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Short Communications

A Neutron Diffraction Investigation on Single Crystals of Titanium Carbide, Titanium Nitride, and Zirconium Nitride

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Single crystals of titanium carbide, TiC, titanium nitride, TiN, and zirconium nitride, ZrN, have been prepared using the floating zone technique. [1] The carbide was grown in helium, and the nitrides were grown in nitrogen. The experimental crystal growth conditions for the samples used in the neutron diffraction investigation are listed in Table 1. The unit cell parameters of the compounds were determined from Guinier powder patterns using $CuK\alpha_1$ radiation, $\lambda = 1.54051$ Å, with NaCl, $a = 5.6389$ Å, as an internal standard. The values obtained are: TiC: $a = 4.328(2)$ Å, TiN: $a = 4.235(2)$ Å, and ZrN: $a = 4.585(2)$ Å. The densities of the compounds were measured using the method of Archimedes, and the values found are: TiC: $\varrho = 4.87(1)$ g/cm³, TiN: $\varrho = 5.02(1)$ g/cm³, and ZrN: $\varrho = 7.29(1)$ g/cm³. Chemical analyses of the metals in the three compounds were made. Titanium in TiC was determined spectrophotometrically as the peroxy titanium ion, and titanium and zirconium in the nitrides were determined gravimetrically by combustion of the nitrides in oxygen at 1 000 °C to TiO_2 and ZrO_2. The results of the chemical analysis are listed in Table 2, where the chemical formulae corresponding to the results of the chemical analysis are listed. The neutron diffraction data were measured at an automatic four-circle diffractometer at DR3, Risø, using 1.07 Å neutrons, and the standard $\omega - 2\theta$ scan technique.[2] A single crystal of TiC with a volume of 0.027 mm³ and linear dimensions in the range 0.17 to 0.55 mm was used in measuring a total of 96 reflections. The diffraction data were reduced using a standard procedure,[3] yielding a total of 16 independent reflections. The single crystal of TiN had the linear dimensions $2.5 \times 2.5 \times 0.8$ mm. A total of 445 reflections was measured. After data reduction the number of independent reflections was 16. The single crystal of ZrN had a volume of 5 mm³ and linear dimensions in the range 1.5 to 3.0 mm. The number of measured reflections was reduced from 337 to 16 independent reflections in the data reduction.

Table 1. Experimental conditions for the growth of TiC, TiN, and ZrN. A: Starting material(s). B: Gas, pressure in atm. C: Length of zone melted specimen in mm. D: Growth rate mm h^{-1}. E: Gear.

Compound	A	B	C	D	E
TiC	TiC	He 17.5	72	7.5	1:1.2
TiN	$Ti + N_2$	N_2 20.4	29	25	none
ZrN	$Zr + N_2$	N_2 15.5	60	7.5	none

Table 2. Densities of crystals and chemical formulae. Standard deviations in parentheses.

Compound	Densities in g/cm³ Obs.	Calc. [a]	Composition from chemical analysis	Composition from neutron diffraction
TiC	4.87(1)	4.908	$Ti_{1.00}\ C_{1.0}$	$Ti_{0.98(3)}\ C_{1.0}$
TiN	5.02(1)	5.394	$Ti_{0.72}\ N_{1.0}$	$Ti_{0.76(4)}\ N_{1.0}$
ZrN	7.26(1)	7.304		
ZrN	7.29(1)	7.304	$Zr_{1.0}\ N_{0.97}$	$Zr_{1.00(1)}\ N_{1.0}$

[a] From unit cell parameters and assuming stoichiometric composition.

Table 3. Results from neutron diffraction. Standard deviations in parentheses.

	Site	Occupancy	B (Å^2)
TiC, $R = 3.8$ %			
Ti	4*a*	0.98(3)	0.24(14)
C	4*b*	1.0	0.36(07)
TiN, $R = 3.7$ %			
Ti	4*a*	0.76(4)	0
N	4*b*	1.0	0
ZrN, $R = 3.9$ %			
Zr	4*a*	1.00(1)	0
N	4*b*	1.0	0

The three compounds are isostructural with sodium chloride, space group $Fm3m$, No. 225. The metal atoms are placed in the site 4*a*, and the non-metal atoms are placed in the site 4*b*. Observed and calculated structure factors were compared using the least squares program LINUS.[4] The neutron scattering lengths used for Ti, Zr, C, and N were -0.335, 0.714, 0.6648, and 0.940, all in units of 10^{-12} cm.[5] The variable parameters for each refinement were a scale factor, isotropic temperature factors for the metal and the non-metal atoms, and an occupancy factor for the metal atom or for the non-metal atom. The results of the refinements are listed in Table 3. A list of observed and calculated structure factors can be obtained from the author at request.

The result of the neutron diffraction investigation is that the investigated specimens of the titanium carbide and zirconium nitride were stoichiometric within experimental errors, and that the titanium nitride investigated is clearly non-stoichiometric with the 4*a* site only partly occupied. The formation of metal atom vacancies should, according to Brager,[6] result in a reduction of the unit cell parameter from 4.235 Å for the N/Ti ratio 1.00 to 4.220 Å for the N/Ti ratio 1.10. Such a reduction of the unit cell parameter has not been observed in the present investigation, as the unit cell parameter for the crystal investigated is 4.235 Å and the N/Ti ratio is 1.30(06).

The temperature factors for the atoms in TiC have been found to have the very small values listed in Table 3. These values are comparable with the temperature factors for the atoms in sodium chloride measured at 4.2 K, B_{Na^+}: 0.35(08) Å, and B_{Cl^-}: 0.27(04) Å,[7] and the low temperature factors for TiC reflect the hardness of the compound. The temperature factors of the atoms in TiN and ZrN are also very small, but become negative values in the least squares refinements. As the numerical values of the temperature factors were from 2 to 4 times the corresponding standard deviations on the temperature factors, the values for the temperature factors were set to zero as listed in Table 3.

Formation of stoichiometric TiC by a zone melting technique is in conflict with previously published phase diagrams for the TiC-system which shows that the maximum in the liquidus curve for TiC is not found for the stoichiometric composition but rather for a compound with the composition $TiC_{0.77}$.[8]

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