The Temperature Factor Parameters of Some Transition Metal Carbides and Nitrides by Single Crystal X-Ray and Neutron Diffraction

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The transition metal carbides and nitrides have been the subject of intensive investigations because of their unusual combination of physical properties. They have metallic conductivity, high melting points, great hardness and brittleness, and some of them show superconductivity. The hardness may be correlated with the temperature factor parameters of the atoms in the crystal lattice. As single crystals of some of these hard materials became available, it was decided to compare the temperature factor parameter of the atoms in these hard materials with the temperature factor parameters of the sodium and the chlorine atoms in the softer compound sodium chloride.

Single crystals were made by zone melting, zone annealing, and annealing crystal growth methods of the compounds TiC, $TiN_{0.90}$, δ-$NbN_{0.90}$, and $Nb_{0.83}Ti_{0.17}N_{0.77}C_{0.05}$.[1,2] All four compounds have the sodium chloride structure, space group *Fm3m*, No. 225, with the metal atoms in site 4*a* and the non-metal atoms in site 4*b*. Further pertinent crystallographic data for the compounds are listed in Table 1. The present communication describes the determination of the temperature factor parameters for the compounds using single crystal X-ray diffraction for TiC, and single crystal neutron diffraction techniques for the other three compounds.

A single crystal of TiC was made from a thin blade obtained when a large specimen was fractured. The blade was placed on a microscope slide on the microscope table and could be cleaved with the edge of another microscope slide. The crystal surfaces were all cleavage planes belonging to class {100}. A total of 76 independent *hkl* reflections with $I > 3\sigma(I)$ were measured on a Picker four circle diffractometer using monochromatic Ag$K\alpha$ radiation ($\lambda = 0.5608$ Å). The $\omega - 2\theta$ scan technique was used. The monochromator was a graphite crystal and the counter was a scintillation counter in conjunction with a pulse height analyzer. Lorentz-polarization corrections were applied and a correction was made for absorption using Well's method.[3]

Single crystals for the neutron diffraction measurements (Table 1) were cut from larger specimens using a diamond cut off wheel. The neutron diffraction data were measured on a four circle diffractometer at DR3, Risø, using 1.07 Å neutrons, and the standard $\omega - 2\theta$ scan technique.[4] The data were reduced using a standard procedure[5] and Lorentz-polarization and absorption corrections were made.

Observed and calculated structure factors were compared using the least-squares program *LINUS*.[6] For TiC the form factors for Ti and C reported by Fukamachi[7] were used in the calculations. The neutron scattering amplitudes used for Nb, Ti, C, and N were 0.711, −0.335, 0.6648, 0.940, respectively, all in units of 10^{-12} cm.[8] The results of the calculations with the values of the refined parameters are listed in Table 2. The corresponding lists of observed and calculated structure factors can be obtained from the author on request.

The result of the investigation shows that the compounds have low values for the isotropic temperature factor parameters, in agreement with the hardness of these materials. Sodium chloride has much higher values for the isotropic temperature factor parameters at 300 K, but at 4.2 K the values of the parameters are comparable with the isotropic temperature factor parameters for TiC at 300 K (see Table 2). This thus reflects the great hardness of titanium carbide. The Debye-temperatures obtained from the temperature factor parameters using the harmonic approximation[11] are listed in Table 2 together with values for θ_B obtained from low temperature specific heat measurements[9]

Table 1. Crystallographic data for compounds with space group *Fm3m*.

Compound	Unit cell parameter in Å	Linear absorption coefficient in cm^{-1}	Volume of specimen in mm^3	Number of reflections	
				Total	Independent
TiC	4.328(2)	34.5[a]	5×10^{-4}	2497	76
$TiN_{0.90}$	4.239(1)	0.42	124	294	19
δ-$NbN_{0.90}$	4.377(1)	0.14	19	225	20
$Nb_{0.83}Ti_{0.17}N_{0.77}C_{0.05}$	4.346(1)	0.55	27	204	19

[a] for X-rays Ag$K\alpha$.

Table 2. Results X-ray (TiC) and neutron diffraction. Standard deviations in parenthesis.

Compound	R %	Scale Factor	Extinction Parameter	Temperature Factor Parameter B(Å^2)		Debye Temperature θ_DK	
				M	X	This work	Ref. 9
TiC	1.6	5.40(3)	0.421(8)	0.26(1)	0.44(3)	604(24)	614–676
$TiN_{0.90}$	3.6	2044(39)	1.4(6)	1.06(17)	1.07(10)	332(17)	636
δ-$NbN_{0.90}$	3.8	487(19)	0.11(2)	0.66(10)	0.64(9)	320(25)	307
$Nb_{0.83}Ti_{0.17}N_{0.77}C_{0.05}$	3.2	632(20)	0.15(2)	0.60(8)	0.70(7)	337(15)	323[a]
NaCl, 295 K, Ref. 10				1.70(10)	1.44(3)		
NaCl, 4.2 K, Ref. 10				0.35(8)	0.27(4)		

[a] For the compound $NbN_{0.81}C_{0.09}$.

and are in acceptable agreement with these values for the Debye-temperatures. Surprisingly, it is found that $TiN_{0.90}$ has higher values for the temperature factor parameters than the three other compounds, and the calculated Debye-temperature is thus correspondingly lower. It is obvious, judged from the hardness of $TiN_{0.90}$ that is comparable with the hardness of TiC, that the isotropic temperature factor parameters arrived at here are too high. It is well-known that systematic errors in the diffraction data or in the calculations can be accummulated in the isotropic temperature factor parameters giving these physically meaningless values. This must be the case for $TiN_{0.90}$. It is observed (see Table 2) that the extinction parameter for $TiN_{0.90}$ is rather large which supports this hypothesis. The data have not been corrected for thermal diffuse scattering. This is a possible error source. An incorrect value for the scattering length of titanium would also have the observed effect on the extinction parameter and the isotropic temperature factor parameters. The Debye-temperature of $TiN_{0.95}$ has recently been determined from Raman scattering experiments[12] as 518 K in acceptable agreement with a Debye-temperature of 485 K obtained for $TiN_{0.99}$ from heat capacity measurements.[13] An average isotropic temperature factor parameter for Ti and N corresponding to the value 518 K would be 0.45 Å^2.

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