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The Defect Structure and Bonding of Zirconium Nitride Containing Excess Nitrogen[1]

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Zirconium nitride, containing 2.0 wt % Hf, is found to have $a_{25} = 4.57560 \pm 0.00005$ A (refraction correction included) and a linear thermal expansion coefficient $\alpha = 5.28 \times 10^{-6}$ deg^{-1} (10–60°). Its composition is $(\mathrm{Zr}, 2\%\ \mathrm{Hf})_{0.95 \pm 0.03}\mathrm{N}$, experimental density $d_{25°} = 6.884 \pm 0.003$ g cm^{-3} (the X-ray density of the stoichiometric compound is 7.284 g cm^{-3}). The unit cell contains 3.913 molecules with 3.5% of all sites (8/unit cell) vacant in the cationic and 1.1% in the anionic (N) sublattice. The excess of N atoms over the stoichiometric formula is 0.19 atom/unit cell. From purely chemical considerations the bonding appears to be more *ionic* than *metallic* and may be described as involving various electronic states of nitrogen (N^{3-}, N^0), imposing a high degree of ionic character on the nitride. However, no quantitative value could be assigned to the degree of ionic bonding.

The phase diagram for zirconium and nitrogen was developed by Domagala, *et al.*;[2a] it showed an α-solid solution and a ZrN homogeneity phase of a range smaller than that for TiN.[2b] Further investigation by Juza, *et al.*,[3] revealed the possibility of an excess nitrogen phase of the composition Zr_3N_4. The ZrN phase may contain defects in the form of vacancies as do TiN and TiO.[4]

Since ZrN closely resembles TiN, the problems of bonding are similar. Klemm and Schüth,[5] Philipp,[6] and Pearson[7] have proposed metallic bonding in TiN and ZrN, whereas Baughan[8] concluded from the lattice energy that the bonding was ionic. Goward and Hershenson[9] and O'Keefe[10] pointed out that the experiments of Philipp were inconclusive. Samsonov and Verkhoglijadova[11] are of the opinion that the bonding is at least in part ionic.

The intention of the present investigation was to study the defects in zirconium nitride (with excess N) by the lattice parameter and density method and to come to some conclusion concerning the bonding in ZrN on the basis of chemical behavior.

Material

Zirconium nitride (from the Carborundum Metals Co., Akron, N. Y.) was a dark gray-brown powder with a greenish tint, displaying under the microscope a golden, metallic color.

The composition (in %) of the ZrN batch was as follows: metallic impurities (Fe, Al, Cr, Mg, etc.), 0.27; Hf, 2.0; N, 11.6; Zr, 86.13.

Inasmuch as the sample was later analyzed, the knowledge of the Hf content was important. Since ZrN and HfN differ in lattice parameters by only 1.4% (4.5756 − 4.5118 = 0.0638 A), they form, according to Duwez and Odell,[12] a continuous series of solid solutions. Therefore the 2% Hf content increased the atomic mass of Zr from 91.22 to 92.12. The influence of other impurities (0.27%) was disregarded. Lattice parameter and density determinations were made to detect the defects in the nitride.

Lattice Constant and Expansion Coefficient

The nitride samples produced sharp X-ray powder lines. However, only chromium Kβ radiation (λ 2.08059 kx) gave a β331 line suitable ($\theta \sim 83°$) to measure precisely the lattice constant (at 10.0, 30.0, 40.0, 50.0, and 60.0°). The 64-mm camera containing the sample was placed into a thermostat for a 40-min exposure by the X-ray beam. As the powder mount was <0.2 mm, no absorption correction was applied,[13] but a refraction correction of 0.00019 A was added to the constants (the conversion factor was 1.00202). At least two photographs were made at each temperature. The one last β-line measurement did not decrease the precision of the a determinations as explained previously.[14]

The average lattice constants are plotted *vs.* temperature in Figure 1. The expansion coefficient α, calculated from the slope of the line of Figure 1, was 5.28×10^{-6} deg^{-1}, in agreement with $(6.0 \pm 0.5) \times 10^{-6}$ deg^{-1}, obtained by Baker.[15]

Using the former, all constants in Figure 1 were reduced to that at 25° and an average of $a_{25} = 4.5756_0 \pm 0.00005$ A (refraction correction included) was obtained. The error represents the probable error. This value of a is in good agreement with previous determinations: van Arkel,[16] 1924, 4.62; Ransley and

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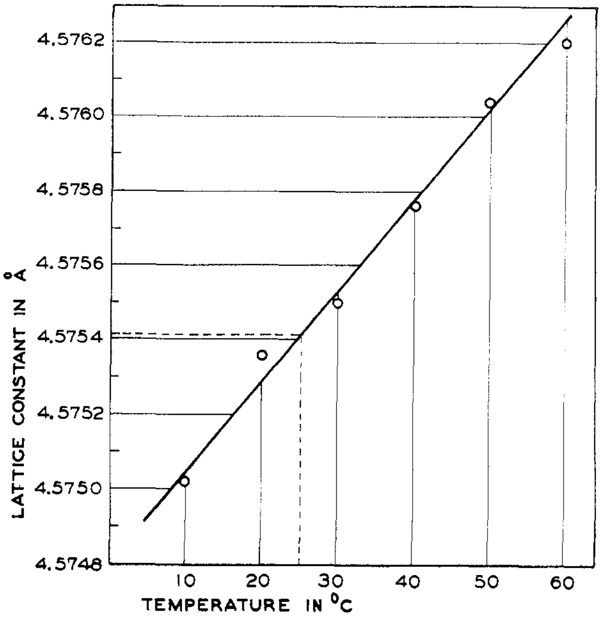

Figure 1.—Lattice constant of cubic ZrN (sodium chloride structure) *vs.* temperature. Refraction correction is *not* added.

Rooksby,[17] 1942, 4.566; Duwez and Odell,[12] 1950, 4.576; Schönberg,[18] 1954, 4.562 A.

Density and Formula of the Nitride

The weighing of the nitride powder (in an Ag crucible) was made at selected constant temperatures in air and xylene, the exact density of which was known over a range of room temperatures.

The powder–xylene mixtures were outgassed under vacuum by vigorous mechanical vibration. The final weighing was performed in air after complete evaporation of xylene from the silver crucible. The densities, reduced to vacuum, were calculated from these data.[19] Eight determinations of each of as many samples gave: 6.8784, 6.8760, 6.8870, 6.8846, 6.8822, 6.8862, 6.8900, and 6.8813 g cm^{-3}. The average was $d_{25°} = 6.884 \pm 0.003$ g cm^{-3} where ±0.03 is again the probable error. The density for ZrN obtained by Friederich and Sittig[20] was 6.93 for a compound prepared from ZrO_2, C, and N_2. The X-ray density of the stoichiometric compound ZrN was higher (7.284 g cm^{-3}).

From the experimental density d and the lattice constants, the formula of a nonstoichiometric compound can be estimated. Assuming that all four nitrogen sites of the unit cell of the (Zr, 2% Hf)$_x$N are filled (because of N excess, as revealed by chemical analyses), the occupied (Zr, Hf) sites are $4x$, where x of (Zr, Hf)$_x$N is <1.[14] From the equation for the number of molecules per unit cell one then obtains

$$x = (vdN_0 - 4N)/4(\mathrm{Zr, Hf}) = 0.926 \qquad (1)$$

where v is the volume of the unit cell and N_0 is Avogadro's number ($= 6.024 \times 10^{23}$ mole^{-1}). The estimated formula of the nitride is therefore (Zr, 2% Hf)$_{0.926}$N, containing N excess. However, the value of x is not very certain, because of the difficulty in density determinations and the assumption made. Therefore, x was also calculated from chemical analyses by determining the amount of metal and of N in separate samples.

Chemical Analyses

Samples of (Zr, Hf)$_x$N were weighed and slowly burned in platinum crucibles in air at about 1100°, and the heating was continued until constant weight was achieved. From the weight of the dioxide the weight of the metal was calculated and the amount of N determined by difference. An average of 13.86 wt % (13.89, 13.83, and 13.86) N was obtained, which resulted in $x = 0.963$.

As the N contents result from difference, direct determinations of N of the nitride by the micro-Kjeldahl method were desirable.

It was found that upon dissolution of the nitride in HF (50% HF, 50% H_2O by volume), large amounts of NH_4F were formed and some gas was evolved, consisting, according to chromatographic analyses with a Wilkins Aerograph, of H_2 and N_2. The formation of H_2 is attributed to the proved reactions

$$\mathrm{Hf\ or\ ZrN} + 3\mathrm{HF} = \mathrm{ZrF_3} + \mathrm{NH_3} \qquad (2)$$

then rapidly

$$\mathrm{ZrF_3} + \mathrm{HF} = \mathrm{ZrF_4} + 0.5\mathrm{H_2} \qquad (3)$$

$$\mathrm{NH_3} + \mathrm{HF} = \mathrm{NH_4F} \qquad (4)$$

As evidence for reaction 3 the gas developed was collected and its volume reduced to standard conditions.[21] About 0.101 ± 0.004 ml mg^{-1} was obtained in comparison with 0.098 ml mg^{-1}, calculated from (2) and (3) assuming $x = 0.926$ (eq 1). This result and the NH_4F found proves that reactions 2–4 certainly occur. The second gas, N_2, was present in a smaller amount, in accord with the difference of the observed volume of the gas and that of the calculated H_2. Conversely, the gas developed during dissolution of TiN was predominantly N_2[22] (the rate of reactions 2 and 3 for TiN is very slow[21]). This N_2 could originate from the nitrogen weakly bound as atoms by the titanium and also the zirconium nitride.

The presence of atomic N in the solid compound might be revealed by heating the nitride under vacuum. According to Agte and Moers[23] and Friederich and Sittig,[20] the melting point of the nitride is 2982 ± 50° and its dissociation occurs just below this point. Clausing,[24] however, found that N_2 is partially released at lower temperatures. According to Kroll, *et al.*,[25] the release under vacuum begins at 500°. Hence, the gas developed could not be absorbed N_2 but rather must have been constitutional. The

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present heating experiments were performed in a "Leco" analyzer at a temperature halfway between the melting point and 500° (at 1250° for 12 min) until no gas was released: an average of 1.1 wt % N_2 (1.1, 1.1, and 1.0 wt %) was obtained. Therefore, it seems plausible that zirconium nitride contains *two kinds* of *nitrogen*, especially if one considers the method of determination: the N content obtained from Dumas analyses is always higher than that found from Kjeldahl, as reported by Hägg[26] and recently by Kern and Brauer.[27] The same was observed by us for Ti nitrides.[22] Whereas the Dumas method and the combustion analyses reveal the *total* amount of N present in a compound, the Kjeldahl method may determine only the N^{3-} ionically bonded, because the atomic nitrogen escapes during digestion in HF (about 0.4 wt % is calculated from the average, subtracting 0.098 ml/mg of H_2). The difference in the results of both methods thus represents the less tightly bonded atomic N, the approximate amount of which can also be found from vacuum-extraction analyses. The correct percentage of nitrogen in the nitride is, therefore, obtained only by adding this (vacuum-extracted) N to the Kjeldahl N, as shown in Table I. In the sample there was an average of 12.38 wt % (12.35, 12.43, and 12.37) Kjeldahl N.[28]

TABLE I

VALUES OF x OF (Zr, 2% Hf)$_x$N OBTAINED FROM CHEMICAL ANALYSES

Method	% N		x
Combustion to ZrO_2, HfO_2	13.86		0.963
Kjeldahl: N → NH_3	12.38	13.48	0.976
Vacuum extraction at 1250°, 12 min	1.1		
Theoretical value + extraction analysis	14.30		0.911
	Av		0.950 ± 0.026

Finally, if it is assumed that, after degassing, a compound of theoretical composition (Ti, 2% Hf)N with 13.198% N is obtained, then, from addition of 1.1% N, x of the starting compound can be calculated. All the values of x obtained are listed in Table I.

The value of $x = 0.95 \pm 0.03$ agrees reasonably with that of 0.926 obtained by a completely different method, using lattice constant and density measurements. It is clear from this result that there are vacancies in the Zr sublattice. Are there vacancies also present in the N sublattice?

The Imperfect Structure of Zirconium Nitride

This question can be answered by calculating the actual number of molecules n' per unit cell (see also eq 1) from

$$n' = vdN_0/M \tag{5}$$

The number of vacant sites in the metal and nitrogen sublattices can then be found as shown in Table II, by inserting the value of M (=101.51 ± 2.58) for (Zr, 2% Hf)$_{0.95}$N into eq 5.

TABLE II

IMPERFECT STRUCTURE OF (Zr, 2% Hf)$_{0.95}$N IN MOLECULES, ATOMS (IONS), AND VACANT SITES PER UNIT CELL

			% vacant sites[a]
Molecules per unit cell, n'	3.913		
Zr + Hf atoms (ions), $n'x$	3.72	8.0	
Vacant sites in the metal sublattice, $n'x - 4$	−0.28		−3.5
N atoms (ions), n'	3.91		
Vacant sites in the nitrogen sublattice, $n' - 4$	−0.09		−1.1
Excess of N atoms, 3.91–3.72	0.19		...
		Total vacant sites	−4.6

[a] Of the total number of sites, 8/unit cell.

Discussion

The appearance of both NH_4^+ (see eq 2 and 4) and N_2 during the dissolution of the ZrN in HF suggests the simultaneous existence of *ionic* and *atomic* states of N in the nitride, of which the more disputed is the first.[6]

Facts in favor of the *ionic* state (Zr^{3+} and N^{3-}) are as follows.

(1) The large amounts of NH_4^+ formed during digestion in HF correspond to those found for the ionic alkali and alkaline earth nitrides. NH_3 formation, assuming metallic bonding, by the reaction of active N and H atoms at the nitride surface,[7] is improbable, especially if one notes that TiN dissolves in HF only in the presence of large amounts of the strongly oxidizing $KMnO_4$.[29,30]

(2) The enthalpies of formation of TiN, ZrN, and HfN are the highest among the nitrides,[22] amounting to −26.8, −27.4, and −29.4 kcal/equiv, respectively.

(3) The high lattice energy of -511 ± 57 kcal mole^{-1} (for N → N^{3-}) as calculated by Baughan,[8] corresponds with that of ionic alkali halides.

(4) The hardness, brittleness, high melting point, and other properties are, according to Pauling,[31] characteristic of multivalent ionic crystals.

The facts which indicate that *atomic* N is also present in the zirconium nitride are as follows.

(1) The excess of 0.19 N atom/unit cell (Table II) constitutes 0.67 wt % nitride as compared with 1.1 wt % obtained at 1250° by vacuum extraction. The difference is reasonable considering the two completely different methods of determination and the temperature.

(2) The N excess is shown by chemical analyses (Table I).

(3) N excess is further shown by vacuum extraction (Table I).

There are three observations which would favor covalent or metallic bonding throughout the nitride, if not explained otherwise.

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(1) The simultaneous appearance of H_2 and N_2 in the gas released upon dissolution of the Zr_xN in HF suggests that the atomic reaction of H and N

$$3H + N \longrightarrow NH_3 \qquad (6)$$

on the nitride surface was incomplete. However, the H_2 obtained could have resulted from reaction 3 and the nitrogen was that in excess in the solid nitride.

(2) The electrical conductivity indicates metallic bonding, but see below.

(3) The lattice parameter (calculated from the atomic radii of N and Zr) is in excellent agreement with the measured values (Table III).

TABLE III

BONDING IN $(Zr, 2\%\ Hf)_{0.95}N$ (NaCl STRUCTURE) AND THE LATTICE PARAMETER a (IN A)

	Metallic	Ionic (Zr^{3+})	Ionic and metallic	a_{measd}
$2r$ for Zr	3.12	1.84[a]	1.84	. . .
$2r$ for N	1.42	3.42[b]	2.84	. . .
a	4.54	5.26	4.68	4.5756

[a] Estimated by interpolation. [b] Ref. 31.

However, if the nitride partakes of both ionic and metallic character, the average r of Zr ions is only slightly larger ($2r$ = 1.84 A) than for Zr^{4+}, and that of N^{3-} is certainly less than that calculated from Pauling's equation using the ligancy of 5 (r = 1.42 A is then obtained in lieu of 1.71 A, calculated with ligancy 7). The former is justified, considering that the nitrogen does not accept its full complement of electrons from the metal atoms and because of the presence of vacancies in the compound (Table II). Thus, the lattice parameter (Table III) does not necessarily rule out ionic bonding.

Conclusion

Therefore, there is sufficient reason to assume that nitrogen is present in atomic and ionic states in equilibrium in the solid nitride with trivalent Zr ion

$$N + 3e \rightleftharpoons N^{2-} + e \rightleftharpoons N^{3-} \qquad (7)$$

whereby N^{2-} could only be present in very small amounts. This model is supported by a study in our laboratory of X-ray scattering factors based on comparison of experimental and theoretical X-ray intensities. The study indicates electronic states intermediate between N and N^{3-}, thus excluding total N (atomic) and positive N ionic states, in agreement with some investigations of other nitrides.[32,33] Hence, the bonding in ZrN is of a mixed or intermediate type involving both *ionic* and *metallic* character.[34] Although the chemical behavior supports a dominantly ionic model, it is difficult to say to what extent. Nevertheless the model (eq 7) explains qualitatively the chemical and physical properties of the nitride, as discussed. As regards the electrical conductivity, it follows from eq 7 that not all of the d electrons from Zr are transferred to available N atoms; a certain concentration of free electrons results which goes into the conduction band responsible for the electrical conductivity. The magnetic properties[5] are determined by the metallic part of the nitride.

Finally, there is the question concerning the contact of the ions within the ZrN structure of the NaCl type. According to Hägg,[35] such contact is established if the radius quotient is ≤ 0.59. Since the relation $r_{Zr^{3+}}/r_{N^{3-}} = 0.64$ is close to 0.59, the ions are nearly in contact with each other, although the small ion is that of Zr (cation) and the large one of N.

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