

# Lattice parameters and thermal expansion of $\text{Ti}(\text{C}_x\text{N}_{1-x})$ , $\text{Zr}(\text{C}_x\text{N}_{1-x})$ , $\text{Hf}(\text{C}_x\text{N}_{1-x})$ and $\text{TiN}_{1-x}$ from 298 to 1473 K as investigated by high-temperature X-ray diffraction

K. Aigner<sup>a</sup>, W. Lengauer<sup>a,\*</sup>, D. Rafaja<sup>b</sup> and P. Ettmayer<sup>a</sup>

<sup>a</sup>Institute for Chemical Technology of Inorganic Materials, Vienna University of Technology, Getreidemarkt 9/161, A-1060 Vienna (Austria)

<sup>b</sup>Department of Semiconductor Physics, Charles University Prague, Ke Karlovu 5, CZ-12116 Prague (Czech Republic)

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## Abstract

The thermal expansion values of the fcc phases  $\text{Ti}(\text{C}_x\text{N}_{1-x})$ ,  $\text{Zr}(\text{C}_x\text{N}_{1-x})$  and  $\text{Hf}(\text{C}_x\text{N}_{1-x})$  with  $[\text{C}+\text{N}]/[\text{Me}] \sim 1$  and  $\text{TiN}_{1-x}$  with  $[\text{N}]/[\text{Ti}] = 1.0$  to 0.67 were determined from lattice parameter measurements made with high-temperature X-ray diffraction (HTXRD) in the temperature range of 298–1473 K. Stoichiometric titanium carbonitrides, zirconium carbonitrides and hafnium carbonitrides obey the Vegard rule up to 1473 K quite well, i.e. at any temperature up to 1473 K the lattice parameter behaves linearly between  $\text{TiN}$ – $\text{TiC}$ ,  $\text{ZrN}$ – $\text{ZrC}$  and  $\text{HfN}$ – $\text{HfC}$ , respectively. The lattice parameter of titanium nitride is also a linear function of the nitrogen/metal ratio in the temperature range investigated.

## 1. Introduction

Refractory carbides, nitrides and carbonitrides of the Group IV transition metals are used as the hard phase in sintered cermet alloys and for protective layers on hard metals. These materials are applied as cutting tools in machining operations where high temperatures are developed due to the intensive tool-workpiece interaction. For a deeper insight into the behaviour of cermets and coated hard metals, it is necessary to know the thermal expansions of the hard phases in relation to the binder phase and, in particular, the difference in the linear thermal expansions between the coating and the substrate. The present study was performed in order to obtain information on the thermal expansion behaviour of the hard materials as determined from accurately characterized samples.

## 2. Experimental setup

The experimental setup consisted of a high-temperature camera manufactured by Anton Paar KG, Graz, Austria. The camera was attached to a vertical Bragg-Brentano Goniometer (Philips). A special feature of

the Paar camera is that the thermal expansion of the heater strip is compensated by constructive means which should avoid significant sample displacements. The temperature was measured internally using a Pt/Pt10%Rh thermocouple tightly squeezed into a borehole in the centre of the heating strip and, additionally, with an optical pyrometer. The original plastic Kapton<sup>R</sup> foil X-ray window was replaced by a Ni foil, the latter being the filter for the Cu radiation used to eliminate the  $K\beta$  radiation. This replacement has several advantages:

- (1) The camera can be operated at high vacuum, without a highly toxic and expensive beryllium window.
- (2) The thermal load of Ni can be higher than that of the previously used Kapton<sup>R</sup> foil; the camera can also be operated at pressures up to 1 bar and at higher temperatures.

- (3) The registered X-ray intensities are higher than with the originally equipped high-temperature camera because the absorbance by the plastic foil is eliminated.

Since the radiation traverses the camera windows twice, the thickness of the Ni foil used was 10  $\mu\text{m}$ , which is about half of the standard filter thickness, in order to obtain optimum Cu- $K\beta$  intensity reduction. This modification also seems to be appropriate for practically all other standard target/filter combinations. Further camera improvements were made in order to obtain *in situ* gas purification by inserting a titanium

\*Author to whom correspondence should be addressed.

getter into the chamber which can be electrically heated prior to and during the high-temperature cycles.

The temperature was regulated by an HTK 2 HC heat controller provided by A. Paar KG. The heat controller was connected to a PC which also controlled the goniometer (stepper motor control and intensity counting). The entire system was operated automatically by a single program which assured that the temperature was changed asymptotically from the current value to the desired value. When the temperature was correct within 0.5 °C, the program started the XRD measurement.

The goniometer setting was calibrated at room temperature with high-purity silicon powder and checked at 1273 K by measuring high-purity corundum. The measured lattice parameters agreed with the values given by Brown *et al.* [1] within the standard deviation, showing that the room-temperature goniometer calibration is also applicable for high temperatures without any further correction being necessary. The sample displacement mentioned by Brown *et al.* was not observed in the present study.

### 3. Sample preparation and characterisation

The samples were prepared by hot pressing powder mixtures of titanium, titanium nitride, titanium carbide, zirconium nitride, zirconium carbide, hafnium nitride and hafnium carbide powders provided by H.C. Starck (Germany).

The powders were mixed and milled in a hard metal ball mill under cyclohexane after which the powder mixture was hot pressed. A zirconium layer inside the dies prevented the diffusion of carbon into the samples. The temperature was 2800 K and the pressure 55 MPa. This treatment led to nearly dense samples which were crushed and ball milled. The powders were analysed with Dumas gas chromatography [2]. The standard deviations were better than 2.5 rel.% for both nitrogen and carbon. The substoichiometric titanium nitrides were obtained by partial nitridation of pure titanium and annealing for homogenization in an Ar atmosphere [3].

### 4. Measurement

The samples were powdered and spread on the surface of the target area of the tantalum strip using a small

TABLE 1. Composition of samples investigated

Sample	at.% C	at.% N	at.% Ti	[C]/[C+N]	
Titanium carbonitrides: $Ti(C_xN_{1-x})$					
TiC	48.6	0.5	50.9	0.99	
TiN2C8	39	10.1	50.9	0.79	
TiN4C6	29.5	19.9	50.6	0.60	
TiN6C4	19.8	29.9	50.3	0.40	
TiN8C2	10.3	38.1	51.6	0.21	
TiN	0.5	49.2	50.3	0.01	
Sample	at.% Hf	at.% Zr	at.% C	at.% N	[C]/[C+N]
Zirconium carbonitrides: $Zr(C_xN_{1-x})$					
ZrC	0.6	48.9	48.9	1.6	0.968
ZrN5C5	0.6	50.6	24.5	23.8	0.507
ZrN	0.0	50.1	0.0	49.1	0.000
Sample	at.% Hf	at.% Zr	at.% C	at.% N	[C]/[C+N]
Hafnium carbonitrides $Hf(C_xN_{1-x})$					
HfC	49.8	0.1	48.3	1.7	0.966
HfN5C5	49.2	1.1	24.5	25.0	0.494
HfN	0.0	50.1	0.0	49.9	0.000
Sample	at.% Ti	at.% N	[N]/[Ti]		
Titanium nitrides $TiN_{1-x}$					
TiN90	52.6	47.4	0.90		
TiN83	54.7	45.3	0.83		
TiN77	56.5	43.5	0.77		
TiN67	59.9	40.1	0.67		

amount of methanol. The camera was then closed, evacuated and flushed with helium gas (< 9.9996 vol.% He). After three evacuation/flushing cycles, the helium pressure was adjusted to 15 mbar. Traces of oxygen were removed from the gas atmosphere by heating the titanium getter wire to *ca.* 900 °C for 20 min prior to the measurements at elevated temperatures. The composition of the atmosphere was checked occasionally by a quadrupole-mass-spectrometer (QMG 421C, Balzers) in order to detect any decomposition of the sample. The diffraction lines at high angles were measured using Cu-K $\alpha$  radiation filtered by the Ni camera windows. The step width of the goniometer was 0.02°, the measurement time 1 s/step. The diffraction lines were measured first at room temperature and then the temperature was raised in steps of 200 K. When the measurement cycle was complete, the sample was cooled down again to room temperature and checked for any changes in the diffraction pattern before and after the high-temperature measurements. With the exception of nitrogen-poor titanium nitrides, no deviations could be detected.

The peaks were approximated by a Pearson VII function in order to correct for the Cu-K $\alpha_2$  contribution and thus the exact K $\alpha_1$  peak position could be determined [4]. The peak positions were corrected against a silicon standard using a third-order polynomial equation and then the lattice parameters were calculated. The polynomials for lattice parameter versus temperature were calculated by means of non-linear least-squares regression.

## 5. Results and discussion

### 5.1. Titanium, zirconium and hafnium carbonitrides

The Ti(C $_x$ N $_{1-x}$ ) lattice parameters versus composition were found to fit eqn. (1) in the temperature region 298–1473 K

$$a([C]/[C+N], T) = 0.42313 + 0.0088 \times [C]/[C+N] + (2.338 - 0.122 \times [C]/[C+N]) \times T \times 10^{-6} + (1.0717 - 0.2258 \times [C]/[C+N]) \times 10^{-9} \times T^2 \pm 0.0002 \text{ nm} \quad (1)$$

where  $a$  is the lattice parameter,  $[C]/[C+N]$  is the carbon/metalloid ratio and  $T$  the absolute temperature. The decrease in the thermal expansion coefficient from TiN to TiC can easily be seen from Fig. 1. The average thermal expansion coefficient in the range investigated was found to decrease according to

$$\alpha_{av} = (9.9 - 1.4 \times [C]/[C+N]) \times 10^{-6} \text{ K}^{-1} \quad (2)$$

The linear thermal expansion coefficient  $\alpha$  is

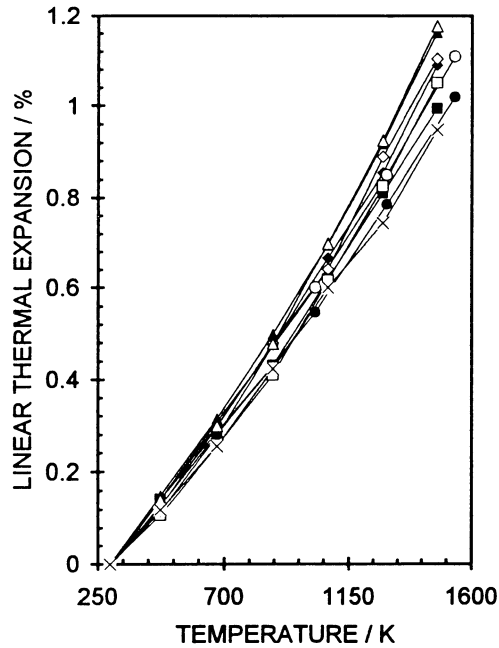


Fig. 1. Thermal expansion of Ti(C $_x$ N $_{1-x}$ ). ■ TiC, □ TiC8N2, ◆ TiC6N4, ◇ TiC4N6, ▲ TiC2N8, △ TiN, ● TiC [5], ○ TiN [5], × TiC [6].

$$\alpha([C]/[C+N], T) = ((2.338 - 0.122 \times [C]/[C+N]) \times 10^{-6} + (2.143 - 0.451 \times [C]/[C+N]) \times 10^{-9} \times T) / a([C]/[C+N], T) \text{ K}^{-1} \quad (3)$$

At higher temperatures, slightly higher thermal expansions were found in the present study than were determined by Houska [5]. For titanium nitride, this could be only partly contributed to the fact that the thermal expansion decreases with decreasing nitrogen/titanium ratio (see below) which was higher for our sample ( $[N]/[Ti]=0.98$ ) than for Houska's ( $[N]/[Ti]=0.95$ ).

The Zr(C $_x$ N $_{1-x}$ ) lattice parameters fit eqn. (4):

$$a([C]/[C+N], T) = 0.45718 + 0.01178 \times [C]/[C+N] + (2.107 + 0.0098 \times [C]/[C+N]) \times T \times 10^{-6} + (8.253 - 0.006 \times [C]/[C+N]) \times 10^{-10} \times T^2 \pm 0.0002 \text{ nm} \quad (4)$$

The value of the linear thermal expansion coefficient  $\alpha$  is

$$\alpha([C]/[C+N], T) = ((2.107 + 0.0098 \times [C]/[C+N]) \times 10^{-6} + (1.650 - 0.0012 \times [C]/[C+N]) \times 10^{-9} \times T) / a([C]/[C+N], T) \text{ K}^{-1} \quad (5)$$

The average linear thermal expansion coefficient is

$$\alpha_{av} = (7.8 + 0.3 \times [C]/[C+N] - 0.6 \times [C]/[C+N]^2) \times 10^{-6} \text{ K}^{-1} \quad (6)$$

As can be seen from Fig. 2, there was good agreement between the literature data for ZrC and ZrN [5] and our measurements.

The lattice parameters of the hafnium carbonitrides are expressed by

$$a([C]/[C+N], T) = 0.45173 + 0.0115 \times [C]/[C+N] + (1.9916 + 0.2875 \times [C]/[C+N]) \times T \times 10^{-6} + (1.124 - 0.877 \times [C]/[C+N]) \times 10^{-9} \times T^2 \pm 0.0002 \text{ nm} \quad (7)$$

The linear thermal expansion coefficient is given by

$$\alpha([C]/[C+N], T) = ((1.9916 + 0.2875 \times [C]/[C+N]) \times 10^{-6} + (2.248 - 1.754 \times [C]/[C+N]) \times 10^{-9} T) / a([C]/[C+N], T) \text{ K}^{-1} \quad (8)$$

Similar to the results for TiC and TiN, the thermal expansion values for HfC and HfN were also higher than those given in the literature [7] (Fig. 3).

The average linear thermal expansion coefficient in the range investigated range increases linearly with the  $[C]/[C+N]$  ratio:

$$\alpha_{av} = (8.5 - 2.4 \times [C]/[C+N]) \times 10^{-6} \text{ K}^{-1} \quad (9)$$

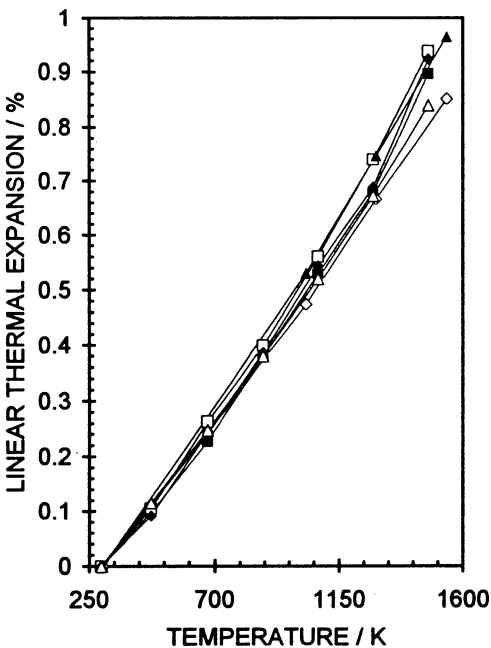


Fig. 2. Thermal expansion of  $Zr(C_xN_{1-x})$ . ■ ZrC, □ ZrC5N5, ◆ ZrN, ◇ ZrC [5], ▲ ZrN [5], △ ZrC [6].

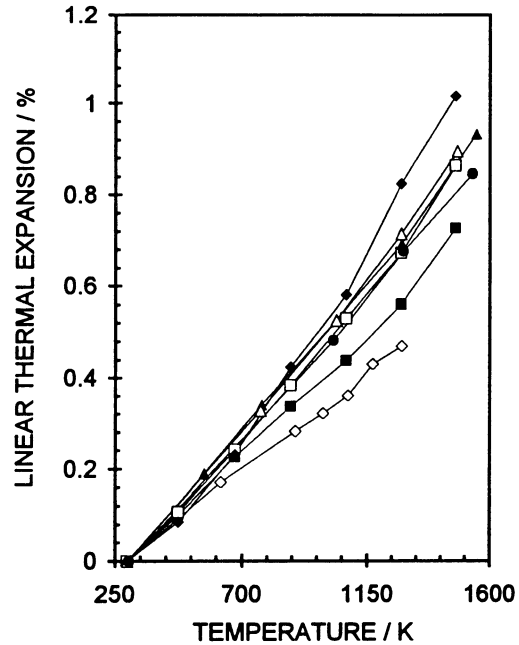


Fig. 3. Thermal expansion of  $Hf(C_xN_{1-x})$ . ■ HfC, □ HfC5N5, ◆ HfN, ◇ HfC [7], ▲ HfC6N4 [7], △ HfN [7], ● HfC [8].

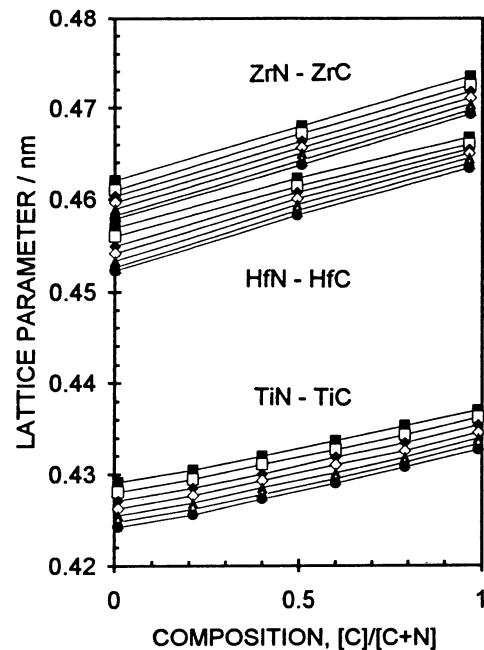


Fig. 4. Lattice parameters versus  $[C]/[C+N]$  ratio for  $Ti(C_xN_{1-x})$ ,  $Zr(C_xN_{1-x})$  and  $Hf(C_xN_{1-x})$ . ■ 1473 K, □ 1273 K, ◆ 1073 K, ◇ 873 K, ▲ 673 K, △ 473 K, ● 293 K.

The thermal expansion coefficients of the nitrides are always greater than those of the carbides. For titanium carbonitride and hafnium carbonitride, the function expansion versus composition is almost linear, while the expansion of the zirconium carbonitrides shows a slight maximum. Titanium carbonitrides, zirconium carbonitrides and hafnium carbonitrides obey Vegard's

rule quite well up to 1473 K (Fig. 4). Except for the hafnium carbonitrides, however, no literature data could be found for the thermal expansion of the carbonitrides for comparison purposes.

### 5.2. Nitrogen-deficient $\delta$ -TiN<sub>1-x</sub>

Figure 5 shows the thermal expansion versus temperature for samples with lattice parameters which were the same before and after the high-temperature investigation. Since the nitrogen-poor samples decomposed at high temperatures, these results were not considered in the following. The lattice parameter fits the equation

$$a([N]/[Ti], T) = 0.41823 + 0.00530 \times [N]/[Ti] + (1.2206 + 0.8348 \times [N]/[Ti]) \times 10^{-6} \times T + (1.3485 - 0.1128 \times [N]/[Ti]) \times 10^{-9} \times T^2 \pm 0.0002 \text{ nm} \quad (10)$$

The linear thermal expansion coefficient is expressed by the equation

$$\alpha([N]/[Ti], T) = ((1.2206 + 0.8348 \times [N]/[Ti]) \times 10^{-6} + (2.697 - 0.2256 \times [N]/[Ti]) \times 10^{-9} \times T) / a([N]/[Ti], T) \text{ K}^{-1} \quad (11)$$

The average linear thermal expansion coefficient in the temperature range of 293–1073 K is

$$\alpha_{av} = (7.0 + 1.9 \times [N]/[Ti]) \times 10^{-6} \text{ K}^{-1} \quad (12)$$

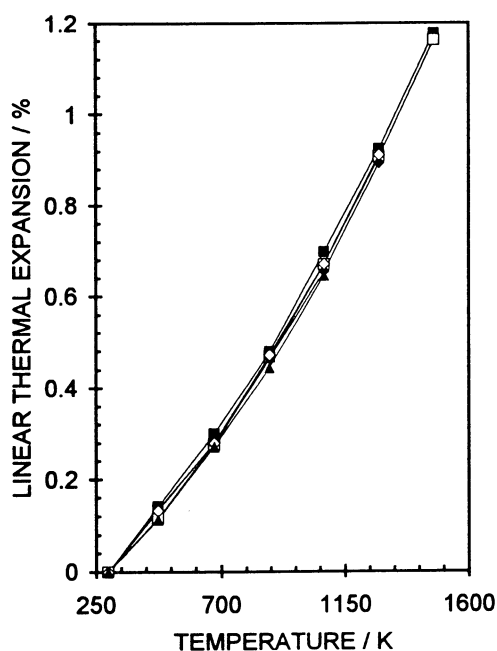


Fig. 5. Thermal expansion of nitrogen-deficient titanium nitride. ■ TiN<sub>99</sub>, □ TiN<sub>90</sub>, ◆ TiN<sub>83</sub>, ◇ TiN<sub>77</sub>, ▲ TiN<sub>67</sub>.

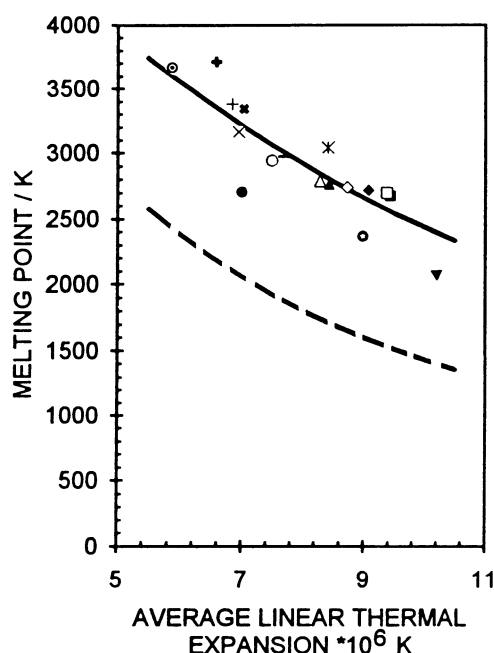


Fig. 6. Average linear thermal expansions of various nitrides, carbides and carbonitrides versus melting points compared to the behaviour of metals. NbN and TaN decompose upon melting (no congruent melting point of NbN could be found in the literature. One has been reported for TaN, but it was probably for Ta<sub>2</sub>N instead). ■ TiN, □ TiC<sub>2</sub>N<sub>8</sub>, ◆ TiC<sub>4</sub>N<sub>6</sub>, ◇ TiC<sub>6</sub>N<sub>4</sub>, ▲ TiC<sub>8</sub>N<sub>2</sub>, △ TiC, ● ZrN, ○ ZrC<sub>5</sub>N<sub>5</sub>, × ZrC, \* HfN, + HfC<sub>5</sub>N<sub>5</sub>, ⊙ HfC, - TaN [12], + TaC [11], ○ NbN [12], × NbC [11], ▼ VN [12], --- cubic metals [11], — regressed values.

In Fig. 6, the average linear thermal expansion coefficients were plotted against the melting points [10,11] of the materials. Thermal expansion data of the carbides and nitrides from the literature [9,12] were included. Except for the nitrides of niobium, hafnium and vanadium, the data fit the line quite well. For NbN<sub>1-x</sub>, the highest reaction temperature NbN ↔ Nb<sub>2</sub>N + 1/2N<sub>2</sub> was used. If a congruent melting temperature is taken, the value of the melting point would shift to a higher temperature. A similar curve is known for pure metals, which however is shifted towards lower melting points (broken line) [13].

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