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PREPARATION AND TG–DTA ANALYSIS OF MANGANESE SILICON NITRIDE

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ABSTRACT

Manganese silicon nitride was prepared quantitatively as a precipitated phase by treating a Mn; Si-alloy (Mn: 1.84 w/o, Si: 1.12 w/o) in a mixture of 2% NH_3 and H_2 at 700°C. Nitriding was carried out in situ in a thermobalance and the nitrogen uptake was recorded as a function of time. The nitride phase was isolated and investigated by means of the combined TG–DTG–DTA technique both in an atmosphere of nitrogen at 25–1600°C and in a mixture of $Ar+O_2$ ($p_{O_2} = 0.20$ atm) at 25–1000°C. In the nitrogen atmosphere $MnSiN_2$ appears to be stable up to 1000°C. Oxidising the nitride in the Ar/O_2 mixture caused three distinct exothermic processes to occur at characteristic temperatures. The final oxidation products as identified by diffractometry and IR-spectroscopy are manganese oxide silicate (braunite) and silicon dioxide.

INTRODUCTION

In studying the precipitated nitride phases in Mn,Si-steels Arrowsmith[1] detected a new phase which was subsequently identified[2,3] as a manganese silicon nitride having the formula $MnSiN_2$. This phase could also be precipitated by treatment of the manganese silicon alloys in various H_2–NH_3 mixtures in the temperature range 400–800°C[4,5]. Studies of the phase isolated from the iron matrix revealed that three structural types of this nitride could occur. The type of nitride formed was shown to be a function of the Mn:Si ratio, the nitriding temperature and presumably also the oxygen potential in the alloy.

The aim of the present work was to prepare the ternary nitride, $MnSiN_2$, quantitatively by nitriding a manganese silicon alloy using a novel thermogravimetric technique. Another aim was to employ the TG–DTG–DTA technique together with other methods in order to determine thermochemical properties of the nitride for identification purposes.

The nitride is known to improve some physical properties of commercial steels and knowledge of the properties of this phase, therefore, is of considerable importance.

EXPERIMENTAL

Preparation of the nitride phase

Samples of two manganese silicon alloys of the compositions, listed in Table 1, were placed in the furnace of the microthermobalance (Mettler). The nitrogen dissolved in the alloys was removed by heating the specimens to 850°C in a hydrogen atmosphere. Nitriding was then carried out in a mixture of 2% NH_3 in H_2 at 700°C. The weight change of the samples was recorded continuously and the stabilized TG curve was taken as an indication of the finished absorption of nitrogen. Full details of this preparation will be published elsewhere[6].

TABLE 1

CONTENTS OF Si, Mn AND N IN ALLOYS C AND D BEFORE NITRIDING, AND TOTAL CONTENT OF N AND O AFTER NITRIDING, IN WEIGHT-%

Sample	*Si*	*Mn*	*N*	N_{tot}	O_{tot}
C	0.42	1.20	0.0120	0.20	0.073
D	1.12	1.84	0.0086	1.02	0.086

The nitride phase was isolated by dissolving the iron matrix according to the method of Beeghly[7] modified by Svedung[8]. Atom absorption photometry (AAP) and X-ray diffractometry were employed in the analysis.

Analysis of the nitride phase

In order to study the thermochemical properties, the samples were heated in a nitrogen atmosphere in the temperature range 25–1400°C and in a mixture of Ar and O_2 ($p_{O_2} = 0.20$ atm) from 25–1000°C.

The TG, DTG and DTA curves were recorded simultaneously as a function of time and temperature. The operational and instrumental parameters used were as follows: Weight of the samples: 5–10 mg; S platinum crucibles; reference substance: Al_2O_3 (SiO_2 and K_2SO_4 in evaluating ΔH); TG–DTG–DTA sensitivity: $5 \cdot 10^{-5}$ g–5 mg/min–100 μV; Pt–Rh thermocouples; temperature control: ±1.5°C; heating rate: 10°C min^{-1}; gas atmospheres: Ar(SR)+O_2, N_2(SR); gas flow-rate: appr. 5 l h^{-1}.

The materials were initially studied over the whole temperature range. Systematic runs were then made at constant temperatures corresponding to the appearing DTA peaks and at other selected temperatures. The heating rate up to a particular constant temperature was 10°C min^{-1}. Each run was terminated when the DTG curve stabilized. The heating of the furnace was interrupted and the samples were allowed to cool in the furnace atmosphere as quickly as possible.

An additional TG–DTA analysis was made, at $p_{O_2} = 0.20$ atm and in the temperature range 25–1100°C, of the oxidation products obtained after heating to constant weight at 1000 °C. The products were examined by X-ray diffractometry and IR-spectrophotometry. Calculations were made on the basis of weight change or peak areas of the DTA curves.

RESULTS

Preparation of the nitride phase

The essential features of the thermograms obtained are shown in Fig. 1. The nitrogen and oxygen content of the samples as determined by AAP are given in weight-% in Table 1. The weight gain of the alloys was in agreement with the total amount of O and N as determined by the above analysis. The total weight gain with respect to Si and Mn in the alloy D minus the amount of oxygen taken up corresponded to the molar ratio Si,Mn:N = 1:2. Nitriding of alloy D thus resulted in a complete precipitation of the ternary nitride. The analysis by AAP showed the molar ratio in the isolated phase Mn:Si:N to be 1:1:2. The X-ray pattern of the phase was consistent with that of pure orthorhombic $MnSiN_2$.

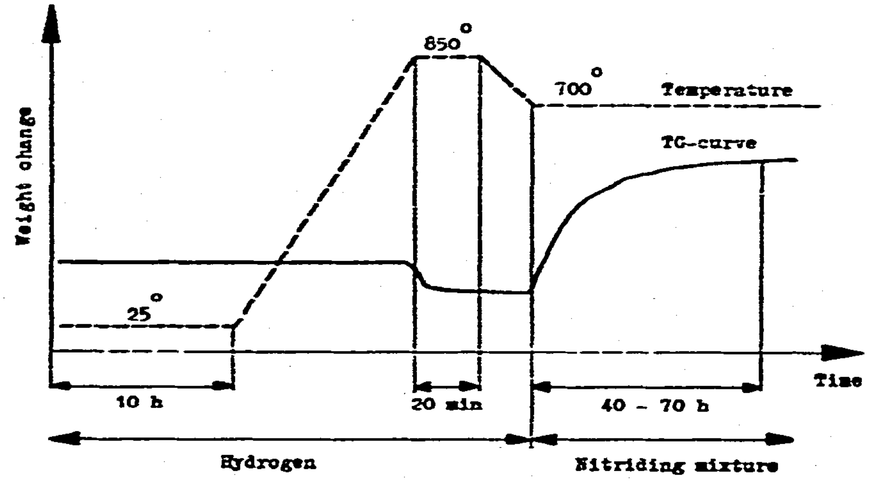

Fig. 1. Diagrammatic appearance of the thermograms after nitriding.

Analysis of the nitride phase

In the nitrogen atmosphere, the nitride appeared stable up to about 1000 °C, above this temperature the material exhibited irreproducible weight changes. This was probably due to an uncontrolable diffusion of O_2 into the furnace. X-ray patterns of the products below 1000 °C were essentially those of orthorhombic $MnSiN_2$. Above 1000 °C, besides the nitride, various structural forms of $MnSiO_3$ or $MnO \cdot 3Mn_2O_3 \cdot SiO_2$ (braunite) and SiO_2 were identified.

On oxidizing the nitride at $p_{O_2} = 0.20$ atm up to 1000 °C and at the heating rate of 10 °C min^{-1} the thermograms obtained are shown diagramatically in Fig. 2.

Exothermic peaks on the DTA curve appeared at the indicated temperatures. At a heating rate lower than 4°C min^{-1}, however, the exothermic response marked in the figure at 895°C was barely discernible and the weight derivative (DTG) did not exhibit any change.

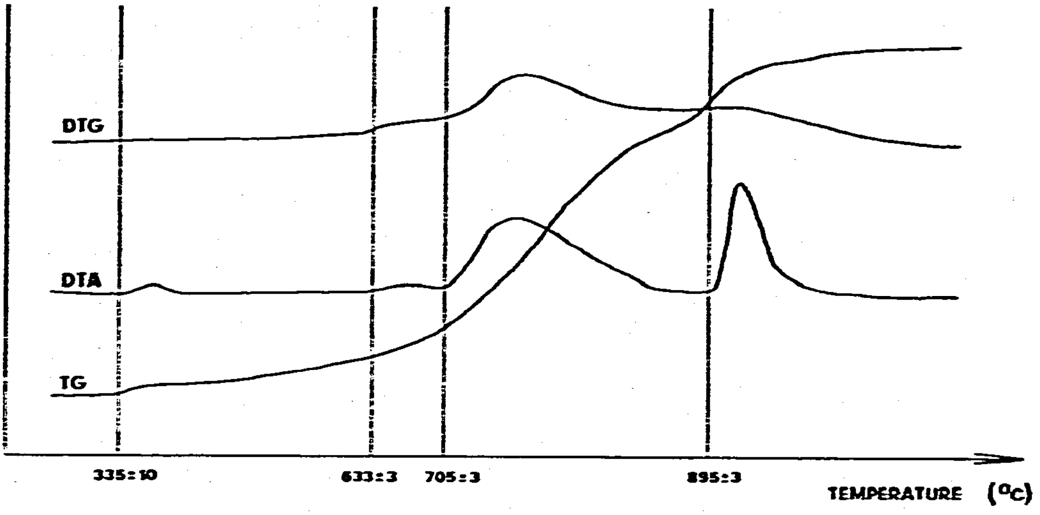

Fig. 2. Appearance of the thermograms after heating the isolated phase to 1000°C at $p_{O_2} = 0.20$ atm and a heating rate of 10°C min^{-1}.

In the systematic runs the DTG curves stabilized within two hours of operation at the constant temperatures. The weight of the samples was then either stable or increased only slightly. The data characteristic of these runs and the products identified by X-ray diffractometry are given in Table 2. $MnSiN_2$ was the only phase identified by X-ray diffraction in the run at 410°C although the colour of the sample was reminiscent of braunite.

TABLE 2

WEIGHT GAIN AND X-RAY DETERMINED PRODUCTS OF THE NITRIDE $MnSiN_2$ OXIDIZED AT $p_{O_2} = 0.20$ atm AND VARIOUS CONSTANT TEMPERATURES

Temp. (°C)	*Weight gain (%)*	*Products*
410	0.3	$MnSiN_2$
700	6.5	$MnSiN_2$, braunite
860	12.5	braunite, some $MnSiN_2$
1000	22.5	braunite

The progressive oxidation of the nitride could also be followed from the IR-spectra of the products. Fig. 2 shows spectra of the isolated nitride and of the products obtained in the tabulated runs.

The thermal study of the products after heating at 1000°C showed that they were subject to a minute weight loss (ca. 0.1% of the sample weight) at 880°C. This weight loss could be reproduced after reheating the sample at 700°C and $p_{O_2} = 0.20$ atm for some hours.

The heat released in the partial oxidation processes at 705°C and 895°C was estimated from the peak area of the DTA curves for reference purposes. Using the reference values of 0.152 kcal mol^{-1} for SiO_2 or 2.14 kcal mol^{-1} for K_2SO_4 the enthalpies were found to be about 24 kcal mol^{-1} $MnSiN_2$ at 705°C and 12 kcal mol^{-1} $MnSiN_2$ at 895°C.

DISCUSSION AND CONCLUSIONS

$MnSiN_2$ could be quantitatively prepared by nitriding the alloy D using the thermogravimetric technique. Furthermore, it was possible to follow the nitriding process as a function of time, thus providing an opportunity to determine the amount of nitrogen which can be taken up by a given alloy at any particular temperature.

As follows from the thermogram in Fig. 2, oxidation seems to be initiated at a temperature of 335°C where the first small exothermic peak appears and the weight begins to increase. The colour of the sample in the run at 410°C suggests that initially, the grains of $MnSiN_2$ are superficially oxidized. A thin layer containing braunite and SiO_2 is presumed to be formed and the oxidation rate is then determined by the diffusion through this outer layer. The total oxidation process may be expressed by a summary formula

$$7MnSiN_2 + 12O_2 \rightarrow MnO \cdot 3Mn_2O_3 \cdot SiO_2 + 6SiO_2 + 7N_2$$

where the total weight gain (24.2%) corresponds almost entirely to the formation of SiO_2.

A very weak exothermic response is obtained reproducibly at 633°C but the major exothermic DTA peak does not appear until 705°C. Its maximum coincides with that of the DTG curve. The prolonged shape of this DTA peak and the change of the weight derivative indicate that the previously formed layer of the oxidation product has become non-protective at this temperature. The oxidation then proceeds rapidly until a new layer is formed on the grains.

The thermal study of the products indicates that braunite can release and reincorporate a small amount of oxygen. The release of oxygen begins close to 880°C. This, together with the high heating rate used, may initiate the rapid final oxidation as indicated by the comparatively narrow DTA peak appearing at 895°C.

The silicon dioxide formed is probably amorphous since no characteristic reflections are observed in X-ray analysis. In the IR-spectra (Fig. 3) SiO_2 may be identified by its stretching frequency (1095 cm^{-1}). The spectrum of pure $MnSiN_2$ indicates that some SiO_2 is already present in the isolated phase. The variation in the relative content of SiO_2, as well as the conversion of $MnSiN_2$ to braunite may then be conveniently followed in the spectra of reaction products obtained in the isothermal runs.

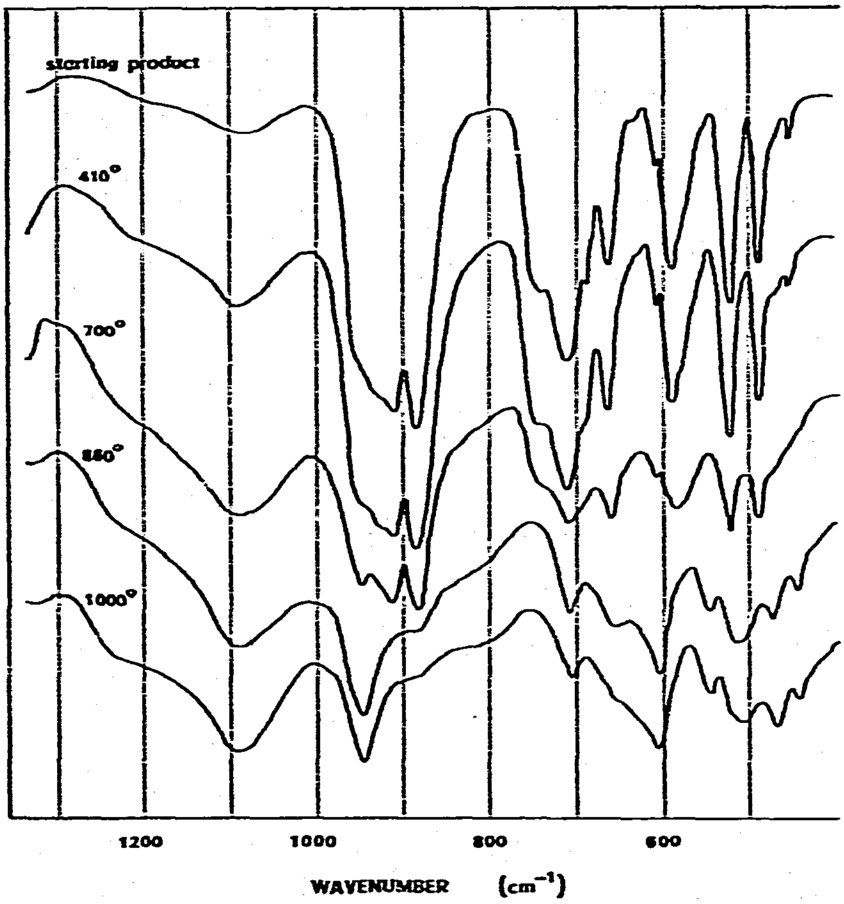

Fig. 3. IR spectra of the isolated phase and of products at various constant temperatures.

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REFERENCES

1 J. M. Arrowsmith, *JISI*, 201 (1963) 699.
2 T. N. Baker, *JISI*, 205 (1967) 315.
3 T. Okada, T. Nakayama, Y. Sakamoto and E. Miyoshi, *Proc, ICSTIS*, 11 (1971) 1144.
4 W. Roberts, P. Grieveson and K. H. Jack, *JISI*, 210 (1972) 931.
5 B. Jonsson-Holmqvist, P. Grieveson and K. H. Jack, *Scand. J. Met.*, 2 (1973) 35.
6 R. Pompe, *Proc. Nortemps 75*, Vol. 1, pp. 177–187.
7 H. F. BEEGHLY, *Anal. Chem.*, 21 (1949) 1513.
8 D. Svedung, Jernkontorskommitté, JK 491/73 (1974).