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Research and Development Report

INTERNAL OXIDATION AND OXIDES OF A
VANADIUM-15 TITANIUM-7.5 CHROMIUM
ALLOY

by

Darrel R. Duncan, William L. Larsen and
Frank X. Kayser

AMES LABORATORY

RESEARCH AND DEVELOPMENT REPORT

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MASTER

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VANADIUM-15 TITANIUM-7.5 CHROMIUM
ALLOY

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Darrel R. Duncan, William L. Larsen and
Frank X. Kayser

August 1969

Ames Laboratory
at
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INTERNAL OXIDATION AND OXIDES OF A
VANADIUM-15 TITANIUM-7.5 CHROMIUM ALLOY

Darrel R. Duncan⁺, William L. Larsen and Frank X. Kayser

ABSTRACT

Sheet samples of V-15 Ti-7.5 Cr alloy have been charged with oxygen by oxidizing under a reduced pressure of oxygen in the temperature range 850-1020°C and annealing in vacuum between 750° and 950°C. The resulting alloys were examined by metallography, X-ray diffraction, microprobe and microhardness.

The single oxygen-affected surface layer observed after oxidation broadens by diffusion into two distinct zones after annealing. The outer (surface) zone is dark-etching and contains appreciable precipitate. Its hardness is approximately 500 DPH as compared with an initial alloy hardness of approximately 250 DPH. The inner light-etching zone contains finer precipitate, is sometimes relatively featureless in structure, contains cracks, and is hardened to 1000 DPH or more.

As annealing temperatures are increased the inner hardened zones disappear and a uniformly distributed oxide is observed. This oxide has been identified as $(\text{Ti},\text{V})_2\text{O}_3$ solid solution. In this particular alloy it has the approximate composition $(\text{Ti}_{2/3}\text{V}_{1/3})_2\text{O}_3$.

Titanium diffuses outward from the unaffected core of the alloy toward the advancing oxygen front where it precipitates internally as $(\text{Ti},\text{V})_2\text{O}_3$. In the most highly oxidized surface zones, all the available titanium is extracted from the alloy leaving a binary vanadium-chromium alloy matrix. Chromium apparently does not participate in the oxidation reaction to any significant degree.

⁺Present address:

A computer program for the indexing and precision determination of hexagonal lattice parameters has been developed. The lattice constants for the $(\text{Ti,V})_2\text{O}_3$ found in this study were $a_0 = 5.042 \pm 0.002\text{\AA}$, $c_0 = 13.933 \pm 0.004\text{\AA}$. An error in the prior indexing of Ti_2O_3 has been found using the present computer program.

The study of alloys prepared by oxidation under a low pressure of gaseous oxygen, followed by a homogenizing anneal, appears to be useful as a way of accelerated testing and evaluation of alloys intended for use in oxygen-contaminated sodium.

INTRODUCTION

The work described in this report was undertaken in order to provide information needed for the ultimate development of a liquid metal fast breeder reactor (LMFBR). The research needs for this development program have been amply described elsewhere.¹ Vanadium-base alloys have been considered as structural and cladding materials for nuclear applications for some time.^{2, 3, 4, 10} Some of these earlier studies have revealed that V-Ti-Cr alloys are worthy of intensive study, particularly for applications involving exposure to liquid sodium. However, "the most critical problem area for vanadium alloys is their questionable resistance to corrosion in sodium containing impurities (especially oxygen) in the amounts expected in the coolant of commercial LMFBRs."¹ Thus this work was directed toward determining the nature of the interaction of oxygen with a promising alloy in the V-Ti-Cr alloy system under conditions simulating reactor exposure to oxygen-contaminated sodium. Since this research program has been suspended indefinitely, this report has been prepared in order to disseminate the results obtained to date.

BACKGROUND

Liquid Sodium Corrosion

Two broad classifications of possible liquid metal corrosion mechanisms given by Litman⁵ are: 1) dissolutive corrosion mechanisms and 2) impurity reaction mechanisms. The first involves loss of material by solution into the liquid metal, or conversely, solution of the liquid metal into the solid. The second describes reactions between the solid metal and impurities dissolved in the sodium.

In the case of vanadium and its alloys, the corrosion mechanism seems to involve impurity reactions rather than dissolutive reactions. This can be inferred from sodium corrosion data, which indicate a direct dependence of weight change upon oxygen content of the sodium. This is shown in Table I.⁶

Table I. Corrosion of vanadium alloys in 550°C sodium

Alloy w/o	Weight change in six weeks at indicated oxygen level	
	8.6 ppm	11.0 ppm
V-15Cr-5Ti (annealed)	+0.43 mg/cm ²	-27.1 mg/cm ²
V-5Cr (annealed)	+0.59	-26.0
V-20Ti (annealed)	+0.55	- 5.52

Weight losses were due to non-adherent corrosion products. As oxygen content decreases, weight changes decrease. Oxygen content can be held below 10 ppm in sodium with existing technology, at least on a small scale. Under these conditions, sodium exposure at 500-700°C causes little change in sample appearance; the only surface effects are brownish tints. However, weight increases caused by penetration of the matrix by interstitial elements will occur as shown in Table II.⁷

It can be seen that oxygen content increases at all temperatures. Hydrogen contents most often decrease, while nitrogen and carbon levels show both gains and losses. Oxygen increases most consistently and in the greatest amounts. Reportedly, the total weight change is usually smaller than the pickup of interstitials, due to some loss of vanadium metal to the sodium.

One effect of this interstitial penetration is an increase in microhardness of the penetrated zone. The embrittled portion can crack under loads that would be supported by uncorroded alloy. Yaggee and Gilbert have studied this effect with V-20Ti.⁸ During their work, V-20Ti tubes were exposed to 650°C sodium with both 10 and 20 ppm oxygen for seven days. Subsequent creep tests indicated shorter rupture times, higher

Table II. Weight changes and interstitial concentration changes

Alloy	Exposure ($O_2 \leq 10$ ppm)		Wt change (mg/cm ²)	Alloy interstitial concentration (ppm)							
	Days	Temp		O_2		N_2		C		H_2	
				a*	b**	a	b	a	b	a	b
V-20Ti	191	650 ^D C	+1.23	2630	575	362	250	620	305	5	5
	155	550	+0.33	1660	575	362	250	116	305	13	5
	134	450	-0.5	1400	575	166	250	413	305	13	5
V-15Ti- 7.5Cr	173	650	+0.72	1550	900	430	250	737	340	3	13
	155	550	+0.32	1850	900	232	250	278	340	9	13
	134	450	+0.02	1940	900	226	250	445	340	7	13
V-5Cr	855	650	+0.06	1030		254		347		14	
	155	550	+0.10	1020		176		377		8	
V-10Cr	134	450	+0.04	1160	705	188	280	360	310	6	22
V-15Cr- 5Ti	66	550	+0.10	1330	815	196	190	320	234	10	47
	134	450	+0.13	1270	815	162	190	417	234	4	47
V	69	650	+0.25	770	390	434	250	552	420	11	50
	155	550	+0.20	1000	390	157	250	294	420	16	50

* a = after exposure.

** b = before exposure.

creep rates, and unchanged ductility when compared to unexposed samples tested under identical conditions. Exposure to the higher concentration of oxygen gave the shortest rupture life. The results were explained by the authors in the following fashion. Oxygen forms a hardened case about 30 microns thick, which is brittle and cracks when strained. The unaffected core of the sample remains ductile and resists crack propagation. Thus total elongation is unchanged but load-bearing area is reduced, resulting in high effective stress and increased creep rate.

The actual depth of embrittled zones formed upon sodium exposure is shown in Fig. 1.⁹

After only 155 days (66 for V-15Cr-5Ti), the depths of the hardened zones for three alloys equal or exceed the acceptable corrosion limit for one year (25 microns) even after exposure to sodium with fairly low O₂ content.

A microprobe study⁹ was performed at Argonne National Laboratory on hardened V-20Ti. This was the sample in Table II which had undergone 191 days exposure to 650°C of ≤ 10 ppm O. The carbon, and to a lesser degree the oxygen, microprobe traces showed maxima corresponding to maxima in microhardness. Titanium also displayed peaks in the same vicinity, pointing to a possible interaction between titanium, carbon,

Figure 1. Microhardness of vanadium alloys exposed to 550°C sodium with oxygen $\leq$ 10 ppm, after Ruth⁹

and oxygen as a cause for hardening.

In summary, the effect of liquid sodium exposure (with oxygen content ≤ 10 ppm) on vanadium and its alloys seems to be predominantly weight gains caused by solution of oxygen, nitrogen and carbon into the matrix. This in turn may initiate formation of the brittle surface zone which cracks with resultant degradation of mechanical properties. Specifically, evidence points to an interaction between titanium, carbon, and oxygen as a possible cause for hardening. Surface corrosion products are noted, but form too slowly to approach the 25 mil/yr limit for acceptable corrosion. Ruther,⁹ in x-ray diffraction studies of vanadium and V-20Ti alloy exposed to 600°C sodium (oxygen < 10 ppm) for 80 days, reports lines corresponding to γ VC ($VC_{.4-.5}O_{0-0.1}$) on the surface, with faint indications of VC or possibly $VO_{0.9}$.

It should be noted that in Fig. 1 only the alloys containing titanium show the hardened surface zone. It appears that the surface hardening and embrittlement of titanium-containing vanadium-base alloys occur by pickup of interstitials with oxygen being the most abundant.

Phase Relationships

Farrar and Margolin¹¹ have constructed isotherms in the V-Ti-Cr system at 700°, 1000° and 1200°C. Although the solubility of titanium and chromium in vanadium diminishes as temperature decreases, a single phase β vanadium solid solution exists at 700°C in the region extending to approximately 45% solute, well beyond the composition of the alloys studied in this investigation. At temperatures below 700°C reaction rates probably would be too slow for the single phase to dissociate under ordinary conditions of cooling even if it became unstable.

No phase equilibrium data were found for either the quaternary system V-Ti-Cr-O or the V-Cr-O ternary system.

Komjathy et al.¹² studied the V-Ti-O system. Their findings on vanadium-rich alloys are presented in Table III.

Table III. Phases identified in vanadium-rich V-Ti-O alloys

Alloy w/o	Phases identified
V-3%Ti-5%O	Solid solution matrix, β (V-O)
V-5%Ti-5%O	Solid solution matrix, β (V-O)
V-5%Ti-10%O	β (V-O), VO (?)
V-15%Ti-5%O	Solid solution matrix, β (V-O), α -Ti
V-27.5%Ti-10%O	Solid solution matrix, β (V-O), α -Ti
V-35%Ti-5%O	Solid solution matrix, β (V-O), α -Ti

All alloys were annealed 16 hours at 1200°C and water quenched. β (V-O) is a body-centered tetragonal distortion of the vanadium lattice found between approximately $\text{VO}_{0.18}$ and $\text{VO}_{0.33}$.

Plan of This Work

The information concerning phase equilibria between the V-Ti-Cr system and interstitial elements has been found to be scanty. Although alloys in this system are known to be hardened upon exposure to liquid sodium, the mechanism of this hardening has not been established. Any new phases formed by interaction of the alloy with sodium contaminants have only been tentatively identified. Since oxygen is absorbed to a greater degree than other interstitials by V-Ti-Cr alloys exposed to contaminated sodium and since it appeared likely that oxygen might preferentially interact with Ti in this alloy to form internal oxides, this research was directed toward the study of the effects of oxygen upon the V-15Ti-7.5Cr alloy. This alloy was selected in preference to the V-5Ti-15Cr alloy since it had the greater amount of titanium and thus presented the possibility of forming greater amounts of oxide phases, should such phases form by reactions with titanium.

A basic assumption of the following work was that the alloys exposed to gaseous oxygen at low pressures would exhibit essentially the same form and distribution of oxygen within the alloy at a given temperature as the same alloy exposed to oxygen in the form of a contaminant in sodium at the same temperature. While the oxygen-metal surface reaction might differ considerably in kind and in kinetics from the reaction of metal with oxygen contained in sodium, it was assumed that once inside the metal, the behavior of the oxygen would depend only upon the temperature and the nature of its surroundings and would be independent of the source from which it came and substantially independent of the kinetics of the surface reaction. Some difference in the final distribution of the oxygen-containing phases could arise because of a difference of the relative rates of oxygen injection and diffusion in the two types of exposures, but unless the differences in the resultant oxygen gradients were very large, the phases present should be similar. While these assumptions and the findings of this research should be checked by comparison with samples exposed to oxygen-contaminated liquid sodium, it was felt that preliminary work on alloys exposed to gaseous oxygen was justified in view of the greatly shortened exposure time and simplicity of experimental apparatus. Therefore it

appeared that useful results could be obtained by preparing high-purity alloys, exposing them to gaseous oxygen at low pressures under simulated reactor conditions, and then examining the contaminated alloys.

EXPERIMENTAL PROCEDURE

Alloy Preparation and Fabrication

Analysis of raw materials, all obtained from the Ames Laboratory, is given in Table IV. Complete quantitative data were available only for vanadium and chromium.

Table IV. Raw material analysis

Vanadium		Chromium		Titanium	Oxygen
Impurity	Conc. (ppm)	Impurity	Conc. (ppm)		
C	206	O	25	Prepared by Kroll process and subsequently electron beam refined.	99.6% pure
O	110	H	1		
N	61	N	<5		
Ni	<50	C	20		
Fe	30	Al	3		
Al	30	Ca	<10		
Si	600	Cu	<10		
Cu	<30	Fe	12		
Mg	<10	Mg	<10		
Ca	<10	Mn	<10		
		Ni	<5		
		Si	10		
		V	<5		

The three metals were arc-melted, using non-consumable tungsten electrodes under 2/3 of an atmosphere of argon, into three 100 g ingots. These ingots were roughly circular in cross-section and measured about 5 in. in length and 1/2 in. in diameter.

Based upon fabrication data of Kramer et al.,¹³ it was decided to hot-roll the alloy at 800°C to produce sheet. The samples were cold-rolled on the final pass to produce a smooth surface. Chemical analysis of as-rolled sheet is given in Table V.

Table V. Average composition of rolled sheet*

Element	Intended composition (w/o)	Actual composition (w/o)	Actual composition (ppm)
V	77.5	75.9	
Ti	15.0	14.7	
Cr	7.5	9.0	
O			325
N			25
C			450
H			100

*Results based upon:

Major constituents	- 2 samples, 6 analyses
Carbon	- 1 sample, 2 analyses
Oxygen	- 2 samples, 2 analyses
Nitrogen	- 2 samples, 2 analyses
Hydrogen	- 2 samples, 2 analyses

Alloy sheet coupons averaging about 1 cm by $1\frac{1}{2}$ cm and weighing $\frac{3}{4}$ g were wet ground through 600 grit silicon carbide paper to insure uniformity of surface in all samples.

Sample Treatment

Oxidation and Annealing

In order to simulate reactor conditions as closely as possible, oxygen was introduced into already-prepared alloys from a surrounding environment, as opposed to including some oxide in the initial alloying process.

Oxidation was performed in a quartz vacuum chamber which was encircled by a tube furnace. Oxygen pressure was controlled by balancing oxygen influx through a controlled leak against the vacuum pumping system. While the specimens were hot the vacuum chamber pressure was kept at or below 5×10^{-6} torr.

In order to maximize the rate of oxygen solution, the highest temperatures and pressures possible were sought. Oxygen pressure was limited by formation of V_2O_5 , which is liquid above 670°C . However, it does not form below oxygen pressures of approximately 70μ . To avoid this liquid oxide, pressures were held below 50μ . However, preliminary studies showed 1000°C to be too high for oxida-

tion. The surface oxide appeared quite spotty and rough upon removal from the furnace, possibly indicating some liquid oxide formation. Subsequent oxidation was carried out near 900°C.

Post-oxidation vacuum annealing treatments were performed on oxidized samples in an attempt to increase particle size of oxygen-containing phases, to minimize oxygen concentration gradients produced during oxidation, and to approach equilibrium microstructures.

Initially, two annealing temperatures were chosen, 900 and 750°C. The former was picked to give maximum reaction rates and the latter was picked because it was representative of expected reactor temperatures.

Calculation of the rate of advance of an internal oxidation interface is possible. However, titanium probably forms too stable a compound to permit application of the equations presented by Rapp.¹⁵ Previous work on sodium corrosion of vanadium-titanium alloys indicates it is impossible to homogenize alloys at reactor operating temperatures. Therefore theoretical calculations of necessary annealing times were felt to be inapplicable. Preliminary post-oxidation anneals at 900°C for 72 hours indicated fairly homogeneous structures,

based on photomicrographs and microhardness. The final choice of 900°C annealing time was 212 hours. Anneals of 750°C were carried out for 331 hours. Homogenization was not expected, but it was hoped a long anneal would give a large oxide particle size.

Annealing was done in a resistance-wound tube furnace. Each sample was sealed in a quartz tube. The tubes were evacuated, flushed several times with helium, and back-filled with helium to 2/3 atmospheric pressure before sealing. Most specimens were allowed to furnace cool. Several samples from both temperatures were water quenched in an attempt to show whether microstructural changes occurred during cooling as well as at temperature. Quenching was done by taking the sample tubes from the furnace while at temperature and breaking them in water at room temperature. The treatments given to the samples used in this study are presented in Table VI.

Analysis

After annealing, all oxide was removed from sample surfaces by wet grinding and samples were metallographically polished. Etching was done with a solution of 50 parts H₂O, 10 parts HF, 5 parts HNO₃ and 5 parts H₂SO₄ by volume, applied for three min. Microhardness tests employed a

Table VI. Sample treatment

Sample	Oxidation time and temperature	Oxidation pressure*	Annealing time and temperature	Post-annealing cooling method
1	925°C (24 h)	45 μ	No anneal	- - -
6	1020°C (24 h)	40	950°C (72 h)	Furnace cool
8	1020°C (24 h)	40	950°C (72 h)	Furnace cool
10	850°C (36 h)	30	850°C (115 h)	Furnace cool
11	850°C (36 h)	30	850°C (115 h)	Furnace cool
12	850°C (36 h)	30	850°C (115 h)	Furnace cool
14	900°C (27 h)	25	900°C (212 h)	Water quench
15	900°C (27 h)	25	900°C (212 h)	Furnace cool
16	900°C (27 h)	25	900°C (212 h)	Furnace cool
17	875°C (24 h)	30	750°C (331 h)	Furnace cool
19	875°C (24 h)	30	750°C (331 h)	Furnace cool
20	875°C (24 h)	30	750°C (331 h)	Furnace cool
21	875°C (24 h)	30	750°C (331 h)	Water quench
22	875°C (24 h)	30	750°C (331 h)	Water quench

*Oxygen pressures mentioned are average values. Actual pressure varied as much as $\pm 25 \mu$ for short periods.

diamond pyramid indenter and a load of 25 g. A portion of each sample was analyzed by the vacuum fusion method for oxygen, nitrogen, and hydrogen. Filtered copper and chromium radiations were used for X-ray studies.

RESULTS AND DISCUSSION

Preliminary Work

A sample of as-rolled sheet was vacuum annealed for 216 hours at 900°C to serve as a comparison standard for oxidized samples annealed at the same time and temperature. Post-anneal grain size was ASTM 7-8. Microhardness was nearly constant throughout the specimen at 250 DPH. The microstructure is shown in Fig. 2, along with a plot of lattice parameter (taken from a Debye-Scherrer powder pattern from a 114.6 cm camera) vs Nelson-Riley function, illustrating the method of determination of lattice parameters by extrapolation. The extrapolated a_0 is $3.054\text{\AA} \pm .002$.

Another specimen was oxidized at 925°C for 23 hours under an oxygen pressure of $45\ \mu$; its cross-section is shown in Fig. 3. An unoxidized zone, similar to the annealed, as-rolled specimen described previously, can be seen flanked by a darkly etching zone and a lighter, faintly-etched microstructure caused by oxidation of the

Figure 2. Sample annealed 216 hours at 900°C
Top: Microstructure at 100X
Center: Microstructure at 1000X
Bottom: Lattice parameter

Figure 3. Specimen oxidized 23 hours at 925°C and furnace cooled
Left: 50X
Right: 250X

alloy.

The oxide coat on the alloy oxidized at 925°C was medium gray and lustrous on the surface, with a thin black sub-layer next to the metal. Some discolored spots on the surface suggested liquid oxide formation. This same oxide appearance was noted at all oxidation temperatures, although spottiness decreased with decreasing temperature. A Debye-Scherrer pattern of this oxide gave lines listed in Table VII.

Matching patterns are also given.

Table VII. X-ray diffraction pattern of oxide formed at 925°C

VO_2^*		Specimen pattern		$\alpha\text{-Fe}^{**}$	
$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I
3.31	30				
3.20	100	3.20	s		
2.68	30				
2.43	40	2.44	w		
2.422	60				
2.418	30				
2.14	50	2.15	m		
2.13	50				
2.05	10				
2.02	30	2.03	vs	2.03	100
1.87	40				
1.73	20				
1.66	30	1.66	m		
1.654	30				
1.650	60				
1.62	10				
		1.60	vw		
		1.43	vw	1.43	19
		1.34	vw		
				1.17	30

*ASTM Powder Diffraction File Card 9-0142.

**ASTM Powder Diffraction File Card 6-0696.

Lines 1, 2, 3 and 5 of the pattern correspond fairly closely to the strongest lines of VO_2 . Line 4 is an iron line arising from fragments of the iron file used to remove the oxide from the sample. The ASTM index card for VO_2 did not give lines of d-spacing low enough to compare with the last three lines of the pattern. However, Hoschek and Klemm¹⁶ present a drawing of a VO_2 powder pattern showing lines close in position to these three. Therefore, the specimen oxide is tentatively identified as containing VO_2 . A sample of oxide formed at 1020°C gave a similar pattern. The detection of this oxide under these conditions was expected on the basis of work by Roy *et al.*¹⁴

Oxidized and Annealed Specimens

Table VIII shows the results of analyses for interstitial elements and relates them to oxidation temperature of each specimen. Annealing conditions and oxidation pressures are not given, since their variations did not influence oxygen content. Analyses of typical starting materials were given previously in Table V.

Results are based upon two analyses per sample. Hydrogen figures are suspect, since in samples 6 and 8 one reported value was close to 200 ppm and the other close to 2000 ppm.

Table VIII. Vacuum fusion analysis results

Sample	Oxidation Temp. °C	Time h	Wt. gain (mg/cm ²)	O(w/o)	N(ppm)	H(ppm)
6	1020	24	64.3	9.54	120	1232
8	1020	24	64.3	11.34	186	1068
10	850	36	27.5	5.15	139	112
11	850	36	27.8	6.32	146	111
14	900	27	32.3	5.58	198	144
15	900	27	32.1	5.91	180	80
16	900	27	33.5	5.95	149	101
17	875	24	20.7	3.90	208	41
17				2.65(edge)*		
17				.97(center)*		
19	875	24	22.8	4.62	235	76
20	875	24	22.6	4.06	217	60
21	875	24	15.9	3.86	366	70
21				1.50(edge)*		
21				.99(center)*		

*Results of microprobe analyses of points at edge and center of specimens.

In view of this and the low H₂ values for all other specimens, near that of the starting alloy, the amount of effect of hydrogen has been assumed to be negligible. Carbon analyses were not available on the oxidized samples at the time of the writing of this report. Since there is no apparent source for further carbon pickup and since oxygen has been added in large amounts, it has been assumed that amounts and relative effects of carbon are also small. While there has been some pickup of nitrogen, it is small compared to the large increase of oxygen content. Therefore all results of

specimen treatment were ascribed to oxygen. Oxygen contents decrease with decreasing oxidation temperature except for the specimens oxidized at 850°C which reflect the influence of longer oxidation time. Only the specimens oxidized at 1020°C and subsequently annealed gave a homogeneous cross-section with respect to microstructure and microhardness. Since oxygen analyses utilize the entire cross-section of the sample, correlations of oxygen content with microstructure or hardness are meaningful only with these specimens. Oxygen concentration gradients, proven by the microprobe for specimens 17 and 21, are expected in all other specimens.

950°C Anneal

The microstructure of specimen 6, oxidized at 1020°C and annealed at 950°C , was completely homogeneous, and is represented in Fig. 4. A coarse, dark, Widmanstätten precipitate is seen within a lighter matrix. Precipitation at grain boundaries is noted, with little depletion of precipitate near grain boundaries. Microhardness is high, averaging 1130 DPH, and substantially uniform throughout the cross section.

The lattice parameter of the bcc solid solution matrix of specimen 8, identical in treatment and

Figure 4. Sample oxidized 24 hours at 1020°C, annealed 72 hours at 950°C and furnace cooled
Top: Microstructure at 100X
Center: Microstructure at 775X
Bottom: Lattice parameter

microstructure to specimen 6, is $3.042 \pm 0.008\overset{\circ}{\text{\AA}}$. There were fourteen lines other than the three assigned to the matrix in this pattern. The stronger lines bore a close resemblance to those of Ti_2O_3 and V_2O_3 , which have a rhombohedral, corundum-like structure. Accordingly these lines were indexed on the hexagonal coordinate system using a computer program for the precision determination of lattice constants.¹⁷ This program used a singly iterative, weighted least-squares method.¹⁸ Given a Bravais lattice, the positions of all lines on the pattern and the correct indices for the first three lines, it indexed the remaining lines, calculated the most probable values of the lattice constants and the systematic errors constant, and provided estimates of their precision. The error limits are the 95% confidence limits assuming a normal distribution of residuals. The results are given in Table IX.

The only significant difference between this pattern and the standard pattern for Ti_2O_3 involves the presence or absence of lines 15 or 16. In this pattern line 15 is indexed as 1.0.10 and no 119 was detected. The standard Ti_2O_3 pattern reports a 119 but not a 1.0.10 reflection.¹⁹ Whereas the indexing of line 15 as a 119 yields nearly the same lattice parameters, the sum of the weighted squares of

Table IX. X-Ray diffraction data for a V-15Ti-7.50r specimen oxidized
at 1020°C then annealed at 950°C.

Lines	(hkl) _{hex}	(hkl) _{bcc}	$\sin\theta_{\text{obs}}$	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	d_{obs}	I
1	012		0.3114	0.0970	0.0974	3.68	m
2	104		0.4226	0.1786	0.1788	2.71	s
3	110		0.4563	0.2082	0.2084	2.51	m
4	006		-	-	-	-	
5	113		0.5191	0.2694	0.2693	2.21	s
6		110	0.5361	0.2874	0.2861	2.14	vs
7	202		-	-	-	-	
8	024		0.6209	0.3855	0.3854	1.845	m
9	116		0.6721	0.4518	0.4517	1.704	s
10	018		-	-	-	-	
11	122		-	-	-	-	
12		200	0.7522	0.5659	0.5678	1.523	vw
13	214		0.7675	0.5921	0.5914	1.489	w
14	030, 300		0.7886	0.6219	0.6207	1.453	m
15	1.0.10		0.8633	0.7453	0.7458	1.327	w
16	119		-	-	-	-	
17	220		0.9093	0.8268	0.8264	1.260	vw
18		211	0.9213	0.8487	0.8483	1.243	m
19	036, 306		0.9289	0.8628	0.8632	1.233	m
20	223		0.9414	0.8863	0.8870	1.217	vw
21	312		-	-	-	-	
22	0.2.10		0.9755	0.9515	0.9514	1.174	w
23	0.0.12		-	-	-	-	

$$a_{\text{bcc}} = 3.049\text{\AA} \pm 0.004$$

$$a_{\text{hcp}} = 5.042\text{\AA} \pm 0.002 ; c_{\text{hcp}} = 13.933\text{\AA} \pm 0.004$$

$$a_{\text{rhom}} = 5.481\text{\AA} ; \alpha = 54^\circ 46'$$

the residuals is very significantly increased and the "fit" of line 15 becomes so poor as to indicate error of nearly 0.6 mm in reading the position of the line. Thus on both a physical and a least-squares basis the indexing above is judged correct. An examination of Cr_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ patterns also indicates that the above is correct.^{20, 21}

Lines 4, 7, 10, 11, 21, and 23 were not detected. Although these are reported for the standard Ti_2O_3 pattern¹⁹ their intensities are either the lowest or among the lowest of all reflections. Also it should be noted that other very weak reflections like 211, 125, 208, and 128 which are reported for $\alpha\text{-Al}_2\text{O}_3$ are not detected in the above pattern or in Ti_2O_3 .^{19, 21}

The only line not listed in Table IX is a single, weak, reflection which had a $d_{\text{obs}} = 2.10$. It remains unidentified. The lines indexed on bcc coordinates are the matrix lines.

The rhombohedral coordinates corresponding to the hexagonal coordinates were obtained using the formulae:

$$\alpha = \cos^{-1} \left(\frac{2c^2 - 3a^2}{2c^2 - 6a^2} \right)$$

$$a_{\text{rhomb}} = \frac{1}{3} \sqrt{3a^2 + c^2}$$

The Ti_2O_3 - V_2O_3 system has been investigated by Nordmark²² and Lin,²³ both of whom found a complete series of solid solutions with lattice parameters varying smoothly but non-linearly between the terminal values. Although a phase transformation has been reported at -100°C for V_2O_3 ²⁴ and at $+200^\circ\text{C}$ in Ti_2O_3 ²⁵ on the basis of dilatometric and electrical evidence, Pearson²⁶ has found no evidence of a structural change in Ti_2O_3 between room temperature and 350°C although lattice parameters do change significantly and non-linearly over this temperature range. At room temperature Pearson found $a_0 = 5.15\text{\AA}$, $c_0 = 13.62\text{\AA}$ and at 350°C , $a_0 = 5.123\text{\AA}$, $c_0 = 13.93\text{\AA}$. Thus, lattice parameter values in a solid solution of Ti_2O_3 and V_2O_3 may depend upon the composition and approach to chemical equilibrium in the solid solution, the temperature and thermal history of the solution and, as in the present case, the constraint of a metallic matrix.

The lattice parameters found in this investigation are shown in Fig. 5 superimposed on the data of Nordmark and Lin. Each parameter suggests independently that the composition of the phase observed is very close to $(\text{Ti}_{2/3}\text{V}_{1/3})_2\text{O}_3$.

The published lattice parameters of Cr_2O_3 are $a_0 = 4.954\text{\AA}$, $c_0 = 13.584\text{\AA}$.²⁰ If Cr_2O_3 were present in solution in the oxide, both parameters would probably be contracted from

Figure 5. Lattice parameters of Ti_2O_3 - V_2O_3 solid solutions.

those of a binary Ti_2O_3 - V_2O_3 oxide solution. A contracted a_0 value would then correspond to a Ti/V ratio of $<2:1$ while the contracted c_0 value would correspond to a Ti/V ratio of $>2:1$, thus suggesting that Cr_2O_3 is not present in significant amounts in the oxide. Microprobe traces, discussed later, suggest that chromium does not become redistributed during oxidation. Moreover, since the free energies of formation of the individual oxides at the oxidizing temperature are approximately in the ratio Ti:V:Cr::95:75:65, it would be expected that the Ti/V ratio in the oxide would be greater than that in the alloy and that chromium would be present in the oxide in insignificant amounts. It would also be expected that the composition of this oxide solid solution would depend upon the composition of the alloy. Thus, all data suggest that the oxide is nearly a true binary solution of Ti_2O_3 and V_2O_3 .

900^o C Anneal

The microstructure of specimen 14, annealed at 900^oC for 212 hours and water quenched, is shown in Fig. 6. The top picture represents virtually the entire cross-section. A light band is seen in the center of the sample, which at 1000X shows a fine Widmanstätten network within grains and some precipitation at grain boundaries. Outside the band the

Figure 6. Sample oxidized 27 hours at 900°C annealed 212 hours at 900°C and water quenched
Top: Microstructure at 100X
Center: Middle of sample, within light band at 1000X
Bottom: Darker microstructure at 1000X

microstructure at 100X looks similar to that of the oxidized, non-annealed specimen in Fig. 3. Higher magnification reveals both irregular and lamellar precipitates within a grayish matrix. The darker portions of specimen 14 resulted from the oxidation treatment, as in Fig. 3, and the structure of the central light band was the result of inward oxygen diffusion during annealing.

Figure 7 relates the microstructure of specimen 14 to microhardness and microprobe results. The dark microstructure seems to be softer by 100-200 DPH than the center; both regions are irregular in hardness. The microprobe indicated uniformity in chromium content from edge to edge at 6%, while titanium reading increased from 15% through the side portions to 18% in the center. This 3% change probably reflects a change in the state of aggregation of titanium rather than a true change in total titanium content of the alloy. There seemed to be an ill-defined drop of several weight per cent in titanium just outside the transition region from dark to light structure. Vanadium content was approximately constant at 77%.

Figure 8 shows the microstructure and microhardness of specimen 16, furnace cooled from 900°C. The similarity between the microstructures of quenched (Fig. 7) and furnace cooled

Figure 7. Sample oxidized 27 hours at 900°C, annealed 212 hours at 900°C and water quenched
 Top: Microstructure at 100X
 Center: Microhardness traverse
 Bottom: Sketch of microprobe tracings drawn to scale

Figure 8. Sample oxidized 27 hours at 900°C, annealed 212 hours at 900°C and furnace cooled
 Top: Microstructure at 100X
 Center: Microhardness traverse
 Bottom: Interface between light and dark micro-structure at 1000X

(Fig. 8) samples shows that substantially all the second phase formation took place at the heat treating temperature, rather than upon cooling.

Lattice parameters for both specimens are $3.013 \pm .004^{\circ}\text{\AA}$. X-ray diffraction lines corresponding to the strongest lines of $(\text{Ti,V})_2\text{O}_3$ were found in addition to lines from the solid solution matrix.

850°C Anneal

The microstructure of specimen 11, oxidized and annealed at 850°C (see Table VI), is given in Fig. 9. Again, the photomicrograph at 100X represents most of the cross-section. The dark microstructure at the sides resembles that of specimens 14 and 16, annealed at 900°C and is likewise assumed to be the product of the oxidation treatment. The double light bands are similar to the single band of specimens 14 and 16, and result from the diffusion of oxygen during annealing into the metal ahead of the front during initial oxidation. Coarse precipitates are noted between the bands. Since the amount of precipitate at the center of the sample is substantially greater than that of samples which are unoxidized (Fig. 2) or unannealed (Fig. 3), these precipitates may represent the first stages of the changes which occur upon diffusion of oxygen into the matrix. At longer times, with

Figure 9. Sample oxidized 36 hours at 850°C, annealed 115 hours at 850°C and furnace cooled
Top left: Microstructure at 100X
Top right: Microstructure of sample center at 1000X
Bottom left: Microstructure of light band at 1000X
Bottom right: Microstructure of area between light band and sample edge at 1000X

more oxygen able to penetrate to the center, the two bands would merge into one, as noted at 900°C. It is of interest to note that the light bands, which are relatively featureless in microstructure, correspond to a higher oxygen content than the sample center which has a well-defined structure with an apparent second phase.

Microhardness, microprobe results, and microstructure are all shown in Fig. 10. The light bands are about 50 DPH harder than those at 900°C, while the outer dark areas remain about the same. The interior is quite soft, having essentially the same hardness as annealed, unoxidized starting material despite the appearance of considerable precipitate.

The lattice parameters of specimens 10 and 12, similar in treatment and microstructure to 11, are 3.016 and $3.014 \pm .004\text{\AA}$, respectively. No lines other than matrix were found in the pattern of specimen 12; the pattern of specimen 10 had three unindexed extra lines.

750°C Anneal

Specimen 17 furnace cooled from 750°C, is shown in Fig. 11. An unoxidized zone is seen in the specimen center. Flanking this are light bands of precipitates showing a lamellar structure at high magnification, with a darker struc-

Figure 10. Specimen oxidized 36 hours at 850°C, annealed 115 hours at 850°C and furnace cooled
 Top: Microstructure at 100X
 Center: Microhardness traverse
 Bottom: Sketch of microprobe tracings, drawn to scale

Figure 11. Specimen oxidized 24 hours at 875°C, annealed 331 hours at 750°C and furnace cooled
 Top left: Microstructure at 100X
 Top right: Center of sample at 1000X
 Bottom left: Narrow, medium-colored band between darkest and lightest etching portions of microstructure at 1000X
 Bottom right: Darkest microstructure at 1000X

tures between the specimen edges and the light bands. The darkest microstructure is similar to that seen at 850 and 900°C and is attributed solely to the oxidation treatment. The lighter bands, assumed to result from inward oxygen diffusion during annealing, show a lamellar pearlite-like precipitate, whereas the two higher temperature anneals gave a Widmanstätten type precipitate. All specimens at this annealing temperature, the temperature most nearly corresponding to reactor operation temperatures, showed cracks in the regions of greatest hardness. These are evident in Fig. 11.

Microhardness and microprobe results are given in Fig. 12. The dark microstructure is seen to be 500-600 DPH, harder than that of the surface regions of samples subjected to higher temperature anneals. The light bands are also harder than the bands found at higher temperatures, 900-1000 DPH at the hardest point. The center is by far the softest portion, and seems softest near the edge of the precipitation front. Microprobe traverses show chromium contents of 7%. Titanium content is 15% at the sides, drops sharply to 8%, and then increases to 20% in the center. Vanadium is 75% at the sides, peaks to 86% where titanium decreased, and is 80% in the center. The titanium-poor regions occur just inside the areas of greatest hardness. The microprobe trace in Fig. 12 shows some mis-

Figure 12. Sample oxidized 24 hours at 875°C, annealed 331 hours at 750°C and furnace cooled
 Top: Microstructure at 100X
 Center: Microhardness traverse
 Bottom: Sketch of microprobe tracings drawn to scale

match with the microstructure because it was made at a different location on the specimen.

The microstructure and microhardness of specimen 19, treated the same as specimen 17 are similar to those of specimen 17. The lattice parameter of sample 19 is $3.016 \pm .004\overset{\circ}{\text{Å}}$. No lines other than matrix were found in the X-ray pattern.

Specimen 21, water quenched from 750°C , gave microstructures, hardness readings, and microprobe results essentially identical to those of the slow-cooled specimen shown in Fig. 12, again suggesting that transformation cannot be arrested by quenching or, more probably, that all the observed reactions took place during oxidation and annealing and not during cooling.

X-ray diffraction patterns of specimens 20 and 21, Table X, were similar and showed a doubling of all lines. Since this made reading of the patterns difficult, the d -spacings could be only approximately determined. Two possible explanations for the line doubling exist.

First, it is possible that $\beta(\text{V-O})$, a phase of variable composition with a body-centered tetragonal structure based upon a distortion of the vanadium structure, may exist as an oxide in this system.

Second, the pattern can be indexed as two independent

bcc structures, one having $a_0 \simeq 3.05\text{\AA}$, the other having $a_0 \simeq 3.01\text{\AA}$. This is the result expected if the X-ray specimen contained material from the unoxidized interior of the alloy ($a_0 = 3.054\text{\AA}$) and from the oxidized zone, which in all other specimens (except those annealed at 950°C) showed a value of $a_0 \simeq 3.015\text{\AA}$. Although the first possibility cannot be ruled out, consistency with other data suggests that the second alternative may be the correct one.

Table X

X-ray diffraction data from specimens 20 and 21

$d(\text{\AA})$	Specimen 20		$d(\text{\AA})$	Specimen 21	
	I	a_0		I	a_0
2.16	vs	3.05	2.15	vs	3.04
2.13	m	3.01	2.13	vs	3.01
1.52	w	3.04	1.52	w	3.04
1.50	w	3.00	1.50	w	3.00
1.25	w	3.06	1.25	m	3.06
			1.23	m	3.01

Discussion

X-ray diffraction results may not be representative of the entire specimen because of possible segregation occurring during grinding or crushing of specimens which were inhomogeneous in hardness. Thus it cannot be said with certainty

that these phases identified represent all those present in the sample. Specimen 8, however, was homogeneous in microstructure and hardness and was easily ground to powder; thus its pattern, shown in Table IX, is considered representative.

The lattice parameters of the metal matrix of all oxidized specimens (except 6 and 8, annealed at 950°C) lie close to 3.015Å. This value is in excellent agreement with that reported by Carlson et al.²⁷ for the composition in the V-Cr alloy system which would occur if all titanium were removed from the V-15Ti-7.5Cr alloy. Thus it appears that in alloys oxidized and annealed at 900°C or below using the treatments shown in Table VI, titanium is not only preferentially, but also totally removed from solid solution. The reason for the lesser removal of titanium at 950°C is not presently understood. However, it is possible that these results could be clouded by sampling errors in the making of X-ray specimens, the total extraction of titanium taking place in the high oxygen content surface layers, which being more friable, were those actually incorporated in the diffraction specimen. The 950°C sample being the only uniform sample studied, may show a re-partitioning of titanium to the matrix after the homogenizing vacuum anneal. However, even in the latter case some lattice contraction is observed.

A rhombohedral oxide was identified in patterns annealed at 950°C, 900°C, and 850°C. Its stoichiometry probably was close to $(\text{Ti}_{2/3}, \text{V}_{1/3})_2\text{O}_3$, and its hexagonal cell constants were $c_0 = 5.042\text{\AA}$ and $a_0 = 13.933\text{\AA}$. The rhombohedral unit cell had an $a_0 = 5.481\text{\AA}$ and $\alpha = 54^\circ 46'$. Lines on patterns of specimens annealed at 950°C and 750°C raised the possibility of $\beta(\text{V-O})$ formation.

The microstructure of all inhomogeneous specimens had a dark etching area existing for some distance in from the edge, which was similar in appearance to that found in a specimen oxidized at 925°C with no anneal. The boundary of this zone is believed to represent the extent of the internal oxidation front produced during the oxidation treatment. Lighter etching areas were found farther into the specimen center in specimens annealed after oxidation. These were assumed to result from inward diffusion of oxygen from the VO_2 scale and the outer oxidized zone during annealing. It is possible that the different microstructures arise from different oxides, but this can not be proven on the basis of the present evidence. The lighter-etching zones were found in the hardest portions of the specimens and generally contained cracks. These hardest areas increased in hardness with decreasing annealing temperatures. However, the highest hardness was found in the

homogeneous specimen oxidized at 1020°C. This may be the result of the greater volume of oxide compared with other specimens.

The microprobe indicated sharply defined titanium-poor zones close to the inside edge of the precipitation fronts in specimens annealed at 750°C. At the 850°C temperature no such areas were found; at 900°C possible shallow titanium-poor zones were present. Depletion of the oxidized element ahead of an oxidation front is expected during internal oxidation, since that element diffuses to the front to combine with oxygen coming from the other direction. Marked titanium-depleted areas were found only in the specimens which had unoxidized areas in specimen centers, and not in specimens annealed at higher temperatures, which had some form of second phase throughout the specimen. Perhaps, then, these titanium-poor zones can be eliminated by additional diffusion after the precipitation fronts meet in the specimen center.

Although the microprobe indicated a redistribution of titanium and vanadium during oxidation and annealing, chromium levels were nearly uniform on all specimens again indicating that chromium apparently does not participate to a significant extent in the oxidation process.

The four different annealing temperatures seem to repre-

sent successive stages in a process of homogenization of oxygen gradients formed during the initial oxidation treatments, the greater mobility of the oxygen at higher temperatures allowing the process to proceed farthest at the highest temperature. At 750°C only fairly thin light-etching bands of precipitate extend into the previously unoxidized matrix. At 850°C some oxygen diffusion as far as the center of the specimen was evident from the coarse precipitates. A second type of structure of higher oxygen content, represented by the two light-etching bands, advanced some distance toward the center. A single such band, similar in microstructure to the two at 850°C, was found at 900°C. Mobility of the oxygen atoms probably was high enough that the double bands met and formed a single band. Finally at 950°C complete homogenization took place.

Correlations between phases identified by x-ray diffraction with microstructure cannot be made with certainty. β (V-O or some other lower oxide may be the finer, light-etching microstructure found at 750°C or the coarse precipitates in the center of the 850°C specimens. The darker precipitate such as that shown in Fig. 4 is probably $(\text{Ti},\text{V})_2\text{O}_3$.

The maximum hardness levels observed in this work are approximately equivalent to those found in comparable alloys

exposed to oxygen-contaminated liquid sodium (Fig. 1). It appears that the light-etching, hard, cracked zones formed on the interior of specimens in this study are comparable in composition and properties to the surface zones formed under lower oxidation potential in specimens exposed to sodium. Thus the dark, soft surface bands and the presence of $(\text{Ti,V})_2\text{O}_3$ probably represent later stages in the corrosion process than have been achieved by testing in sodium.

Future work in this area should include attempts to separate the various zones of oxidized alloys, to identify the phases found in each and correlate these phases specifically with the microstructure. Particular attention should be paid to the possible occurrence of lower oxides such as $\beta(\text{V-O})$, to the variation in composition of $(\text{Ti,V})_2\text{O}_3$ as a function of initial alloy composition, and to the identification of the precipitate formed in the central zone of the alloy at 850°C . Although it appears that oxidation under low oxygen pressures followed by diffusion annealing gives a result comparable to long term exposure to sodium, and this is a useful accelerated test for possible cladding materials, further work is required to establish with certainty the correlation between these two types of testing.

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