

Vacancy Short-Range Order in Substoichiometric Transition Metal Carbides and Nitrides with the NaCl Structure. I. Electron Diffraction Studies of Short-Range Ordered Compounds

BY J. BILLINGHAM, P. S. BELL AND M. H. LEWIS

Department of Physics, University of Warwick, Coventry, England

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The structure of cubic transition metal compounds VC_{1-x} , NbC_{1-x} , TiC_{1-x} , VN_{1-x} and TiN_{1-x} has been studied by electron diffraction. These compounds occur with large deviations from the stoichiometric composition and the carbides have been observed with long-range ordered carbon distributions for certain compositions and temperatures. For crystals of other compositions and temperatures electron diffraction patterns frequently contain diffuse bands of intensity which have a periodic distribution with respect to the reciprocal lattice points. The diffuse intensity follows a continuous surface of complex curvature in reciprocal space, is observed for all compounds except VN_{1-x} , and has the symmetry of the b.c.c. reciprocal lattice. These features indicate a short-range ordered non-stoichiometric vacancy distribution which is analysed in Part II of this series [Sauvage & Parthé (1972), *Acta Cryst.* A28, 607].

Introduction

Compounds of the group IV and V transition metals with carbon or nitrogen have been classified as Hägg phases whose crystal structures are based on simple packing arrangements of component atoms which have a large size difference. Thus the transition metal atoms may be arranged in either f.c.c. or h.c.p. stacking with the second component (C or N) occupying octahedral sites within these structures. These compounds are notable for their accommodation of large departures from stoichiometric compositions. For compounds based on the f.c.c. metal atom arrangement non-stoichiometry occurs by subtraction of atoms from octahedral sites such that the compound formula may be written, *e.g.*, MC_{1-x} . This paper is concerned only with 'cubic' compounds of this type which occur in both groups IV and V (VC_{1-x} , NbC_{1-x} , TiC_{1-x} , TiN_{1-x} , VN_{1-x}).

Recent electron diffraction work on some of these compounds has indicated a long-range ordered distribution of non-stoichiometric vacancies for particular compositions (Venables, Kahn & Lye, 1968; Billingham & Lewis, 1970; Billingham, Bell & Lewis, 1972). A comprehensive electron microscopic and diffraction analysis has been made in this laboratory of the series of compounds listed above throughout the stability limits of temperature and composition for the nominally cubic phases. Long-range ordered vacancy distributions and their stability limits have been identified for the compounds VC_{1-x} , NbC_{1-x} and TiC_{1-x} (Lewis, Billingham & Bell, 1972). Reference is made in this paper to the various superstructures determined for these compounds. The main purpose of this paper is to present, in detail, the electron diffraction observations made for these compounds for composition and temperature limits outside those in which long-range

order has been defined but for which the non-stoichiometric vacancy distribution is still non-random, *i.e.* it exhibits short-range order. These observations will indicate a similarity in short-range ordered distribution for all compounds listed above except for VN_{1-x} . An analysis of this short-range ordered distribution will be presented as a separate paper (Part II: Sauvage & Parthé, 1972) and is based on the observations presented in this paper.

Experimental

The compounds, with varying deviations from the stoichiometric composition, were prepared from the available commercial powders of highest purity (generally >99.9%). The powders were pressed at room temperature and sintered in vacuum at temperatures between 1500 and 1700°C. The rod-shaped specimens produced in this way were used for crystal preparation, either by zone melting [for the VC_{1-x} compounds (Billingham, Bell & Lewis, 1971; Billingham & Lewis, 1971)] or by an additional reaction solid-state sintering treatment at temperatures near to the compound melting point (for NbC_{1-x} , TiC_{1-x} , TiN_{1-x} and VN_{1-x}). The latter technique resulted in the formation of homogeneous fine grain polycrystalline material. Compositions of the resulting compounds were determined only for the V-C compounds by chemical analysis. For the other compounds compositions were assumed to be those of the starting mixtures.

Thin sections for transmission electron diffraction were prepared from the VC_{1-x} compound crystals using standard electropolishing techniques (Billingham, 1971). This technique was only possible when large melt-grown single crystals were available and enabled thin sections of predetermined orientation to be obtained. Thin sections from NbC_{1-x} , TiC_{1-x} , TiN_{1-x}

and VN_{1-x} were obtained by fragmentation of the small brittle crystals in a pestle and mortar and mounting the fragments on adhesive electron microscope grids. The greatest areas of electron transparent section obtained with the latter method were not comparable with those obtained by electropolishing. Hence the electron diffraction study reported here has involved detailed observations from the VC_{1-x} compounds followed by a comparative study for other compounds. This has revealed a marked similarity in the diffraction patterns obtained from all compounds (with the exception of VN_{1-x}) which obviates the need for detailed presentation of results for the sections obtained by the fragmentation technique. All diffraction patterns were recorded in a JEM 200 kV electron microscope fitted

with a large-angle tilting stage which enabled the observation of a large number of reciprocal lattice sections for a single specimen.

Electron diffraction observations

The observations are described here under headings for each non-stoichiometric compound. For each compound the compositions and temperatures defining the extent of short-range or long-range ordered vacancy distributions are given together with a brief description of the long-range ordered structure.

VC_{1-x}

Following the investigations of vacancy distributions for particular compositions by X-ray diffraction [$\text{VC}_{0.87}$ (de Novion, Lorenzelli & Costa, 1966)] and electron diffraction [$\text{VC}_{0.83}$ (Venables, Kahn & Lye, 1968)] two different superlattice structures have previously been defined for these compositions. A more recent study by electron diffraction and microscopy (Lewis, Billingham & Bell, 1972) has defined the stability limits for two long-range ordered phases within the range $\text{VC}_{0.7}$ – $\text{VC}_{0.9}$ and examined the mechanism for the transformation to long-range order. A partial phase diagram which illustrates these phase limits is reproduced in Fig. 1. The shaded area labelled V_8C_7 is that for a long-range ordered phase, (based on that metal/carbon ratio), with cubic superlattice symmetry and a structure identified with that previously determined by X-ray diffraction (de Novion, Lorenzelli & Costa, 1966). This structure is stable up to the boundary at which graphite becomes a stable phase and has been observed in a eutectic of the cubic carbide with graphite which has been cooled to ambient temperature following solidification (O'Sullivan & Lewis, 1972).

The area labelled V_6C_5 is that for a non-cubic superstructure for which a detailed interpretation has been given in a recent electron diffraction study (Billingham, Bell & Lewis, 1972). It has been shown that well annealed crystals, in which a marked reduction in 'as-grown' planar defect substructure has occurred, contain a 'duplex' structure. This may briefly be described with reference to layers of the octahedrally coordinated carbon atoms parallel to $\{111\}$ cubic lattice planes. Alternate layers contain sites which are only $\frac{2}{3}$ filled (at the exact V_6C_5 composition), the vacant carbon atom sites being distributed within these part-filled layers with an ordered distribution having sixfold rotational symmetry about the plane normal. These part-filled layers may be 'stacked' with different position of projection of the vacant sites onto $\{111\}$ planes. The various possible stacking sequences may generate structures which may be assigned to either monoclinic or trigonal space groups, both of which have been identified by electron diffraction combined with dark-field electron microscopy. There is a small free-energy difference between the two structures at any particular temperature and composition within the shaded area

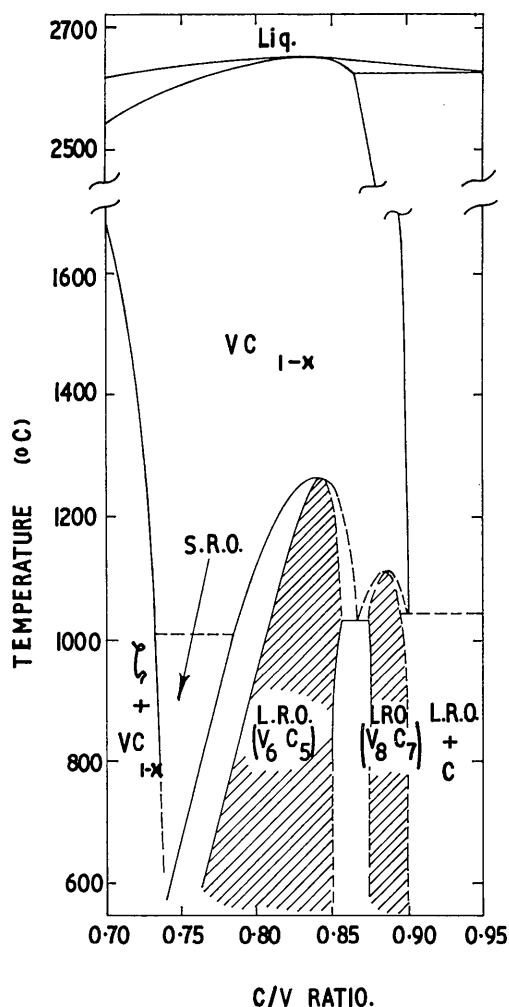


Fig. 1. Part of a phase diagram for the V-C system showing the boundaries of sub-solidus ordered phases (derived from Lewis *et al.*, 1972) and a region in which short-range order has been detected. The liquidus and solidus are derived from Rudy, Windisch & Brukl (1968) but with the liquidus maximum at the composition V_6C_5 , consistent with crystal growth data of Precht & Hollox (1968).

(Fig. 1) such that both occur within adjacent small regions of microstructure even after long heat treatment. It is significant that the structures with various stacking sequences for part-filled layers all have the same nearest and next-nearest neighbour coordination for vanadium atoms. Thus all vanadium atoms have one vacancy in the nearest neighbour shell of carbon atoms while one third of the vanadium atoms have two vacancies and two thirds have one vacancy in the next-nearest neighbour shell. This information is relevant to the short-range ordered distribution of carbon atoms (discussed in Part II) for which diffraction evidence will now be presented.

The rapid fall in order-disorder critical temperature with carbon content in VC_{1-x} compounds makes possible examination of the matrix structure in which long-range order is nucleated. Thus the nucleation of long-range order may be suppressed by quenching (air cooling of thin disc specimens) from within the region labelled S.R.O. in Fig. 1. Above the upper limit of temperature for this region the diffusion rate of carbon atoms is too high to prevent long-range ordering of the carbon distribution. Compounds above $VC_{(0.78-0.80)}$ are fully ordered in the quenched state. Crystals quenched from within the indicated area all exhibit electron diffraction patterns which contain bands of diffuse intensity, in addition to primary diffraction spots which are 'structure-factor' allowed for a completely disordered NaCl structure type. These diffuse bands of intensity, in certain reciprocal lattice sections, cross over the positions of the long-range ordered superlattice reflexions. These patterns, which are indicative of the retention of a short-range ordered carbon distribution, have been recorded from a number of crystals with varying composition quenched from different temperatures following a long isothermal anneal. The patterns have also been recorded during specimen heating in the electron microscope column (up to 900°C) to ensure that the short-range ordered state is present above the phase boundary and is not formed during the quenching process. These patterns have been recorded for a large number of orientations of the cubic structure with respect to the electron beam and some of these are reproduced in Fig. 2. The primary diffraction spots are indexed for the cubic parent structure and electron beam directions are indicated. The occurrence of short-range order above the boundary indicated in Fig. 1 has not been ascertained due to the limitation in temperature of the electron microscope hot stage and the inability to suppress the formation of complete long-range order above $VC_{0.80}$. The observations presented for the NbC_{1-x} compounds below indicate that short-range order is likely to persist above the critical temperature for higher carbon contents in VC_{1-x} compounds.

NbC_{1-x}

The occurrence of long-range order for this compound has been detected only following extensive an-

nealing below 900°C (Lewis, Billingham & Bell, 1972). Thus for all compositions in the nominally cubic phase field ($NbC_{0.7}-NbC_{0.95}$), the order-disorder critical temperature occurs where carbon diffusion rates are slow, unlike the VC_{1-x} compounds. The approximate position and variation of the critical temperature with composition is shown in Fig. 3. A briefly reported electron diffraction and microscopy study (Lewis *et al.*, 1972) has determined that the long-range ordered structure is based on the composition Nb_6C_5 (near to the peak in the critical temperature) analogous to the V_6C_5 structure described above. The cubic superstructure, based on the M_8C_7 composition, has not been detected for this system even after prolonged annealing of high carbon compounds ($NbC_{0.87}-NbC_{0.95}$).

Crystals of all compositions quenched from above the critical temperature at different rates all exhibit the same diffuse electron scattering as for the low carbon VC_{1-x} crystals. Thus the state of short-range order is believed to exist for all compositions, as suggested for the vanadium compounds above. Examples of diffraction patterns recorded for the NbC_{1-x} compounds are

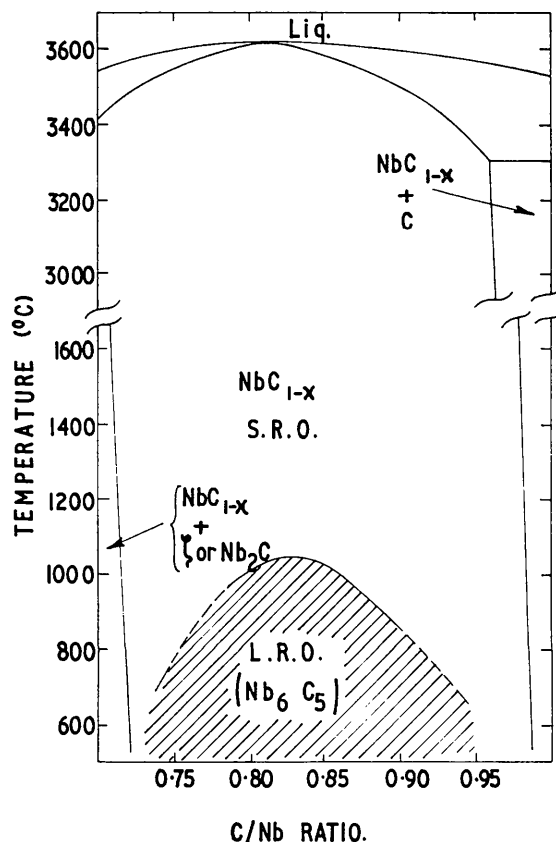


Fig. 3. Part of a phase diagram for the Nb-C system showing the approximate limits for long-range ordered phase formation and the extent of the short-range ordered state. The liquidus and solidus have been derived from Rudy *et al.* (1968).

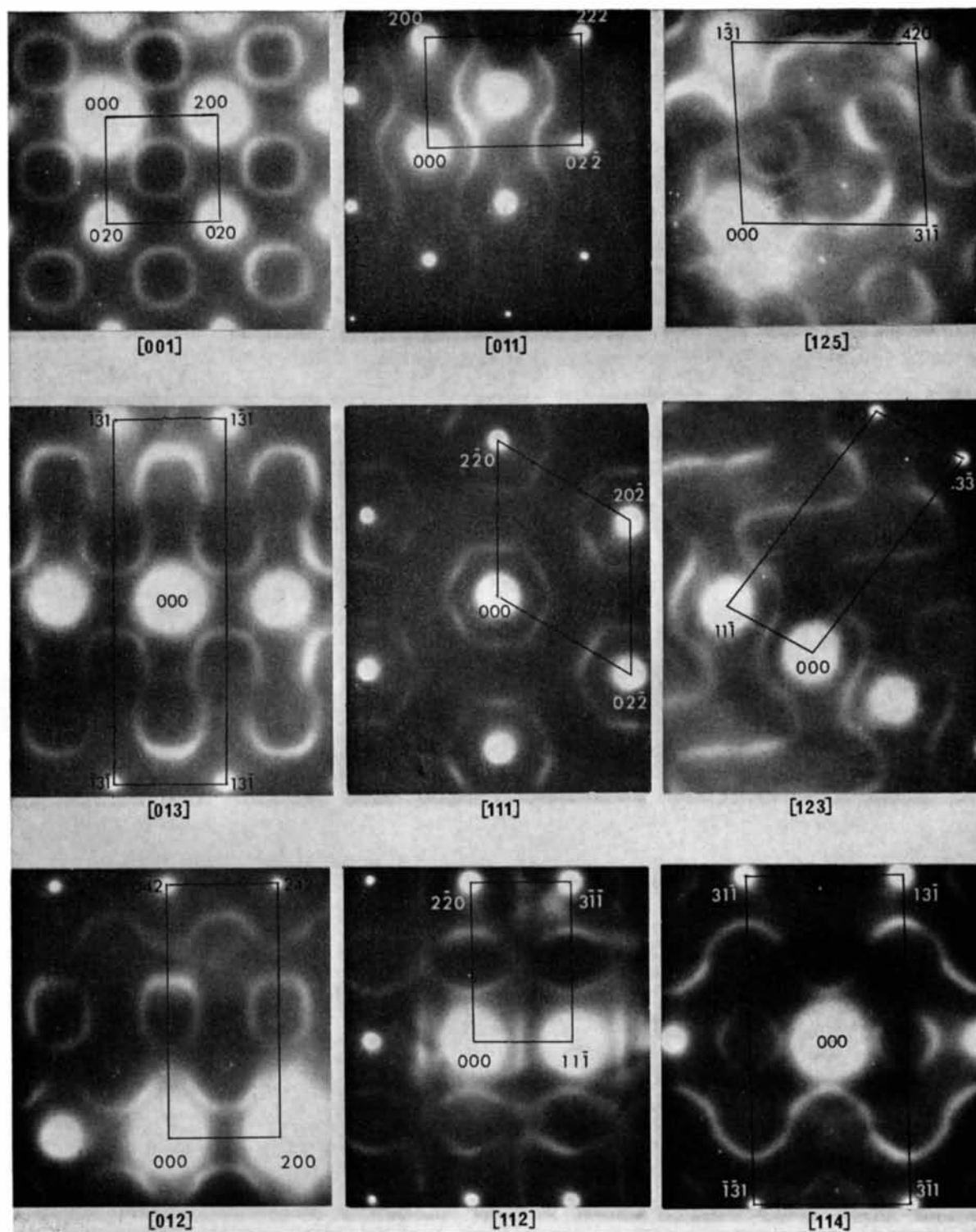


Fig. 2. Electron diffraction patterns from crystals of VC_{0.75} grown by zone melting. Electron beam directions relative to the cubic crystal axes are indicated for each pattern.

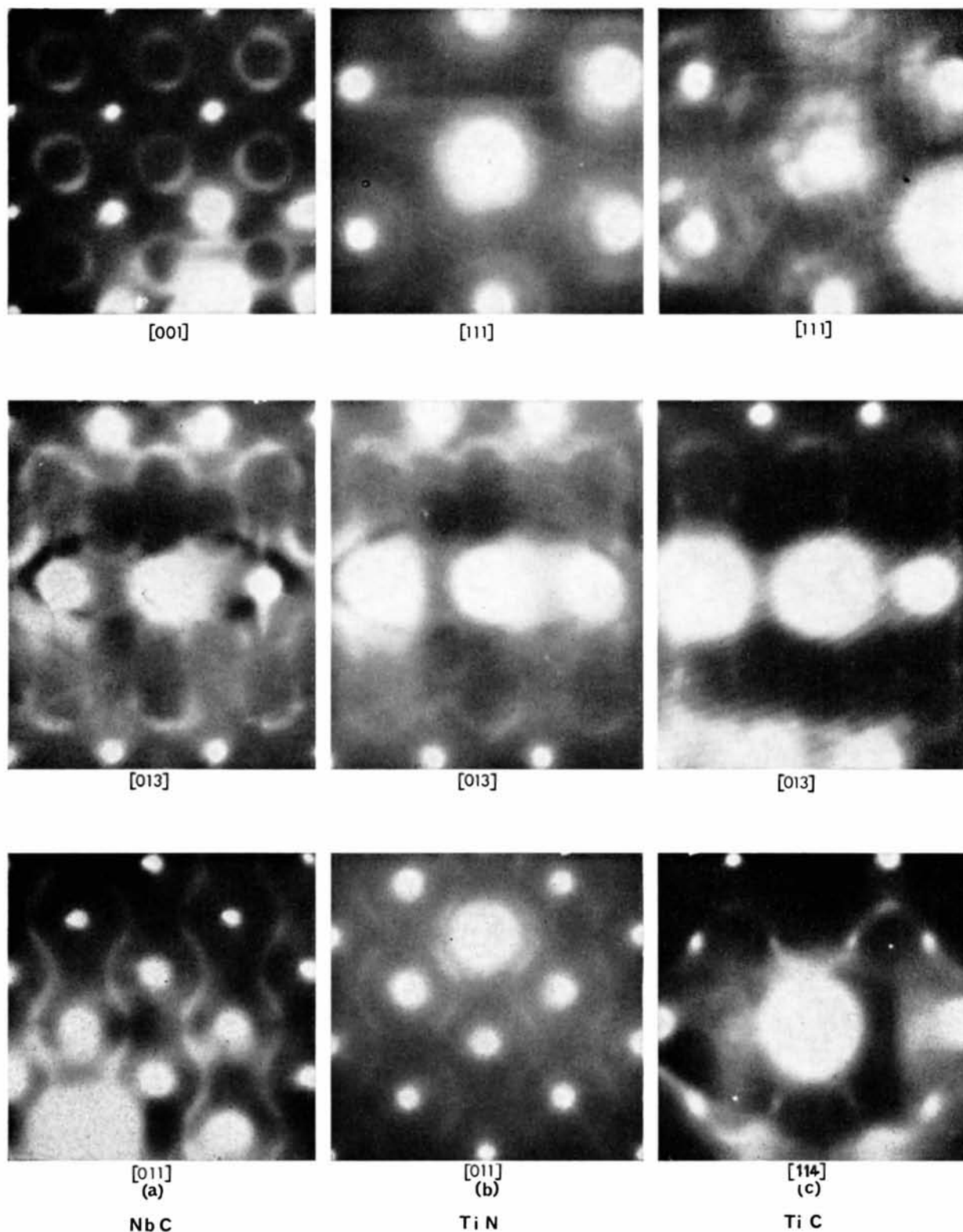


Fig. 4. Electron diffraction patterns from thin crystals of: (a) NbC_{1-x} in the 'quenched' state, where $x=0.5$ to 0.05 . (b) TiN_{1-x} in the 'as-grown' state, where $x=0.4$ to 0.25 . (c) TiC_{1-x} in the 'as-grown' state, where $x=0.5$ to 0.4 . Electron beam directions relative to the cubic crystal are indicated for each pattern.

given in Fig. 4(a) and may be compared with the equivalent patterns in Fig. 2. The bands of diffuse intensity in Fig. 4(a) are slightly weaker than for the vanadium compounds. This may arise from the greater ratio in scattering power of niobium and carbon but is also associated with the smaller area of thin crystal which may be selected for diffraction when prepared by the fragmentation technique. It has been observed that a preferred crystal thickness exists for ease of observation and recording of the diffuse bands. This optimum thickness is just below the level for observation of Kikuchi bands where the proportion of inelastic electron scattering is high.

TiC_{1-x}

The occurrence of a long-range ordered carbon atom distribution near to the composition TiC_{0.5} has recently been confirmed by Bell & Lewis (1971). Using electron microscopy and diffraction they have unambiguously identified a cubic superstructure similar to that suggested (on the basis of neutron diffraction) by Goretzki (1967). This structure (space group *Fd3m*) may conveniently be described with $\frac{1}{2}$ and $\frac{2}{3}$ occupancy of alternate octahedral {111} carbon layers. This ordered arrangement has the same coordination of titanium by carbon atoms as that calculated for the average coordination for a random array of the same composition.

The approximate phase-boundary position for this cubic superstructure is illustrated in Fig. 5(a). The uncertainty in its position stems from the difficulty in quenching crystals such that diffraction patterns contain uniform bands of diffuse contrast. The diffuse bands, which occur only for crystals below TiC_{0.6} in composition, usually have intensity maxima at positions corresponding to diffraction spots for long-range order. The diffuse bands, which are of very weak in-

tensity compared with those from group V compounds, are illustrated in the patterns of Fig. 4(c).

TiN_{1-x}

Neither of the 'cubic' nitrides examined in this work, TiN_{1-x} and VN_{1-x} exist with long-range ordered nitrogen distributions throughout their composition limits of stability. Further, only the titanium compound showed evidence for short-range order in diffraction patterns with diffuse banding reproduced in Fig. 4(b). These patterns, which are comparable in form with those from the other compounds, have been obtained only for compositions indicated in Fig. 5(b).

Diffuse diffraction and short-range order

Using the planar sections of Fig. 2 it is possible to construct a reciprocal space lattice which includes the position of the bands of diffuse electron intensity. Observation of the electron diffraction patterns during specimen tilting confirms the continuity of these bands. The 'surface' of diffuse intensity in reciprocal space has the cubic symmetry of the reciprocal lattice for the parent disordered crystal. A model illustrating the curvature of this surface and its relation to the reciprocal lattice has been constructed from the diffraction data and will be presented in Part II.

The high intensity and small spread of the diffuse intensity normal to the surface in reciprocal space indicates that the correlation in carbon or nitrogen atomic site occupancy may extend over many interatomic spacings. Hence in particular crystallographic directions the distribution of interstitial atoms within the f.c.c. metal-atom substructure resembles that for the highly periodic long-range ordered state. The concentration of scattered intensity at positions $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in reciprocal space (Fig. 2 for <110>, <211> and <321> sections) is expected if successive {111} layers of octahedral sites are unequally populated. There is an obvious correlation with the long-range ordered distribution based on the compositions M₆C₅ in which sites in alternate layers are $\frac{2}{3}$ occupied and gives rise to sharp $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ diffraction spots. The crossing of weaker bands of diffuse intensity near to $\frac{2}{3}\frac{2}{3}0$ and $\frac{4}{3}\frac{4}{3}0$ (the positions for long-range order spots in M₆C₅ for certain superlattice orientations) indicates the retention of a partial long-range order within the octahedral layers. The structures of long-range ordered (monoclinic and trigonal) phases based on the M₆C₅ composition are characterized by each vanadium atom having one vacancy and five carbon atoms in the nearest-neighbour shell. This coordination condition has been explained by Lye (1970) in terms of the electronic structure for vanadium carbide. A model for atomic bonding in these carbides is that of a division of the *d*-electron energy band into 'bonding' and 'anti-bonding' states. The composition of maximum cohesive energy for vanadium carbide occurs near V₆C₅ at which the 'bonding' states are fully occupied. The long-range ordered structure with five-

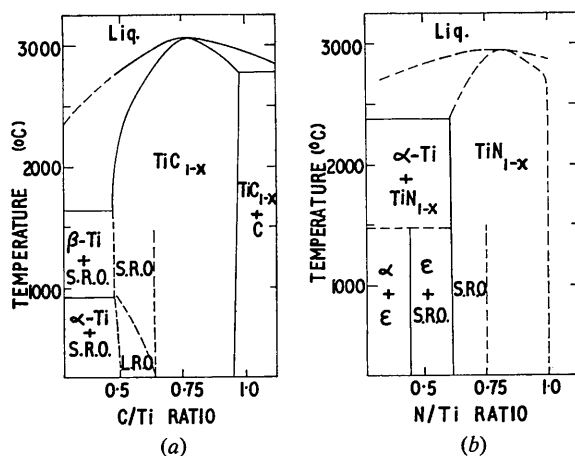


Fig. 5. Part of a phase diagram for (a) the Ti-C system and (b) the Ti-N system. The approximate limits for either long or short-range ordered phases are superposed on diagrams showing phase boundaries derived from Storms (1967) for Ti-C and Toth (1971) for Ti-N.

fold coordination is the condition for satisfying this criterion homogeneously, down to atomic dimensions. Deviations in composition from the ideal $\frac{c}{3}$ ratio and an increase in temperature prevent the retention of this condition. However it is anticipated that the number of metal atoms with fivefold carbon atom coordination will exceed that for a random carbon-atom distribution. It is significant that the additional long-range ordered compound in the vanadium carbide V_5C_7 has a cubic superstructure with a greater concentration of vanadium atoms with the fivefold coordination than for a disordered compound of this composition. For compounds of lower carbon content, e.g. $VC_{0.75}$, Froidevaux & Rossier (1967) using n.m.r. techniques have also measured a higher than random concentration for fivefold-coordinated vanadium atoms. This technique does not distinguish between long-range and short-range order.

A crystallographic description of the short-range ordered state in compounds may extend from the statistical model on non-random atom-pair probabilities to the 'microdomain' model in which discrete regions of a structure, which may have long-range atom correlation, is dispersed in a matrix which may be disordered. Attempts were made to reveal a microscopically inhomogeneous state, characterized by the latter description, with high-resolution dark-field imaging using regions of diffuse electron intensity maxima from the vanadium carbide crystals. No microdomains were visible in these images such that either they are of a size below the resolution limit of the electron microscope or the structure is more appropriately described by the statistical model for short-range order. A description of a structure which is consistent with the diffraction evidence presented above and with the model for cohesive energy based on electronic structure is presented in Part II.

Finally, Venables & Meyerhoff (1971) have recently examined a tantalum-carbon compound ($TaC_{0.83}$) following different heat treatments. This compound does

not form with a long-range ordered carbon atom distribution but exhibits the same distribution of diffuse banding as for the short-range ordered vanadium and niobium compounds described here.

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