Monatshefte für Chemie 117, 713–719 (1986)

Monatshefte für Chemie
Chemical Monthly

Lattice Parameters and Thermal Expansion of δ-VN_{1-x} from 298–1000 K**

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(Received 13 November 1985. Accepted 16 December 1985)

The thermal expansion of VN_{1-x} was determined from measurements of the lattice parameters in the temperature range of 298–1 000 K and in the composition range of $VN_{0.707}$–$VN_{0.996}$. Within the accuracy of the results the expansion of the lattice parameter with temperature is not dependent on the composition. The lattice parameter as a function of composition ([N]/[V] = 0.707–0.996) and temperature (298–1 000 K) is given by

$$a([N]/[V], T) = 0.38872 + 0.02488\,([N]/[V]) - \\ - (1.083 \pm 0.021) \cdot 10^{-4}\, T^{1/2} + (6.2 \pm 0.1) \cdot 10^{-6}\, T.$$

The coefficient of linear thermal expansion as a function of temperature (in the same range) is given by

$$\alpha(T) = a([N]/[V], T)^{-1}\,[(-5.04 \pm 0.01) \cdot 10^{-5}\, T^{-1/2} + (6.2 \pm 0.1) \cdot 10^{-6}].$$

The average linear thermal expansion coefficient is

$$\alpha_{av} = 9.70 \pm 0.15 \cdot 10^{-6}\,\mathrm{K}^{-1}\,(298\text{–}1\,000\,\mathrm{K}).$$

The data are compared with those of several fcc transition metal nitrides collected and evaluated from the literature.

(Keywords: B1 Vanadium nitride; Lattice parameter; Thermal expansion)

Gitterparameter und Wärmeausdehnung von δ-VN_{1-x} *bei 298—1 000 K*

Die thermische Ausdehnung von VN_{1-x} wurde durch Messung des Gitterparameters im Temperaturintervall von 298—1 000 K und im Homogenitätsbereich von $VN_{0.707}$—$VN_{0.996}$ bestimmt. Innerhalb der erzielten Genauigkeit ist die temperaturbedingte Ausdehnung des Kristallgitters nicht abhängig von der

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** Dedicated to Professor Dr. *Kurt L. Komarek* on the occasion of this 60th birthday.

Stöchiometrie. Der Gitterparameter als Funktion der Zusammensetzung ([N]/[V] = 0.707—0.996) und Temperatur (298—1 000 K) ergibt sich zu

$$a([\mathrm{N}]/[\mathrm{V}], T) = 0.38872 + 0.02488\,([\mathrm{N}]/[\mathrm{V}]) - \\ - (1.083 \pm 0.021) \cdot 10^{-4}\, T^{1/2} + (6.2 \pm 0.1) \cdot 10^{-6}\, T.$$

Der lineare thermische Ausdehnungskoeffizient als Funktion der Temperatur (gleicher Bereich wie oben) beträgt

$$\alpha(T) = a([\mathrm{N}]/[\mathrm{V}], T)^{-1}\,[(-5.04 \pm 0.01) \cdot 10^{-5}\, T^{-1/2} + (6.2 \pm 0.1) \cdot 10^{-6}].$$

Der mittlere lineare thermische Ausdehnungskoeffizient ist

$$\alpha_{\mathrm{av}} = 9.70 \pm 0.15 \cdot 10^{-6}\,\mathrm{K}^{-1}\,(298\text{—}1\,000\,\mathrm{K}).$$

Die erhaltenen Meßergebnisse werden mit aus der Literatur verfügbaren Daten von fcc-Nitriden der Übergangsmetalle verglichen.

Introduction

Refractory compounds such as the transition metal carbides and nitrides often exist over extended composition ranges with appreciable vacancy concentrations in the non-metal sublattice. A high concentration of vacancies affects their physical, thermodynamic and mechanical properties [1]. While the thermal expansion behaviour of the transition metal carbides has been extensively studied, there is a considerable lack of experimental values for the transition metal nitrides [2, 3]. This fact can be attributed not only to the greater technical interest in the refractory carbides but also to the difficulties in preparing homogeneous and well characterized nitride samples with low oxygen contents.

In addition, high-temperature investigations of the properties of transition metal nitrides would require that the nitrogen equilibrium pressure be adjusted to avoid a composition shift—something which is not necessary for the refractory carbides. Since considerable experimental difficulties would arise in imposing a higher-than-atmospheric nitrogen equilibrium pressure during high-temperature lattice parameter measurements of the less stable nitrides, such investigations are resticted to a temperature range where the equilibrium pressure is comparably low and/or the diffusion of nitrogen in the lattice is slow.

The thermal expansion of δ-VN_{1-x} on a single sample was reported by *Ajami* and *MacCrone* [4] who found that the volume coefficient of thermal expansion of $\mathrm{VN}_{0.96}$ increases from $\alpha = 20 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at 298 K to $\alpha = 39 \cdot 10^{-6}\,\mathrm{K}^{-1}$ at 977 K (a graph showing α vs. T is given in their later review [3]). *Bogdanov* et al. [5] measured the linear coefficient of thermal expansion on $\mathrm{VN}_{0.93}$ ($\alpha = 6.988 \cdot 10^{-6} + 6.441 \cdot 10^{-9}\, T$ (T in °C), 298–873 K). The low-temperature lattice expansion of $\mathrm{VN}_{0.98}$ was measured by *Timofeeva* and *Shvedova* [6] from lattice parameters at 93 and 298 K ($\alpha = 5.0 \cdot 10^{-6}\,\mathrm{K}^{-1}$).

Since values given by different authors hardly allow statements as to whether or not the composition influences the thermal expansion of VN_{1-x}, this study was carried out on several samples covering the homogeneity range of the fcc phase.

Experimental

Sample Preparation and Characterization

The samples were prepared by reacting compact vanadium pieces ($\geqslant$ 99.7 wt% V; main impurities: 0.15 wt% Si, 0.05 wt% Fe, 0.02 wt% C, and 0.01 wt% O) with nitrogen gas (> 99.999 vol% N_2) at various temperatures and under nitrogen pressures of 6.8 kPa to 4 MPa.

The chemical analyses were made for nitrogen (*Dumas* method), vanadium (combustion) and oxygen (vacuum hot extraction). A detailed description of the preparatory conditions and characterization procedures is given in a previous paper [7].

The lattice parameters were measured using a high-temperature X-ray attachment to a commercial Philips goniometer manufactured by A. Paar, Graz (Austria), and described in detail by *Ebel* and *Nowak* [8]. This attachment was equipped with an internal resistively heated molybdenum strip (cross section: 0.3 × 10 mm). The temperature was measured with a Pt/Pt 10% Rh thermocouple tightly squeezed into a bore hole in the center of the target area of the molybdenum strip.

Examination Procedure

The samples were powdered and spread on the surface of the target area of the molybdenum strip using a small amount of methanol. Subsequently the attachment was closed, evacuated and flushed with nitrogen gas (> 99.999 vol% N_2). After three evacuation/flushing cycles the nitrogen pressure was adjusted to 40 kPa. The angles of the (420) and (422) diffraction lines were measured using Ni-filtered Cu-K_α radiation. The diffraction lines were measured first at room temperature and then going from the highest temperature (1 000 K) back down to room temperature. In order to check for any changes in composition the diffraction angles at room temperature before and after the high-temperature measurements were compared. In each case the deviations were below $7 \cdot 10^{-5}$ nm. The goniometer setting was calibrated at room temperature with high purity silicon powder and at higher temperatures with gold, using the lattice parameters vs. temperature given by *Merryman* and *Kempter* [9]. The deviations of the goniometer readings from the reference angles were fitted against a linear function of θ and the measured diffraction angles were corrected accordingly.

Results and Discussion

The lattice parameters of nine VN_{1-x} samples vs. temperature are shown in Fig. 1. They fit the following equation quite closely:

$$a(T) = a(298) + A\,T^{1/2} + B\,T \qquad (1)$$

where $a(T)$ is the lattice parameter at a given absolute temperature T (298–1 000 K), $a(298)$ is the lattice parameter at 298 K, and A and B are

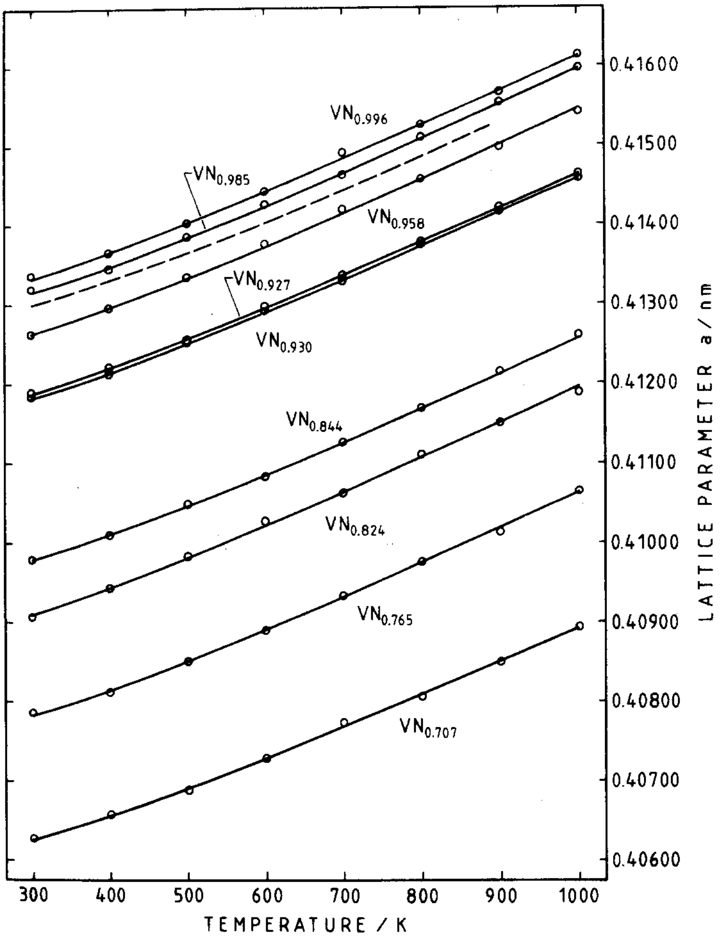

Fig. 1. Lattice parameters of VN_{1-x} vs. temperature. Since most data points for $VN_{0.991}$ and $VN_{0.996}$ coincide, only those for $VN_{0.996}$ are shown. — — — Data from *Bogdanov* et al. [5]

coefficients which can be calculated by a least-squares fit of the obtained data. Eq. (1) was also used to calculate $\alpha(T)$ from literature data where no $\alpha = f(T)$ relation was given. It approximates the experimentally determined data points quite well but is not based on a physical model.

With respect to the slope of the curve the values of *Bogdanov* et al. [5] for $VN_{0.93}$ agree quite well with our own results for a sample of the same composition (VN 9). The room temperature lattice parameter however is significantly higher. The coefficient of linear thermal expansion as a function of temperature can be derived from equation (1):

$$\alpha(T) \equiv \frac{1}{a(T)} \cdot \frac{\mathrm{d}\,a(T)}{\mathrm{d}T} = \frac{1}{a(T)}\left(\frac{A}{2\sqrt{T}} + B\right). \tag{2}$$

The values of A and B as well as the average linear thermal expansion coefficient α_{av} [obtained from a least-squares fit of $a(T)$ vs. T] are included in Table 1.

Table 1. *Lattice parameters and thermal expansion of* δ-VN_{1-x}

Sample	Composition $[N]/[V] = 1 - x$ ± 0.002	Lattice parameter ($T = 298$–$1\,000$ K) $a(T) = a(298) + A \cdot T^{1/2} + B \cdot T$			Average linear thermal expansion coefficient $\alpha_{av} \cdot 10^6$ K
		$a(298)$ nm	$A \cdot 10^4$	$B \cdot 10^6$	
VN 1 A	0.707	0.40625	− 1.05	6.00	9.38
VN 1	0.765	0.40787	− 1.10	6.27	9.79
VN 2 A	0.824	0.40912	− 1.10	6.37	9.89
VN 2	0.844	0.40982	− 1.12	6.29	9.77
VN 3 A	0.927	0.41187	− 1.07	6.13	9.66
VN 3	0.930	0.41183	− 1.08	6.21	9.76
VN 4	0.958	0.41264	− 1.07	6.19	9.69
VN 7	0.985	0.41318	− 1.09	6.25	9.78
VN 8	0.991	0.41337	− 1.09	6.23	9.75
VN 9	0.996	0.41341	− 1.06	6.09	9.52
$\bar{x}$			− 1.083	6.20	9.70
standard deviation		± 0.00007	± 0.021	± 0.11	± 0.15

The coefficients of eq. (2) and the average linear thermal expansion coefficient show that within the accuracy of the experimental results the nitrogen content does not influence the thermal expansion of VN_{1-x}. Similar results were reported by *Aronson* et al. [10] for ZrC_{1-x} in the range $x = 0.28 - 0.09$. This behaviour is quite different from that obtained for δ-NbN_{1-x} where the lattice expansion increases with increasing nitrogen content [11]. Since the values of A, B, and α_{av} do not change significantly with composition, average values were calculated from all samples (Tab. 1).

The room temperature lattice parameter $a(298)$ of δ-VN_{1-x} is a linear function of the composition:

$$a(298) = 0.38872 + 0.02488\,([N]/[V]). \tag{3}$$

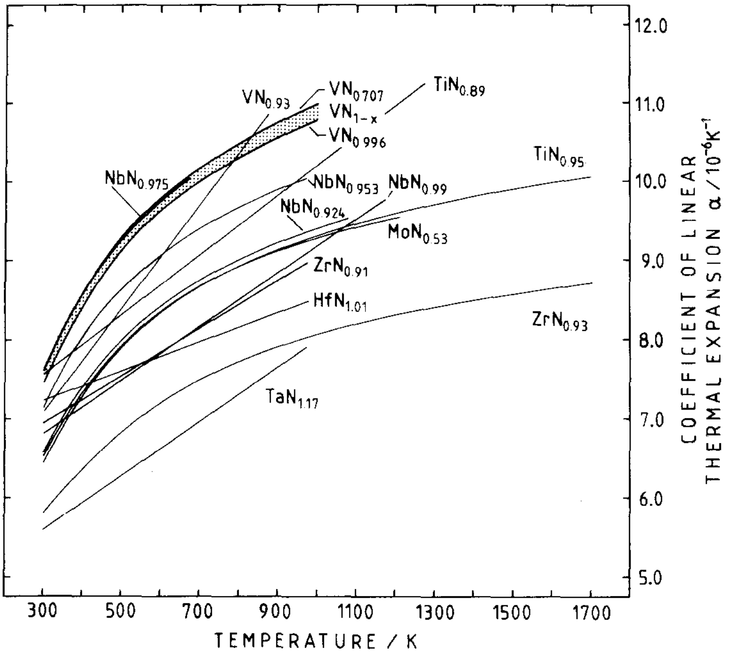

Fig. 2. Linear thermal expansion coefficient for VN_{1-x} vs. temperature compared with other fcc transition metal nitrides. The dotted area represents the variation of the lattice parameter with composition within the homogeneity range of VN_{1-x}. References: $TiN_{0.89}$, $ZrN_{0.91}$, $HfN_{1.01}$, $VN_{0.93}$, $NbN_{0.99}$, $TaN_{1.17}$ Ref. [5]; $TiN_{0.95}$, $ZrN_{0.93}$ Ref. [12]; $NbN_{0.924}$, $NbN_{0.953}$, $NbN_{0.975}$ Ref. [11]; $MoN_{0.53}$ Ref. [13]

With eq. (3) eq. (1) and (2) can be extended to following expressions:

$$a([\mathrm{N}]/[\mathrm{V}], T) = 0.38872 + 0.02488\,([\mathrm{N}]/[\mathrm{V}]) - (1.083 \pm 0.021)\cdot 10^{-4}\,T^{1/2} + (6.2 \pm 0.1)\cdot 10^{-6}\,T \tag{1 a}$$

$$\alpha(T) = a([\mathrm{N}]/[\mathrm{V}], T^{-1}[(-5.04 \pm 0.01)\cdot 10^{-5}\,T^{-1/2} + (6.2 \pm 0.1)\cdot 10^{-6})] \tag{2 a}$$

The values of $\alpha(T)$ vs. temperature of the samples with the largest and smallest lattice parameters (the two composition extremes) are graphically presented in Fig. 2. Also data for several fcc transition metal nitrides—taken from various sources—are included which show considerable scatter. *Bogdanov* et al. [5] did not report their measurements in explicit form but gave a linear function $\alpha = f(t)$ which is included in that form in Fig. 2. However, the data reported by *Houska* [12] (linear expansion in percentages relative to the room temperature lattice parameter) as well as the data of *Ettmayer* [13] (lattice parameter at a given temperature) were used to calculate $\alpha = f(T)$ analogous to eq. (2).

Apparently VN_{1-x} exhibits the highest degree of thermal expansion among these compounds. It is noteworthy that the coefficient of linear thermal expansion of δ-NbN_{1-x} is dependent upon stoichiometry [11] (α increases with increasing nitrogen content) whereas a dependence, if any, is scarcely noticable for δ-VN_{1-x}.

The set of data available is not sufficient to draw a uniform picture due to the lattice dynamics in these refractory compounds. This is especially true if this view is extended to the isotypic transition metal carbides [3].

Acknowledgements

The authors wish to express their appreciation for the financial support given by the Austrian Fonds *zur Förderung der wissenschaftlichen Forschung.*

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