Reaction Diffusion and Phase Equilibria in the V-N System

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The formation of phase bands in *in situ* diffusion couples of the V-N system was studied by the reaction of vanadium sheet with pure nitrogen within the temperature range 1100 °C to 1700 °C and the nitrogen pressure range 2 to 24 bar. Under these conditions, phase bands of β -V₂N and δ -VN_{1-x} develop. The morphology of the β -V₂N/ α -V(N) interface depends on the saturation state of the α -V(N) core. If the nitrogen content in α -V(N) is high, the interface has a jagged appearance, whereas at low nitrogen contents of the α -V(N) phase, the interface is planar. Electron probe microanalysis (EPMA) was used to measure the diffusion profiles within the couples. The homogeneity regions of the nitride phases were established and the phase diagram accordingly corrected. From the growth rates of the phase bands, the mean composition-independent nitrogen diffusivities in β -V₂N and δ -VN_{1-x} were derived. These diffusivities follow an Arrhenius equation with activation energies of 2.92 (β -V₂N) and 2.93 eV (δ -VN_{1-x}). By using δ -VN_{1-x} as a starting material and a low nitrogen pressure during annealing, it could be shown that the direction of nitrogen diffusion can be reversed, *i.e.*, β -V₂N is formed on the surface of the couple as a result of out-diffusion of nitrogen.

I. INTRODUCTION

THE phase equilibria in the vanadium-nitrogen system have been reviewed by Carlson *et al.*,^[1] who also published the first complete version of a tentative V-N phase diagram. Relevant studies, which were published later or were not considered by these authors, cover the preparation and properties of δ -VN_{1-x} within the homogeneity range,^[2] thermodynamic data of coexistence of β -V₂N with δ -VN_{1-x},^[3] and thermodynamic and kinetic effects of nitrogen diffusion in δ -VN_{1-x}.

The δ -VN_{1-x} attains a stoichiometric composition at relatively high nitrogen pressures (depending on the temperature) only.^[2] In the temperature range 1400 °C to 1700 °C, the nitrogen-poor boundary was determined by Kieda *et al.*^[3] to lie at [N]/[V] = 0.65 to 0.60. For β -V₂N there is substantial disagreement concerning the phase boundaries (Table I). According to Brauer and Schnell,^[6] the nitrogen-rich composition of β -V₂N is at 32.8 at. pct N, and according to Kieda et al.^[3] it is at 33.8 at. pct N ([N]/[V] = 0.51), the boundary supposedly being independent of temperature. However, in the compilation of Carlson et al.,^[1] a composition close to 31 at. pct N was adopted for the phase diagram based on data by Arbuzov et al.[7] and Khaenko and Fak.^[8] The nitrogen-poor boundary was stated to be rather uncertain; values between 25 and 30 at. pct N were reported.^[1]

The aim of the present study was to describe phenomena occurring within the nitriding of vanadium metal and to investigate vanadium nitride layers that develop during the reaction of vanadium metal with nitrogen, in order to establish the homogeneity regions of the vanadium nitrides

Table I. Literature Data of Different Authors for the Phase Boundary of the β -V₂N Phase

Temperature (°C)	N-Poor	N-Rich	Author(s)
1500	28 to 30		Carlson et al. ^[1]
1408 to 1710		33.8	Kieda et al. ^[3]
1500	28 to 30	32.8	Brauer and Schnell ^[6]
700 to 1500		31.0	Arbuzov et al. ^[7]
1500	approx. 25	_	Arbuzov et al. ^[7]
700, 1500		31.3	Khaenko and Fak ^[8]
1500	26.7	_	Khaenko and Fak ^[8]
700	28.7	_	Khaenko and Fak ^[8]
1500	27	—	Fromm and Gebhardt ^[10]

by electron probe microanalysis (EPMA) measurements of diffusion bands and to derive nitrogen diffusivities. No information on the nitridation of vanadium metal and the reactive diffusion-band formation in V-N₂ diffusion couples was available in the literature.

II. EXPERIMENTAL PROCEDURES

Vanadium rods (10-mm diameter, purity >99.8 wt pct V, Heraeus, Hanau, Germany) were cut into 1- to 3-mmthick slices, the faces of the slices were ground with SiC paper of 4000 mesh, and the slices were placed in a sample container lined with Zr foil as an oxygen getter. The samples were placed in a cold-wall high-temperature autoclave at pressures of 2 to 24 bar and heated at temperatures of 1100 °C to 1700 °C, which were recorded with a Pt/Pt10 pct Rh thermocouple. The samples were cooled down to room temperature within a few minutes. Temperatures where diffusion is too slow to give perceptible changes in the microstructure (approximately 1000 °C) were reached in approximately 30 seconds.

To prepare single-phase, homogeneous δ -VN_{1-x} samples for the investigation of nitrogen out-diffusion, the starting material was heated in the same manner at 1700 °C for long periods at two different nitrogen pressures in order to obtain two different equilibrium compositions. The out-diffusion couples cooled slower to room temperature (about 2

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Fig. 1—Diffusion couple annealed at 1700 °C showing the principle phase band sequence. The α/β phase boundary is straight or irregularly shaped, depending on the time of the annealing process and/or thickness of the sample (Fig. 2). Top right (hatched region): presence of metastable vanadium nitrides. Etched with HF/HNO₃.

minutes to 1000 °C) because of the lower pressure in the autoclave.

The samples were cut, embedded in resin, and polished with diamond and SiO_2 paste. Occasionally they were etched with aqueous HF/HNO₃ solutions.

For measurements of the nitrogen diffusion profiles, a Cameca SX50 microprobe was used. For the measurement of the N K_{α} line, a W/Si multilayer crystal was used, and for the V K_{α} line, a LiF crystal was employed. Chemically analyzed δ -VN_{1-x} standards were used for calibration. Details of the light-element EPMA analysis of diffusion couples were recently reported.^[9] The samples that were subjected to microprobe analysis were reannealed for a few minutes at the same temperatures at which the diffusion process was performed, and were then quenched to room temperature onto a copper plate mounted within a vacuum furnace. This should reestablish the high-temperature conditions and provide a suppression of precipitations upon quenching. Only these samples were used for the determination of the homogeneity ranges of phases.

III. RESULTS AND DISCUSSION

A. Nitriding and Layer-Formation Phenomena and Homogeneity Ranges

Two layers, one of δ -VN_{1-x} and one of β -V₂N, and an α -V(N) core (Figure 1), developed at all applied temperatures and pressures. The δ -VN_{1-v}/ β -V₂N interphase boundary was almost a straight line, due to the isotropic nitrogen diffusion in fcc δ -VN_{1-x}. The β -V₂N/ α -V(N) boundary had a jagged appearance, particularly at extended annealing times, or, because of the reciprocal relationship of diffusion distance and time, in thinner specimens. In wedge-type samples, the two situations can be observed together (Figure 2). Near the tip of the wedge, the crystallites of β -V₂N grow dendritelike irregular forms into the α core phase, whereas at greater sample thickness a planar α/β interface can be observed. This phenomenon can be explained by the fact that near the tip, the core becomes saturated with nitrogen at the annealing temperature. During the cooling-down cycle, precipitation of β -V₂N from



Fig. 2—Cross section of a wedge-shaped diffusion couple where the influence of sample thickness on the shape of the α/β interface and on the layer thickness can be seen. At small thicknesses (corresponding also to long annealing times), an irregularly shaped α/β interface is observed, whereas at large sample thicknesses (corresponding also to short annealing times), a straight α/β interface is observed. The diffusion layer thickness increases with decreasing sample thickness. Etched with HF/HNO₃.

the supersaturated α -V(N) phase takes place. The formation of precipitates is favored by lateral nitrogen diffusion (diffusion direction other-than-perpendicular to the phase bands), because of the flat nitrogen concentration profile. The β -V₂N phase band formed during high-temperature diffusion serves as nucleation center for the precipitation, so that the resulting β phase band shows a jagged nitrogenpoor boundary. The α phase is free from small β precipitates near the α/β interface. At a large sample thickness, the nitrogen profile in the α phase is steeper and the overall dissolved amount of nitrogen is smaller, so that only small precipitates form homogeneously within the α phase and no acicular crystals are formed. The contribution of lateral diffusion is much smaller here, because of the steep nitrogen profile (the driving force for perpendicular diffusion is higher the steeper the nitrogen profile). Similar observations were made in the Nb-N system.

Especially for the samples annealed at the highest temperature (1700 °C), it was observed that in the nitrogenpoor region of δ -VN_{1-x}, a Widmannstätten-type pattern formed, representative of the oriented precipitation of β -V₂N upon cooling (Figure 1). The same has been observed for the N-poor region of β -V₂N, where α -V(N) forms, and in the α -V(N) core some β -V₂N is precipitated during cooling.

Interestingly, no difference in the phase band widths of δ -VN_{1-x} between diffusion experiments at different nitrogen pressures could be detected. Such a difference could be expected, because different nitrogen pressures result in different surface concentrations of δ -VN_{1-x}. However, since the diffusivity decreases with increasing occupancy of nonmetal sites, as shown for some isostructural carbides, the effect of the thickness increase that would be expected to go with an increase of the homogeneity range is probably canceled out.

Figure 3 shows four microprobe scans representative of the four different temperatures. It can be seen that the composition of the nitrogen-poor phase boundary of δ -VN_{1-x} shifts to lower nitrogen values with higher annealing temperatures (Table II). The maximum nitrogen concentration of β -V₂N is not significantly different from 33.3 at. pct N, in agreement with expectations from structural considerations, and does not change within the investigated temperature range. This result is significantly different from the values adopted by Carlson *et al.*^[1] for the V-N phase diagram compiled from the results of Arbuzov *et al.*^[7] and Khaenko and Fak^[8] (Table I). Much better agreement is



Fig. 3—Microprobe scans for samples quenched at four different temperatures. Some discontinuities in the scans stem from cracks in the samples, which occur during cooling/reheating/quenching because of different thermal expansivities of the phases or due to isolated β -V₂N grains. (a) 1100 °C, (b) 1338 °C, (c) 1503 °C, and (d) 1700 °C.

Table II. Homogeneity Ranges of α -V(N), β -V₂N, and δ -VN_{1-x} for Four Different Temperatures (from 4 to 6 Line Scans on Each Sample; Standard Deviations in At. Pct N in Parentheses)

α -V(N)	Homogeneity Range (At. Pct N)		
1100 °C 1338 °C 1503 °C 1700 °C	0 to 9.0 (0.6) 0 to 12.8 (0.8)		
β -V ₂ N	Homogeneity Range (At. Pct N)		
1100 ° C 1338 °C 1503 °C 1700 °C	30.2 (0.2) to 33.2 (0.2) 29.0 (0.1) to 33.3 (0.4) 28.0 (0.5) to 33.1 (0.4) 27.1 (0.5) to 33.5 (0.2)		
δ -VN _{1-x}	Nitrogen-Poor Boundary (At. Pct N)*		
1100 °C 1338 °C 1503 °C 1700 °C	42.2 (0.3) 41.3 (0.2) 40.9 (0.7) 39.5 (0.2)		
*Nitrogen-rich bou	undary depends on the nitrogen pressure.		

found with the values of Brauer and Schnell^[6] and of Kieda *et al.*^[3] Also, the nitrogen-poor boundary of β -V₂N could

be established by means of the diffusion couples, which is in good agreement with the value for 1500 °C of Khaenko and Fak^[8] and Fromm and Gebhardt.^[10] This phase boundary shifts to lower nitrogen composition upon increasing temperature.

For diffusion couples annealed at 1100 °C and 1338 °C, the nitrogen content of α -V(N) as observed in the present study was higher (approximately 11 at. pct for both temperatures) than that given in the literature, whereas for the couples annealed at higher temperatures excellent agreement was found.

Table II lists the homogeneity ranges at the four different annealing temperatures, together with standard deviations. These data were included into the phase diagram that is shown in Figure 4.

B. Nitride Layer Growth

From the layer growth as a function of time, the nitrogen diffusivities in δ -VN_{1-x} and β -V₂N could be determined. This was performed by a computer program^[11] that takes into account the dependency of layer thickness as a function of sample thickness. The influence was shown recently^[12] on plane-sheet and wedge-type samples to be of crucial importance already in samples of several millimeter thick-



Fig. 4—Phase diagram of the V-N system^[1] corrected on the basis of the results of the present study. — present study; ---; possible phase boundaries; ---- phase boundaries of β -V₂N and δ -VN_{1-x} from Ref. 1; and — phase boundary of α -V(N) from Ref. 1.



Fig. 5—Arrhenius plot of concentration-independent nitrogen diffusivities in α -V(N), β -V₂N, and δ -VN_{1-x} together with literature data^[13,14] on the nitrogen diffusion in α -V(N). x: V(N); o: β -V₂N; and +: δ -VN_{1-x}.

ness. In plane-sheet samples, the layers are thicker than in corresponding samples of semi-infinite diffusion geometry (thick samples). For the calculation of diffusivities, molar volumes were calculated from the microprobe measurements and well-established lattice parameters^[1,2,6] in order to obtain the concentrations in mol N/cm3. Only nitrogen was assumed to diffuse, and the diffusivities were assumed to be concentration independent. This is a first approximation for phases with a large homogeneity range such as δ -VN_{1-x}; the obtained diffusion coefficient is thus an average one and applies to an average composition $VN_{\sim 0.84}$. If only one plane-parallel diffusion couple was prepared at a given temperature, it was necessary to know the nitrogen diffusivity in α -V(N) for calculating the diffusivities in the outer nitride phases. Therefore, data calculated from different sources by Wasz and McLellan^[13] (including the data of Schmidt and Warner^[14]) were taken. Our own data on α -V(N) were determined by using samples with different thicknesses or wedge-type samples,[15] but were collected



200µm

Fig. 6—Microstructures of out-diffusion couples of the series [N]/[V] = 0.68 (40.5 at. pct N) obtained by heating δ -VN_{1-x} at 1600 °C for 1 h (top), 5 h (center), and 15 h (bottom). W: Widmannstätten-type microstructure.

only at the high-temperature region of this investigation. It should be noted that small differences in diffusivity data used for α -V(N) did not change the calculations for the nitride phases significantly. Figure 5 shows the Arrhenius-type dependency of the nitrogen diffusion in δ -VN_{1-x} and β -V₂N. The diffusion coefficients can be expressed numerically by the following:

$$\delta$$
-VN_{1-x}: $D_N = 12.7 * \exp(-2.93 \text{ eV}/k_BT) \text{ cm}^2/\text{s}$
 β -V₂N: $D_N = 13.6 * \exp(-2.92 \text{ eV}/k_BT) \text{ cm}^2/\text{s}$

where k_{B} is the Boltzmann constant. This result shows that the diffusion rate of nitrogen in both phases is almost identical. The identical activation energy in both phases (error: ± 0.03 eV) is representative for the same transport mechanism, which is a migration of nitrogen *via* octahedral nitrogen vacancies. The small difference in diffusivity is thus



Fig. 7-Microprobe scans across the diffusion couples shown in Fig. 6.

reflected by the pre-exponential factor only. This factor is proportional to the jump probability of nitrogen atoms to empty next-neighbor positions, which is larger in β -V₂N, where about half of the octahedral positions are unoccupied, than in δ -VN_{1-x}. The only available literature value^[16] for the activation energy of nitrogen diffusion in "VN" of 0.82 eV is very unlikely for a vacancy diffusion mechanism in a NaCl-type solid and does not agree with the present findings.

C. Out-diffusion Couples

Because vanadium nitride has a relatively high nitrogen equilibrium pressure (as opposed to the group IVB transi-



Fig. 8—EPMA scans across out-diffusion couples of starting composition [N]/[V] = 0.94 (48.4 at. pct N) annealed for 5 h at 1600 °C in a rotary pump vacuum. The nitrogen profile in the center remains constant as opposed to the series of lower nitrogen content. W: Widmannstätten-type microstructure.

tion metal nitrides) decomposition of δ -VN_{1-x} is already possible by applying a rotary pump vacuum during hightemperature annealing. Therefore, the phase band formation was investigated in the reverse manner, by out-diffusion of nitrogen from δ -VN_{1-x} and decomposition of the sample. Two series were investigated, one with a starting composition of [N]/[V] = 0.94 (48.4 at. pct N) and one with [N]/[V] = 0.68 (40.5 at. pct N). In the first series the growth of β -V₂N is slower than in the second, representative for the lower nitrogen diffusivity at the higher nitrogen content of δ -VN_{1-x}.

A series on the latter composition is shown in Figure 6, and the corresponding EPMA scans are given in Figure 7. It can be seen that β -V₂N forms on the surface of the couple (Figure 6, top) because of nitrogen loss of δ -VN_{1-x}. The α -V(N) did not form on the surface, because the pressure in the heating chamber could not be reduced to values where β -V₂N decomposes. The thickness of the β -V₂N phase band increases upon increasing annealing time, and the process can be seen just as the reverse process as the in-diffusion. The β -V₂N layer growth is faster for the samples of composition [N]/[V] = 0.68 than for the composition [N]/[V]= 0.94, because the critical composition that leads to a phase change is reached earlier because of a faster depletion in nitrogen. In the samples of the latter series, the nitrogen profile remains flat in the center of the sample, although the β -V₂N phase is already formed (Figure 8).

It can be seen that an intense formation of a Widmannstätten-type pattern occurs first in the outer and nitrogenpoor regions of the δ -VN_{1-x} phase, because of nitrogen loss and subsequent precipitation of β -V₂N upon cooling. This pattern extends throughout the core of the sample (Figure 6, center) if the annealing time increases. Within the Widmannstätten pattern, the profile is rather steep and the data scatter because of the two-phase mixture (the samples were slower cooled than than the in-diffusion couples so that the precipitation is more intensive). Finally, when the sample is single-phase β -V₂N (Figure 6, bottom), a flat profile in β -V₂N is observed (Figure 7, bottom), representative of the attainment of a very homogeneous sample. Such a sample was analyzed by bulk chemical analysis and proved to have practically the same composition as that found by EPMA.

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Note added in the proof:

After this study was submitted, Schmid-Fetzer and coworkers [17] performed a thermodynamic assessment of the V-N system and included also the data of the present study.

REFERENCES

- O.N. Carlson, J.F. Smith, and R.H. Nafziger: *Metall. Trans. A*, 1986, vol. 17A, pp. 1647-56.
- 2. W. Lengauer and P. Ettmayer: J. Less-Common Met., 1985, vol. 109, pp. 351-59.

- 3. N. Kieda, N. Mizutani, and M. Kato: J. Less-Common Met., 1988, vol. 144, pp. 293-99.
- 4. W. Lengauer: J. Phys. Chem. Solids, 1988, vol. 49, pp. 59-63.
- 5. W. Lengauer: J. Phys. Chem. Solids, 1991, vol. 52, pp. 393-99.
- 6. G. Brauer and W.D. Schnell: J. Less-Common Met., 1964, vol. 6, pp. 326-32.
- M.P. Arbuzov, B.V. Khaenko, and O.A. Frenkel: *Inorg. Mater.*, 1975, vol. 11, pp. 236-41.
- B.V. Khaenko and V.G. Fak: *Inorg. Mater.*, 1978, vol. 14, pp. 1011-16.
- 9. W. Lengauer, J. Bauer, M. Bohn, H. Wiesenberger, and P. Ettmayer: *Mikrochim. Acta*, in press.
- E. Fromm and E. Gebhardt: Gase und Kohlenstoff in Metallen, Springer, Berlin, 1976.
- D. Rafaja: Program DIFDK, Vienna University of Technology, unpublished research 1994.
- 12. W. Lengauer, D. Rafaja, R. Täubler, C. Kral, and P. Ettmayer: Acta Metall. Mater., 1993, vol. 41 (12), pp. 3505-14.
- M.L. Wasz and R.B. McLellan: J. Phys. Chem. Solids, 1992, vol. 53, pp. 629-30.
- 14. F.A. Schmidt and J.C. Warner: J. Less-Common Met., 1967, vol. 13, p. 493.
- D. Rafaja, W. Lengauer, and P. Ettmayer: Acta Mater., 1996, vol. 44, pp. 4835-44.
- G.V. Samsonov and G.S. Kaplina: cited in *Defect Diffus. Data*, 1973, vol. 7, p. 458.
- 17. Y. Du, R. Schmid-Fetzer and H. Ohtani: Z. Metallkunde, 1997, in press.