PHASE TRANSFORMATIONS INVOLVING INTERSTITIAL ORDERING
IN THE VANADIUM-NITROGEN SYSTEM

MASTER

Donald Irwin Potter
Department of Metallurgy and Mining
and Materials Research Laboratory
University of Illinois, Urbana, Illinois

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J. H. Kahn / amh
DATE 3/22/71

February 1971

This technical information document is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Metallurgical Engineering in the Graduate College of the University of Illinois, 1971. This research was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198 and in part by the National Aeronautical Space Administration.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

P8864

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PHASE TRANSFORMATIONS INVOLVING INTERSTITIAL ORDERING
IN THE VANADIUM-NITROGEN SYSTEM

Donald Irwin Potter, Ph.D.
Department of Metallurgy and Mining Engineering
University of Illinois at Urbana-Champaign, 1970

Alloys of vanadium containing up to 14.0 atomic percent nitrogen were examined in the as-quenched and aged conditions. X-ray diffraction showed the room temperature material to be body centered cubic for nitrogen contents of less than 6.9% and body centered tetragonal for nitrogen contents greater than 7.4%. Electrical resistivity, measured during quenching, also indicated a change in behavior near 6.0% nitrogen.

Transmission electron microscopy was used to follow the progress of aging in alloys containing less than 6.0% nitrogen. When aged, these alloys contained a disc shaped precipitate whose habit plane was determined to be $\{100\}$. The matrix remained cubic and the interstitial nitrogen atoms in the matrix were not ordered. The structure of the precipitate was determined from selected area diffraction patterns and consisted of an ordered array of nitrogen atoms in a body centered tetragonal vanadium sublattice. The unit cell of the superlattice, i.e., vanadium sublattice plus nitrogen sublattice, enclosed sixteen vanadium sublattice cells, being $4 \times 4 \times 1$ such cells. The nitrogen sublattice was found to be base centered orthorhombic with $c = 0.036 \text{ \AA}$, $b = 12.504 \text{ \AA}$, and $a = 12.140 \text{ \AA}$. The superlattice cell, which

is enclosed by the nitrogen sublattice cell, has these same lattice constants. Stoichiometrically the compound corresponds to $V_{16}N$. It is shown that the nitrogen atoms occupy octahedral interstitial sites rather than the tetrahedral sites predicted from theoretical considerations.

Alloys containing greater than 6.0% nitrogen transformed to a banded structure during radiation quenching. The vanadium sublattice showed tetragonal distortion with $\frac{c}{a}$ varying from 0.974 in a 7.4% alloy to 0.955 in a 10.0% alloy. X-ray Laue patterns together with two surface analysis showed that adjacent bands were twin related across $\{110\}$ twin planes, which were the boundaries between bands. There was a fine banding ($\sim 100\text{\AA}$) within the main bands. This occurred on the other set of $\{110\}$ twin planes of the tetragonal system as well as the remaining $\{110\}$ planes which are not twin planes in the tetragonal system. Electron diffraction showed that the nitrogen atoms in this structure are ordered.

A macroscopic shape change as well as audible "clicking" accompanied the transformation in alloys containing between 6.0% and 8.0% nitrogen.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ACKNOWLEDGEMENT

The author gratefully acknowledges the stimulating discussions and continued guidance provided by Professor Carl J. Altstetter throughout his period of graduate study. The support provided by the United States Atomic Energy Commission during the latter years of graduate study as well as that provided by the National Aeronautics and Space Administration in the earlier years of study is likewise acknowledged and was greatly appreciated. Special thanks are owed to Dr. Brian Eyre for help in interpreting the electron micrographs. The author would also like to acknowledge the many interesting discussions with Mr. Ronald Geils concerning this work. Thanks are owed to Union College of Schenectady, New York, for typing the final manuscript. Last but not least the author wishes to thank his family who provided much of the encouragement required for him to complete his work.

TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
2. EXPERIMENTAL PROCEDURE	12
2.1 Material and Specimen Preparation	12
2.2 Electrical Resistivity Measurements	18
2.3 Preparation of Samples for Electron Microscopy	18
2.4 X-ray Diffraction and Two Surface Analysis ..	19
3. RESULTS	20
3.1 Vanadium Starting Material	20
3.2 Electrical Resistivity of Doped Materials	21
3.3 The Precipitate Structure in the Low Composition Alloys	26
3.4 Tetragonality in the Vanadium Sublattice ..	98
3.5 Progress of Precipitation in the Low Composition Alloys	102
3.6 Transformation of the High Composition Alloys	126
4. DISCUSSION	171
4.1 Crystal Structure Refinements and Stoichiometry of the Precipitate	171
4.2 Choice of Interstitial Site; Growth Twins	174
4.3 The High Composition Alloys	180
5. SUMMARY	182
LIST OF REFERENCES	184
VITA	186

1. INTRODUCTION

Vanadium as well as niobium and tantalum belong to group V of the periodic table. Vanadium is used as an alloying agent in steels and has potential applications relating to nuclear energy conversion, principally as a nuclear fuel cladding material. It is referred to as a refractory metal, with a melting point near 1900°C .

The interactions of both niobium and tantalum with the principal atmospheric gases, nitrogen and oxygen, have been extensively investigated and reported in the literature⁽¹⁻⁴⁾. The equilibrium phases existing in these systems are readily studied by classical techniques, such as pressure measurements as a function of temperature for a fixed composition material. Corresponding measurements and data for vanadium are missing, as a literature search reveals. It is the objective of this study to investigate the interaction of vanadium with nitrogen in alloys containing less than fifteen atomic percent nitrogen in order to provide some of this missing data.

A search of the literature reveals the absence of even a tentative phase diagram for the vanadium-nitrogen system. Hahn⁽⁵⁾ found the solubility of nitrogen in vanadium to be small and reported the existence of the hexagonal V_2N phase. Rostoker and Yamamoto⁽⁶⁾ reported the solubility to be at least 3.5 atomic percent at the melting point and less than this at 900°C . A sample containing about 16 atomic percent nitrogen which showed irregular twinning led these latter

authors to postulate the existence of a V_6N phase. The existence of the V_6N phase and the interpretation of the microstructures involving this phase, as given by Rostoker and Yamamoto, require the existence of a low temperature allotropic transformation in pure vanadium. Rostoker and Yamamoto attempted to substantiate this⁽⁷⁾, but later work⁽⁸⁾ showed that no such allotropic transformation took place.

Hahn⁽⁵⁾ did not detect any phase corresponding to V_6N . Schönberg⁽⁹⁾ later confirmed the work of Hahn, suggesting the V_6N phase and the tetragonality observed by Rostoker and Yamamoto was due to the presence of oxygen in their sample.

Cost and Monroe⁽¹⁰⁾ have reported the low temperature solubility of nitrogen in vanadium as determined by internal friction techniques. The solubility was represented by the following equation:

$$C = 50 \exp \left(- \frac{5500}{RT} \right)$$

where C is the nitrogen concentration in atomic percent, R is the gas constant, and T is the temperature expressed in degrees Kelvin. Cost and Monroe assumed that the above equation described the equilibrium between nitrogen in the α solid solution and than in V_2N .

In recent years with the ready accessibility of electron diffraction equipment, it has become well known that interstitial atoms in body centered cubic (bcc) metals often exhibit a tendency to order. As early as 1951, Jack⁽¹¹⁾ had confirmed the ordering of nitrogen atoms in iron-nitrogen

martensites by noting the systematic displacements of the host iron atoms as evidenced by x-ray diffraction peak shifts. A few extremely weak superlattice reflections due to this interstitial ordering were also noted.

The use of x-ray diffraction to observe interstitial ordering is limited due to the low scattering power of these elements for x-rays. The numerical value of the electron scattering power is about 10^4 times greater than that for x-rays so that superlattice reflections are much more easily observed with electron diffraction techniques. Superlattice reflections attributed to interstitial ordering have been observed for vanadium-oxygen,⁽¹²⁻¹³⁾ niobium-oxygen,⁽¹⁴⁾ tantalum-nitrogen,⁽¹⁵⁾ tantalum-oxygen,⁽¹⁶⁾ and tantalum-carbon⁽¹⁷⁾.

The suggested type of superlattice varies from one system to another. In the case of Ta-O solid solutions the oxygen atoms are said to take up interstitial positions so as to form a superlattice in the orthorhombic metal lattice cell with double lattice spacing between oxygen atoms along cube directions^(16,18). The analysis of this system is incomplete.

In Ta-C solid solutions the interstitial atoms are reported⁽¹⁷⁾ to order on a bct sublattice with lattice parameters approximately four times that of the host tantalum lattice. In the Ta-N system the nitrogen atoms are said⁽¹⁵⁾ to occupy a bcc sublattice with lattice parameter three times that of the host tantalum lattice. It has been

suggested in each instance that these ordered solutions correspond stoichiometrically to $Ta_{64}C$ and $Ta_{27}N$ respectively. The unit cell proposed for $Ta_{64}C$ by Villagrana and Thomas⁽¹⁷⁾ is presented in Figure 1.

The body centered cubic structure possesses two sets of interstitial sites, the tetrahedral and octahedral sites, as shown in Figure 2. The atoms surrounding octahedral sites are not symmetrically disposed, there being two neighboring atoms at $\frac{a}{2}$ and four more at $\frac{\sqrt{2}}{2} a$. Insertion of an interstitial atom into an octahedral site creates a strain dipole with tetragonal symmetry. Note that there are three subsets of octahedral sites, each giving rise to tetragonality along a different cube axis. When interstitials in octahedral sites order, as in Figure 1, they give rise to tetragonal domains in the crystal, i.e., regions wherein all octahedral atoms occupy the same subset of sites. If the interstitials are randomly distributed in all three subsets of octahedral sites, the lattice maintains its cubic symmetry.

The undistorted octahedral site can accommodate an atom with a diameter of $0.067a$, while the tetrahedral site can hold an atom of $0.126a$ diameter. The tetrahedron of atoms surrounding a tetrahedral site is not regular as two sides have length a while the remainder have length $a\frac{\sqrt{3}}{2}$. The departure of the tetrahedron from regularity may be described as a contraction along the line joining the midpoints of the two edges of length a ; this line is then the axis of the

Figure 1. The unit cell of Ta_{64}C proposed by Villagrana and Thomas..

Figure 2. The octahedral (O) and tetrahedral (T) sites in the body centered cubic lattice.

tetrahedral site. The atoms forming the tetrahedron are all a distance $a\sqrt{5}/4$ from the tetrahedral site.

Calculations⁽¹⁹⁻²⁰⁾ based on minimizing the strain energy associated with the two types of sites indicate that octahedral site occupancy is favored in iron, either kind of site occupancy is possible in niobium and tantalum, and tetrahedral site occupancy is favored in vanadium.

The morphology of these ordered phases when they precipitate has been investigated. Carbon in tantalum⁽¹⁷⁾ is said to order such that tetragonal domains ($c/a = 1.128$) come into contact with one another, giving rise to domain boundaries analogous to those found in ordered substitutional alloys. The boundaries separating ordered regions lie parallel to $\{110\}$ planes.

The ordered phase in Ta-O appears in platelets surrounded by body centered cubic matrix⁽²¹⁾. The ordered sub-oxide is orthorhombic⁽²²⁾ with $a = 3.271\text{\AA}$, $b = 3.201\text{\AA}$, and $c = 3.610\text{\AA}$. The formation of these platelets is described well by the crystallographic theory of martensite formation. The predicted habit plane is in agreement with the observed $\{320\}$ habit plane. The sub-oxide platelets show internal twinning on $\{110\}$ planes.

The superlattice structure in Ta-N was associated⁽¹⁵⁾ with regions giving rise to anomalous transmission effects in thin foil electron microscope specimens. During the beam heating of a homogeneous specimen a maze of ordered regions developed which, with continued heating, broadened in texture

and finally transformed. The authors noted that the sequence was identical to that found in the Fe-Ni-Co system where there is an ordering reaction followed by a martensitic transformation.

In niobium thin foils containing ~0.5 atomic percent oxygen, a homogeneous phase transformation to an fcc lattice occurs in localized regions during annealing in the electron beam⁽¹⁴⁾. This transformation was said to initiate by diffusion of interstitials until the local concentration is high enough to produce an appreciable ordering of oxygen atoms on {101} planes of the niobium. The precipitate then forms as prisms bounded by these planes. In bulk specimens the observed habit plane is {201} niobium in accordance with the predictions of the crystallographic theory for martensite formation.

In vanadium containing oxygen, platelets of a sub-oxide were observed⁽¹³⁾ to form in the bcc matrix for compositions near 6.4 atomic percent, while compositions near 9.5 atomic percent were found to be completely transformed to a bct phase. The $\frac{c}{a}$ ratio was 0.98 in the former case and 0.96 in the latter case. Twinning on {110}, {112} and {120} planes was observed within the platelets.

The present study investigates the vanadium-nitrogen system using classical gas-equilibrium techniques as well as electron microscopy to study the precipitation phenomena in dilute alloys. In the higher composition alloys, where a more complex structure is formed, x-ray

diffraction and two surface analysis were employed in addition to electron microscopy in order to delineate the important crystallographic features of the structure. Where applicable, electrical resistivity measurements were used to follow the progress of the transformation.

2. EXPERIMENTAL PROCEDURE

2.1 Material and Specimen Preparation

The vanadium used in this work was purchased from Wah Chang Albany in the form of $\frac{3}{8}$ " rod of approximately 99.9% purity. The supplier's analysis is presented in Table 1. Samples for internal friction and electrical resistivity measurements were fabricated by swaging this stock to 0.037" wire. Samples used for electron microscopy were fabricated by rolling the $\frac{3}{8}$ " stock to a thickness of 0.009" and then cutting into strips $\frac{1}{8}$ " wide. No intermediate annealing was required in either the swaging or the rolling process.

Doping the vanadium with known quantities of nitrogen was performed in an ultra-high vacuum Sieverts apparatus. A schematic diagram of this is presented in Figure 3. The pumping system consisted of a mechanical roughing and fore pump, a three stage glass oil diffusion pump, and an 8 liter/second ion pump. Dynamic vacuums in the 10^{-10} torr range were obtained under optimum conditions. With the sample heated to 1300°C , vacuum of 10^{-8} torr were typical. System pressures were measured with a Varian "Millitorr" gauge in the 10^{-5} torr to 10^{-1} torr range, and with an inverted Bayard-Alpert gauge in the 10^{-10} torr to 10^{-5} torr range.

Known amounts of gas were introduced into the closed chamber containing the hot specimen, which absorbed the gas

Table 1 Supplier's Analysis of Starting Vanadium
(in maximum weight ppm)

interstitial elements		substitutional elements*	
C	100	Al	50
H	10	Cr	100
N	150	Fe	100
O	200	Mo	50
		Si	500
		Ti	50

*substitutional elements other than those listed were present in amounts less than 40 ppm and totaled less than 150 ppm.

Table 2 Supplier's Nitrogen Analysis, Maximum ppm

element	maximum amount present
O ₂	1
H ₂	1
Ar	5
He	1
Ne	1
CO ₂	0.5
hydrocarbons	0.5
dewpoint	-105°F

Figure 3. Schematic diagram of the ultra-high vacuum Sieverts' apparatus used in this work.

completely. The quantity of gas was determined by measuring its pressure in a known volume at a standard temperature. The volume of a short length of pyrex tubing between two valves was accurately determined using a water manometer and gas displacement techniques. The volume of this tube was found to be 32.65 ± 0.10 ml. Pressures established in this calibrated volume, typically in the 1 to 50 torr range, were measured with an LVDT pressure transducer which had been calibrated against a McLeod gauge. The atomic percent nitrogen, x , introduced into the sample chamber, the pressure, p , in torr in the calibrated volume at 300°K and the weight, w , of the sample in grams are related by:

$$p = 5460 w \left(\frac{x}{100-x} \right)$$

The sample was heated by passing a current through it. The sample temperature was read with a micro-optical pyrometer, the reading then being corrected for sample emissivity using an emissivity of 0.44 for vanadium⁽²³⁾. This value has been verified by Diercks⁽²⁴⁾ for the particular sample preparations used in this investigation. The temperature was also corrected for sight glass absorption.

Samples were recrystallized at 1225°C and pressures of less than 10^{-7} torr for one hour prior to doping. The doping temperature was 1335°C except when noted differently. Following doping the samples were annealed for one hour at 1335°C and then either radiation quenched or helium quenched using high purity helium which was dried by passing it over liquid nitrogen-cooled CaSO_4 .

During radiation quenching of an 0.009" foil from 1300°C, the temperature fell to about 650°C in 10 seconds and to 300°C in about 50 seconds. The times to reach the same temperatures during helium quenching were about 4 and 7 seconds respectively. An upper limit on the contamination due to pick up of gases during annealing is completely negligible, being of the order of 10^{-2} atomic percent per day at 10^{-8} torr. During aging treatments the pressure never rose above 10^{-7} torr and was typically less than 2×10^{-8} torr.

The nitrogen used in doping was of the highest commercially available purity. The supplier's analysis is presented in Table 2. The process of nitrogen sorption by the sample was followed by monitoring the pressure with the millitorr gauge. In the case of doping the 0.037" vanadium wires, the pressure initially rose into the 10^{-1} torr range when the valve between the sample chamber and the calibrated volume was opened. It returned to less than 5×10^{-5} torr within 10 minutes. The sorption times for the 0.009" foils were much less, typically one or two minutes.

To avoid temperature gradients in the specimen grip region, 0.040" molybdenum lead wires were spot-welded to the specimens. This reduced the temperature difference between the grip region and the bulk of the sample to less than 30°C at 1335°C. The nitrogen sorption by the molybdenum is negligible. (25)

2.2 Electrical Resistivity Measurements

Electrical resistivity was measured by the four lead method. The wire sample was mounted inside the Sieverts apparatus and nitrogen was added incrementally, the resistivity versus temperature curve after each increment being recorded during radiation quenching. The voltage drop across the sample for fixed current, a quantity proportional to the resistivity, was used as input to the y-axis of an x-y recorder while the emf generated by a 0.010" tungsten-tungsten rhenium thermocouple spot welded to the sample was used as input to the x-axis of the recorder.

2.3 Preparation of Samples for Electron Microscopy

After doping with nitrogen the 10" x 0.125" x 0.009" foils were cut by electro-discharge machining into rectangular specimens of length 0.160", width 0.125". Dimples were jet machined into both sides simultaneously using an electrolyte of 20 volume percent H_2SO_4 in methanol and a potential of 155 volts for a jet size of 1 mm. Jet machining was continued to a depth just short of breakthrough, this requiring two to three minutes in most instances. The sample was then transferred to a stationary bath of the same electrolyte maintained at 32°F and electropolishing continued with a 12 volt potential until pinpoint breakthrough.

The microscope employed for this work was a Hitachi HU-11A equipped with a 10° tilt, 360° rotate stage.

Electron micrographs were produced from negatives oriented emulsion side up. The microscope was calibrated for image rotation and magnification by the author for this work.

2.4 X-ray Diffraction and Two Surface Analysis

Powder pattern samples were prepared by grinding; the entire sample was made to pass a 325 mesh sieve and then rolled into cylinders of less than 0.5 mm diameter, using Duco cement as a binder. An 11.46 cm Debye Scherrer camera and nickle-filtered copper radiation was employed. A 0.005" nickel filter was placed between the sample and the film to reduce the background radiation.

Laue patterns of individual grains were taken with a 5 centimeter, back-reflection camera using wet film techniques. Radiation from a tungsten tube was collimated with a 0.015" diameter tube, giving a beam size on the sample of approximately 0.018".

For the two surface analysis, a portion of a wire sample was mounted in bakelite, sectioned longitudinally and polished using standard metallographic techniques. A reference edge was cut in the bakelite approximately parallel to the wire axis. This reference edge was used for orientation work and for later second surface cutting. The grain selected for analysis was masked off from adjacent grains with PbO_2 in glycerine and its orientation determined from a Laue pattern. The second surface was then cut at 90° to both the polished surface and the reference edge.

3. RESULTS

Initial experiments were designed to measure the equilibrium partial pressure of nitrogen over solid solutions of nitrogen in vanadium as a function of temperature. Thermodynamic arguments coupled with the data of Brauer and Schnell⁽²⁶⁾ on the partial pressures of nitrogen over V_2N , reportedly the first nitride to form, indicated that this was a feasible project. Extensive effort proved that in solid solutions containing as great as 10% nitrogen (all compositions are stated in atomic percent unless otherwise noted), the equilibrium partial pressure was less than 10^{-7} torr at temperatures above $1000^{\circ}C$. The temperature had to be kept below $1350^{\circ}C$ due to vanadium sublimation and the resultant gettering action of the vanadium on the cool chamber walls.

It was concluded that the data of Brauer and Schnell was in error. It is noteworthy that these same authors claim to have purified vanadium of nitrogen by heating in a vacuum, while others⁽²⁷⁻²⁹⁾ as well as the present work show this to be impossible at temperatures of $1400^{\circ}C$ and pressures as low as 10^{-11} torr.

3.1 Vanadium Starting Material

A preliminary study was performed on the starting vanadium, that is the undoped material. Internal friction measurements at 1 cps in a Ke type pendulum⁽³⁰⁾ revealed

the presence of only one peak in the spectrum between room temperature and 375°C . The peak position corresponded to the relaxation of interstitially dissolved oxygen and its height indicated an oxygen content of about 0.10 atomic percent,⁽²⁸⁾ somewhat higher than that stated in the supplier's analysis.

No peak was observed at the position corresponding to the relaxation of nitrogen atoms, indicating that the initial nitrogen content was less than 10 ppm, which is lower than that stated in the supplier's analysis.

Metallographic examination of the starting material after it had been recrystallized showed a structure typical of a pure metal. An electron micrograph of this material is presented in Figure 4 for comparison with later micrographs. No second phase was observed in any of the annealed pure vanadium specimens by transmission electron microscopy.

3.2 Electrical Resistivity of Doped Materials

Typical electrical resistivity results are presented in Figure 5. The effect of adding nitrogen was to displace the resistance versus temperature curve to higher resistance at a given temperature, but to maintain the shape of the curve at higher temperatures. That is, in accordance with Mathesson's rule, the temperature coefficient of resistance was not significantly altered by adding nitrogen. This was true for nitrogen concentrations of less than 6.0%; nitrogen in excess of this amount tended to alter the temperature

Figure 4. Recrystallized starting vanadium in approximate (111) orientation. A grain boundary crosses the field of view. Magnification: 80000X.

Figure 5. Typical resistance versus temperature curves observed during radiation quenching.

coefficient somewhat, as well as displacing the curve in its entirety.

If one superposes all the R versus T curves at higher temperature, then the point at which deviation from the curve occurs as the temperature is reduced may be plotted as a function of composition as in Figure 6. The point of deviation may be associated with the onset of a phase transformation, and the drastic change in slope of this plot is taken to indicate two different transformations, one operating up to about 6.0% nitrogen and the other in alloys containing greater than this amount of nitrogen. The existence of these transformations is substantiated in the remainder of this work.

For classification purposes, alloys containing less than 6.0% nitrogen will be termed "low composition alloys" and those containing more than 6.0% nitrogen will be termed "high composition alloys."

3.3 The Precipitate Structure in the Low Composition Alloys

When the as-quenched, low composition alloys were aged, isolated precipitate particles nucleated and grew. This process was studied by transmission electron microscopy, and the results of this study will be presented in the next section. To fully interpret the details observed in the electron microscope images during the precipitation process, it is essential to know the crystal structure of the precipitate, as well as the habit plane and lattice correspon-

Figure 6. The temperature at which curves typified by those of Figure 5 change slope plotted as a function of nitrogen composition.

dence between the precipitate and matrix. This will be established in the present section.

As will soon become evident, it is necessary in determining the structure of the precipitate not only to observe electron diffraction spots which arise from the precipitate, but also to determine which of these spots are associated with each precipitate orientation. In order to fulfill each of these demands the structural analysis was performed on a well aged 3.0% alloy. The results were found to apply to all compositions in the range of 1.5% to 6.0% nitrogen.

Figure 7 presents the 3.0% alloy aged 47 hours at 350°C. It can be seen from this figure that the precipitate is disc shaped, the discs being viewed either normally or in profile. Noting that the foil orientation is such that a {100} plane is perpendicular to the electron beam, it is evident that the habit plane of the precipitate is {100}.

The presence of superlattice spots, i.e., the weaker spots which are present in addition to the strong matrix spots, is evident in Figure 8, the diffraction pattern from the region shown in Figure 7. This diffraction pattern is nearly identical to that presented by Villagrana and Thomas⁽¹⁷⁾ for a tantalum - 1.5% carbon alloy. A pattern showing the same arrangement of spots as well as similar streaking effects was presented by Edington and Smallman⁽¹²⁾ for vanadium heated in air.

The internal structure of the precipitate which when viewed normal to the disc, consists of two perpendicular sets of parallel boundaries making 45° angles with the <001>

Figure 7. V-3% N aged 47 hours at 350°C. Foil is in the exact {100} orientation. Selected area diffraction pattern is presented in Figure 8. Magnification: 40000X.

Figure 8 Selected area diffraction pattern from image presented in Figure 7. A large selected area aperture was used and all precipitate orientations contribute to the pattern.

directions, is also similar to that observed in the Ta-C system by Villagrana and Thomas. The explanation of these boundaries to be presented shortly is entirely different from that presented by these latter authors. In the profile view the internal precipitate boundaries intersect the foil surface along cube directions. Thus these internal boundaries must lie parallel to $\{110\}$ matrix planes, in particular, parallel to planes of this type which are parallel to the normal of the disc shaped precipitate.

To better appreciate the nature of these internal boundaries, several images were observed under different diffracting conditions - see Figures 9, 10 and 11. From such studies it was noted that the boundaries went out of contrast whenever $\vec{g}$ was normal to the boundary. This sort of behavior is associated with boundaries across which the displacement vector is parallel to the boundary. Such boundaries include, for example, stacking faults, anti-phase boundaries in ordered structures and twin boundaries.

If one were to consider only the diffraction pattern of Figure 8, then he might conclude, as did Villagrana and Thomas, that the crystal structure of the precipitate was of the $Ta_{64}C$ type proposed by these authors. However, there are certain subtle indications in Figure 8 which suggest that this conclusion is incorrect. Note, for example, that along one of the cube directions in this pattern those superlattice spots lying between matrix spots are noticeably more intense than the remaining superlattice spots. Such an occurrence would not be expected from a $Ta_{64}C$ type of structure.

Figure 9. V-3% N aged 47 hours at 350°C, demonstrating the effect of imaging with an $\langle 002 \rangle \vec{g}$.
Magnification: 40000X.

Figure 10. V-3% N aged 47 hours at 350°C, demonstrating the effect of imaging with a $\langle 110 \rangle \vec{g}$. Magnification: 40000X.

Figure 11. V-3% N aged 47 hours at 350⁰C, demonstrating the effect of imaging with the perpendicular, coplanar $\langle 110 \rangle$ $\vec{g}$ of that used in Figure 10. The sample has not been rotated between these two images. Magnification: 40000X.

In order to correctly interpret the precipitate structure it is necessary to examine the diffraction patterns of each individual precipitate orientation. Various precipitate orientations and the associated patterns for a $\{100\}$ foil are presented in Figures 12 through 16 while equivalent results for a $\{111\}$ foil are presented in Figures 17 through 20. The particular precipitates indicated in Figures 12 through 17 are not necessarily the precipitate giving rise to the associated diffraction patterns but have the same orientation as these precipitates. In general the particular precipitates giving rise to the patterns lay very close to the pinhole in the foil. Such precipitates were selected because they were thin and gave more intense spots. In thicker regions of the foil the diffuse background radiation, due to inelastic scattering effects and the strong matrix spot intensities, obscured the relatively weak superlattice spots. Having previously oriented the foil with the Kikuchi line pattern in the thicker regions, care was taken to assure that no bend contours were crossed in moving to a thinner region. In performing these diffraction experiments the aperture illuminated a 0.65 micron diameter region on the foil, drawn to scale on Figures 12 and 17.

Note that the diffraction patterns of Figures 14, 15 and 16 represent the arrangement of points on three orthogonal reciprocal lattice planes of the precipitate. The fact that they are not identical suggests that the precipitate

Figure 12. V-3% N aged 47 hours at 350°C, showing precipitate orientations associated with selected area diffraction patterns of Figures 13 through 16. The area circled corresponds in size to that illuminated by the aperture. The foil was positioned so that a {100} plane was exactly perpendicular to the beam. Magnification: 40000X.

Figure 13. Selected area diffraction pattern associated with the matrix shown in Figure 12. Note the absence of superlattice spots.

0/0,00

Figure 14. Selected area diffraction pattern associated with precipitate orientation A of Figure 12.

Figure 15. Selected area diffraction pattern associated with precipitate orientation B of Figure 12.

Figure 16. Selected area diffraction pattern associated with precipitate orientation C of Figure 12.

Figure 17. V-3% N aged 47 hours at 350°C, showing precipitate orientations associated with diffraction patterns of Figures 18 through 20. The aperture size is drawn to scale. Foil is in exact {111} orientation. Magnification: 40000X.

Figure 18. Selected area diffraction pattern associated with precipitate orientation A of Figure 17.

$\frac{0.1T}{10T}$

Figure 19. Selected area diffraction pattern associated with precipitate orientation B of Figure 17.

Figure 20. Selected area diffraction pattern associated with precipitate orientation C of Figure 17.

A hand-drawn diagram on a white page. It features a collection of approximately 15 small circles of varying sizes, some of which are interconnected by thin lines. There are also several small dots scattered throughout the diagram. In the lower right quadrant, there is a small coordinate system with two axes: a vertical axis labeled '1' and a horizontal axis labeled '10T'. The origin of this coordinate system is marked with a small dot.

1
10T

structure does not have three orthogonal four-fold symmetry axes. Note similarly in Figures 18, 19 and 20 that the pattern of superlattice spots does not have three-fold symmetry.

Figure 13 demonstrates that no superlattice spots originate from the matrix, and thus it may be concluded that the nitrogen atoms in the matrix form a random solid solution. Note that weak spots which occur at the outer edges of these patterns arise because the selected area aperture is displaced for higher order reflections⁽³¹⁾ and regions not intended to be included, in this case a precipitate particle, are included.

One may note again in Figure 14 the appearance of superlattice spots along one of the $\langle 100 \rangle$ directions which are brighter than the remaining superlattice spots. This is a very characteristic feature and should be explained by any proposed structure. Figure 16, typical of precipitates in the normal view, shows systematic absences of superlattice spots and leads to the complete abandonment of any suggestion that the structure is of the Ta_{64}C type illustrated in Figure 1.

In the $\langle 111 \rangle$ patterns presented in Figures 18, 19 and 20 the superlattice spots form a diamond pattern, with spots along two $\langle 110 \rangle$ directions but absent along the third. Superlattice spots exist only between adjacent matrix spots. Note that as one proceeds from one orientation of precipitate to another the absent spots are along the $\langle 110 \rangle$ which

is parallel to the trace of the platelet.

Extensive attempts to explain the diffraction patterns on the basis of a single crystal precipitate structure failed. It was then assumed that these patterns consist of the superposition of two separate patterns, each being associated with a single crystal region in the precipitate but differing in orientation from the other region.

It was noted that Figure 16 could be resolved into two twin-related patterns as shown in Figure 21. Furthermore, it was noted that one of these components results if only the bright spots in Figure 14 were plotted. Both these facts, coupled with the contrast experiments on the internal boundaries, suggest that these boundaries are twin boundaries of the superlattice. If it were not for the superposed twin pattern in Figure 14 the diffraction pattern would consist of a uniform intensity fcc array of superlattice spots.

A proposed reciprocal lattice structure which includes one of the components of Figure 21 as well as the fcc array mentioned above is presented in Figure 22. It will be demonstrated shortly that this structure together with its twin across the appropriate $\{110\}$ planes will generate all the diffraction patterns found in this work. Note in Figure 22 that only one fourth of the vanadium sublattice reciprocal cell is shown.

It is at this point that a lattice correspondence between vanadium atoms in the precipitate and vanadium atoms in the matrix will be presented. Clearly the absence of extraneous spots in any of the patterns thus far presented indicates

Figure 21. (a) reproduction of the basic pattern appearing in Figure 16. Large circles represent matrix reflections; small circles represent nitrogen atom reflections. Filled in small circles are double intensity spots. (b) and (c) are the components contributing to the pattern in (a).

(c)

(b)

Figure 22. Proposed reciprocal lattice structure consistent with the diffraction patterns presented in Figures 12 through 20. Only one-fourth of the vanadium sublattice is shown. Small circles are superlattice spots, large circles are matrix spots.

that the vanadium sublattice of the precipitate is also essentially bcc and that its cube axes are aligned with those of the matrix. Evidence more clearly establishing this point will be presented in the next section where the spots actually arising from the vanadium sublattice will be indicated. They are, in fact, hidden by the matrix spots. For now the following lattice correspondence will be employed:

$$[001]_V \parallel [001]_M$$

$$[010]_V \parallel [010]_M$$

$$[100]_V \parallel [100]_M$$

This correspondence was assumed in constructing Figure 22.

The real lattice corresponding to Figure 22 may be generated using the well known relations between the reciprocal and real lattices. The reciprocal of the vanadium reciprocal lattice is the bcc lattice. To determine how the nitrogen atoms are distributed in this lattice, we write the reciprocal nitrogen sub-lattice vectors in terms of the reciprocal vanadium sub-lattice vectors, thus:

$$\vec{b}_1^* = \frac{1}{4} (\vec{a}_1^* + \vec{a}_2^*)$$

$$\vec{b}_2^* = \frac{1}{4} (\vec{a}_2^* - \vec{a}_1^*)$$

$$\vec{b}_3^* = \vec{a}_3^*$$

It can be shown that

$$\vec{b}_1 = 2 (\vec{a}_1 + \vec{a}_2)$$

and that

$$\vec{b}_2 = 2 (\vec{a}_2 - \vec{a}_1)$$

$$\vec{b}_3 = \vec{a}_3$$

Hence the nitrogen sublattice may be constructed within the vanadium sublattice in real space to form the superlattice of the precipitate as presented in Figure 23. It is a direct consequence of the diffraction patterns associated with each disc orientation that the disc normal must be perpendicular to the tetragonal axis of the nitrogen sublattice and lie along a cube direction in the matrix. Note that in Figure 23 the nitrogen atoms were placed in octahedral sites. The justification for this choice will be presented in Section 4.2.

As Figure 23 illustrates the nitrogen atoms occupy a primitive tetragonal sublattice with a c parameter of a_V and an a parameter of $8 a_V$, a_V being the lattice parameter of the metal atoms in the precipitate. Letting the subscript N refer to the nitrogen sublattice and V refer to the vanadium sublattice in the precipitate, the lattice correspondence may be stated as:

$$[100]_N \parallel [110]_V$$

$$[010]_N \parallel [\bar{1}10]_V$$

$$[001]_N \parallel [001]_V$$

Figure 23. The real lattice corresponding to the reciprocal lattice of Figure 24. Each cube represents a vanadium lattice unit cell; the circles represent interstitial nitrogen atoms.

Parallel planes in the nitrogen sublattice and vanadium sublattice are related by the following matrix transformations:

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}_V = \alpha \begin{bmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 4 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}_N$$

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}_N = \beta \begin{bmatrix} 2 & 2 & 0 \\ -2 & 2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}_V$$

where α and β are arbitrary constants which may be adjusted so that the resulting indices have no common factor.

Reciprocal lattice points may also be referred to either set of reciprocal lattice vectors, the transformations between points (planes in the real lattice) being given by the above relations with $\alpha = \frac{1}{4}$ and $\beta = 1$. Of course, due to the coincidence of axes of metal atoms in precipitate and matrix, the subscript V may be replaced by M in any of the above relations, M referring to the matrix.

In predicting and indexing the various diffraction patterns associated with different orientations of the superlattice of Figure 23 the aid of a stereographic projection was indispensable. The lattice planes contributing to an electron diffraction pattern are those nearly parallel to the electron beam. If one constructs a stereographic projection of the crystal and the beam is normal to the projection, those planes whose poles project to the basic circle

give rise to diffracted spots provided, of course, the structure factors for these planes are not zero. From such a plot one may obtain the angular relations between the diffraction spots by direct measurement on the projection. The distance of the spot from the origin may be calculated for the nitrogen sublattice spots using the relation

$$\frac{1}{d} = \frac{1}{a_v} \left[\frac{h^2 + k^2}{8} \right] + \ell^2 \cdot 1/2$$

On a given pattern the distance of a spot from the origin is proportional to $\frac{1}{d}$, the proportionality constant henceforth being denoted as K . The proportionality constant may be easily deduced by examination of a spot of known indices, e.g., a matrix spot.

The lattice and structural correspondence between metal atoms in matrix and precipitate eliminates the need to predict spots associated with the vanadium sublattice in the precipitate. It is only the diffraction spots associated with the nitrogen sublattice which must be considered. The stereographic projections of the nitrogen sublattice presented in Figures 24 and 25 were prepared to aid in this indexing. Note all values of (hkl) give equally intense reflections because the nitrogen sublattice is primitive. In preparing these figures the tetragonal axis of the nitrogen sublattice was chosen to be $[001]_N$. The disc normal was chosen to be the $[010]_V \parallel [010]_M$ direction. Thus the operative twin planes are $(101)_V$ and $(10\bar{1})_V$. Though these are twin planes of the superlattice, they are mirror planes in the vanadium sublattice.

Figure 24. Stereographic projection of plane poles of nitrogen sublattice shown in Figure 23. Projection is constructed with $[001]_v$ normal to the projection. The nitrogen sublattice projects as .

Figure 25. Stereographic projection of plane poles of nitrogen sublattice shown in Figure 23. Projection is constructed with $[001]_v$ normal to the projection. The nitrogen sublattice cell projects as .

The diffraction patterns predicted for a single nitrogen sublattice orientation for various matrix cube directions are presented in Figure 26. The symbols included in these and the following figures ( ) are shorthand notations for how the nitrogen sublattice unit cell looks when viewed along the incident electron beam. The orientation of these symbols relative to the diffraction patterns is in turn dictated by the particular orientation of precipitate being considered.

Thus in a view normal to a precipitate disc, i.e., along an $[010]_V \parallel [010]_M$ direction, the two twin-related unit nitrogen cells project as + as a study of Figure 23 reveals. When the precipitate is viewed in profile the two twin-related orientations project as + , with the latter projection parallel to the disc normal. To obtain the predicted patterns one superposes the patterns of Figure 26 in appropriate fashion, thus obtaining the patterns presented in Figure 27. Note the detailed agreement between predicted patterns and the actual diffraction patterns, in particular the nitrogen spots which are doubled in intensity. Note that in Figure 27a the rows of double intensity spots lie parallel to the disc normal. Figure 14 demonstrates that this is as it should be.

A pole figure representing the (111) matrix plane was likewise prepared for one of the orientations in the precipitate; this is presented in Figure 28. The nitrogen atom planes whose normals fall on the basic circle were reflected about the twin plane trace shown and also recorded on this

Figure 26. (a) Diffraction pattern from structure of Figure 23 when viewed along $[001]_V$. This will be symbolized by . Medium size circles designate nitrogen sublattice reflections from this sublattice orientation. (b) Diffraction pattern from structure of Figure 23 when viewed along $[010]_V$. This will be symbolized by . Smallest circles designate nitrogen sublattice reflections from this sublattice orientation. Largest circles represent matrix reflections. The orientation symbolized by will be represented by small black dots.

Figure 27 (a) Predicted diffraction pattern for a disc viewed in profile. Disc normal is horizontal

(b) Predicted diffraction

pattern for a disc viewed normally. .

Figure 28. Stereographic projection of plane poles of nitrogen sublattice shown in Figure 23. Projection is constructed with $[111]_V$ normal to the projection. Only those planes parallel to the normal are shown. The twins of these planes about the $(10\bar{1})_M$ twin plane shown are included and denoted with a prime. The $\{100\}_V$ plane normals are also indicated.

figure. The twins of planes lying inside the basic circle were not recorded, as they are not necessary for this discussion. Using angles and indices from this pole figure the diffraction pattern presented in Figure 29 was constructed. Note the excellent agreement between the constructed pattern and the observed diffraction patterns of Figures 18 through 20. Recalling that the precipitate disc normal lies along the $[010]_M$ direction, one sees from Figure 28 that the precipitate orientation is such that the trace of the platelet is always parallel to the row of missing spots. This is as observed and noted previously.

To establish beyond any doubt that the precipitate structure was as presented in Figure 23, several more diffraction patterns were generated by tilting angles between 10° and 20° both about $\langle 100 \rangle$ and $\langle 110 \rangle$ directions in a $\{100\}$ foil. The Kikuchi lines were used to accurately establish the orientation of the foil. The pole figures presented in Figures 24 and 25 were used to predict the appropriate diffraction patterns. In the cases presented in Figures 30 through 35 the agreement between prediction and observation was exact. The indexed schematic patterns following each observed pattern are those predicted from the structure of Figure 23 and its twin.

Four orientations, other than those presented, were also checked and found to be in perfect agreement. No patterns were observed which were not fully consistent with the proposed structure.

Figure 29. Predicted $\{111\}$ diffraction pattern for a single orientation of precipitate. Largest circles represent vanadium atom reflections while two smaller sets of circles represent spots arising from two twin-related nitrogen sublattices. Trace of disc is parallel to $[110]_V$ direction along which no nitrogen sublattice spots appear.

Figure 30. Diffraction pattern from a $\{100\}$ foil tilted approximately 16° about an $\langle 001 \rangle$ direction. The tilt axis as well as the precipitate orientation are noted in Figure 31. The precipitate was nearly in the profile position.

Figure 31. (a) The Kikuchi pattern associated with the foil orientation producing the diffraction pattern of Figure 30. (b) The diffraction pattern predicted by the structure of Figure 23 for a {100} foil tilted as described in Figure 30. Symbols are as defined in Figure 26.

(a)

(b)

Figure 32. Diffraction pattern from a {100} foil tilted approximately 14° about an $\langle 010 \rangle$ direction. The tilt axis as well as the precipitate orientation are noted in Figure 33. The precipitate was nearly in the profile position.

Figure 33. (a) The Kikuchi pattern associated with the foil orientation producing the diffraction pattern of Figure 32. (b) The diffraction pattern predicted by the structure of Figure 23 for a {100} foil tilted as described in Figure 32. Symbols are as defined in Figure 26 except for the use of larger filled in circles to represent the spots. Disc normal is approximately horizontal.

(a)

(b)

Figure 34. Diffraction pattern from a {100} foil tilted approximately 11° about an $\langle 011 \rangle$ direction. The tilt axis as well as the precipitate orientation are as noted in Figure 35. The precipitate was in the nearly normal position.

7

d

v

x

x

d

v

7

B

d

v

d

v

d

Figure 35. (a) The Kikuchi pattern associated with the foil orientation producing the diffraction pattern of Figure 34. (b) The diffraction pattern predicted by the structure of Figure 23 for a {100} foil tilted as described in Figure 34. Symbols are as defined in Figure 26. The indices for the set of superlattice spots arising from one orientation of nitrogen sublattice are denoted by a prime while the set for the other twin-related orientation is not primed. Disc normal is approximately horizontal.

(a)

(b)

Some of the patterns in Figures 30 through 35 show redissual or "ghost" spots along the tilt axis; these are not included in the predicted patterns. Such spots are due to the finite length of the relrods associated with reciprocal lattice points which are slightly off the Ewald sphere. Taking the foil thickness in the selected area region to be of the order of $100\text{\AA}$, the relrod half length is about $10^{-2}\text{\AA}^{-1}$. The relpoints closest to the tilt axis are about $\frac{1}{4a} \approx 0.1\text{\AA}^{-1}$ removed from this axis. The distance of these points to the Ewald sphere is approximately $0.1\text{\AA}^{-1} \sin 14^\circ = 0.02\text{\AA}^{-1}$, and hence they are expected to appear on the pattern close in to the tilt axis.

3.4 Tetragonality in the Vanadium Sublattice

In the previous section the vanadium sublattice in the precipitate was treated as if it were body centered cubic. A closer inspection of the diffraction patterns indicates that this is not the case. A selected area diffraction pattern of a profile view precipitate in a $\{100\}$ foil was taken to specifically demonstrate this effect. The condenser lens on the microscope was defocused so as to constrict the diffraction spots as much as possible, thus producing the pattern of Figure 36. Only the matrix spots have been indexed in this figure, the superlattice spots are indexable as in Figure 26a.

Note that the matrix spots in this figure are often resolved into two separate spots, e.g., the $(\bar{2}\bar{2}0)_M$ and $(020)_M$

Figure 36. V-3% N aged 47 hours at 350°C. The beam is exactly perpendicular to a $\{100\}_M$ plane. A precipitate in profile view with the disc normal along the $\langle 020 \rangle_M$ direction causes the observed pattern.

020

010 100
11000

spots. The weaker of these two spots is associated with the set of superlattice spots, while the stronger belongs to the set of matrix spots. The weaker spot originates not only from the nitrogen sublattice of the precipitate, but also from the vanadium atoms in the precipitate. Hence, as can be seen from Figure 36 the superlattice spots adjacent to matrix spots are considerably brighter than the other superlattice spots.

If the vanadium sublattice in the precipitate were cubic with the same lattice parameter as the matrix, the set of spots discussed above -- those adjacent to matrix spots -- would be indistinguishable from the matrix spots. The fact that they do not superpose exactly on the matrix spots indicates that the vanadium sublattice is not cubic.

In proceeding away from the origin along the $[200]_M$ direction of Figure 36, the rows of superlattice spots at right angles to this direction remain aligned with rows of matrix spots. Along the $[020]_M$ direction, however, the rows of superlattice spots parallel to $[200]$ are displaced inwards relative to the parallel rows of matrix spots. This indicates that the vanadium sublattice in the precipitate is tetragonal. Measurements of this displacement fix the $\frac{c}{a}$ ratio as lying between 1.03 and 1.04. Note that the tetragonal axis of the vanadium sublattice is parallel to the disc normal.

In order to more accurately determine the various lattice parameters, a 6.0% alloy was investigated using x-ray diffraction. From electron diffraction patterns the 6.0% alloy was

known to contain the same precipitate as the 3.0% alloy. In the as-quenched condition the 6.0% alloy was found to be body centered cubic with $a = 3.050 \pm .001\text{\AA}$. After aging for 6 hours at 350°C , x-ray lines developed which could be associated with the c direction tetragonal distortion in the precipitate. Those lines arising from the precipitate "a" parameter were not distinguishable from those of the matrix. It was found that $c = 3.13 \pm .01$, $a = 3.037 \pm .02$, $\frac{c}{a} = 1.031$. Aging for 315 hours at 350°C produced no change in the values of c and a, but did increase the intensity of the precipitate lines as would be expected. A 4.5% alloy produced similar results except that in the as-quenched condition it had a lattice parameter of $3.042 \pm .001\text{\AA}$.

3.5 Progress of Precipitation in the Low Composition Alloys

When a 1.5% alloy was radiation quenched, the structure presented in Figure 37 resulted. Indications of a precipitate are present in the form of small black dots, but on such a fine scale that the precipitate is not clearly resolvable. Helium quenching of a 3.0% alloy produced a structure with little or no precipitate. Compare Figure 38 with that for the pure vanadium, Figure 4. As the concentration was increased to 6.0% and above, the electron micrographs showed an increased amount of finely divided precipitate. At 7.4% the structure consisted of a mottled background and isolated bands of a second phase. Alloys having a banded microstructure belong to the high composition category to be discussed in the next section.

Figure 37. V-1.5%N, radiation quenched. Plane of foil
is approximately {111}. Magnification:
80000X.

Figure 38. V-3.0%N, helium quenched. Plane of foil is approximately {111}. Magnification: 80000X.

The electron diffraction patterns give some indication of change as the composition increases from 1.5% to 6.0% nitrogen. The Kikuchi lines, which give exact indication of lattice orientation and qualitative indication of lattice perfection, are clearly evident in the starting material and alloys up to about 6.0%. However they become weaker as the composition increases until in the 6.0% alloy they are just barely visible. In the 7.4% alloy the Kikuchi lines are no longer useful for orientation determination although there is slight indication of their presence as they sweep across the diffraction pattern during sample manipulation. In such samples orientations were determined by tilting the foil until equivalent diffraction spots had equal intensity.

The 1.5, 3.0 and 4.5% alloys showed no superlattice spots in the as-quenched condition. Very weak superlattice spots between the matrix spots along $\langle 100 \rangle$ directions are present in the 6.0% alloy as can be seen in Figure 39a. These superlattice spots are accompanied by streaking in the $\langle 110 \rangle$ directions. In the 7.4% alloy's diffraction pattern, Figure 39b, the superlattice spots are very prominent.

Figures 40 and 41 show the precipitate in the 1.5% alloy after aging for 100 minutes at 280°C . Several individual precipitates are marked in these pairs of pictures. Note that the temperature of 280°C has some significance, being the temperature at which the nitrogen atoms make about 1 jump per second.

Figure 39. Diffraction patterns showing the presence of superlattice spots:

- (a) 6.0% alloy, radiation quenched. Foil was in exact $\{100\}$ orientation.
- (b) 7.4% alloy, radiation quenched. Foil plane is approximately parallel to $\{111\}$ plane.

Figure 40. V-1.5%N, aged 100 minutes at 280°C. (a) and (b) are images of the same region on the foil viewed using two different $\langle 110 \rangle$ diffraction vectors, as indicated. Corresponding precipitates in the two images are indicated. Magnification: 160000X.

(d)

(q)

Figure 41. V-1.5%N aged 100 minutes at 280°C. (a) and (b) are images of the same region viewed with complementary $\langle 112 \rangle$ diffraction vectors. Corresponding precipitates in the two images are labeled; these exhibit the inside-outside contrast typical of disc shaped precipitates. Magnification 160000X.

(a)

(b)

Figures 40a and b were taken with two different diffraction vectors, $\vec{g}$, both of the $\langle 110 \rangle$ type but non-complimentary, i.e., having directions differing by other than 180° . Note that the precipitates appear as pairs of crescents, separated by a line of no contrast. Such an effect is typical of precipitates in the $100\text{\AA}$ to $1000\text{\AA}$ size range which are too small to be visible due to structure factor contrast, i.e., differences in absorption between precipitate and matrix. Due to misfit between precipitate and matrix, however, there is localized bending of the lattice planes in the matrix in the vicinity of the precipitate. This gives rise to matrix strain contrast. Hirsch et al⁽³¹⁾ provide an elementary treatment of this effect, demonstrating that for precipitates which produce spherical strain fields there is no contrast in regions where $\vec{g} \cdot \vec{R} = 0$, $\vec{R}$ being the matrix displacement vector.

Inspection of Figure 40a or b reveals that there are sets of precipitates in each figure having different orientations of the line of no contrast. Neither of these lines in either figure is perpendicular to $\vec{g}$, as would be the case if the displacements of the surrounding matrix were spherically symmetrical. Furthermore, comparison of Figures 40a and b shows that there are in fact three orientations of the line of no contrast, although only two of these directions appear at the same time in either figure. The missing one in both instances is parallel to $\vec{g}$. The orientation of precipitate in contrast in both figures has its line of no

contrast parallel to the third coplanar $\langle 110 \rangle \vec{g}$.

Evidence to be presented shortly suggests that even at this early stage in the precipitation process the precipitate exists as discs. As a first approximation, one may resolve the matrix displacements due to such discs into two components: $\vec{R}_1$ along the disc normal and $\vec{R}_2 = \vec{R}_3$ in the plane of the disc.

Since one set of discs in either figure goes completely out of contrast for a given $\vec{g}$, it may be concluded that $\vec{R}_2 (= \vec{R}_3)$ is small or zero. The set of discs which are out of contrast for a given $\vec{g}$ are those for which $\vec{g} \cdot \vec{R}_1 = 0$.

A second feature to note is that for discs the line of no contrast is no longer perpendicular to $\vec{g}$. Instead it becomes a function of $\vec{R}_1$, $\vec{R}_2$ and $\vec{R}_3$: Here only the case where $\vec{R}_2 = \vec{R}_3 = 0$ will be considered. If the disc normal is appreciably inclined to the beam, then $\vec{R}_1$ will cause some displacement of planes which are parallel to the beam, i.e., those contributing to the image. However, there is no component of $\vec{R}_1$, and hence no lattice distortion, along the line of intersection of the plane normal to the beam and the plane of the disc. When the foil surface is perpendicular to the beam this latter line corresponds to the trace the disc would make if it intersected the surface. The line of no contrast lies along this line of intersection.

The above discussion in conjunction with the images presented in Figure 40 are sufficient to fix the habit planes of these precipitate discs as either $\{100\}$ or $\{111\}$. Results

presented in earlier and later parts of this work favor the former habit plane.

Figures 41a and b were included to further substantiate the disc-shaped character of the precipitate during its early stages. In Figure 41a several precipitates are circled which exhibit excellent matrix contrast. Maher and Eyre⁽³²⁾ delineate carefully the conditions under which discs or loops in the 100-500⁰Å size range show particular shapes in matrix contrast. Such discs or loops are said to show inside or outside contrast according to whether the image lies inside or outside the actual loop projection. The contrast can be changed from inside to outside or vice-versa by changing the sign of $\vec{g}$. Thus when the sign of $\vec{g}$ is changed in Figures 41a and b, the precipitates circled show the characteristic inside-outside contrast change.

Annealing the 1.5% alloy for 6 hours at 350°C caused considerable growth of the particles as shown in Figure 42. Some of the particles have grown at the expense of others, becoming larger discs. The disc shaped nature of the precipitate is not so readily observable in the {111} foils since the three orientations are equally inclined to the foil surface. One may infer the shape from the fringe patterns which will be dealt with shortly.

In the case of the 1.5% alloys only {111} foils were available for analysis. This was the common foil plane found in these materials; rarely a {100} or {331} foil plane occurred.

Figure 42. V-1.5%N, aged 6 hours at 350°C. Plane of foil was approximately parallel to a {111} plane. Magnification: 40000X.

The habit plane of the discs in the 1.5% alloy aged 6 hours at 350°C was established from the {111} foils. This cannot be done simply by inspection as in the case of the {100} foils. Although the presence of three orientations with traces along $\langle 110 \rangle$ directions strongly indicates a {100} habit plane, there is always the possibility, admittedly remote, that there is a disc lying parallel to the foil surface which is out of contrast. To establish beyond a doubt that the habit planes of the discs were {100} planes, the angle of inclination of these discs with the foil surface was measured using both $\langle 110 \rangle$ and $\langle 112 \rangle$ two beam conditions. From several such measurements this angle was found to be consistently about 55°, precisely the angle expected for the {100} planes.

In general, whenever the precipitates were inclined to the foil surface at an angle other than 90°, the presence of fringe patterns was noted. In imaging with a $\langle 110 \rangle \vec{g}$, fringes were observed on two orientations but absent on the third orientation, for {111} foils. The orientation without fringes was always that with its trace in the {111} foil surface parallel to $\vec{g}$. Imaging with a $\langle 112 \rangle \vec{g}$ produced fringes on all three precipitate orientations.

The fringe patterns on these precipitates are actually composed of two superposed patterns, one pattern lying parallel to the trace of the precipitate disc in the foil surfaces, and a second pattern concentric with the center of the disc. The former pattern arises from displacement fringe contrast and the latter patterns consist of thickness fringes arising within the precipitate.

Displacement fringe contrast is associated with the matrix displacement at the interface. It arises when there is an abrupt change in phase of the incident and diffracted waves as they encounter a sheet of precipitate which has displaced the matrix planes in opposite directions on either side of it. Although it has not been pointed out in detail previously, the precipitate discs in this system are coherent, i.e., the metal atom planes match across the flat face of the disc. The lattice parameter matching across the habit plane, as presented in Section 3.4 of this work, together with the absence of any Moire fringes when the precipitate is viewed normally establishes this. The displacement $\vec{R}$ of such a coherent disc is normal to the plane of the disc. When a normal displacement, R_n , is substituted into the equations of the dynamical theory (neglecting absorption), the intensity of the transmitted wave is given by⁽³³⁾

$$I = \cos^2 \frac{\alpha}{2} \cos^2 \frac{\pi t}{\epsilon g} + \sin^2 \frac{\alpha}{2} \cos^2 \frac{2\pi Z}{\epsilon g}$$

where $\alpha = 2\pi \vec{g} \cdot \vec{R}_n$, Z is the thickness of the foil, ϵg is the extinction distance and z is the distance from the foil surface to the precipitate. Clearly when $\alpha = 0$ there will be no fringes.

Figure 43 is a pole figure showing the $\{100\}$ and $\{110\}$ plane poles for all three precipitates and the matrix in the (111) orientation. Note that $\alpha = 2\pi \vec{g} \cdot \vec{R}_n$ is zero when imaging with a $\langle 110 \rangle$ $\vec{g}$ only for the precipitate whose trace is parallel to $\vec{g}$. Imaging with a $\langle 112 \rangle$ $\vec{g}$ does not make $\alpha = 0$ for any precipitate orientation.

Figure 43. (111) matrix pole figure. The matrix poles are indexed with the larger set of numbers. The poles from the three precipitate orientations are also shown and designated by smaller numbers; one orientation is unprimed, another singly primed and the third is doubly primed. A precipitate tetragonality of 10% was used to construct this figure.

The situation may be viewed in a more geometrical fashion. Referring again to Figure 43, imaging with a particular $\langle 110 \rangle \vec{g}$ produces one orientation of precipitate, and only one, in which the planes used for imaging do not change in either spacing or orientation across the precipitate/matrix interface. This orientation of precipitate would hence show no displacement fringes. As previously noted, its trace is parallel to $\vec{g}$.

The thickness fringes, those concentric with the center of the disc, arise from the disc shaped nature of the precipitate and delineate regions of constant precipitate thickness. These are separated by a fixed thickness which is not necessarily equal to the extinction distance in the matrix but depends on the properties of the precipitate. From the intersections of the disc with the foil surface the thickness is estimated to be about 200 to 300 Å while the diameter is about 5,000-10,000 Å.

The mottled contrast remaining in those discs oriented such that $\vec{g} \cdot \vec{R}_n = 0$ arises from the twin boundaries within the precipitate. Earlier studies presented in Section 3.3 showed that these boundaries are out of contrast when $\vec{g}$ is normal to the twin plane. An inspection of Figure 43 will show this is the case for only one set of twin planes in the precipitate orientation, the other set remains in contrast and gives rise to the mottled appearance. The effect is also noticeable in Figure 44 which presents a $\{111\}$ image of the 3.0% alloy aged 6 hours at 350°C.

Figure 44. V-3%N, aged 6 hours at 350°C. Note the presence of fringes on two orientations of precipitate and the absence of fringes on that precipitate whose trace with the foil surface lies parallel to $\vec{g}$. Magnification: 40000X.

In comparing Figures 42 and 44, the appearance of the precipitate in the 1.5% and 3.0% alloys is similar. To test whether precipitation was complete or not, these alloys were aged for longer times. The results of aging these alloys for 47 hours at 350°C are presented in Figures 45 and 46. Comparison of these figures with Figures 42 and 44 demonstrates that growth is complete prior to 6 hours at 350°C in the 1.5% alloy, but that further growth takes place in the 3.0% alloy. This indicates that the precipitate is richer in nitrogen than the matrix and its growth requires long range diffusion of nitrogen, resulting in depletion of nitrogen in the matrix. The relatively small volume fraction of precipitate in the 1.5% alloy requires that the precipitate composition be considerably greater than 1.5%. We note in passing that the 1.5% alloy corresponds stoichiometrically to $V_{64}N$.

Increasing the nitrogen content up to about 6.0% had the effect of producing more precipitate for a given aging treatment. The as-quenched material in the 4.5% and 6.0% alloys looked much the same as the 1.5% alloy of Figure 37. In the aged materials the precipitate was so prevalent that individual discs linked up to form a lattice work of precipitate whose interstices contained the solid solution. A typical sample is presented in Figure 47.

3.6 Transformation of the High Composition Alloys

As the electrical resistivity measurements of Section 3.2 indicated, there is a different phase transformation occurring

Figure 45. V-1.5%N, aged 47 hours at 350°C. Comparison of this figure with Figure 42 shows that precipitate growth in the 1.5% alloy is essentially complete within 6 hours at 350°C. Foil plane is approximately parallel to {111}. Magnification: 40000X.

Figure 46. V-3%N, aged 47 hours at 350°C. Comparison of this figure with Figure 44 shows that growth is not complete in this alloy when it is aged 6 hours at 350°C. Foil plane approximately parallel to {111}. Magnification: 40000X.

Figure 47. V-4.5%N aged 6 hours at 350°C. Plane of foil is approximately parallel to {111}. The top figure shows a region near the edge of the foil while the bottom figure shows a region where the foil is thicker. Magnification: 80000X.

during quenching in the high composition alloys. This was further substantiated by x-ray diffraction. In the 7.4% alloy the x-ray pattern showed the structure to be body centered tetragonal with $c = 3.00 \pm 0.01 \text{ \AA}$, $a = 3.08 \pm .01 \text{ \AA}$ and $\frac{c}{a} = 0.974$. Increasing the composition to 10.0% shifted these parameters to $c = 2.97 \pm .01 \text{ \AA}$, $a = 3.11 \pm .01 \text{ \AA}$ and $\frac{c}{a} = 0.955$. Considering the as-quenched materials only, the a parameter increased in essentially a linear fashion from $3.04 \text{ \AA}$ in the 4.5% alloy to $3.11 \text{ \AA}$ in the 10.0% alloy.

In the 7.4% alloy irregularities in the form of long thin bands showing contrast different from the matrix were observed in the transmission electron microscopy images, as shown in Figure 48.

In a 7.8% alloy evidence of a new phase could also be seen in the optical microstructure in the form of striations, as shown in Figure 49. Alloys in the 6.0% to 8.0% composition range underwent considerable macroscopic deformation during quenching, also shown in Figure 49. This deformation was abrupt, occurring at about $500\text{--}600^\circ\text{C}$ depending on composition and was also reversible, the wire sample returning to its original shape at about the same temperature on heating. Accompanying the distortion was a clicking noise similar to tin "cry."

Above about 8.0% nitrogen the macroscopic shape deformation ceased and optical examination revealed the presence of a banded microstructure. Figure 50 is typical of alloys in this range. Increased nitrogen content caused no further

Figure 48. V-7.4%N, radiation quenched. Note the presence of ribbons of a second phase. Foil surface approximately parallel to {111}. Magnification: 40000X.

Figure 49. V-7.8%N (a) Wire specimen at temperature of 1355°C . (b) Macroscopic deformation of specimen during radiation quenching. Temperature is 25°C in this picture. (c) Optical micrograph showing striations produced during radiation quenching. Magnification: 200X.

(a)

(b)

(c)

Figure 50. V-12.3%N. Optical micrograph of a radiation quenched wire sample. The microstructure is typical of alloys containing more than 8.0% nitrogen. Magnification: 1000X.

microstructural changes except when the solvus line at the doping temperature of 1335°C was exceeded. In this latter case a nitride layer formed on the surface of the wire.

From several samples of varying composition equilibrated at 1335°C , the solubility of the nitride in the α -solid solution was found to be between 9 and 10 atomic percent. The nitride layer on a 15.0% sample was examined using an electron microprobe and was found to contain 89.5 ± 0.5 weight percent vanadium. This corresponds to about 30 atomic percent nitrogen and represents the composition of nitride in equilibrium with the solid solution at 1335°C . This is probably the previously reported V_2N .⁽²⁶⁾

In order to determine the crystallographic features of the banded microstructures, both two surface analysis and transmission electron microscopy were employed. Accurate orientation determinations in the electron microscope were not possible due to the absence of Kikuchi lines. This made any trace analysis in the microscope very approximate. Fortunately the blades were large enough so that two surface analysis techniques were applicable.

Five different grains in alloys containing 10.2, 12.3 and 15.0% nitrogen were oriented using a Laue camera and their surfaces prepared for analysis. A typical Laue pattern is presented in Figure 51. In such patterns it was found that if split and/or streaked Laue spots were treated as single spots, the pattern could be completely indexed as being due to a single orientation of crystal. Thus the

Figure 51. (a) Laue pattern taken from a V-12.3%N radiation quenched wire. This pattern, in the orientation portrayed, was taken from the longitudinal surface of the sample shown in Figure 52, in the orientation in which it is portrayed. (b) Some indexed spots of the pattern shown in (a).

(a)

(b)

orientational change between adjacent bands must be small and is manifested in the splitting of Laue spots.

The two surfaces of the grain whose Laue pattern appear in Figure 51 are presented in Figure 52. Each set of bands which intersect both surfaces was used to establish the boundary plane between them. From eleven such sets of bands, the boundary plane was determined to be a $\{110\}$ plane.

The high composition alloys are tetragonal. Since the $\{110\}$ planes which are parallel to the C axis are twin planes of this system, it is suggested that adjacent bands are twin related. As Figure 51 shows, the Laue spots of the $[010]$ zone are split into pairs separated by about 2° . This splitting was attributable to twinning on the particular $\{110\}$ plane whose traces are present in both surfaces of Figure 52. The magnitude of the splitting to be expected from twinning on a $\{101\}$ plane in a tetragonal lattice is given by

$$\cos \left(45^\circ \pm \frac{\theta}{2} \right) = \frac{c/a}{[1 + (c/a)^2]^{1/2}}$$

when θ is the splitting along the $[010]$ zone of spots. A value of $\theta = 2^\circ$ corresponds to a $\frac{c}{a}$ ratio of 0.96 or 1.03. The agreement of the former value with that established by x-ray diffraction is evidence that the bands are, in fact, twin related.

The Laue spots are also split or streaked along the $[100]$ direction of Figure 51. This sort of streaking is also found in the electron diffraction patterns to be

Figure 52. The two surfaces of the grain whose Laue pattern appears in Figure 51. The sample was in the form of an 0.037" wire.
Magnification: 100X.

presented shortly. It is associated with internal structure within the bands, which is nicely brought out in the surface replica of Figure 53.

Electron transmission techniques were employed to better delineate this fine structure internal to the bands. A foil with its surface approximately parallel to a cube plane is presented in Figure 54, while a foil showing a single band in approximate $\{111\}$ orientation is shown in Figure 55.

In Figure 54 the darker lines running vertically and horizontally within the band are $\{110\}$ planes, a fact also demonstrated in Figure 55. In both instances these planes are nearly parallel to the electron beam. Since in Figure 55 the fine structure traces are at 60° to one another, the $\{110\}$ planes causing the structure cannot belong to the same $\langle 100 \rangle$ zone, as was the case for the fine twins in the ordered precipitate of the low composition alloys.

Figures 56 through 62 present several selected area electron diffraction patterns. It is obvious from these patterns that, although the vanadium atoms remain body centered tetragonal, the ordered structure of the nitrogen atoms is not the same as that occurring in the low composition alloys. The structure which gives rise to these patterns is considerably more complex and has not yet been deduced. Note that the most intense superlattice spots in Figure 57 do not appear in Figure 58. Note also that the various superlattice spots do not fall at any simple fraction of the distance between matrix spots. Both these facts complicate the analysis.

Figure 53. Surface replica showing the presence of structure internal to the bands which occur in the high composition alloys. Magnification: 15000X.

Figure 54. V-11.0%N, as quenched. Foil surface
approximately parallel to {100}.
Magnification: 80000X.

Figure 55. V-11.0%N, as quenched. Foil surface
approximately parallel to {111}.
Magnification: 80000X.

017
101

Figure 56. V-11.0%N, radiation quenched. Foil surface approximately parallel to {100}. Showing regions used for selected area diffraction patterns presented in Figures 57 and 58. Magnification: 40000X.

Figure 57. Selected area diffraction pattern from region
A of Figure 56.

010
100

Figure 58. Selected area diffraction pattern from region B of Figure 56.

Figure 59: V-11.0%N, radiation quenched. Foil surface approximately parallel to {111}. Selected area diffraction regions associated with Figures 60 through 62 are noted. Magnification: 40000X.

Figure 60. Selected area diffraction pattern of region
A in Figure 59.

Figure 61. Selected area diffraction pattern of region B in Figure 59.

Figure 62. Selected area diffraction pattern of region
C in Figure 59.

Despite the fact that the structure of these alloys is different from the low composition structure, they do share some features. One may, for example, resolve the patterns in Figures 57 through 62 into components, each component arising from a single crystal region which is twin related to the other areas a $\{110\}$ plane. It should be noted that these twins may be twins in the nitrogen sublattice, twins in the matrix, or both. A detailed analysis of this twinning must await the deduction of the structure.

Note the rotation of the diamond patterns of superlattice spots in Figures 60 through 62 as adjacent bands are examined. This too has its counterpart in the low composition alloys. Figures 60 and 62 demonstrate that although adjacent bands differ in orientation, alternate bands have the same orientation. As the x-ray results showed, the orientation of the vanadium atom sublattices in these bands changes by less than 2° between adjacent bands. The electron diffraction patterns establish a nitrogen atom sublattice correspondence in alternate bands.

When two sets of non-parallel bands met, either one set ended abruptly or else one set penetrated the other. When this latter event occurred, the penetrating set tapered to a point. This sort of intersection can be seen in Figure 50. A surface replica showing the fine structure within bands at such intersections is presented in Figure 63.

Figure 63. Surface replica showing regions where bands intersect. Magnification: 20000X.

Intersecting twin bands and the conditions under which such intersections occur have been discussed by Cahn.⁽³⁴⁾ The tapering of such bands after intersection may be a result of the fine structure within the bands, as was the case for In-Tl⁽³⁵⁾ alloys.

4. DISCUSSION

4.1 Crystal Structure Refinements and Stoichiometry of the Precipitate

Certain details were omitted in the initial presentation of the crystal structure in order to avoid confusion. Such details will now be examined.

The primitive nitrogen sublattice is actually not tetragonal as it was presented in Section 3.3. Due to the tetragonality of the vanadium sublattice in the precipitate, the nitrogen sublattice is actually monoclinic with $a_N = b_N = 2.875 a_V$, $c_N = a_V$, $\alpha = \gamma = 90^\circ$ and $\beta = 88^\circ 20'$. It is helpful for future discussion to redefine the unit superlattice cell in terms of the non-primitive nitrogen cell presented in Figure 64. In this cell the nitrogen atoms occupy a base centered orthorhombic lattice which includes the superlattice cell. From the figure it can be seen that $c_S = A_V = 3.035\text{\AA}$, $b_S = 4.12 a_V = 12.504\text{\AA}$, $a_S = 4.0 a_V = 12.140\text{\AA}$, $\frac{b}{a} = 1.03$ and $\frac{c}{a} = 0.25$, the S subscript referring to the superlattice. This cell has the further advantage that the axes of the two sublattices are parallel. Note that the interstitial nitrogen atoms lie in rows parallel to $\vec{a}_2$ with the distance between rows nearly three times the distance between atoms in a row.

Assuming, for the moment, that each nitrogen sublattice site is occupied by only one nitrogen atom, the unit cell is seen to contain two nitrogen atoms and thirty two

Figure 64. The unit cell of $V_{16}N$ defined in terms of a non-primitive nitrogen sublattice unit cell.

vanadium atoms. Thus the precipitate corresponds under these circumstances to $V_{16}N$ and contains 5.88% nitrogen (1.69 wt.% nitrogen).

The various aging treatments give qualitative indication that the composition of the precipitate is close to $V_{16}N$. Visual estimates indicated that the 1.5% foils contained from 10 to 20 volume percent of precipitate after aging 315 hours at $350^{\circ}C$, while the 3.0% alloys contained 30 to 40 volume percent of precipitate. Assuming the Cost and Monroe⁽¹⁰⁾ data actually represent the equilibrium between the ordered structure and the solid solution, the solubility is about 0.62% at $350^{\circ}C$. If the precipitate is $V_{16}N$, the lever rule predicts about 17 volume percent for the 1.5% alloy and 45% for the 3% alloy. These predictions, in reasonable agreement with observation, indicate that the precipitate is indeed $V_{16}N$.

4.2 Choice of Interstitial Site; Growth Twins

It has been assumed that the interstitial nitrogen atoms occupy octahedral sites. It will now be demonstrated that tetrahedral site occupancy is inconsistent with the experimental findings of this work.

The electron diffraction studies presented in Section 3.3 establish both the shape and orientation of the nitrogen cell pictured in Figure 64. They also establish the orientation of the tetragonal axis of the vanadium sublattice in the precipitate, indicated $\vec{a}_3$ in Figure 64. This tetragonal

axis is parallel to the disc normal. In the lower right hand corner of Figure 64, a single vanadium sublattice cell is redrawn and the three subsets of tetrahedral sites are indicated as A, B and C. The three subsets of octahedral sites are indicated as D, E and F.

It is sufficient for purposes of this discussion to use a hard sphere model for describing the displacements of the vanadium sublattice associated with an occupied interstitial site. These displacements are assumed to be radial, an assumption justified by more detailed calculations. (36)

The tetrahedral site has a 4-fold rotation-inversion axis parallel to the tetrahedral axis ($\vec{a}_1$ is the tetrahedral axis for site A). The octahedral site has a 4-fold rotation axis along the octahedral axis ($\vec{a}_1$ is the octahedral axis for site D). Both of these symmetry axes are contained in the tetragonal crystal system, and occupancy of either type of site gives rise to vanadium sublattice distortions having tetragonal symmetry. If the displacements associated with an isolated tetrahedral site are resolved along $\langle 100 \rangle$ directions, the displacement along the tetragonal axis is only half of that along the other two cube directions. Octahedral site occupancy gives rise to a strain dipole which expands the vanadium sublattice along the octahedral axis and contracts it slightly in directions perpendicular to this axis.

When rows of sites are considered, as in Figure 64, the displacements are somewhat modified. Selection of a B-type of site for the ordered array of interstitial results in

vanadium sublattice displacements of equal magnitude along $\vec{a}_1$ and $\vec{a}_3$ due to the symmetry of the nitrogen sublattice and the symmetry of the tetrahedral displacements mentioned above. Any tetragonality of the vanadium sublattice must be associated with $\vec{a}_2$ for type B site occupancy. This is inconsistent with the observed $\vec{a}_3$ axis of Figure 64. Suppose then that the ordered array of nitrogen atoms takes up A-type tetrahedral sites. In this case the largest displacements will clearly be along $\vec{a}_2$ and the smallest along $\vec{a}_1$ with displacements along $\vec{a}_3$ intermediate between these two. The resulting lattice distortion, aside from not having tetragonal symmetry, does not have its greatest extension along $\vec{a}_3$ as experimental findings indicate must be the case. Similar reasoning leads to the rejecting of C-type tetrahedral sites.

From the above reasoning it is concluded that the nitrogen atoms in the $V_{16}N$ precipitate occupy octahedral sites. In Figure 64 the D and E type octahedral sites have strain dipoles perpendicular to $\vec{a}_3$ and thus cannot produce the observed vanadium sublattice tetragonality. Only that subset of octahedral sites labeled F has strain dipoles directed along $\vec{a}_3$, hence only these sites are consistent with the experimental findings of this work.

It has already been pointed out that the superlattice is observably orthorhombic. The extent of this orthorhombicity has been experimentally determined in this work. A more subtle point is that the vanadium sublattice itself is most probably orthorhombic, not tetragonal -- an effect of insufficient magnitude for measurement by techniques employed

in this work. The equal contractions normal to $\vec{a}_3$ for an isolated F-type octahedral site may be expected to become unequal when the nitrogen atoms are placed in rows. The contraction along the rows would be greater than between the rows, making $\vec{a}_2 < \vec{a}_1$. Thus the vanadium sublattice becomes slightly orthorhombic. Some evidence for this may be gotten from the electron diffraction patterns, which show that the boundaries internal to the precipitate are twin planes of the nitrogen sublattice. If the vanadium sublattice is tetragonal such planes are mirror planes to the vanadium atoms. To the extent that the vanadium sublattice is orthorhombic, these planes are also twin planes for the vanadium sublattice. Figure 65 is a view normal to the flat face of a precipitate disc (parallel to a twin plane) in which the orthorhombicity of the vanadium sublattice has been accentuated for illustrative purposes. There would be no effect on the vanadium sublattice, if it were tetragonal. An $\frac{a_2}{a_1}$ ratio of slightly less than 1.0 would cause a slight rotation of the vanadium atoms across the twin plane, as shown in the figure. In crossing the twin plane the rows of nitrogen atoms are rotated about the $\vec{a}_3$ axis by approximately 90° .

As figures such as Figure 7 demonstrate, the twin planes in the precipitate are regularly spaced by distances of the order of $100\text{\AA}$ and they extend long distances along the $\langle 110 \rangle$ direction contained in the twin plane. It is suggested that these twins provide a means of minimizing the distortion in

Figure 65. Growth twin occurring in the $V_{16}N$ precipitate. The view presented is normal to the flat face of a precipitate disc, i.e., parallel to the twin plane. The orthorhombicity of the vanadium sublattice has been accentuated.

the habit plane.

Let the $\vec{R}_i$ in Figure 65 connect the atoms in their twinned crystal positions to their positions without the twin present. The $\vec{R}_i$ are parallel to the twin plane both for the nitrogen atoms and for the much smaller displacements of the vanadium atoms. Thus as observed in the contrast experiments of Section 3.3 such boundaries should be out of contrast when $\vec{g}$ is normal to the twin plane because $\vec{g} \cdot \vec{R}_i = 0$.

4.3 The High Composition Alloys

Banded structures similar to that presented in Figure 50 are observed in some martensitic transformations, for example, that occurring in the indium-thallium system.⁽³⁵⁾ In-Tl undergoes a cubic to tetragonal martensitic transformation in cooling from high temperatures. The bands in In-Tl lie parallel to $\{110\}$ planes. The fine structure within the bands in this system always lies parallel to one or the other of two $\{110\}$ planes which lie at 60° to the band boundary and at 90° to each other. The remaining set of $\{110\}$ planes, those not observed, are the set which are not twin planes in the tetragonal system.

In vanadium with greater than 7.4% nitrogen the bands are parallel to $\{110\}$ twinning planes, planes which rotate the major distortion axis by 90° . One orientation of fine structure within the bands in both Figures 54 and 55 is parallel to the $\{110\}$ planes lying at 60° to the band boundaries, as is the case for In-Tl. The presence of a second set of fine structure at 60° to the first set in

images such as Figure 55 is consistent with either a nitrogen sublattice twinning in an ordered tetragonal structure or vanadium sublattice twinning in a slightly orthorhombic structure.

In the In-Tl system both the main band boundaries and the fine structure within are due to shearing, but not the twinning shear as explained by Barrett et al. (35). In the high composition alloys of this work the electron diffraction patterns indicate that the various regions across the $\{110\}$ planes are twin related. It is probable, then, that during cooling the original cubic crystal becomes orthorhombic by pronounced expansion along one direction and rather slight contraction along an orthogonal direction. This change to a slightly orthorhombic structure could be caused by the ordering of the nitrogen atoms in one or more subsets of interstitial sites. In the polycrystalline samples used in this work such a transformation would lead to high internal stresses which could be relieved by twinning on $\{110\}$ planes, all such planes being possible twin planes.

Verification of any mechanism describing the transformation of the high composition alloys must await further experimentation.

5. SUMMARY

1. Alloys containing less than 6.0% nitrogen appeared to be single phase when examined with an optical microscope. Closer examination using transmission electron microscopy showed the presence of an extremely fine ($\sim 20\text{\AA}$) precipitate whose presence became more pronounced as the nitrogen content was increased from 0% to 6.0%. Helium quenching of a 3.0% alloy essentially eliminated the presence of this precipitate. X-ray diffraction showed that these alloys in the as-quenched condition were body centered cubic, the lattice parameter increasing slightly with nitrogen content.

2. No tendency for interstitial ordering in the 1.5% and 3.0% alloys in the as-quenched condition was detected by electron diffraction. Alloys containing nitrogen in excess of 3.0% showed superlattice electron diffraction spots indicating that some interstitial ordering had occurred during quenching. This tendency increased with increased nitrogen content.

3. The precipitate in aged alloys was disc shaped and its habit plane was determined to be $\{100\}$. The precipitate was found to consist of a twinned orthorhombic superstructure containing an ordered array of nitrogen atoms in sixteen body centered tetragonal vanadium cells.

4. The precipitate was shown to correspond to $V_{16}N$ in composition.

5. During aging, the nitrogen atoms in the matrix surrounding the precipitate remain in random interstitial solid solution.

6. A phase transformation occurring during radiation quenching in alloys containing more than 6.0% nitrogen was observed. Alloys of between 6.0% and 8.0% showed macroscopic deformation of the wire sample accompanied by audible "clicking" sounds.

7. Alloys containing greater than 8.0% nitrogen showed a banded microstructure. The transformed product was tetragonal, the $\frac{c}{a}$ ratio being less than one and decreasing with increased nitrogen content. The main bands were twin related across $\{110\}$ planes, which were the boundaries between adjacent bands.

8. There was a fine band structure ($\sim 100\text{\AA}$) within the main bands mentioned in 7 above. This fine structure also occurred on $\{110\}$ planes. Electron diffraction showed that the nitrogen atoms were ordered in these high composition alloys.

LIST OF REFERENCES

1. J.R. Cost and C.A. Wert, *Acta Met.* 2, 231 (1963).
2. E. Gebhardt, H.D. Seghezzi, E. Fromm, *Z. Metallk.* 52, 464 (1961).
3. H. Inouye, *Refractory Metal Alloys*, 165 (1968), Plenum Press.
4. E. Fromm, *Thermodynamics Volume II*, 455, International Atomic Energy Agency, Vienna, 1966.
5. H. Hahn, *Z. Anorg. Chem.* 258, 58 (1949).
6. W. Rostoker and A. Yamamoto, *Trans. ASM* 46, 1136 (1954).
7. W. Rostoker and A. Yamamoto, *Trans. ASM* 47, 1002 (1955).
8. J.A. Hren, M.S. Thesis, University of Illinois, Champaign-Urbana, Illinois.
9. N. Schönberg, *Acta Chem. Scand.* 8, 211 (1954).
10. J.R. Cost and F.M. Monroe, *Trans. AIME* 245, 1079 (1969).
11. K.H. Jack, *Proc. Roy. Soc.* A208, 200 (1951).
12. J.W. Edington and R.E. Smallman, *Acta Met.* 13, 155 (1965).
13. M. Cambini and M. Heerschap, *Mat. Res. Bulletin* 4, 633 (1969).
14. L.I. Van Torne and G. Thomas, *Acta Met.* 12, 601 (1954).
15. D.P. Seraphim, N.R. Stemple and D.T. Novick, *J. Appl. Phys.* 33, 136 (1962).
16. J. Van Landuyt and C.M. Wayman, *Acta Met.* 16, 803 (1968).
17. R.E. Villagrana and G. Thomas, *Phys. Stat. Solidi* 9, 499 (1965).
18. N. Schönberg, *Acta Chem. Scand.* 8, 240 (1954).
19. D. Beshers, *J. App. Phys.* 36, 290 (1965).
20. G.A. Shatalov and A.G. Khachaturyan, *Phys. Metals and Metallog.* 25, 56 (1969).
21. C.M. Wayman and J. Van Landuyt, *Acta Met.* 16, 815 (1968).

22. G. Brauer, H. Müller and G. Kühner, J. Less Comm. Metals 4, 533 (1962).
23. W. Dürschnable and G. Hörz, Naturwissenschaften 15, 2 (1964).
24. D. Diercks, University of Illinois at Urbana-Champaign, Dept. of Metallurgy and Mining Engineering, private communication.
25. J.H. Evans and B.L. Eyre, Acta Met. 17, 1109 (1969).
26. G. Brauer and H. D. Schnell, J. Less Comm. Metals 6, 326 (1964).
27. J.T. Stanley and C.A. Wert, Acta Met. 3, 107 (1955).
28. G. Hörz, Z. Metallk. 59, 832 (1968).
29. W.E. Anable, Bureau of Mines publication TN 23.U7, No. 7014, 622. 06173.
30. T.S. Ke, Phys. Rev. 71, 533 (1947).
31. P.B. Hirsch et al., Electron Microscopy of Thin Crystals, Butterworth and Co., London (1965).
32. D.M. Maher and B.L. Eyre, "Characterization of Small Resolved Perfect Dislocation Loops by Transmission Electron Microscopy," to be published in Phil. Mag.
33. M.J. Whelan and P.B. Hirsch, Phil. Mag. 2, 1121 (1957).
34. R.W. Cahn, Acta Met. 1, 49 (1953).
35. J.S. Bowles, C.S. Barrett, L. Guttman, Trans. AIME 188, 1478 (1950).
36. R.A. Johnson, G.J. Dienes and A.C. Damask, Acta Met. 12, 1215 (1964).

VITA

Donald Irwin Potter was born May 28, 1941, in Detroit, Michigan. He graduated as salutatorian of his class from Salesian Catholic Boys' High School, Detroit, in 1959. He entered Monteith College, Wayne State University in June of 1959 and received his Ph.B. degree with high honors in 1964. He entered the College of Engineering, Wayne State University in 1964 and received his B.S. in Metallurgical Engineering with highest honors in 1966. In September of 1966 he entered graduate school at the University of Illinois at Urbana-Champaign. He has held a National Aeronautics and Space Administration fellowship as well as the position of research assistant and teaching assistant in the Department of Metallurgy and Mining Engineering during his graduate work. He received his M.S. degree in June 1967.

He is a member of Tau Beta Pi, Sigma Xi, Phi Lambda Upsilon, American Society for Metals, and the Metallurgical Society of AIME. He has published the paper "Prediction of the Operative Slip Systems in Cs Cl Type Compounds Using Anisotropic Elasticity Theory" which appeared in Materials Science and Engineering, Vol. 5 (1970), p. 201. He has co-authored the paper "Recovery Processes and Ordering in Ni_3Al " which appeared in the Journal of Applied Physics, Vol. 38 (1967), p. 3894.