation of decomposition of Mn_4N and Mn_5N_2 was observed at ca. 600 °C. The reaction then started quantitatively (DTG base line departure) at 650–660 °C. On further heating the decomposition process differed between Mn_4N and Mn_5N_2. Figure 6 shows a thermogram obtained for Mn_5N_2 at 10 °C min^{-1}. An endothermal DTA peak may be seen between 658–963 °C. The N content of the specimen decreases from 28.6 (Mn_5N_2) to 15.8 at.% in this temperature range.

In evaluating the enthalpy change from this peak the partial DTA area, which according to the TG-change corresponded to the reaction of ζ to ε

$$Mn_5N_2(s) \rightarrow 5/4\ Mn_4N(s) + 3/8\ N_2(g)$$

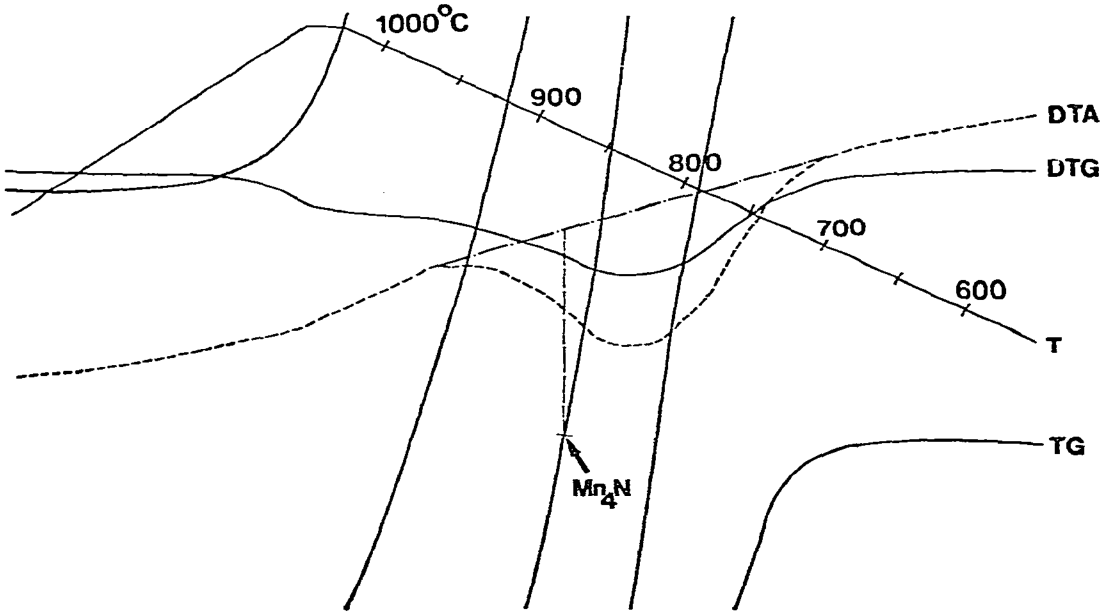

Fig. 6. Decomposition of Mn_5N_2 in argon up to 1000°C at 10°C min^{-1}.

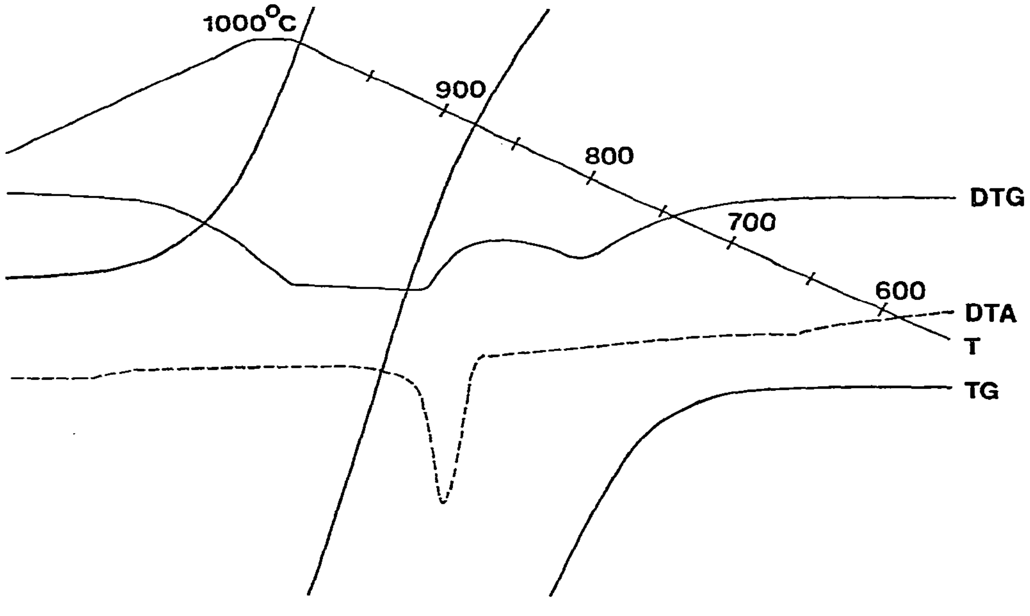

Fig. 7. Decomposition of Mn_4N in argon up to 1000°C at 10°C min^{-1}.

was considered. Using K_2SO_4 as the reference substance this value was found to be 8.0 ± 1.5 kcal mole^{-1} Mn_5N_2. A thermogram obtained for Mn_4N at 10°C min^{-1} is shown in Fig. 7. Unlike the Mn_5N_2 decomposition, no marked response from DTA appeared when the reaction rate (DTG) started increasing. Only an endothermal deflection of the DTA base line was observed while the DTG response displayed a local maximum at 810°C. However, at 872°C a sharp endothermal DTA peak ap-

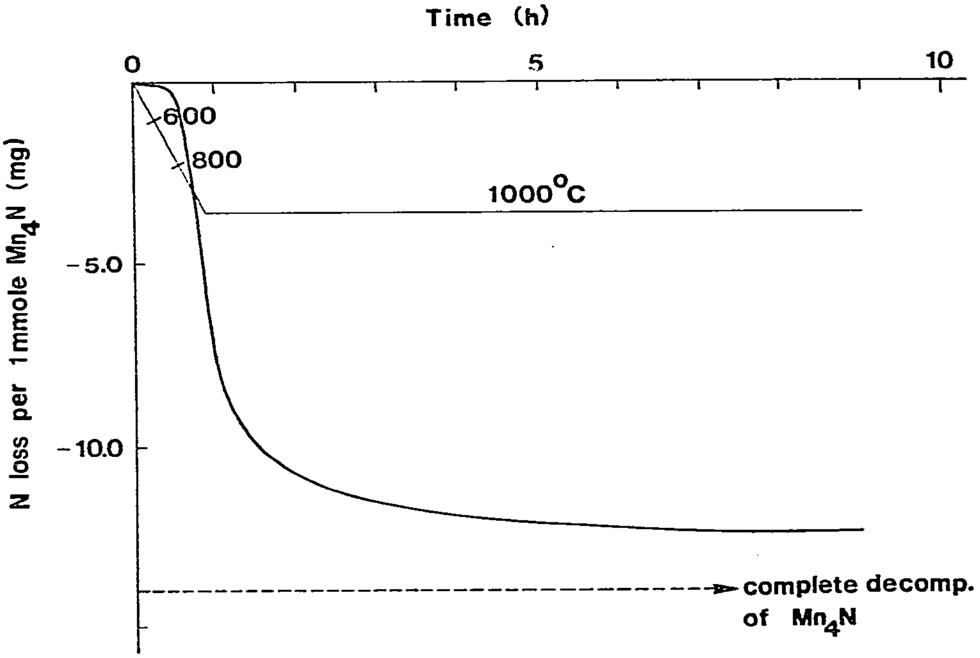

Fig. 8. Nitrogen loss per 1 mmole Mn_4N as a function of time up to 1000°C (10°C min^{-1}) and at 1000°C.

peared. During this response the reaction rate increased to about twice the maximal value at 810°C. It was then nearly constant up to 1000°C. As the decomposition kinetics varied slightly in different runs the initiation of this DTA peak varied in the range 870–880°C.

Figure 8 shows the weight loss per 1 mmole Mn_4N vs. time plot when Mn_4N was decomposed at 1000°C. The heating rate up to 1000°C was 10°C min^{-1}. The dotted line indicates the weight loss corresponding to the complete decomposition of Mn_4N to Mn(s) and N_2(g). It follows from Fig. 8 that the weight loss curve virtually stabilized after approximately 8 h. It then converged towards a definite, rather than zero, N content. After heating for approximately 10 h at 1000°C the N content was 2.5 at.%.

DISCUSSION

The formation of interstitial solutions or compounds such as the ε- or ζ-phase involves diffusion of N atoms or ions through the Mn particles. The mobility of N within the Mn metal can be expected to be low in the initial stages of nitridation (450–650°C). This will result in the establishment of a N concentration gradient. The phases present at a certain temperature may then be all of those which are stable at this temperature and $P_{N_2} = 1$ atm, as schematically outlined in Fig. 9 ($T > 600$°C).

The phase studies collected in the diagrams[1, 2] suggest that, initially, the N solution in α-Mn and an increasing amount of the ε-phase are mainly present in the specimen below 605°C. The endothermal DTA response at 605 ± 3°C then seems

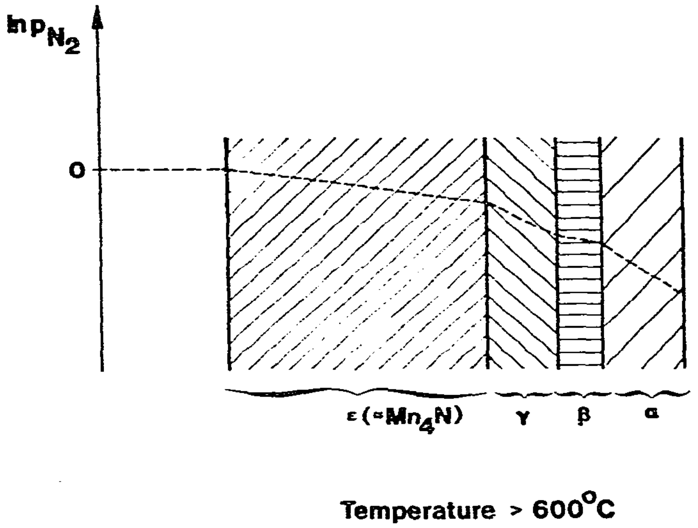

Fig. 9. Schematic profile of a Mn particle showing the phases which may be stable within certain regions of N pressures when nitriding at P_{N_2} = 1 atm and the temperature above 600°C.

to indicate the phase transition of α-Mn. This transition temperature can be reproducibly obtained. At different heating rates the DTA response is observed at total N contents in the range 6.8/11.2 at.% (corresponding to ca. 40–70 mole % α-Mn). These responses thus seem to define the phase boundary line for α-Mn.

As suggested[2, 4], this transition should be that of α-Mn to β-Mn. This is in accordance with ref. 2 where the boundary is placed at 600°C. The ε- and β-phases, however, have been shown[2] to coexist within a small temperature region (ca. 25°C). The β-phase is then expected[1, 3, 5, 7] to transform to the γ-phase. At the high heating rates used a large part of the transitions α → β → γ may occur simultaneously. This is suggested by the estimated transition enthalpies. The enthalpy for α → β extrapolated[17] to 605°C is 0.50 kcal mole^{-1}. The value obtained for extrapolation at the heating rate of 10°C min^{-1} is 0.44 kcal. However, the amount of α-Mn at this temperature and heating rate is less than 50 mole %. The ΔH value is therefore almost twice as large as that expected. This indicates that still another transition (β → γ) will be involved.

After completion of these transitions the formation of the ε-phase will occur between γ-Mn and N_2(g). The uptake of N_2(g) by the specimen with the N content above that corresponding to the ε-phase is, of course, dependent on the heating rate. The uptake is interrupted when the equilibrium temperature for a given N content (Fig. 3) is reached in the surface region of the specimen.

In decomposing Mn_5N_2 in Ar(g), the process occurs smoothly while a sharp increase in decomposition rate is observed for Mn_4N at 870–880°C. Consideration of this part of the equilibrium Mn–N diagram[7] (see also Fig. 3) clearly suggests that the ε-phase becomes unstable at these observed temperatures and the observed total N contents in the samples. Because of the high mobility of N within Mn metal at these temperatures (see Fig. 4) the N content at a given temperature may be close to that at equilibrium.

A complete removal of N from Mn does not seem to be possible in Ar(g) at 1000 °C (Fig. 8). This is in accordance with a similar observation in H_2(g) at 1200 °C[18]. Some nitrogen may tend to remain in solution, stabilizing the metal structure at this temperature.

The reaction enthalpies of Mn_4N and Mn_5N_2 obtained from the DTA peak areas should be comparable with the reported values after making the necessary corrections for their variation with temperature. The standard values for Mn_4N and Mn_5N_2 (25 °C) determined from their enthalpies of oxidation to Mn_3O_4 (bomb calorimetry)[12, 19] are -30.3 ± 0.4 and -48.2 ± 0.6 kcal mole^{-1}. A more recent work[20] yields -30.75 and -48.8 kcal mole^{-1} at 25 °C. The temperature variations of these enthalpies are given[19, 21] for the temperatures up to 1500 K (Mn_4N) and 800 K (Mn_5N_2). A plot of these enthalpies vs. temperature suggests a moderate and nearly linear decrease for Mn_4N (-29.75 kcal at 900 K)[19]. According to ref. 21 the enthalpy decreases more rapidly (-27.95 kcal at 800 K). The expected ΔH values are calculated[16] using the TG curve in Fig. 1 for the reaction

$$4\alpha\text{-Mn(s)} + 1/2\ N_2(g) = Mn_4N(s)$$

In the observed range 470–780 °C they are -29.8[19] and -27.5[21] kcal mole^{-1} Mn_4N. The experimental enthalpy should be expected to be larger than these values by approximately 2 kcal. In the run shown in Fig. 1 (10 °C min^{-1}) approximately 50% of the reaction occurred with the higher Mn-phases (β, γ)[22]. The heat released during this reaction was probably given off mainly into the surroundings. However, a part of it would have been consumed in heating up the specimen. It may be roughly assumed that the molar heat capacity $C_p \approx 3$ R and 4.5 moles react on average. For the reaction range 470–780 °C the heat absorbed is then as large as 8.3 kcal mole^{-1} Mn_4N or approximately 30% of the total reaction enthalpy. The experimental enthalpy obtained from DTA (-27 ± 2 kcal) is lower by 2–4 kcal than the expected one. A partial adsorption of heat by the specimen may thus be responsible for this difference.

For the decomposition of Mn_5N_2 no expected ΔH values are calculated. Above approximately 600 K the enthalpy of formation of Mn_5N_2 is found to decrease in a non-linear manner[21]. The necessary extrapolation above 800 K is thus very unreliable. The decomposition enthalpies obtained from DTA may be comparable with that of the decomposition of the stoichiometric ζ to ε ($Mn_5N_2(s) \rightarrow 5/4Mn_4N(s) + 3/8N_2(g)$). The enthalpy value for this reaction is 10.3 kcal at 25 °C[12]. The experimental enthalpies for the decomposition in Ar(g) (8.0 ± 1.4 kcal) and N_2(g) (7.5 ± 2.5 kcal) are mutually in good agreement and they are in the same order of magnitude as the above ΔH value.

The expected ΔH values for the oxidation of the nitrides to Mn_2O_3 were calculated[16] using the TG curves of the runs at 6 °C min^{-1} from the data[17, 19, 21]. Comparison of these values, -401 kcal mole^{-1} Mn_4N and -491 kcal mole^{-1}

Mn_5N_2, shows good agreement with the experimental ones (−403 ± 15 and −489 ± 15 kcal mole^{-1}). The enthalpies of formation of the nitrides comprise less than 10% of these enthalpies. The DTA evaluation from the oxidation enthalpies seems therefore to only allow a very rough estimation of the enthalpies of formation for Mn_4N and Mn_5N_2.

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