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MATERIALS NOTE 128

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by

T. MILLS

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NITRIDING OF CHROMIUM IN NITROGEN GAS AT HIGH TEMPERATURE

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SUMMARY

Parabolic rate constants of the reaction of chromium with nitrogen gas under oxygen-free conditions have been determined over a range of temperature (1000–1250°C) and nitrogen pressure (0·265–101·33 kPa). The growth rate of the subnitride was measured by a thermogravimetric technique using a single specimen. Wagner's oxidation theory is used to calculate the self-diffusivity and intrinsic diffusivity of nitrogen in the subnitride from a theoretical analysis of the parabolic rate constant. The calculated diffusivities varied with the composition of the subnitride, having minimum values at intermediate compositions of the non-stoichiometric chromium nitride Cr_2N.

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16. *ABSTRACT*

Parabolic rate constants of the reaction of chromium with nitrogen gas under oxygen-free conditions have been determined over a range of temperature (1000–1250°C) and nitrogen pressure (0·265–101·33 kPa). The growth rate of the subnitride was measured by a thermogravimetric technique using a single specimen. Wagner's oxidation theory is used to calculate the self-diffusivity and intrinsic diffusivity of nitrogen in the subnitride from a theoretical analysis of the parabolic rate constant. The calculated diffusivities varied with the composition of the subnitride, having minimum values at intermediate compositions of the non-stoichiometric chromium nitride "Cr_2N".

CONTENTS

Page No.

1. INTRODUCTION 1

2. EXPERIMENTAL 1

3. RESULTS 1

4. DISCUSSION 2

5. CONCLUSIONS 3

TABLE

REFERENCES

FIGURES 1-6

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A

1. INTRODUCTION

The mechanical properties of chromium and chromium-base alloys are adversely affected by their reaction with nitrogen at high temperatures and a knowledge of nitriding kinetics is expected to be helpful in the development of chromium-base alloys for gas turbine applications. Although the rate of nitriding of chromium has been studied by several investigators,[1-4] the data are very limited: only Schwerdtfeger[4] studied the effect of nitrogen pressure and his study was restricted to two temperatures, 1100 and 1200°C. The subnitride 'Cr_2N' film formed on chromium is uniform in thickness, dense and adherent, and its formation follows parabolic kinetics. It has been clearly established[1,3,4] that the growth of the film occurs by the diffusion of nitrogen through the nitride film.

The present work was undertaken to study the kinetics of the growth of chromium subnitride on chromium in nitrogen gas over the temperature range 1000–1250°C as a function of nitrogen pressure, and to analyse the kinetic data using the detailed equilibrium measurements on the Cr–N system previously reported by the present author.[5,6]

2. EXPERIMENTAL

A gravimetric technique was used to determine the rate of nitriding. The thermobalance was a Cahn automatic recording R.G. Electrobalance and the apparatus for temperature control, pressure control and nitrogen purification has been described in detail elsewhere.[5] The important feature of the system is the use of a 150 mm tube of nitrided titanium at the bottom of the alumina reaction tube. The specimen was suspended in the centre of this tube, which eliminated the possibility of oxidation of the specimen by residual oxygen and water vapour in the apparatus.

Only one specimen, with dimensions 8 × 8 × 2·4 mm, was used in the experiments. It was prepared from rolled strip of high-purity electrolytic chromium by polishing with abrasive papers under kerosene down to 4/0, then washing (in turn) in petroleum ether, alcohol and acetone. The specimen was de-oxidized in the apparatus in hydrogen at 1200°C for 3 hours prior to the nitriding studies. Before each test, the specimen was equilibrated at the test temperature in nitrogen at a pressure just below the dissociation pressure of "Cr_2N". The pressure was then raised to the value selected for the test. At the end of a test, the pressure was reduced so that the "Cr_2N" dissociated and the chromium specimen was regenerated for the next test. With this procedure, the measurements were made in a very short time and the uncertainties associated with the use of separate specimens for each test were eliminated.

3. RESULTS

It was found, in agreement with the results of other workers, that the nitriding of chromium follows the parabolic law

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t \qquad (1)$$

where ΔW = weight change during nitriding, A = surface area of the specimen, k_p = parabolic rate constant, and t = reaction time. Figures 1 and 2 show typical results in accordance with this law. Dependence of k_p (Table 1) on nitrogen pressure and temperature is shown in Figure 3 where k_p is plotted against $\log p_{N_2}$. For clarity and compactness, the values of k_p are scaled by a factor B and displaced by a constant C (shown on figure). The relation between k_p and $\log p_{N_2}$ is best represented by a sigmoidal-shaped curve. The inflection is more evident at the lower temperatures, where, with nitrogen pressures restricted to 1 atmosphere, it was possible to study the reaction with compositions at the subnitride nitrogen interface close to the upper limiting composition of "Cr_2N". Above 1100 C, much higher pressures are required to study the same composition range e.g. at 1250 C, the "Cr_2N"/CrN equilibrium pressure is about 1160 kPa[5].

Schwerdtfeger's[1] results are also plotted in Figure 3. At 1200 C, at the high pressure end, his values for k'' are lower than the present results. At 1100 C, Schwerdtfeger ignored one value of k'' and his curve showed no inflection. If equal weight is attached to each point, agreement with the present work at 1100 C is very good and a sigmoidal-shaped curve is obtained.

4. DISCUSSION

Wagner[7] derived an expression relating the parabolic rate constant and the diffusion coefficients of the anions and cations in the scale formed on a metal through reaction with a gas. In the case of "Cr_2N", where nitrogen is the diffusing species, Wagner's equation gives the following relation between k'' and the self-diffusivity of nitrogen D_N^*.

$$k'' = \int_{a_{N_i}}^{a_{N_s}} 2c^2 D_N^* \, d\ln a_N \qquad (2)$$

where k'' is in [(g nitrogen)^2 m^{-4} min^{-1}], c is the concentration of nitrogen in (g nitrogen m^{-3}), D_N^* is in (m^2 min^{-1}), and a_N is the nitrogen activity with the indices s and i referring to the subnitride-gas and subnitride-chromium interfaces respectively. Differentiating Equation (2) and setting $a_N = p_{N_2}^{1/2}$ gives:

$$D_N^* = \frac{1}{c^2\, 2{\cdot}303} \, \frac{dk''}{d\log p_{N_2}} \qquad (3)$$

A simplifying assumption involved in the derivation of Equations (2) and (3) is that the concentration c is essentially constant and that the unidirectional diffusional flux at a given time is the same in all planes throughout the tarnish layer; this is a reasonable assumption for phases of narrow composition range.

For "Cr_2N", which has a relatively wide composition range, Schwerdtfeger[1] derived the following modification of Wagner's equation, based on the assumption that the nitrogen concentration profile across the subnitride is linear.

$$k''\left(\frac{4c_i - 2c_s}{3(c_i - c_s)^2}\right) = \int_{a_{N_i}}^{a_{N_s}} c\, D_N^* \, d\ln a_N \qquad (4)$$

where c_s and c_i are the nitrogen concentrations at the subnitride-gas and subnitride-chromium interfaces, respectively. Differentiating Equation (4) and setting $a_N = p_{N_2}^{1/2}$ gives

$$D_N^* = \frac{4}{3 \cdot 2{\cdot}303\, c_s (c_i - c_s)^2} \left[(2c_i - c_s) \frac{dk''}{d\log p_{N_2}} \; [illegible] \; \frac{k''}{d\log p_{N_2}} \right] \qquad (5)$$

Schwerdtfeger's[1] data for the concentration of nitrogen in the subnitride c and the composition x in Cr_2N_x, fit the linear relation

$$c = (684x - 92) \, 10^3 \qquad (6)$$

Equation (5) may be modified using $dc/dx = 684 \cdot 10^3$ to give

$$D_N^* = \frac{1}{1{\cdot}727\, c_s (c_i - c_s)^2} \left[(2c_i - c_s) \frac{dk''}{d\log p_{N_2}} \; 684 \cdot 10^3 \; [illegible] \right] \qquad (7)$$

Values of c_i, c_s and $dx/d\log p_{N_2}$ were calculated from the present [illegible] pressure data (Ref. 6, Fig. 1); k'' and $dk''/d\log p_{N_2}$ were obtained from Figure [illegible] of the curves were calculated using a five-point formula for the first derivative of an experimental function (Lanczos[8]).

If diffusion in chromium subnitride is accomplished essentially by random motion of nitrogen vacancies, the self-diffusivity should be proportional to the ratio of the number of vacant nitrogen sites to the number of occupied nitrogen sites $(n_N \quad n_N)$ $(1 \quad)$. Values of D_N^* calculated using Equation (7)† are plotted as a function of $n_N \quad n_N$ in Figures 4 and 5. The proposed linear relationship was not obtained. Instead the curves passed through a minimum which suggests that the intrinsic diffusivity D_N of nitrogen varies with the composition of the subnitride.

The diffusivity D_N can be related to the self-diffusivity D_N^* by the equation

$$D_N^* \quad 2\,D_N \frac{d \ln c}{d \ln p_{N_2}} \tag{8}$$

which may be re-arranged to give

$$D_N^* \quad \frac{2\,D_N}{2{\cdot}303\,c} \cdot \frac{dc}{dx} \cdot \frac{dx}{d \log p_{N_2}} \tag{9}$$

Values of D_N calculated using Equation (9) are plotted as a function of composition in Figure 6. The intrinsic diffusivity of nitrogen is shown to depend on composition, increasing towards both the lower and upper limits of the composition range of the subnitride, the minimum shifts to lower nitrogen contents with increasing temperature.

D_N^* was calculated using Equation (9) and constant values for D_N. The results for the temperatures 1100 and 1250 C are plotted in Figures 4 and 5. The values of D_N used were the minimum values for the curves in Figure 6 and it is seen that the equilibrium data (Ref. 6, Fig. 1) give a linear relation between D_N^* and $n_N \quad n_N$ if D_N is independent of composition; however, the curves do not pass through the origin.

It was not possible to calculate meaningful values of activation energies from the data due to the large variations of c_i and the dissociation pressure of the subnitride with temperature, and the complex dependence of the diffusivity on composition and temperature.

Schwerdtfeger[1] measured the intrinsic diffusivity of nitrogen in chromium subnitride at 1200 C and concluded that it was essentially independent of composition. The variations in diffusivity values calculated from the kinetic data are large enough to be readily measured experimentally. A study of the diffusivity of nitrogen in chromium subnitride will be undertaken to assess the validity of the calculations of diffusivities in the present work.

5. CONCLUSIONS

A new technique with a single specimen has been used successfully to determine the kinetics of the reaction of nitrogen with chromium over a wide range of temperature and nitrogen pressure.

Nitrogen diffusivities in chromium subnitride calculated using Wagner's oxidation theory indicate that the diffusivity varies with composition, passing through a minimum value at intermediate compositions. The composition having the minimum diffusivity varies with temperature

† Equation (7) reduces to Equation (3) on putting $c_i \quad c$ and neglecting the second term in the brackets; this second term was found to be 10% or less of the first term, and putting $c_i \quad c$ increased the first term by a corresponding amount, so that values of D_N^* calculated from Equation (7) agreed with those calculated from Equation (3) to within 1 %.

TABLE 1

Parabolic Rate Constants for the Formation of Chromium Subnitride Layer on Chromium in Nitrogen

p_{N_2} kPa	k'' $g^2\,m^{-4}\,min^{-1}$	p_{N_2} kPa	k'' $g^2\,m^{-4}\,min^{-1}$	p_{N_2} kPa	k $g^2\,m^{-4}\,min^{-1}$
1000°C		*1050°C*		*1100°C*	
0·265	0·95	0·465	2·0	0·400	2·2
0·665	1·46	0·615	2·6	0·665	3·6
1·335	1·76	0·835	3·1	1·335	5·3
2·665	1·94	1·630	3·6	1·705	7·7
5·865	2·45	3·505	4·6	5·415	8·7
13·335	2·80	8·725	5·3	13·335	10·3
26·665	3·13	14·895	5·9	21·335	11·4
		28·475	6·8	66·665	13·0
		58·465	7·5	101·330	14·2
1150°C		*1200°C*		*1250°C*	
0·605	1·56	1·145	4·5	2·110	12·3
0·740	3·5	1·165	8·4	3·475	33·9
1·120	7·1	1·970	14·7	5·880	51·9
1·730	10·0	2·915	21·6	10·730	73·5
2·775	13·0	4·440	29·1	20·875	87·6
4·670	16·0	7·010	34·5	46·845	105·3
8·415	19·4	11·550	41·4	89·150	119·7
11·620	21·4	20·420	46·2		
16·485	22·9	39·355	54·3		
36·520	25·9	85·795	61·2		
98·190	30·2				

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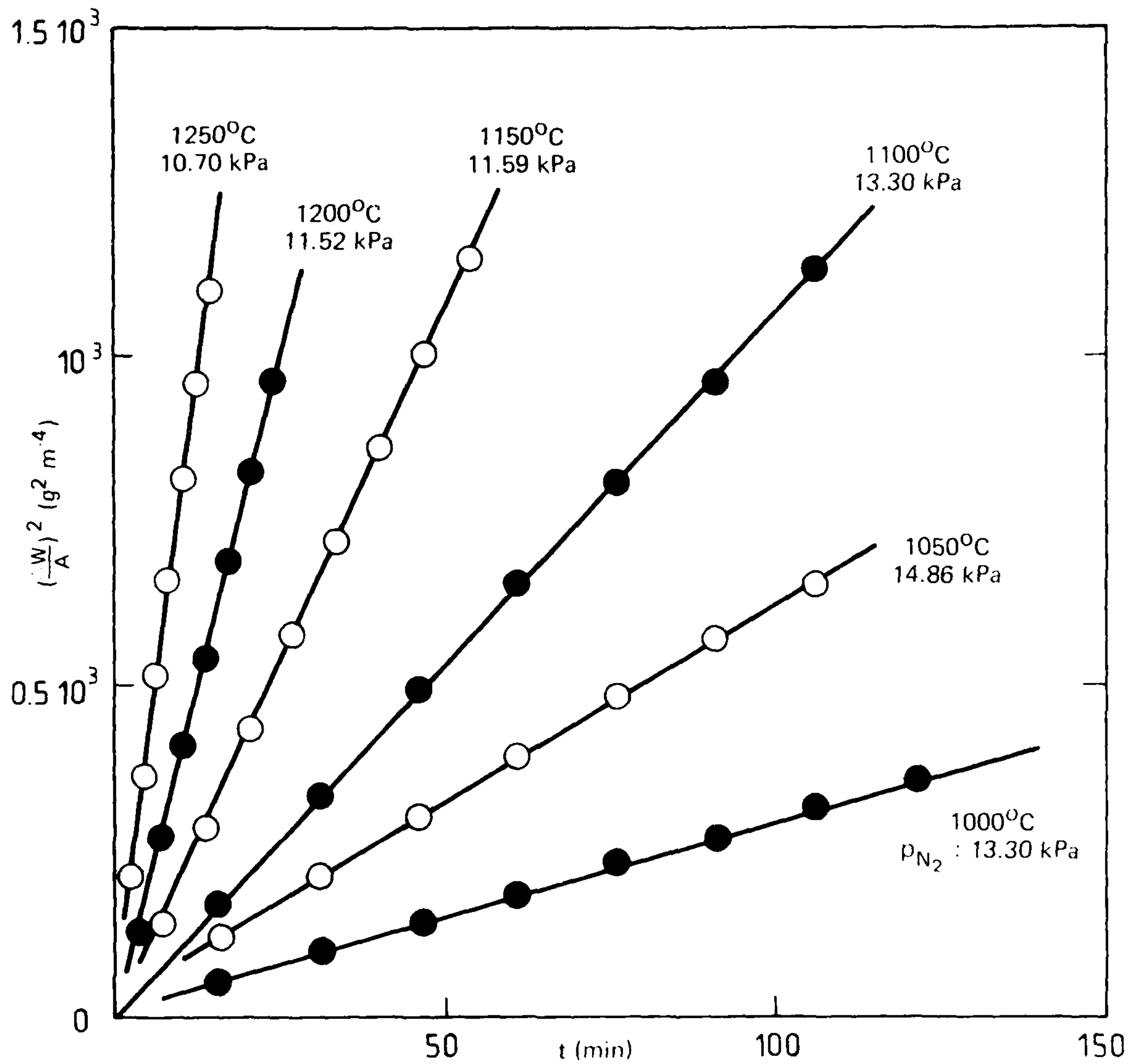

Fig. 1. Typical examples showing that a parabolic rate law is obeyed in the nitriding of chromium over the temperature range 1000 – 1250°C.

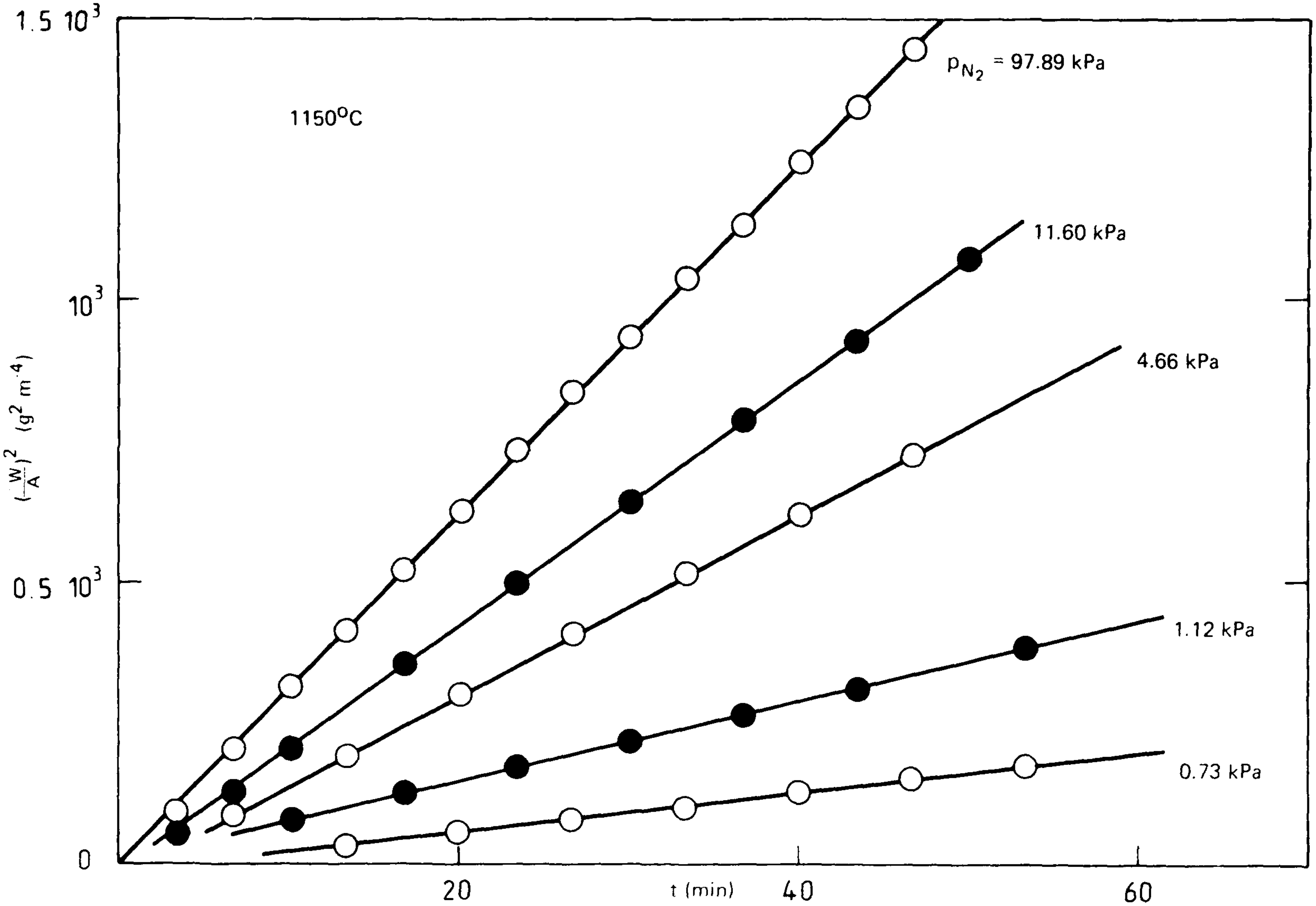

Fig. 2. Curves showing the effect of nitrogen pressure on nitriding kinetics of chromium at 1150°C.

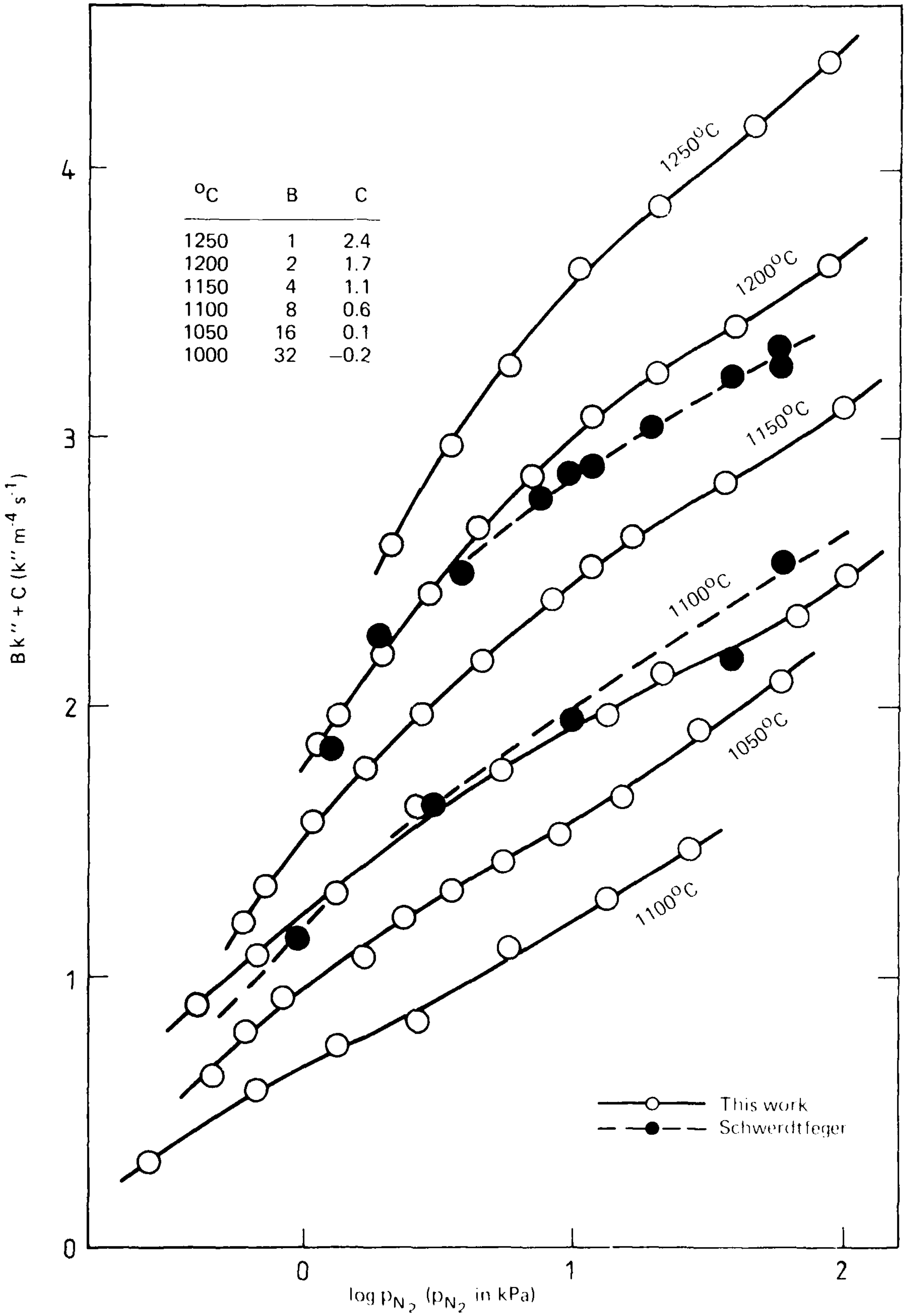

Fig. 3. Parabolic rate constant for the nitriding of chromium as a function of nitrogen pressure at six temperatures.

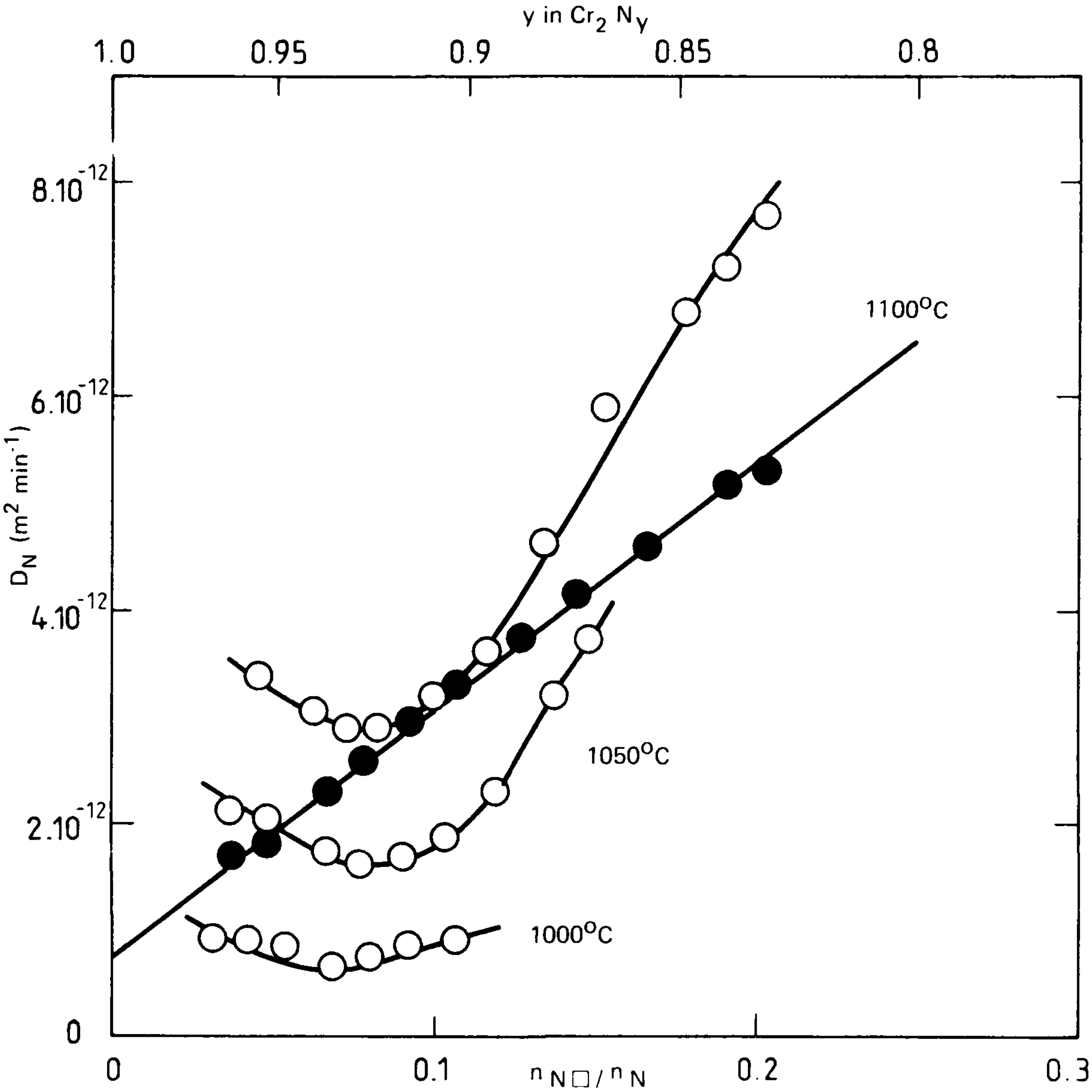

Fig. 4. Self-diffusivity of nitrogen in chromium subnitride at 1000°, 1050° and 1100°C as a function of composition, —O— calculated from Eq. (7), —●— calculated from Eq. (9) for 1100°C assuming D_N constant.

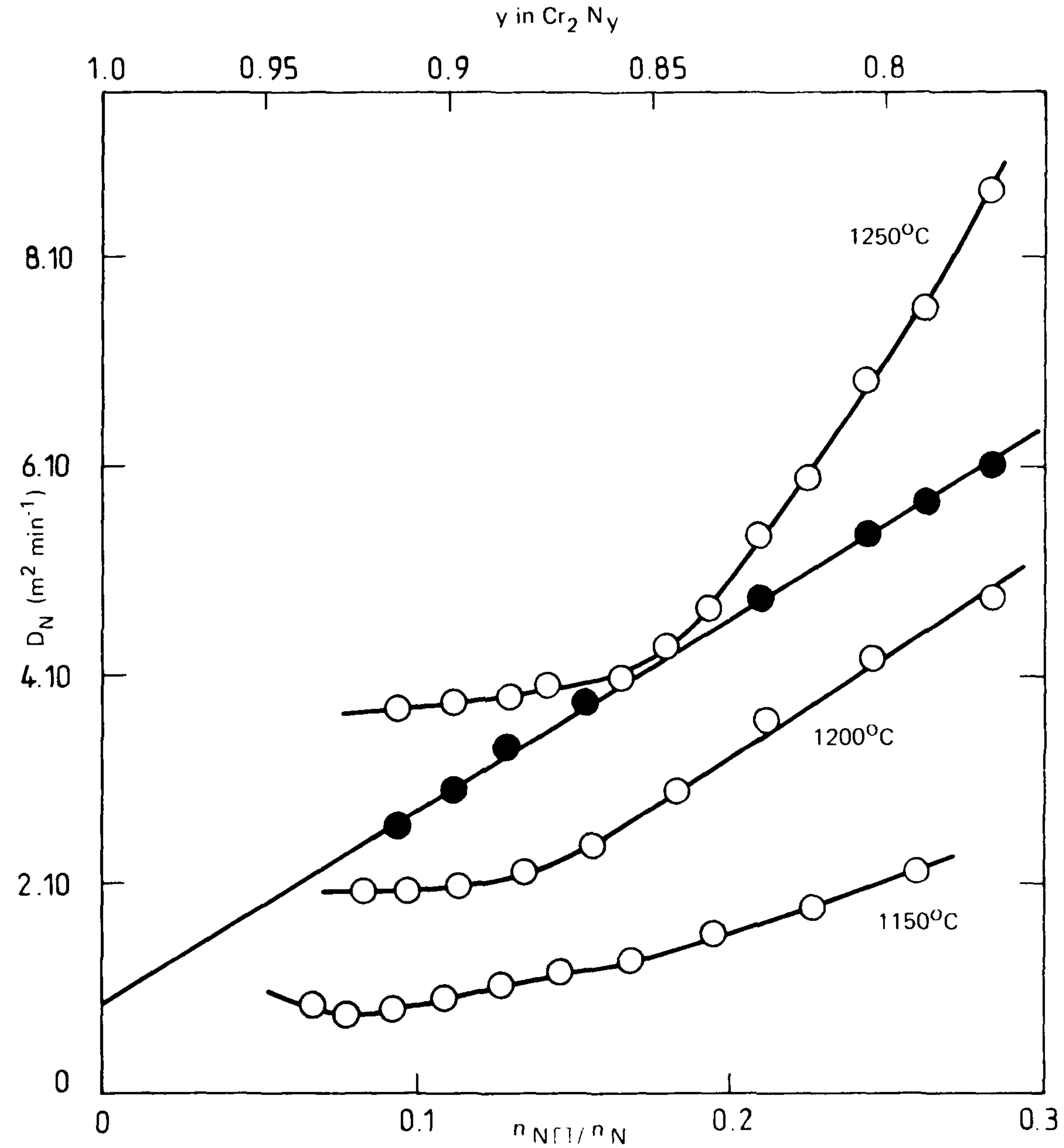

Fig. 5. Self-diffusivity of nitrogen in chromium subnitride at 1150°, 1200°and 1250°C as a function of composition, –O– calculated from Eq. (7), ● calculated from Eq. (9) for 1250°C assuming D_N constant.

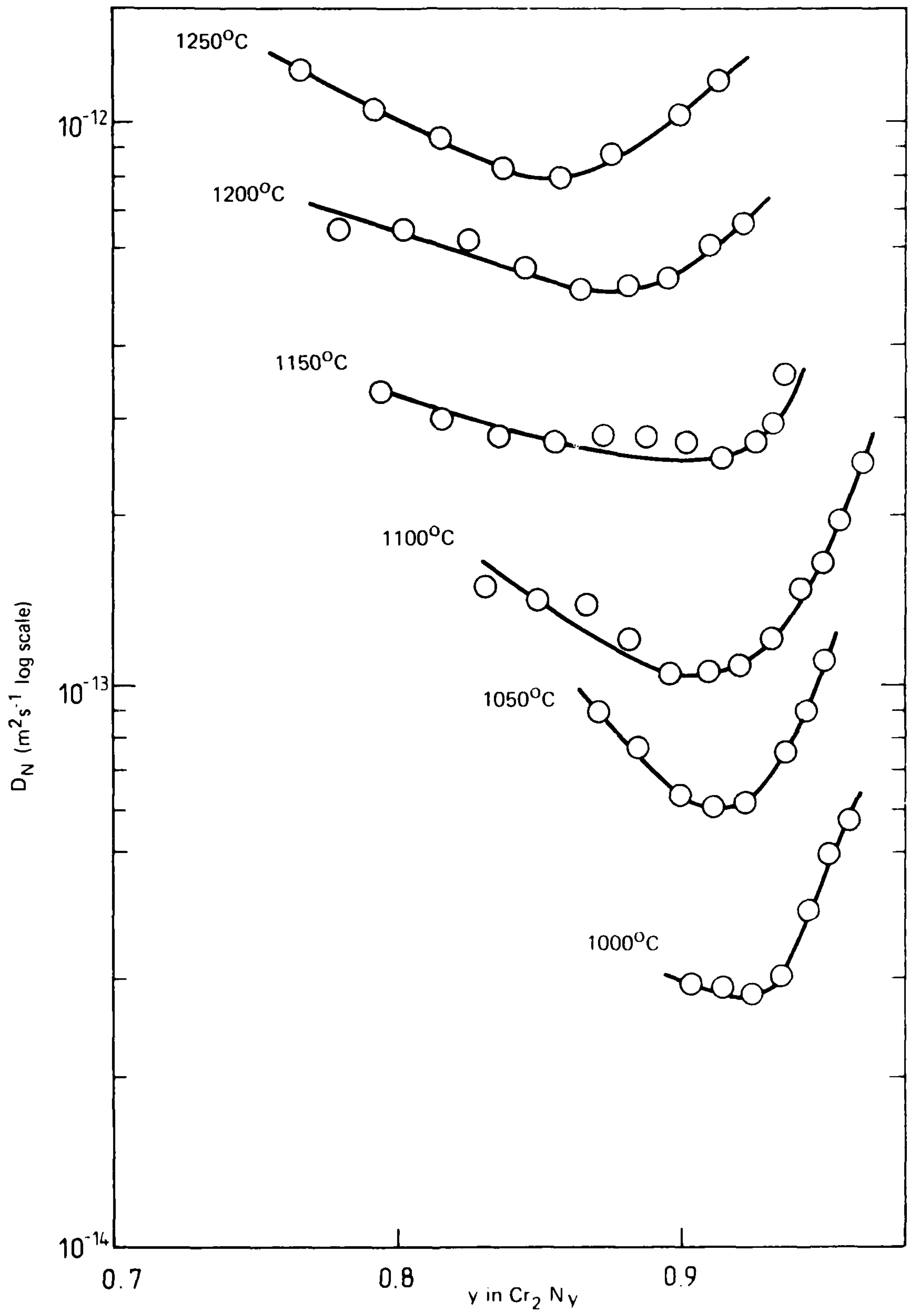

Fig. 6. Intrinsic diffusivity of nitrogen in chromium subnitride as a function of composition at six temperatures.

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