Low-temperature thermal expansion of refractory nitrides

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While high-temperature thermal expansion of several transition metal nitrides has been studied and the results recently compiled [1], no detailed investigation in the low-temperature range could be found in the literature. Only a single lattice parameter at 93 K has been given by Timofeeva and Shvedova [2] for some group IVb and Vb nitrides. As the refractory nitrides are of considerable interest in technical applications, we decided to investigate their low-temperature expansion behaviour from X-ray powder diffraction.

Samples of Sc, Ti, Zr, Hf, V, Nb and Ta nitrides were produced by direct nitridation of the metals with pure nitrogen in a cold-wall autoclave at various pressures and temperatures in the ranges 10 mbar–30 bar and 1500–1900 K. Care was taken to avoid oxygen contamination (Zr-getter foil). X-ray powder diffraction analysis using Ni-filtered Cu radiation showed clear Ka1/Ka2 splitting at high diffraction angles. Nitrogen analysis was carried out by Dumas and/or Dumas–gas chromatography analysis with an accuracy of better than [N]/[Me]=±0.01. The samples ScN, TiN, ZrN and HfN had stoichiometric compositions within this range, whereas the two vanadium nitride samples had the compositions VN0.72 and VN0.90.

For the low-temperature diffraction experiments a computerized Guinier diffractometer [3] operating with a helium cryostat was used. Strictly monochromatized (Si crystal) Cu Ka, radiation (1.540 562 Å) was applied. The temperature was measured with an Si diode. Si powder was used as an internal standard by admixing it intimately with the powdered sample material. The goniometer settings were calibrated as a function of temperature using the parameter values of Batchelder and Simons [4]. Diffraction data were recorded in the theta range 10°–50° with a step width of 0.005° and a counting time of 1–2 s step−1 in steps of 40–50 K in the temperature range 8–300 K.

In order to detect possible deviations from cubic lattice symmetry at low temperatures, such as those observed for CrN-1.00 [5, 6] and VN-1.00 [7], some
diffraction profiles were more precisely measured at 8 K with a counting time per step ($\Theta = 0.01^\circ$) of up to 100 s. There was no indication (such as line broadening or splitting) of a phase transition.

Four to five diffraction lines for both the silicon standard and the nitride phase were used for lattice parameter determination at each temperature step. The raw data from a peak search routine were introduced into a computer program [8] which fitted the standard lines to a third-order polynomial equation and corrected the diffraction lines accordingly. The standard deviation of the obtained lattice parameters was smaller than 0.0001 nm.

**TABLE 1**

Coefficients for the function $a_T = a_{3K} + A(T - 8) + B(T - 8)^2$ and $a_T = a_{3K}^{-1}[A + 2B(T - 8)]$ in the interval 8–300 K for the nitrides investigated.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$a_{3K}$</th>
<th>$A \times 10^4$</th>
<th>$B \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScN</td>
<td>0.45004(3)</td>
<td>-1.2344</td>
<td>6.2099</td>
</tr>
<tr>
<td>TiN</td>
<td>0.42348(5)</td>
<td>0.5853</td>
<td>2.9737</td>
</tr>
<tr>
<td>ZrN</td>
<td>0.45717(6)</td>
<td>1.3838</td>
<td>1.9787</td>
</tr>
<tr>
<td>HfN</td>
<td>0.45213(5)</td>
<td>0.0734</td>
<td>4.0308</td>
</tr>
<tr>
<td>VN$_{632}$</td>
<td>0.40593(9)</td>
<td>-0.3497</td>
<td>5.2731</td>
</tr>
<tr>
<td>VN$_{636}$</td>
<td>0.41235(5)</td>
<td>-0.7980</td>
<td>8.4676</td>
</tr>
<tr>
<td>NbN$_{6197}$</td>
<td>0.43880(4)</td>
<td>0.7862</td>
<td>2.8002</td>
</tr>
<tr>
<td>TaN$_{301}$</td>
<td>0.43341(6)</td>
<td>0.4213</td>
<td>3.2342</td>
</tr>
</tbody>
</table>

![Fig. 1. Normalized linear thermal lattice expansion, $(a_T - a_{3K})/a_{3K}$, as a function of temperature for ScN$_{1038}$ and group IVb and Vb transition metal nitrides, as calculated from coefficients in Table 1. The bar represents the error range.](image-url)
The lattice parameters vs. temperature were fitted by a parabolic least-squares fit of \( (a_T - a_{30K})/T \) vs. \( T \). Table 1 contains the coefficients of the polynomials of \( a_T \) as a function of temperature. With the exception of VN\(_{0.72}\) and VN\(_{0.96}\), all nitrides exhibit coefficients of linear thermal expansion \( \alpha \) in the range \( (5.5-6) \times 10^{-6} \, \text{K}^{-1} \) at room temperature. The expansivity of VN\(_{1-x}\) is substantially higher \( (\alpha = (7-8) \times 10^{-6} \, \text{K}^{-1}) \) and increases with nitrogen content.

A graphic representation of the linear thermal lattice expansion for the various nitrides investigated is shown in Fig. 1. Except for scandium nitride and vanadium nitride, all compounds show a monotonic increase in their lattice parameters with increasing temperature. ScN, VN\(_{0.72}\) and VN\(_{0.96}\) exhibit a lattice parameter minimum centred around 30 K, 50 K and 100 K respectively, i.e. their expansion coefficients are negative below these temperatures. For ScN the anomaly is more pronounced than for the vanadium nitrides; its origin is not yet clear.

Together with the expansion values from high-temperature X-ray diffraction [1] the expansivities of most transition metal nitrides are now available in a broad temperature range from 8 K to at least 1000 K. It is thus possible to predict any lattice mismatch for nitrides which are to be joined to materials such as binder phases in cermet or substrates in layer technology.

Acknowledgment

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References