JOURNAL OF SOLID STATE CHEMISTRY **96**, 442–445 (1992)

Crystal Structure and Chemical Reactivity of Transition Metal Carbides and Nitrides

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Received June 10, 1991; in revised form August 5, 1991

Trends in melting points, stoichiometry, and crystal structures in early transition metal carbides and nitrides are discussed in terms of the Engel–Brewer valence bond theory. It is deduced that carbon and nitrogen combine their valence *sp* electrons with the metal *spd* bands. As a consequence crystal structure and chemical reactivity of the compounds resemble those of elements further to the right in the Periodic Table. This is in accord with the original suggestion of Levy and Boudart [*Science* **181,** 547 (1973)]. © 1992 Academic Press, Inc.

This communication points out simple trends in the melting points and crystal structures of early transition metal carbides and nitrides which provide insights into the nature of their bonding and their chemical reactivity. The carbides and nitrides are formed by the incorporation of carbon and nitrogen atoms into the interstitial spaces between metal atoms. These interstitial alloys are interesting because they combine the physical properties of ceramics (*1*) and the electronic properties of metals (*2*). Thus, they are extremely hard and strong, but at the same time, good conductors of heat and electricity.

The carbides and nitrides have attracted attention because they are excellent catalysts for a number of reactions carried out by the more expensive noble metals (*3–5*). The alloys can now be prepared with stable, ultra-high surface areas (*6, 7*).

The similarity of carbides and nitrides to the Group VIII metals was first pointed out by Levy and Boudart (*8*), who noted the Pt-like catalytic behavior of WC. Their explanation was that carbon added its valence electrons to those of tungsten, so that it resembled its neighbor, platinum, four atoms to the right in the Periodic Table.

The direction of electron transfer has been a subject of controversy (*9*). X-ray photoelectron chemical shifts indicate electron donation from $M \rightarrow \mathrm{C}$ (*10*), but this could be a secondary effect due to backdonation or screening. APW and related calculations have been reviewed (*11*) and these also indicate $M \rightarrow \mathrm{C}$ electron transfer, but calculations by Gelatt *et al.* (*12*) suggest covalent bonding with little electron donation. Meanwhile, the valence bands and core levels in WC have been reported to be similar to those in Pt (*13*).

Electronegativity considerations would also suggest simple $M \rightarrow \mathrm{C}$ electron dona-

0022-4596/92 $3.00

tion, and indeed compounds of C and N with the electropositive alkali and alkaline earth metals do result in ionic-type compounds with negatively charged nonmetals. These compounds are characterized by lack of electrical conductivity, transparency, and ready hydrolysis to produce the metal oxide and hydrocarbons or ammonia. However, these properties are not found in the alloys of C and N with transition metals. The interstitial alloys are excellent electrical conductors, have shiny metallic colors, and are hydrolytically stable. It is likely that *simple* electronegativity charge transfer concepts do not apply when C and N are dissolved interstitially in metal lattices. This has been discussed by Gelatt *et al.* (*12*), who point out that the amount and direction of charge transfer depends on the property considered. For example, when considering band occupation, electron transfer is from C → *M*, but this reverses when considering integrated charges around atoms.

Trends in melting points in carbides and nitrides are revealing. In the transition metals, the maximum in melting point occurs in Group VI, whereas for the carbides the maximum is displaced to Group V, and for the nitrides to Group IV (*2*). A crude interpretation of this trend is that the maxima are associated with the formation of a half-filled *d*-shell and to achieve this carbon and nitrogen donate, respectively, one and two electrons to the metal.

Examination of crystal structures can shed light on this subject. Table I presents the structures adopted by metals of the second and third rows of the Periodic Table. The first row follows a similar but more complicated trend and will not be discussed here. On moving from left to right in the table, the crystal structure evolves from body centered cubic (bcc), to hexagonal closed packed (hcp), and finally to cubic closed packed (ccp). This progression is well understood from the Engel–Brewer valence bond theory (*14–16*). According to this theory, crystal structure is determined by the number of outer-shell *sp* electrons per atom (e/a). These are itinerant and control long range order. Thus, for up to 1.5 *sp* e/a the bcc structure is obtained, for 1.7–2.1 e/a the hcp structure is produced, and for 2.5–3 e/a the ccp structure is attained. The number of *sp* electrons may be deduced from compilations of promotion energies determined from spectroscopic data (*17*) or predictions (*18*).

TABLE I

VARIATION OF CRYSTAL STRUCTURES ACROSS THE PERIODIC TABLE

Metals					
V	VI	VII	VIII		
Nb bcc	Mo bcc	Tc hcp	Ru hcp	Rh ccp	Pd ccp
Ta bcc	W bcc	Re hcp	Os hcp	Ir ccp	Pt ccp

The crystal structures of transition metal carbides and nitrides are generally simple and are similar to those found in pure metals. This is in contrast to other Main Group compounds, like the borides, oxides, and sulfides, which adopt complex crystalline forms. The simplicity found in the carbides and nitrides is probably related to the metallic nature of the compounds. Interestingly, although the carbides and nitrides have simple structures, they are rarely the same as those of the parent metal. Considering first Group VI elements, Table II shows that mo-

TABLE II

CRYSTAL STRUCTURE PROGRESSIONS

	INTERSTITIAL ALLOYS	
Mo bcc	β-Mo_2C hcp	γ-Mo_2N, MoO_xC_y ccp
W bcc	β-W_2C hcp or hex′	β-W_2N ccp

lybdenum converts from bcc to hcp in forming the carbide and to ccp in forming the nitride (or oxycarbide). Similarly, in forming the carbide, tungsten converts from bcc to hcp or hex′ (cadmium iodide hcp variant, found at low temperatures) and to ccp in forming the nitride. Discounting the minor difference between the two hexagonal forms (hcp and hex′) (*19*), the progression in Mo and W is the same as that found for the pure metals, and correlates with the number of valence electrons in C, N, and O. In forming the solids, these electrons hybridize with the metal *spd* band. For these Group VI metals, geometry does not account for the variation in crystal structure because the sizes of the C, N, and O atoms are similar, and the interstitial sites in the hcp and ccp structures are identical.

In the Group VI compounds the stoichiometry M_2X is prevalent (X = C,N). In contrast, the earlier Group III–V compounds show primarily an MX stoichiometry, whereas the Group VII–VIII compounds display preferentially M_3X or M_4X formulas. This can be understood from simple band-filling considerations, as discussed below.

The high-temperature crystalline form of the early transition metals (Groups III–V) is bcc. On forming carbides and nitrides these metals adopt preferentially the limiting MX stoichiometry, where every octahedral interstitial site is occupied. The bcc structure transforms to the B1 cubic structure in which the metal atoms form a ccp lattice. Thus, for these compounds the hexagonal structure is bypassed entirely. This probably occurs because the MX structure represents a high ratio of *sp*-electron-rich nonmetal to metal (X/M), which according to the Engel–Brewer rules would produce the ccp structure. The MX formula results because the host metals have incompletely filled bands and are able to fully accommodate the *sp* atoms.

Similar inferences may be drawn when considering interstitial compounds of the late transition metals (Groups VII and VIII). Here it is found that, aside from the first row elements, metals of Groups VII and VIII *do not form* stable carbides and nitrides. This is consistent with the filling of antibonding levels in the metal bands. Where compounds are formed, in the first row, the rejection of the electron-rich C and N atoms is manifested by high metal (M) to nonmetal (X) atom ratios. Thus, stoichiometry such as Mn_3C, Fe_3C, Co_3C, Mn_4N, and Fe_4N appears. Note the higher M/X ratio in the nitrides.

The transformation of the structure in all cases appears to be related to an increase in the number of valence *sp* electrons, as predicted by Engel–Brewer theory. Thus, trends in melting point, stoichiometry, and crystal chemistry support greater occupation of metallic *spd* bands in forming compounds, in agreement with the original assertion of Levy and Boudart (*8*). This can occur without specifying the direction of electron transfer, as explained by Gelatt *et al.* (*12*). The trends help explain the observed noble metal-like catalytic reactivity (*3–5*) of the early transition metal carbides and nitrides. It should be noted that relationships between bulk and surface properties have been proposed in the past, for example, in the form of the Tanaka–Tamaru (*20*) or Sachtler–Fahrenfort correlations (*21*). Detailed explanations of surface reactivity will require more intimate considerations of composition, structure, and bonding.

Acknowledgments

This paper was written with support from the Center for Advanced Materials Processing at Clarkson University and from the U.S. Department of Energy under the Advanced Coal Research at U.S. Universities Program (Grant No. DE-FG22-91PC91298).

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