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AN ELECTRON MICROSCOPY STUDY
OF CARBIDE PRECIPITATION IN A VANADIUM-TITANIUM ALLOY

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I. INTRODUCTION

In the past few years, extensive work has been done on the development of vanadium alloys¹⁻⁵. Vanadium and certain vanadium alloys are of interest as a possible fuel element cladding in sodium cooled Liquid-Metal-Fast-Breeder-Reactor (LMFBR). Carbon, nitrogen and oxygen are known to affect the mechanical properties of vanadium⁶, as well as that of the other Group V-B transition metals. From the beginning of the development of vanadium alloys, titanium has been one of the most important alloying elements because of its strong affinity towards interstitial impurities.

Internal friction results for a V+1.31% Ti alloy strongly indicate that titanium act as a scavenger of interstitials. However other investigators have concluded that above approximately 3% Ti, the complete binding of the interstitial impurities by titanium is not maintained with increasing titanium content. The solubility of interstitial increases and hence, the scavenging action of titanium must decrease or cease^{2,3,8}. Finally, according to Hasson and Arsenault⁹, the scavenging action of titanium appears not to be a function of titanium concentration. The internal friction results for the V-4% Ti and V-20% Ti alloys show no evidence of a Snoek peak at 2.52 at.% oxygen addition, which is greater than the solubility limit of oxygen in vanadium.

Electron microscope investigations of V-Ti alloys by Kramer², with oxygen content between 200 and 1600 ppm and heat treatment around 1000°C, indicate that the alloys show a precipitation of a cubic phase of NaCl structure of the B1 lattice type, i.e. TiO particles. The number of TiO particles precipitated increases with increasing oxygen content. The particle size in this case does not change, only the distance between particles is diminished. With increasing titanium content, the number and volume fraction of the precipitated particles decrease. The plate-shaped TiO particles precipitate on the (001) planes and are coherent with the matrix. The orientation relationship between the matrix and the precipitates are:

$$(001)_M // (001)_{TiO}$$

$$[100]_M // [110]_{TiO}$$

Ryan and co-workers studied the precipitation of Group IV A carbides and nitrides in molybdenum¹⁰ using electron microscopy. The precipitates display a characteristic plate-like morphology. The zirconium and hafnium carbides and nitrides exhibit a cubic {100} habit plane. However the titanium carbides and nitrides exhibit an apparent {310} habit plane.

An interesting feature of the refractory metal-interstitial systems is the great variety of second phases possible depending upon composition and thermal treatment. Roubin and Paris obtained a series of carbonitrides in vanadium (formula VC_yN_{1-y} , $0 < y < 1$)¹¹. Multi-stage precipitation processes have been observed in the systems Nb-O¹², Nb-O-N¹³, Ta-O¹⁴, Fe-N¹⁵ and Fe-C¹⁶⁻¹⁷.

Precipitation in the refractory metal-carbon systems has not been studied as extensively as in the oxygen and nitrogen systems. The solubility of carbon is in general very small and it is difficult to retain appreciable amounts of carbon in these metals by quenching. Diercks and Wert¹⁸ studied precipitation in V-C alloys and found it to be at least a two stage process. The formation of a metastable coherent carbide on $\{310\}$ planes of the matrix preceeds the appearance of the final equilibrium carbide (hexagonal V_2C). Subsequently Viswanadham and Wert¹⁹ conducted a similar study on Nb-C system. Electron microscopy observations showed two similar well defined precipitate structures and morphologies. Electrical resistance and hardness measurements were consistent with the formation of three more intermediate structures. They have the same $\{310\}$ habit plane but differ in carbon content and degree of carbon order. They are respectively carbon clusters, GP I and GP II zones.

The fact that the interstitial atoms in Bcc metals are not distributed randomly among the available interstitial sites is well known. Internal friction measurements demonstrate that, in all but the most dilute solutions of interstitial atoms, the solute atoms cluster in two, three, four or more atoms. Such studies have been conducted for the systems Nb-O²⁰, Ta-N²¹, and V-N²². At higher concentration, of the order of 5 at.% or more, these interstitials often exhibit a tendency to long range order. As early as 1951, Jack²³ had confirmed the ordering of nitrogen atoms in iron-nitrogen martensites. Such interstitially

ordered superstructures have been observed in Ta-C²⁴, Ta-N²⁵⁻²⁷, Ta-O²⁸⁻²⁹, Nb-O³⁰⁻³², V-N³³, V-O³⁴⁻³⁹, and V-H⁴⁰.

The interstices in the Bcc metals are commonly divided in two sets, the tetrahedral and octahedral sites as shown in Figure 1. Calculations⁴¹ based on minimizing the strain energy associated with the two types of sites indicate that octahedral site occupancy is expected for oxygen in vanadium, carbon and nitrogen in iron and carbon in tantalum. The energy required for intrusion of an impurity atom into an octahedral or tetrahedral interstitial site of a Bcc lattice was calculated by Shatalov and Khachaturyan⁴². They found that interstitial atoms occupy octahedral sites in iron, either kind of sites in tantalum and niobium and only tetrahedral sites in vanadium. A number of arguments relative to the strain energy⁴³, the anisotropy of the Snoek relaxation strength⁴⁴ and others, are in favor of the general acceptance of octahedral sites⁴⁵, the case for tetrahedral occupancy remaining a possibility.

In the Ta-C solid solutions a superstructure of composition Ta₆₄C was suggested²⁴ with the interstitials in octahedral sites ordered on a Bct sublattice. Thomas and Villagrana³⁵ proposed an ordered phase identical to that of Ta₆₄C in order to interpret the micrographs of Edington and Smallman³⁴ in the V-O system. On the other hand Gunwaldsen and Potter³⁹ explained the pattern obtained from the V₉O phase using a long period superlattice which is 4 x 4 x 6 vanadium atom cells in dimension. They showed that the sites of this long period superlattice correspond to tetrahedral positions.

Figure 1. The octahedral (O) and tetrahedral (T) sites in the body centered cubic lattice.

In the V-N system Potter and Alstetter³³ identified a precipitate with the stoichiometry $V_{16}N$. The structure consists of a base centered orthorhombic array of Bct vanadium unit cells. The nitrogen atoms are found to occupy the octahedral interstitial sites.

In the Ta-N system Schönberg defined the compound Ta_2N with the metal atoms in a closed packed hexagon and the non-metal atoms in one of the two octahedron centers of the unit cell. Seraphim and co-workers²⁵ found an ordered structure in interstitial solid solutions as dilute as 0.1 at.% nitrogen in tantalum. On the basis of the symmetry of the ordered structure, tetrahedral rather than the octahedral sites are considered appropriate. Usikov and Khachaturyan have proposed a superlattice corresponding to the composition Ta_9N . In this superlattice the nitrogen atoms are situated in three sublattices of octahedral interstices. Finally Geils and Potter found that the composition was higher than Ta_9N . The composition would be Ta_9N_2 and the unit cell defining this structure is a cube consisting of 27 Bcc tantalum cells with the nitrogen atoms placed in the tetrahedral sites.

Other examples could have been taken in the Ta-O and Nb-O systems. They express the difficulty to define general laws of occupancy of the interstitials in the refractory metals. The present study investigates the vanadium-titanium-carbon system using electron microscopy and electron diffraction to study the precipitation phenomena in dilute alloys.

II. EXPERIMENTAL PROCEDURE

A. Specimen Preparation

The vanadium used in this investigation was purchased from Materials Research Corporation in the form of 0.25" rods of Grade Marz purity. The titanium was obtained from the same company in the form of 0.062" wires of Grade Marz purity. The chemical analysis furnished by the supplier are given in Tables I and II.

The vanadium-titanium alloy was obtained by a zone refining process in a MRC Model EBZ-93 Electron Beam Zone Refiner. Alloys can be prepared in a floating zone apparatus provided the constituent materials do not differ too widely in melting point from each other and from the alloy. A hole of 0.063" diameter was drilled into the vanadium rod and the titanium wire was placed inside. Several melting passes were used to improve homogeneity in a dynamic vacuum of less than 1×10^{-6} torr. The rods and wires were cleaned in a solution of $\text{HNO}_3 : \text{H}_2\text{O} = 1 : 1$. The alloy was cold swaged to 0.050" diameter wire and specimens were prepared to check the composition using the microprobe. The homogeneity was quite satisfactory (± 0.1 weight %) and the composition was close to 5 weight % of titanium. These were then cold rolled into 0.010" thick foils approximately 1/8 inch wide.

1. Annealing and Degassing

Sixteen inch strips of the foil were cleaned again and mounted in a modified Sievert's apparatus with a well trapped

Table I. Supplier's analysis of vanadium starting material
(analysis for impurities given in weight ppm).

O	10.0	K	1.0	Zr	6.0
N	N.D. <5	Ca	.6	Nb	30.0
H	1.4	Sc	.7	Mo	1.0
C	87.0	Ti	5.0	Rh	< 2.0
Li	< .02	Cr	< 3.0	Cd	< .3
Be	< .02	Mn	< 0.3	In	< 1.0
B	2.0	Fe	30.0	Sn	< .7
F	< .4	Co	1.0	Te	< .7
Na	1.0	Ni	1.0	I	.5
Mg	1.0	Cu	2.0	Ba	< 2.0
Al	50.0	Zn	1.0	Ta	< 30.0
Si	500.0	Ga	< .7	W	30.0
P	10.0	Ge	< 2.0	Pt	1.0
S	6.0	As	.4	Au	< 1.0
Cl	2.0	Sr	< .5	Hg	< .4
				Pb	1.0
				U	1.0

All others non-detected to 0.1 ppm.

Table II. Supplier's analysis of titanium starting material
(analysis for impurities given in weight ppm).

O	350.0	V	20.0	Mo	10.0
N	50.0	Cr	20.0	Pd	< .7
C	140.0	Mn	20.0	Ag	< 2.0
H	10.0	Fe	80.0	Cd	< 3.0
Be	.06	Co	< .3	In	< .7
F	< .4	Ni	20.0	Sn	15.0
Si	20.0	Cu	20.0	Sb	.5
P	.2	Zn	< .4	Te	< 1.0
S	3.0	As	.5	Ta	< 2.0
Cl	10.0	Br	< .4	Ir	< .7
K	.3	Zr	< 1.0	Au	< 2.0
Ca	.6	Nb	< 2.0	Pb	4.0
				Bi	20.0

mercury diffusion pump. The apparatus was pumped to a vacuum better than 5×10^{-7} torr and the foils were heated to a temperature of 1400°C by direct resistance heating. After one hour the vacuum returned equal or below the initial value. This treatment not only recrystallizes the sample (with a grain size of 1 to 2 mm) but also removes interstitial oxygen, nitrogen and carbon. The final total interstitial content is estimated to be of the order of 10 atomic ppm. Figure 2 is a micrograph of a degassed specimen.

2. Carburizing

After annealing, the specimens were removed, carefully weighed and remounted in the Sievert's apparatus. They were pumped again and reheated to 1350°C . The foils were isolated from the vacuum system and a calculated amount of research grade purity methane gas was admitted to the chamber in order to produce a nominal composition of about 0.3 atom % carbon. The strip was carburized for at least thirty minutes. In spite of the formation of hydrogen gas after decomposition of methane, no hydrogen is expected to enter the metal at this high temperature. The samples were then radiation cooled by cutting off the power and opening the chamber to vacuum to prevent the absorption of hydrogen.

3. Quenching

The carburized foils were cut into five inch lengths and one inch long grips of 0.036" degassed vanadium-titanium wire were spot welded to both ends of the foil. The apparatus used was a modified version of one designated by Evans and Eyre⁴⁶. The specimens were mounted on two pivoting stainless steel arms

Figure 2. Micrograph of annealed and degassed vanadium-titanium alloy.

which also served as electrodes and were held in place by a thin copper wire. The system was pumped to a vacuum of less than 5×10^{-7} torr and the specimens were heated to a temperature of about 1300°C for two minutes. The quenching bath employed was a low melting point eutectic alloy with low vapor pressure. The composition of the alloy is (in weight percent) Bi-49, Pb-18, Sn-12 and In-21. The melting point of the alloy is 55°C . After this homogenizing heat treatment which removes any hydrogen picked during doping, the sample was dropped into the molten quenching bath by melting the copper wire. The quenching rates obtained are in excess of 10^4 $^{\circ}\text{C}/\text{sec}$. After the quench the foils were cleaned in warm water and then chemically polished in a solution of 50% HNO_3 in water to remove any additional quench metal. Figure 3 is an electron micrograph of a 0.3 atomic percent carbon quenched foil and reveals no trace of any second phase.

4. Aging

The quenched specimens were usually aged at elevated temperatures prior to examination in the electron microscope. The samples were wrapped in vanadium-titanium foil and encapsulated in quartz under a vacuum of better than 10^{-6} torr. For aging below 800°C a salt bath (sodium nitrate) with a temperature control of $\pm 2^{\circ}\text{C}$ was used. Aging at higher temperatures was accomplished in a small air furnace.

B. Electron Microscopy

Specimens for electron microscopy were prepared by a combination jet- and electropolishing techniques. This gave

Figure 3. Micrograph of an alloy containing 0.3 atom % carbon in the as quenched condition.

1000 Å

excellent thin areas with the added advantage that the thin area is never directly handled.

1. Jet Polishing

The jet polishing solution consisted of an electrolyte of 20 volume percent H_2SO_4 in methanol, as suggested by Edington and Smallman⁴⁷ for vanadium. Two symmetrical dimples were jet machined into the sample using stainless steel jets 1 mm in diameter spaced 5 mm apart. The jet polishing was carried out at 150 V and 200 mA. The process was continued to just short of breakthrough with times typically on the order of 2 minutes. After jet polishing the samples were washed in methanol.

2. Electropolishing

The final electropolishing was carried out in a stationary bath of the same electrolyte maintained at 0°C with a potential of 10 volts. A stainless steel sheet served as a cathode. The electropolishing operation was observed under a 30 power microscope and continued until pinhole breakthrough with times typically being 10 to 20 minutes. The samples were washed in methanol followed by a final wash in absolute ethyl alcohol. They were dried between filter papers and stored in air tight vials.

3. Electron Microscope

The microscope used was a JEOL type JSEM-200 with a $\pm 60^\circ$ tilt stage. All electron micrographs reproduced here were photographed at an accelerating voltage of 200 kV and 35,000X.

4. Indexing and Notation

Following the suggestion of Bedford and Miller⁴⁸, the three index Miller notation is used to index the hexagonal diffraction patterns which occur, as well as to designate all hexagonal planes and directions. All micrographs were taken under strong two beam bright field conditions and the $\underline{g}$ vector is indicated by an arrow on the micrographs.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Microstructures for Isochronal Aging from 300°C to 600°C

In order to study precipitate morphology, an isochronally aged series of specimens were prepared from foils carburized to a nominal 0.3 atomic percent carbon level and quenched. The isochronal aging was carried out for sixty minutes in the temperature range from 300°C to 600°C.

The first specimen, aged for 60 minutes at 300°C, is shown in Figure 4. This treatment has produced a very fine precipitate dispersed uniformly throughout the matrix.

Aging for sixty minutes at 350°C produces the microstructure shown in Figure 5. The precipitates have grown to diameter about 100Å. The particle size estimated from micrographs are only maximum limits since the strain field of the particle rather than the particle itself is being observed. It is very difficult to distinguish a precipitate from its neighbors. In contrast to carbide precipitation in pure vanadium, displacement fringes similar to that displayed by stacking faults have not been found. The stage of coherent precipitation occurring on $\{310\}$ habit planes, where the vanadium atoms arrangement in the precipitate is very nearly Bcc, does not seem to exist. Furthermore this structure does not give streaking in the diffraction patterns as it was found in pure vanadium or in pure niobium¹⁹. The scavenging action of titanium seems to prevent the formation of G.P. zones and the precipitation of coherent carbide.

Figure 4. Microstructure of an alloy aged for 1 hour at 300°C. Beam direction close to [113], diffraction vector shown.

Figure 5. Microstructure of an alloy aged for 1 hour at 350°C. Beam direction close to [113], diffraction vector shown.

The structure produced by aging for sixty minutes at 400°C , Figure 6, confirms this result. Instead of showing the plate-like morphology, the carbides coalesce into irregular three dimensional particles.

Figures 7, 8, 9 and 10, corresponding to sixty minute agings at 450°C , 500°C , 550°C and 600°C respectively, show the fully developed incoherent precipitate. The diffraction patterns from this structure show faint second phase spots superimposed on the matrix pattern. This phase has the same structure as hexagonal V_2C or Nb_2C and the results of the diffraction studies of this incoherent precipitate are discussed in the next section.

Aging at 600°C results in dislocations emitted from the particle matrix interface. Approximately 10 minutes are sufficient to drive the reaction to completion and the earlier stages observed at much lower temperature do not appear.

Finally Figures 11 and 12 show very large precipitates corresponding to aging at 800°C for 10 minutes. The micrographs show the faulting inside the incoherent precipitate as previously observed with Nb_2C in Nb. On the contrary V_2C in V is almost perfect with no faulting. When the precipitate transforms to the hexagonal structure, the misfit becomes very high.

The relatively low number of dislocations observed on the micrographs is consistent with the fact that the misfit is accommodated by faulting of the carbide rather than by misfit dislocations.

Figure 6. Microstructure of an alloy aged for 1 hour at 400°C. Beam direction close to [113], diffraction vector shown.

Figure 7. Microstructure of an alloy aged for 1 hour at 450°C. Beam direction close to [113], diffraction vector shown.

Figure 8. Microstructure of an alloy aged for 1 hour at 500°C. Beam direction close to [113], diffraction vector shown.

Figure 9. Microstructure of an alloy aged for 1 hour at 550°C. Beam direction close to [113], diffraction vector shown.

Figure 10. Microstructure of an alloy aged for 1 hour at 600°C. Beam direction close to [111], diffraction vector shown.

Figure 11. Microstructure of an alloy aged for 10 minutes at 800°C. Beam direction close to [113], diffraction vector shown.

Figure 12. Microstructure of an alloy aged for 10 minutes at 800°C. Beam direction close to [113], diffraction vector shown.

B. The Incoherent Carbide Precipitate

The micrographs for aging from 400°C to 800°C have clearly shown the development of the three dimensional incoherent carbide which can grow to very large dimensions. This can be seen in Figure 12 where the largest dimension is about 2μ . The carbides produced at the higher temperatures give rise to additional spots in selected area diffraction patterns. Figure 13 shows such a diffraction pattern from a single precipitate. The matrix is in a [011] orientation. In addition to the bright spots due to the vanadium-titanium solid solution there are additional rows of spots. The brightest spot in each row appears to form the pattern for a hexagonal structure in the [001] orientation (Figure 14).

It is assumed that the faults inside the incoherent precipitates give rise to the rows of spots around the precipitate spots. These are due to Fraunhofer effects^{49,50}. They are also very similar to those observed in Rutile^{51,52}. The rows of spots in that case were due to the formation of shear structures in highly non-stoichiometric TiO_2 . Usually shear structures are observed in compounds of gross non-stoichiometry by long range ordering of point defects in the lattice.

On the diffraction pattern one can also notice the alignment of the $(\bar{2}11)_m$ spot with the $(1\bar{1}.0)_p$ spot (the subscripts "m" and "p" referring to the matrix and the precipitate respectively). Aligned spots on the diffraction pattern correspond to parallel planes in real space. This causes the $(\bar{2}11)_m$ and $(1\bar{1}.0)_p$ planes to be misaligned by $10^\circ 32'$ and as well the angle between $(011)_m$ and $(0\bar{1}.0)_p$ planes to be $5^\circ 16'$. An equivalent situation would

Figure 13. Selected area diffraction pattern from an area containing a large incoherent carbide.
The matrix orientation is $[011]$.
The precipitate is in a $[001]$ orientation.

Figure 14. Diagram showing indexing of Figure 13.

have been to consider the $(2\bar{1}1)_m$ and $(10.0)_p$ planes parallel. On this basis the incoherent carbide is tentatively identified as belonging to a hexagonal structure with the basal plane (00.1) parallel to the (011) cubic plane.

From crystallographic considerations one can expect the $(11.0)_p$ to be parallel to the $(1\bar{1}1)_m$. This situation is presented in Figure 15 where the matrix is in $[1\bar{1}1]$ orientation and the precipitate in a $[110]$ orientation. The pattern is indexed in Figure 16. Actually the additional spots on the diffraction are situated on two sets of parallel lines at an angle of 60° . This situation occurs when two precipitate particles or a precipitate including two different orientations are present in the selected area. Here we consider the case where the $(00.1)_{p2}$ basal plane of the second precipitate is parallel to the $(110)_m$, with $(00.1)_{p1}$ parallel to $(011)_m$. When the matrix is in the (111) orientation we have at the same time the $(11.0)_{p1}$ and the $(11.0)_{p2}$ orientations for the precipitates. Since the angle between $(00.1)_{p1}$ and $(00.1)_{p2}$ is 60° , the diffraction pattern shown in Figure 15 results. Furthermore for each hexagonal pattern we again find the presence of rows of spots through each precipitate spot.

The $(00.1)_p$ spot is aligned with the $(011)_m$ and the $(\bar{1}1.0)_p$ spot is aligned with the $(2\bar{1}1)_m$. The indexing of this pattern is consistent with the diffraction pattern of Figure 13. This relationship can be further verified by use of other matrix orientations. A selected area diffraction pattern with the matrix in the $[1\bar{1}3]$ orientation is shown in Figure 17. The pattern is

Figure 15. Selected area diffraction pattern from an area containing a large incoherent carbide.
The matrix orientation is $[11\bar{1}]$.
The precipitate is in a $[110]$ orientation.

Figure 16. Diagram showing indexing of Figure 15.

Figure 17. Selected area diffraction pattern from an area containing a large incoherent carbide. The matrix orientation is $[\bar{1}13]$. The precipitate is in a $[\bar{1}\bar{1}1]$ orientation.

Figure 18. Diagram showing indexing of Figure 17.

indexed in Figure 18. The precipitate orientation is $[\bar{1}\bar{1}\bar{1}]$ corresponding to a plane between $(\bar{1}\bar{1}.5)_p$ and $(\bar{1}\bar{1}.6)_p$. The rows of spots through each precipitate spot are again present. The $(\bar{1}\bar{1}.0)_p$ spot is aligned with the $(2\bar{1}\bar{1})_m$ spot. Figure 19 shows two hexagonal patterns from two areas whose orientations are a mirror image of each other.

Finally in Figure 20 the matrix is shown in (010) orientation and the pattern is indexed in Figure 21. It is still consistent with the relationship established previously. The precipitate is in the $[12\bar{1}]$ orientation, corresponding almost to the $(01.2)_p$ plane, with a few degrees of misalignment.

All these patterns are consistent with the conclusion that the incoherent carbide has a hexagonal structure and it is tentatively identified as $(V,Ti)_2C$. The relationship between the incoherent carbide and the matrix is summarized in Figure 22 (after D. R. Diercks and C. A. Wert¹⁸). This orientation relationship is identical to that of V_2C in vanadium¹⁸, Nb_2C in niobium¹⁹, W_2C in tungsten⁵³ and epsilon carbide in martensite⁵⁴. It is known as the Burgers relationship.

The diffraction patterns shown in Figures 13, 15, 17 and 20 were not the only ones obtained with these particular orientations of the matrix. Given the relationship described in Figure 22, one can notice that the $(010)_m$ and the $(\bar{1}00)_m$ directions are not equivalent relative to the precipitate orientation. If the matrix has the $(\bar{1}00)$ orientation, the diffraction pattern is different from Figure 20 and is shown in Figure 23. The precipitate has a $[\bar{1}00]$ orientation corresponding to the $(\bar{2}\bar{1}.0)_p$

Figure 19. Selected area diffraction pattern from an area containing two precipitates in an equivalent orientation which is a mirror image of each other.

Figure 20. Selected area diffraction pattern from an area containing a large incoherent carbide. The matrix orientation is $[010]$. The precipitate is in a $[121]$ orientation.

Figure 21. Diagram showing indexing of Figure 20.

Figure 22. Stereographic projection showing the orientation relationship between the matrix and the incoherent carbide (after Diercks and Wert¹⁸).

- CUBIC PLANES
- HEXAGONAL PLANES
- ⊙ COINCIDENT PLANES

Figure 23. Selected area diffraction pattern from an area containing a large incoherent carbide. The matrix orientation is $[\bar{1}00]$. The precipitate is in a $[\bar{1}00]$ orientation.

Figure 24. Diagram showing indexing of Figure 23.

Figure 25. Selected area diffraction pattern from an area containing a large incoherent carbide. The matrix orientation is $\langle 113 \rangle$.

plane. The $(\bar{1}00)_m$ and $(21.0)_p$ planes are misaligned by $5^\circ 16'$. The pattern is indexed in Figure 24.

As well the three matrix orientation $[\bar{1}11]$, $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ are not equivalent. Only $[\bar{1}11]_m$ gives the diffraction pattern shown in Figure 15; the two others do not correspond to any precipitate orientation which could give additional spots.

Finally with the matrix in a (113) type orientation, a diffraction pattern such as that shown in Figure 25 was obtained. There are seven different (113) type matrix orientations relative to the precipitate orientation. Besides the $(\bar{1}13)_m$ orientation the $(\bar{1}31)_m$ orientation should also give the diffraction pattern from the $(10.0)_p$ plane. However it was not possible to find enough evidence to assert the exact orientation corresponding to this pattern.

C. Microstructures for Isothermal Aging at 1000°C

A second series of heat treatments were performed using the same foils carburized to a nominal 0.3 atomic percent carbon level and quenched. The wrapped and encapsulated specimens were aged at 1000°C in air furnace for times varying from 1 to 24 hours. The general aspect and size of the precipitates did not change very much with longer aging times. Furthermore some foils were aged at 950°C and a few at 1050°C without noticeable changes in the structure. A series of micrographs taken with different matrix orientations are shown in Figures 26 to 29. The carbide precipitate gives rise to stacking fault type of contrast with fringes running parallel to lines of intersection

Figure 26. Microstructure of an alloy aged for 17 hours at 1000°C. Beam direction close to [100], diffraction vector shown.

Figure 27. Microstructure of an alloy aged for 5 hours at 1000°C. Beam direction close to [113], diffraction vector shown.

Figure 28. Microstructure of an alloy aged for 5 hours at 1000°C. Beam direction close to [111], diffraction vector shown.

Figure 29. Microstructure of an alloy aged for 5 hours at 1000°C. Beam direction close to [331], diffraction vector shown.

of the plate shaped particle with the matrix plane, as the micrograph in the $\langle 111 \rangle$ orientation shows.

This type of contrast arises because a thin partly coherent precipitate in a foil causes a displacement of adjacent matrix planes on either side of it in opposite direction⁵⁵. If the displacement vector R is not an integral multiple of the lattice vector, the matrix planes are displaced from their normal positions and displacement fringes result. Application of the dynamical theory of electron diffraction leads to the prediction that the intensity I of the transmitted electron wave will vary with the distance z of the precipitate from the center of the foil according to the relationship⁵⁶, $I = \cos^2 \frac{\alpha}{2} \cos^2 \left(\frac{\pi t}{\xi_g} \right) + \sin^2 \frac{\alpha}{2} \cos^2 \left(\frac{2\pi z}{\xi_g} \right)$ where $\alpha = 2 \pi \mathbf{g} \cdot \mathbf{R}$.

If the precipitate is inclined to the foil surface, z will vary continuously along the plane of the precipitate, and the transmitted intensity will show a periodic variation. The result is that the image of the precipitate appears as alternating light and dark fringes.

In Figure 25 the particles have precipitated on different planes and appear either on edge or contained within the specimen. The precipitates on edge have their largest dimension oriented exactly in the $[100]$ and $[010]$ matrix direction and it is then concluded that the particles precipitate on the (001) habit plane. Indeed the $\langle 001 \rangle$ directions form a trirectangular base.

This habit plane is the most common and it can be explained on the basis that $\langle 100 \rangle$ is a "soft" direction, i.e. one of minimum modulus. It has been already observed in the case of the

precipitation of TiO in vanadium-titanium alloys². In molybdenum the titanium carbides and nitrides precipitate on (310) planes, but it was shown that misfit and strain energy are minimum for such a habit¹⁰.

The size of the particles can be estimated from these micrographs. It turns out to be between $.1 \times .1 \mu\text{m}^2$ and $.5 \times .3 \mu\text{m}^2$ for the largest section and around 200Å in thickness.

D. The Ordered Superstructure

Selected area diffraction patterns of regions containing precipitates reveal supplementary spots in a regular arrangement between the matrix spots. A number of foil orientations have been examined, e.g. of the type $\langle 100 \rangle$, $\langle 120 \rangle$, $\langle 112 \rangle$, $\langle 133 \rangle$ and $\langle 111 \rangle$ (Figures 30 to 35). The last one, $\langle 111 \rangle$, as well as $\langle 113 \rangle$ did not show extra spots.

Dark field microscopy demonstrated that the supplementary spots were associated with the precipitate particles. Figure 36 is a dark field image of a specimen. With the matrix in the $\langle 100 \rangle$ orientation, diffraction patterns could be observed with two sets of additional spots in the two $\langle 100 \rangle$ directions. This was only the case when the selected area contained precipitates on edge in two perpendicular $\langle 100 \rangle$ directions. Figure 37 shows a diffraction pattern obtained with the selected area placed equivalently to the position A drawn on Figure 26. The selected area in position B gave the diffraction pattern shown in Figure 30.

Figure 30. Selected area diffraction pattern from an area containing carbides. The matrix orientation is [100].

Figure 31. Selected area diffraction pattern from an area containing carbides. The matrix orientation is $[110]$.

Figure 32. Selected area diffraction pattern from an area containing carbides. The matrix orientation is $[120]$.

Figure 33. Selected area diffraction pattern from an area containing carbides. The matrix orientation is $[112]$.

Figure 34. Selected area diffraction pattern from an area containing carbides. The matrix orientation is $[331]$.

Figure 35. Selected area diffraction pattern from an area containing carbides. The matrix orientation is $[111]$.

Figure 36. Dark field image of an alloy aged for 17 hours at 1000°C. Beam direction close to [100].

Figure 37. Selected area diffraction pattern from an area containing carbides as shown in position A on Figure 26. The matrix orientation is $[100]$.

The observation of supplementary spots indicates that a superlattice has been formed. The most reasonable process whereby such a superlattice could be introduced in the alloy is the ordering of carbon interstitials.

The lattice of the ordered structure was determined in the following way. From the diffraction patterns for different foil orientations and from the position of the supplementary spots, the reciprocal lattice was constructed. This is sketched in Figure 38 where the open circles represent the face centered cubic reciprocal matrix lattice. For a particular foil orientation, six supplementary reciprocal lattice points appear regularly spaced between two matrix spots in the $\langle 100 \rangle$ direction. This shows that in real space the interplanar spacing of the superlattice will be seven times that of the matrix in that direction.

All the observed diffraction patterns are consistent with a reciprocal lattice for which a unit cell is shown in Figure 38. A possible primitive unit cell for the reciprocal superlattice is indicated in heavy lines. From that unit cell the smallest possible unit cell of the superlattice in real space can be deduced. As a primitive cell, one can choose a tetragonal centered cell with $a_1 = a_2 = a_{\text{matrix}}$ and $a_3 = 7 a_{\text{matrix}}$.

The question of whether the carbon atoms occupy an octahedral or tetrahedral superlattice cannot be solved from this study. If we suppose an octahedral sites occupancy, a possible structure for the superlattice could be that shown in Figure 39.

Figure 38. Proposed reciprocal lattice structure consistent with the diffraction patterns presented in Figures 30 to 37. Open circles are matrix spots.

Figure 39. The real lattice corresponding to the reciprocal lattice of Figure 38. The vanadium-titanium unit cells are shown as squares. The spheres represent carbon atoms in $(0, \frac{1}{2}, 0)$ octahedral positions, defining a Bct cell.

Considering the contents of a unit cell of the superstructure, the ratio vanadium-titanium to carbon atoms would be 7:1, i.e. the corresponding composition would be $(V,Ti)_7C$.

It was also not possible to determine the exact composition of the precipitate for the vanadium to titanium atoms ratio.

Considering the value given by Murdock and McHargue⁵⁷ for the coefficient of diffusion of titanium in vanadium-titanium alloys ($>1.6 \cdot 10^{-12} \text{ cm}^2/\text{sec}$ at 1100°C), the titanium should have the possibility of diffusing during the heat treatments performed. However no trace of formation of the face centered cubic titanium carbide was detected.

IV. CONCLUSIONS

The result of this investigation can be summarized as follows:

1. The precipitation of carbon from supersaturated solid solution in vanadium-titanium alloy occurs in at least two stages: an incoherent $(V,Ti)_2C$ precipitate and an ordered superstructure $(V,Ti)_7C$.

2. The incoherent $(V,Ti)_2C$ precipitate is hexagonal and the orientation relationship with the matrix may be expressed:

$$(00.1) \text{ hcp} // (011) \text{ cubic}$$

$$[\bar{1}\bar{1}.0] \text{ hcp} // [11\bar{1}] \text{ cubic}$$

3. The misfit between the incoherent carbide and the matrix gives rise to internal faulting in the carbide. The formation of shear structure is possible.

4. The precipitation of the ordered superstructure occurs on $\{100\}$ habit planes and the plate-shaped particles are no more than $200\text{\AA}$ thick.

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