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**TECHNICAL ASSESSMENT OF VANADIUM-BASE
ALLOYS FOR FUSION REACTOR APPLICATIONS**

**Volume 2. Review of Properties: Vanadium and
Vanadium-Base Alloys. Final Report**

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MASTER

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TECHNICAL ASSESSMENT OF VANADIUM-BASE ALLOYS FOR FUSION REACTOR APPLICATIONS

FINAL REPORT

Volume 2

Review of Properties: Vanadium and Vanadium-Base Alloys

Westinghouse Electric Corporation
Pittsburgh, Pennsylvania 15236

APRIL 1978

Prepared For

The U.S. Department of Energy
Under Contract EG-77-C-02-4540

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FOREWORD

This report was prepared by Westinghouse Electric Corporation under Contract EG-77-C-02-4540 for the Department of Energy, Office of Fusion Energy. Dr. T. C. Reuther of the Materials and Radiation Effects Branch was the cognizant DOE program monitor. Coprincipal investigators for Westinghouse were R. E. Gold and D. L. Harrod of the Research and Development Center.

The Final Report is presented in two volumes. Volume 1 presents the results of the technical assessment of vanadium alloys for fusion reactor applications. A complete documentation of the technical literature which was reviewed for Task 1 of this assessment is provided in Volume 2.

The authors wish to acknowledge valuable review comments and suggestions by J. H. DeVan of the Oak Ridge National Laboratory and D. L. Smith of the Argonne National Laboratory with regard to the material provided in Section 3 of Volume 2.

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ABSTRACT

A review of those properties and characteristics of vanadium and vanadium-base alloys which are likely to determine the acceptability of these materials for fusion reactor applications has been carried out. The open technical literature and reports made on government-supported development programs have been consulted to provide the data base surveyed here. Emphasis has been placed on the radiation response, mechanical properties, corrosion/compatibility behavior, and gas-metal interactions of vanadium and vanadium alloys. In addition, a review is presented of the state of the art in the consolidation and fabrication of vanadium alloys. Temperatures up to about 650°C have been emphasized; this is felt to represent an approximate upper limit for long time applications of these materials.

1.0 RADIATION EFFECTS IN VANADIUM AND VANADIUM-BASE ALLOYS

CONTENTS

Introduction	Summary-Void Swelling and Precipitation Due to Neutron Irradiations
Radiation Anneal Hardening in Vanadium	• Void Swelling
Background	• Precipitation
Experimental Data for RAH in Vanadium	Mechanical Properties of Neutron Irradiated or Helium-Injected V-Base Alloys
• Fluence and Irradiation Temperature Effects	V Alloys-Low Temp. Neutron Irradiations
• Internal Friction Experiments	• V-Ti Binary Alloys
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Discussion of RAH in Vanadium	V-20Ti Alloy-Elev. Temp. Neutron Irradiations
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1.1 INTRODUCTION

Various aspects of the radiation response of vanadium and vanadium-base alloys have been the subject of experimental investigations since at least 1966. By far the majority of these investigations have been as the result of interest in the radiation response of vanadium alloys as candidate structural materials in nuclear power reactors or because of the fundamental interest in the creation and annealing/recovery behavior of defect structures in body centered cubic (bcc) metals. The literature on both of these aspects will be reviewed here.

Interest in vanadium alloys for nuclear reactor applications initially focused on their potential as a fuel cladding material in fast fission breeder reactors. This interest derived primarily from the better high temperature mechanical properties of vanadium alloys relative to the stainless steels. The results of very early irradiation testing further stimulated this interest when vanadium alloys were found to apparently resist elevated temperature irradiation embrittlement effects.

Major alloy development and characterization programs were carried out in the United States, under the sponsorship of the (then) AEC, and in West Germany, primarily at Karlsruhe. A significant portion of the AEC-sponsored program was aimed at the evaluation of the effects of high fluences of fast neutrons on the microstructural characteristics and mechanical behavior of vanadium alloys. Before this program was terminated, in about 1970, the results of these evaluations were reported as informal accounts of in-progress work at Working Group Meetings held between 1966 and 1970. The present review was initiated with the intention of assessing the results generated on that program in order to provide a clearer perception of the radiation response of vanadium alloys as it might be relevant to the current fusion reactor first wall alloy development activities. By the nature of the Working Group Meetings on the AEC Cladding Development Program, viz, reports of in-progress experiments or work planned for future experiments, the information available from the meetings themselves were of very limited value. Fortunately, most of this experimental research was ultimately reported in the open literature; this body of information provided the bulk of the data reviewed here.

The radiation effects literature on vanadium and vanadium-base alloys can be separated, for convenience in discussions, into the following categories;

- Radiation Anneal Hardening (RAH) Studies⁽¹⁻¹¹⁾
- Void Swelling, Precipitation, and Other Microstructural Studies⁽¹²⁻²¹⁾
- Mechanical Behavior Characterizations^(17,20,22-30)
- Ion Irradiation-Simulation Studies^(26,31-39)

There are obvious regions of overlap in the above classification. For example, most RAH studies involve some form of mechanical property measurement in order to follow changes in behavior with fluence or annealing parameters. Also, precipitation phenomena have been reported in several of the references listed in other categories. Nevertheless, the above groupings do tend to be representative of different fluence or temperature ranges of emphasis. The ion irradiations represent a unique set of data and are treated separately since the precise correlation between these results and those of neutron irradiations is still unclear at the present time.

Helium effects are not treated separately in this review; rather, those studies which have examined the effects of helium on either void swelling, on mechanical properties, or during ion irradiations, are included in the appropriate subsections.

1.2 RADIATION ANNEAL HARDENING IN VANADIUM

1.2.1 Background

Radiation anneal hardening (RAH) is a phenomenon unique to the bcc metals and certain of their alloys. Just as the name implies, RAH is an additional hardening or strengthening of the irradiated metal which occurs due to post-irradiation annealing. This incremental strengthening is in addition to the normally observed "radiation hardening" seen in all types of metals and alloys following neutron irradiations. While it was early agreed upon that radiation hardening was likely the product of increased resistance to dislocation movement due to radiation-produced defect clusters, the specific mechanism(s) responsible for RAH phenomena remain the focal point of discussion and disagreement to the present time. Further comment on these issues is provided in Section 1.2.3.

Apparently the earliest reports of RAH in vanadium were made in the period 1969-1970 by Venetch, et al.,⁽¹⁾ Perepezko, et al.,⁽⁴⁰⁾ and various researchers at Ames Laboratory,^(2,3) although reports of similar effects in niobium appear as early as the 1959 work by Makin and Minter.⁽⁴¹⁾

Most of the early observations are the unintentional by-products of experimental studies whose primary purpose was the investigation of the annealing/recovery stages in the bcc metals. By analogy to the annealing stages observed in fcc metals due to the motion and annihilation of intrinsic point defects (vacancies and self-interstitials), the "annealing" stage associated with RAH in bcc metals was designated as "Stage III" annealing. Excellent discussions of the evidence for and against such a classification exist in the literature. The review papers by Nihoul^(42,43) and the interpretation of recent experimental investigations by Smidt,⁽⁴⁾ Shiraishi, et al.,^(6,11) McIlwain, et al.,⁽⁷⁾ and Wechsler, et al.,⁽⁸⁾ are particularly noteworthy.

In common with other thermally activated processes, an "activation energy" can be determined for RAH. In fact, most of the investigations which have been carried out on RAH phenomena have been focused on determination of the activation energy in the hope this would shed some light on the operating mechanism. The most common technique employed in this regard has been the measurement of changes in the electrical resistivity upon isochronal annealing of irradiated specimens. As will be discussed in Section 1.2.3, these efforts have met with only limited success.

In vanadium, RAH is generally observed to have a maximum effect at about 160-200°C ($\sim 0.2 T_m$) although this temperature range can vary somewhat due to both irradiation and specimen (composition) variables.

In the following subsections the experimental data are reviewed, followed by a brief discussion of the possible mechanisms of RAH, an analysis of the observed strengthening effects, and comments on the potential technological importance of RAH to reactor structural material applications.

1.2.2 Experimental Data for RAH in Vanadium

A summary of the major experimental investigations of radiation anneal hardening (RAH) in vanadium is presented in Table 1. Note that the irradiation temperatures are generally quite low, as are the fluences. The low irradiation temperatures -- generally in the 50-110°C range -- are necessary to avoid thermally-induced

Table 1. Summary of radiation experiments for RAH studies on vanadium.

Location of Work	Irradiation Conditions			Starting Material ^(c)					Post-Irrad'n. Examinations ^(b)		Reference
	Max. Fluence ^(a)	T _{irrad.}	Environment	C	O	N	H	Heat Treat	Testing Techniques	Other Notes	
BNL-Graph. Reactor	$\sim 10^{18}$	60°C		526	266	320	9	975°C-1 hr.	Tensile		1
ALRR	4×10^{19}	107		166	136	95	7	900°C-1 hr.	Tensile		2
ALRR	6×10^{18}	-190	Liq. N ₂	77	586	78	1	1000°C-6 hr.	Tensile		2,3
U. Carbide Res. React.	1.0×10^{19}	50	Helium	57	112	3	3	900°C-2 hr.	Hardness	Microstr.	4
ORNL-BSR	1.4×10^{18}	60	Helium	-	85	350		1400°C-2 1/2 hr.	Intern. Friction, Resistivity		5
ORNL-BSR	1.4×10^{18}	60	Helium	80	140	280		1200°C-1 hr.	Intern. Friction, Resistivity		5
JRR-2	8.2×10^{19}	180-220		32	240	41	6	900°C-1 hr.	Tensile	Microstr.	6
ALRR	2.7×10^{18}	-190	Liq. N ₂	46/70	50/600	5/10	30/15		Intern. Friction, Resistivity		7
ALRR	1.2×10^{19}	106	Heavy Water	46/70	50/600	5/10	30/15		Tensile		7
ALRR	1.2×10^{19}	105	Heavy Water	7	60/640	1		900°C	Tensile		8
ALRR	1.5×10^{19}	85	Helium	9	70/3160	2		900°C	Tensile		8
ORR	1.6×10^{19}	60-80		72/91	90/157	12/87		1000°C-1 hr.	Compression, Intern. Friction		9
ALRR	1.3×10^{19}	105			60/640				Tensile	Microstr.	10
JRR-2	2×10^{17} to 10^{20}	70	Helium	38	190	5	15	950°C-1 hr.	Tensile	Microstr.	11
JRR-2	1.2×10^{20}	70-600	Helium	32	240	41	6	900°C-1 hr.	Tensile	Microstr.	11
JMTR	1.2×10^{21}	70	Helium	50	430	4	21	900°C-1 hr.	Tensile	Microstr.	11

(a) For $E_n > 1$ MeV

(b) Post-irrad'n annealing employed for all experiments

(c) Interstitial analyses in wt. ppm

rearrangements of the irradiation produced defect structures since this would severely compromise post-test interpretation efforts. The low neutron fluences -- typically in the 10^{18} to 10^{19} n/cm² range -- were initially the maximum practical levels which could be attained in thermal research reactors. This factor is significant, however, since RAH has been found to "saturate" at fluences above about 10^{20} to 10^{21} n/cm². (11)

The normal or typical procedure for a RAH experiment consists of the following steps:

- Irradiation at some temperature below the temperature range where RAH is most prominent (~150-200°C typically for V)
- Post-irradiation annealing at temperatures from $T_{\text{irrad.}}$ to as high as 500-700°C.
- Measurement of some critical property to follow and define the effects of the RAH. This might be by in-situ measurements of $\rho_{\text{electrical}}$ during isochronal annealing or by post-anneal mechanical property tests.

A schematic illustration of the variation in room temperature hardness and lower yield stress with post-irradiation annealing temperature for neutron irradiated vanadium is presented in Figure 1. The considerable incremental hardening/strengthening due to RAH is obvious.

● Fluence and Irradiation Temperature Effects - The dependence of the increase in the room temperature yield stress on fluence, and on irradiation temperature, is presented as a function of post-irradiation annealing temperature in Figures 2 and 3, respectively. Although the unirradiated yield stress was not given by the authors, from the interstitial impurity levels quoted, the room temperature yield stress would be approximately 15 ksi. Hence, the data in Figure 2 represent a considerable strengthening due to irradiation and post-irradiation annealing. Note in Figure 2 that the peak in the yield stress increase is shifted to slightly higher temperatures by increasing the fluence from 2×10^{17} n/cm² to 1×10^{18} n/cm². Note also that after irradiation to 1×10^{20} n/cm² no RAH is observed; the large increase in yield stress due to radiation hardening decreases monotonically with increasing annealing temperature. This monotonic decrease is the kind of behavior normally observed in neutron irradiated fcc metals.

Figure 1. The variation of room temperature hardness and tensile yield stress as a function of post-irradiation annealing temperature for vanadium.

Figure 2: The increase in room temperature yield stress of vanadium as a function of post-irradiation annealing temperature and neutron fluence.

Figure 3. The increase in room temperature yield stress of vanadium as a function of irradiation temperature and post-irradiation annealing temperature. All data for specimens irradiated to $1 \times 10^{20} \text{ n/cm}^2$ ($E_n > 1 \text{ MeV}$).

The effects of increased irradiation temperature on yield stress changes due to post-irradiation annealing are shown in Figure 3 for vanadium irradiated to 1×10^{20} n/cm². These data have been interpreted by Shiraishi, et al.,⁽¹¹⁾ to indicate RAH occurs for irradiation temperatures as high as 460°C. Shiraishi, et al.,⁽⁶⁾ have reported a similar effect of irradiation temperature on RAH in vanadium irradiated at 180-220°C to a fluence of 8.2×10^{19} n/cm² ($E_n > 1$ MeV). The peak in the yield stress increase occurred for specimens post-irradiation annealed at about 400°C.

- Internal Friction Experiments - Several investigators have employed internal friction measurements in an effort to gain information on the possible role of interstitial impurities in RAH.^(5,7,9) Internal friction is a common and powerful technique for monitoring the anelastic strain which occurs upon preferential ordering of interstitial atoms in solution in bcc metals under an applied stress. From measurements of the rate at which the anelastic strain appears, the jump frequency, and hence the diffusion coefficient and activation energy for diffusion of the mobile species, can be determined. Comparison of these values with known values for the activation energy of diffusion for a given interstitial species can provide important information regarding the rate-controlling mechanisms.

Internal friction (Snoek) peaks in unirradiated vanadium occur at about 170°C ($0.2 T_m$) and 275°C ($0.25 T_m$). Activation energies calculated for these give ~ 1.2 eV for the $0.2 T_m$ peak and ~ 1.5 eV for the $0.25 T_m$ peak. It is fairly well accepted that the lower temperature peak is due to the migration of oxygen and/or carbon; the activation energies for diffusion of these interstitials in vanadium are 1.26 eV and 1.18 eV, respectively.⁽⁴⁴⁾ The high temperature peak corresponds very closely to that expected for the migration of nitrogen which has an activation energy for diffusion in vanadium of 1.5 eV.⁽⁴⁴⁾

In vanadium which has been irradiated with neutrons and subjected to post-irradiation annealing, the Snoek peaks are found to occur at the same temperatures, but their amplitudes are reduced by as much as 50%, depending upon interstitial content and annealing temperature.⁽⁵⁾

- Resistivity Measurements - Changes in the electrical resistivity, as it is lowered by post-irradiation annealing from the as-irradiated value, can be a convenient and useful way to observe and measure the recovery/annealing process. By using the ratio-of-slopes method with resistivity-time curves, Stanley, et al.,⁽⁵⁾ determined the activation energy for the 0.2 T_m annealing peak as $1.2 \pm 0.1 \text{ eV}$ for vanadium irradiated at 60°C to $1.4 \times 10^{18} \text{ n/cm}^2$ ($E_n > 1 \text{ MeV}$).

McIlwain, et al.,⁽⁷⁾ performed isochronal resistivity annealing measurements on vanadium specimens containing 50 to 800 weight ppm oxygen which had been irradiated at fluences up to $3 \times 10^{18} \text{ n/cm}^2$ ($E_n > 1 \text{ MeV}$) at -190°C. Post-irradiation annealing temperatures ranged up to 220°C. The results of low temperature resistivity measurements are shown in Figure 4 for vanadium containing high (600-800 wppm), medium (140-200 wppm), and low (50-80 wppm) levels of oxygen. Notice that the peak height increases with increasing neutron fluence for similar oxygen concentrations; the peak height also increases with increasing oxygen concentration for the same fluence. Moreover, the peak temperature decreases slightly with increasing neutron fluence and increasing oxygen level. This latter observation was interpreted as the result of more rapid arrival of oxygen atoms at trapping sites⁽⁷⁾ since the concentration of both oxygen atoms in solution and irradiation-produced defects in the matrix would be higher for these cases.

- Alloying Effects - Hasson,⁽⁹⁾ in an attempt to test the hypothesis that RAH was due to oxygen interstitial impurity migration, performed a radiation-anneal hardening experiment on a V-3.5Ti alloy; no RAH effect was noted.

In a recent study of the interaction between interstitial impurities and substitutional solutes in vanadium binary alloys, Shikama, et al.,⁽⁴⁵⁾ have examined the effects of small additions of titanium on the internal friction peaks in unirradiated specimens. For a V-0.72Ti alloy, they found an approximately six-fold reduction of the oxygen and nitrogen Snoek peaks relative to unalloyed vanadium with the same total interstitial content. Additional damping peaks were observed which are possibly due to interactions of oxygen or nitrogen with the titanium. Although these data are for unirradiated specimens, they are not inconsistent with Hasson's observation since irradiation and subsequent annealing should lower the amount of oxygen in solution even more.

Figure 4. Derivative curves for electrical resistivity as a function of the isochronal annealing temperature for high-, medium-, and low-oxygen vanadium. All irradiations done at -190°C ; annealing times, one hour; annealing temperature interval, 15°C ; measurements at -196°C . Data from Ref. (7).

1.2.3 Discussion of RAH in Vanadium

- Mechanisms - Arguments have been developed which explain the radiation-anneal hardening observed in vanadium and the other bcc transition metals as the result of either the migration of intrinsic point defects (vacancies and self-interstitials) to radiation-produced defect clusters or traps,^(46,47) or the migration of interstitial impurities (carbon and/or oxygen) to radiation-produced defect clusters where they are trapped and removed from solid solution.^(2-10,48)

The specific details of each of these models, and in particular their relationship to Stage III annealing in bcc metals, have been documented by Nihoul^(42,43) and discussed at some length in the literature cited previously. These discussions will not be repeated here; the bulk of the evidence seems to endorse the latter interpretation -- that RAH in vanadium is due to the diffusion of interstitial impurity atoms, probably oxygen, to radiation-produced defect clusters during the post-irradiation annealing treatment. Observations which tend to support this conclusion include:

- RAH was observed in vanadium containing ~600 wppm oxygen, but not in vanadium with ~100 wppm oxygen⁽³⁾
- Vanadium which had been RAH'd was re-irradiated and re-annealed; no further increase in strength due to the second radiation-anneal was observed⁽³⁾
- The activation energies determined for RAH are very close to those for the diffusion of carbon and oxygen in vanadium^(5,7)
- The resistivity following post-irradiation annealing falls below that of the unirradiated material, indicating a removal of interstitial impurities from solid solution⁽⁵⁾
- No microstructural evidence has been noted of a change in the irradiation-produced defect density, or average size, during RAH; this is difficult to reconcile with vacancy or interstitial migration which should either increase or decrease the size of the observable aggregates⁽⁴⁾
- The magnitude of the resistivity annealing stage is increased by increasing the oxygen and carbon contents^(5,7)
- The Snoek internal friction peaks due to oxygen and carbon decreased upon post-irradiation annealing^(5,7) indicating removal of these species from solid solution.

While exception can be taken with each of the above observations with regard to its individual merits for or against one mechanism or the other, the sheer weight of the evidence seems to strongly favor the interstitial impurity model.

● Analysis of Strengthening Due to RAH - Radiation hardening of metals is generally explained in terms of a dispersed barrier model where the strengthening increase is expressed by:⁽⁴⁹⁾

$$\Delta\tau = \alpha \frac{\mu b}{\ell} \quad (1)$$

where $\Delta\tau$ is the increase in shear stress

μ is the shear modulus

b is the Burgers vector

α is a dislocation-defect interaction parameter which is assumed to be constant for a given barrier, and describes the barrier strength

and, ℓ is the separation between barriers.

For strengthening due to forest dislocations, equation (1) is usually written as,

$$\Delta\tau = \alpha\mu b \sqrt{\rho} \quad (2)$$

where ρ is the dislocation density

For very fine defect aggregates, voids, or very small interstitial or vacancy loops,

$$\Delta\tau = \alpha\mu b \sqrt{Nd} \quad (3)$$

where N is the concentration or density of defects, voids, or loops

and, d is their (avg.) size.

The strengthening which occurs due to radiation-anneal hardening in vanadium has been analyzed by Smidt,⁽⁴⁾ Shiraishi, et al.,^(6,11) and Bajaj and Wechsler.⁽¹⁰⁾

The character, concentration, and sizes of the various irradiation-produced defects believed to be contributing to the observed strengthening have been determined by electron microscopy.

From equation (3) there are clearly two ways in which radiation hardening, or RAH, can increase the yield stress. These are by either increasing the concentration (N) and/or the size (d) of the defects responsible for strengthening, or by increasing the strength of the barriers (i.e. increasing α).

Smidt⁽⁴⁾ analyzed the strengthening of vanadium irradiated at 50°C to 1.0×10^{19} n/cm² ($E_n > 1$ MeV) and anneal-hardened at 100-500°C by comparing the observed strengthening with that which can be achieved for impenetrable point obstacles (Orowan barriers); this should represent an upper limit. On this basis, he found radiation-anneal hardening could only be explained if the value of α approaches unity. For specimens which were radiation hardened but not annealed, the strengthening could be explained if α is about 0.55. Smidt found no evidence of changes in either N or d due to the annealing treatments and, hence, concluded that the RAH could be best explained on the basis of migration and precipitation of interstitial impurities on radiation-produced defects. Changes in α from ~ 0.55 to unity imply a major hardening of the impurity-defect atmospheres as barriers to dislocation motion.

Shiraishi, et al.,⁽⁶⁾ analyzed the strengthening in vanadium irradiated to 8.2×10^{19} n/cm² ($E_n > 1$ MeV) at 180-220°C and annealed at temperatures up to 700°C. Based on measurements of the dislocation loop density and the loop diameters, the strength increases calculated using a form of equation (3) with $\alpha = 0.5$ were much less than the measured values. In agreement with Smidt, Shiraishi, et al.,⁽⁶⁾ found no changes in dislocation loop density or size and attributed the strengthening to interstitial impurity "clusters" formed on post-irradiation annealing.

Bajaj and Wechsler⁽¹⁰⁾ irradiated vanadium at 105°C to 1.3×10^{19} n/cm² ($E_n > 1$ MeV) and used post-irradiation anneals from 100 to 600°C to study radiation-anneal hardening effects on the room temperature yield stress. Using the results of TEM to give information on the concentration and sizes of the defect clusters, and the measured increases in the yield stress, the apparent dislocation-defect interaction parameter was found to vary with the oxygen content of the specimens. Again, no changes were observed in the concentration or sizes of the defect clusters due to RAH anneals up to about 400°C. These results were interpreted as indicating RAH is due to strengthening of the defect clusters by interstitial impurity trapping.

Shiraishi, et al.,⁽¹¹⁾ analyzed the strengthening observed in vanadium irradiated to 10^{20} - 10^{21} n/cm² at 70-600°C in terms of equations (2) and (3). Using the results

of transmission electron microscopy for the dislocation and void parameters, the calculated strengthening was much less than the measured values. The authors concluded that this discrepancy was probably due to contributions to the strength from defect clusters which are below the resolution limit of the electron microscope.

- The Technological Significance of RAH in Vanadium - There are several factors regarding radiation-anneal hardening phenomena in vanadium which suggest it is likely to have little impact on the suitability of this metal and its alloys for fusion reactor applications. First, RAH is primarily a low fluence effect and is seen to saturate at $\sim 10^{20}$ n/cm², a neutron exposure which will be achieved in a few months of reactor operation. In addition, with admittedly a very sparse experimental data base, RAH has not been observed in a vanadium alloy. It seems highly unlikely that unalloyed vanadium will find application in reactor structures. If the interstitial impurity model is the appropriate mechanism for RAH, it would seem unlikely that significant hardening would occur in any alloy containing a strongly reactive alloying addition; most of the vanadium alloys which have been found to have attractive mechanical, chemical and radiation effects properties contain intentional additions of titanium or zirconium.

- Summary - Based on the preceding data and discussions, radiation-anneal hardening in vanadium can be summarized as follows:

- RAH is primarily a low fluence phenomenon; "saturation" occurs at $\sim 10^{20}$ n/cm²
- RAH is additive to radiation hardening effects seen in as-irradiated specimens
- Increases in the room temperature yield stress after post-irradiation annealing can be up to $\Delta\sigma \approx 25-30$ ksi
- The tensile ductility usually decreases due to RAH; this decrease is probably only serious if plastic instability due to dislocation channeling occurs
- The incremental strengthening due to RAH in vanadium is sensitive to the interstitial impurity level; in particular, the oxygen level appears very important, with increases in oxygen level accompanied by increased radiation-anneal hardening

- The most probable mechanism of RAH in vanadium is the migration of interstitial impurity atoms to radiation-produced defect aggregates, thereby enhancing their effectiveness as dislocation barriers
- RAH has not been reported in vanadium alloys or in ultra-pure vanadium.

1.3 VOID SWELLING AND PRECIPITATION IN NEUTRON IRRADIATED VANADIUM AND VANADIUM-BASE ALLOYS

The results of studies of void formation and other microstructural rearrangements occurring due to fast neutron irradiation have been reported for vanadium^(12-18,21) and a few vanadium-base alloys.^(12,16-19) Table 2 presents a summary of the major results of these investigations.

Before beginning a discussion of the various experimental results, a few important points should be noted with regard to the data base. While in general the fluences reported in Table 2 are considerably higher than those used in the RAH studies discussed in Section 1.2, they are still only a fraction of the $1-3 \times 10^{23} \text{ n/cm}^2$ fluences which a fusion reactor first wall will experience; the neutron spectra are also obviously mismatched. Also, with the exception of the work done at Oak Ridge by Wiffen and co-workers,^(12,16,19) documentation of the interstitial impurity levels is almost nonexistent. This is unfortunate since, in addition to their critical role in determining the mechanical properties of the bcc refractory metals, the interstitial impurities are believed to strongly influence the development of as-irradiated microstructures in these metals. Finally, the lack of information on combined helium-damage investigations should be noted. This is an unavoidable experimental limitation of the available test reactors.

Where only one irradiation temperature is listed this is usually the temperature where maximum void swelling was observed. The helium (α particle) irradiation data of Ehrlich and Kaletta⁽²⁰⁾ are reported here because of the swelling phenomena observed. Even a superficial review of Table 2 emphasizes the lack of an adequate data base for these materials relative to that of the face centered cubic stainless steels.

Table 2. Summary of experimental studies of void swelling in neutron irradiated vanadium and vanadium-base alloys.

Metal or Alloy	Location of Work	Irradiation Experimental Details					Starting Material ^(b)					Post-Irradiation			Reference
		Dose/Damage Info.			T _{irrad.}	Environment	C	O	N	H	Ht. Treat, etc.	ΔV (%)	Precipn.	Notes & Others	
		Fluence ^(a)	DPA	appm He											
V	EBR-II	$1.7 \times 10^{22(c)}$			630°C	Helium	520	278	186	21	"Annealed"		Carbides (?)		12
V-20Ti	EBR-II	$1.7 \times 10^{22(c)}$			630	Helium	289	420	291	50	"Annealed"			No Voids	12
V	CEA	5×10^{20}			600	Helium					"Well Annealed"	0.38			13
V	EBR-II	1.4×10^{22}			550	Helium						1.77			14
V	EBR-II	1.4×10^{22}			575	Helium						1.58			14
V	EBR-II	1.4×10^{22}			600	Helium						1.47			14
V	EBR-II	3×10^{21}			450							0.2			15
V	EBR-II	5.7×10^{21}			385	Helium	350	670	230		Recrystall.	0.56			16
V	EBR-II	4.9×10^{21}			385	Helium	79	110	31		Recrystall.	0.08			16
V-20Ti	EBR-II	1.4×10^{22}			600	Helium					Recrystall.	-	Ppts.	No Voids	16
V	EBR-II	1.1×10^{22}			525							1.10			17
V	EBR-II	2.5×10^{22}			625							1.54			17
V-1, 3, 5Ti	EBR-II	1.1×10^{22}			525		120	200	30	15	Stress-Relieved	0.01	Coher. Ppts.		17
V-10, 20Ti	EBR-II	1.1×10^{22}			525		120	200	30	15	Stress-Relieved	-		No Voids	17
V-20Ti	EBR-II	6×10^{22}			600						Stress-Relieved	~0		A Few Voids	17
V-10, 15Cr	EBR-II	1.1×10^{22}			525							~0	Ppts.	A Few Voids	17
V-1Ti-0.550 ₂	EBR-II	2.5×10^{22}			625							1.36	Ppts.	Int.	17
V-15Cr-5Ti	EBR-II	2.65×10^{22}			600							~0		Friction	17
V-15Ti-7.5Cr	EBR-II	2.65×10^{22}			600							~0		Few Voids	17
V	DFR	3.6×10^{22}			550		Commercial				800°C-1 hr.	0.9		Few Voids	18
V	DFR	3.6×10^{22}			600	In Mo Powder	Zone Refined				800°C-1 hr.	0.8			18
V-15Cr-5Ti	DFR	3.6×10^{22}			550	In Mo Powder					1500°C-1 hr.	~0		Isolated Voids	18
V-10Cr	EBR-II	1.5×10^{22}	17 ^(e)	~1.8	496-805	Helium	140	77	550		1100°C-1 hr.	1.35 (max)	Ppts.		19
V-20Ti	EBR-II	1.3- 6.1×10^{22}	15 to 69 ^(e)	~1.8	470-780	Helium	145	575	46		900°C-1 hr.	-	1 Vol. % Ppts.	No Voids	19
VANSTAR-7	EBR-II	1.5×10^{22}	17 ^(e)	~1.8	496-805	Helium	500	760	90		1200°C-1 hr.	0.04 (max)	ZrC		19
V	Darmstadt	α -Particles	up to 22	125 to 200,000	575-700	Vacuum					1030°C-1 hr.	8 (at 625°C)			20
V-20Ti	Darmstadt	α -Particles	up to 22	125 to 200,000	575-700	Vacuum					1030°C-1 hr.	"Same as V"	TiO ₂ (?)		20
V	HFR	$3.5 \times 10^{20(d)}$			445	Inert Gas	30 appm total				1000°C-1 hr.	0.05			21
V	HFR	$3.5 \times 10^{20(d)}$			445	Inert Gas	800 appm (oxygen)				1000°C-1 hr.	0.16			21
V	HFR	$3.5 \times 10^{20(d)}$			445	Inert Gas	2000 appm total				1000°C-1 hr.	0.05	Carbides (?)		21

(a) For $E_n > 0.1$ MeV unless otherwise stated.

(b) Interstitial analyses in wt. ppm unless noted.

(c) For $E_n > 0$.

(d) For $E_n > 1$ MeV.

(e) $E_d = 25$ eV used to calculate DPA.

In the paragraphs which follow, no attention will be given to specific values of void concentrations or sizes; we are not interested here in void nucleation, growth, and annihilation details. Rather, a brief description of the data reported for vanadium and its alloys will be presented and reviewed for its relevance to fusion reactor applications.

1.3.1 Unalloyed Vanadium

• Voids and Void Swelling - The earliest reports of void formation in unalloyed vanadium were by Wiffen and Stiegler⁽¹²⁾ (1968-69), and Elen,⁽⁵⁰⁾ followed shortly thereafter by several papers given at the 1971 Albany Conference.⁽¹³⁻¹⁶⁾ Most of these were the results of very early investigations into whether void development, which had been recently reported for fcc stainless steels, was going to occur in the high temperature bcc metals. General features of the void formation and development processes were found to be similar to other "pure" metals. Irradiations at 385°C (0.3 T_m) produced a very high concentration of very small voids, whereas increasing the irradiation temperature to 600°C (0.4 T_m) produced a much lower concentration of larger voids.^(14,16) Maximum swelling values were less than about 2% for fluences to 1.4×10^{22} n/cm².⁽¹⁴⁾ The peaks in the swelling versus irradiation temperature curves were in the range 550-600°C (0.38-0.40 T_m).^(13,14,16) Void ordering on a superlattice, which had been observed in other bcc metals such as Nb, Ta, and Mo, did not occur in vanadium.⁽¹⁶⁾

Bartlett, et al.,⁽¹⁸⁾ reported void swelling of 0.9% for commercial vanadium irradiated at 550°C in the Dounreay Fast Reactor to a fast fluence of 3.6×10^{22} n/cm² ($E_n > 0.1$ MeV). Zone refined vanadium had a maximum swelling value of 0.8% at 600°C for the same dose. No interstitial chemistries were reported.

Ehrlich and Kaletta⁽²⁰⁾ studied the swelling behavior of vanadium which was irradiated with 240 keV alpha particles at temperatures from 575° to 700°C. At a dose equivalent to 250,000 appm helium, a total of 8% swelling was observed for irradiations at 625°C. The authors report swelling values of ~2% for doses of 25,000 appm helium at the same temperature. Swelling was less, but still considerable, for irradiations at 575°C and 700°C. Although neutron irradiations were not coupled to this work, displacement damage due to the ion irradiations was reported to be 22 dpa and 2 dpa, respectively, for the doses reported

above. While range and displacement damage plots were not shown, the bubble concentrations and mean bubble diameters varied in a complex fashion through the specimen thickness. The precise interpretation of these results is unclear.

- Effects of Oxygen on Void Swelling - Carlander, et al.,⁽¹⁷⁾ found that increasing the oxygen content of commercial purity vanadium (from 200 wppm) to 8900 wppm had the effect of slightly reducing the void concentration and void swelling due to irradiation at 525°C to $1.1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$). Bressers and Cambini⁽²¹⁾ looked at the effects of varying the total interstitial impurity level (mainly oxygen) on the void-swelling of vanadium irradiated at 445°C to a fluence of $3.5 \times 10^{22} \text{ n/cm}^2$ ($E_n > 1 \text{ MeV}$). Vanadium containing very low (30 appm total) levels of interstitials and very high (~ 2000 appm total) levels were found to behave in essentially identical fashion; void swelling was $\sim 0.05\%$ and void number density was less than 10^{16} cm^{-3} . Vanadium containing 800 appm (mostly oxygen) displayed a void number density of $\sim 5 \times 10^{16} \text{ cm}^{-3}$ and exhibited about 0.16% swelling. The vanadium containing 2000 appm impurities contained extensive precipitation, tentatively identified as carbides. These results were interpreted in terms of an increase in the void number density with oxygen level provided the impurity remains in solution.

- Precipitation in Neutron-Irradiated Vanadium - The only published reports of precipitation in neutron irradiated unalloyed vanadium have been by Wiffen and Steigler⁽¹²⁾ and Bressers and Cambini.⁽²¹⁾ In the work by Wiffen and Steigler, the starting vanadium contained nearly 1000 wppm interstitials (520 wppm carbon). Following irradiation to a total neutron fluence of $1.7 \times 10^{22} \text{ n/cm}^2$ at 630°C, precipitates were observed which had a platelet morphology and were aligned on {012} planes with their long axis along $\langle 100 \rangle$ directions. Bressers and Cambini found similar precipitation in Marz-grade vanadium containing 2000 appm (~ 700 wppm) total interstitials. Neither of these observations are consistent with the results of electron microscopic investigations of precipitation phenomena in unalloyed vanadium conducted by Kramer.⁽⁵¹⁾ Kramer reported only the semi-coherent precipitate VO forms in vanadium containing up to 2030 wppm oxygen, 600 wppm nitrogen and 385 wppm carbon. The crystallography of the precipitates reported by Wiffen and Steigler, and Bressers and Cambini appears very similar to

that observed by Agarwal, et al.,⁽³⁹⁾ in ion-irradiated vanadium. These were not identified but were seen in vanadium, vanadium-oxygen, and vanadium-carbon alloys only after irradiations.

1.3.2 V-Ti Binary Alloys

- Void Observations - V-Ti binary alloys have been the subjects of more experimental observations on the effects of neutron irradiations than any other class of vanadium-base alloys. At least part of the reason for this interest is due to the early observations reported by Wiffen and Stiegler,⁽¹²⁾ and by Moteff, et al.,⁽⁵²⁾ of the lack of void formation in V-20Ti. Since voids had been observed to form in neutron-irradiated vanadium, several investigations were undertaken in an attempt to explore and better define the boundaries of the void-inhibiting action imparted by titanium additions.

Elen⁽⁵³⁾ reported that addition of 3% Ti was sufficient to completely suppress void swelling in neutron-irradiated V-Ti alloys. Carlander, et al.,⁽¹⁷⁾ prepared a series of binary V-Ti alloys containing 1, 3, 5, 10 and 20 Ti and found after irradiation to 1.1×10^{22} n/cm² ($E_n > 0.1$ MeV) at 525°C that only the V-1Ti alloy developed voids. Even in the V-1Ti alloy the (0.01%) swelling was lower by a factor of 100 relative to commercial purity vanadium. The effect of oxygen was examined by preparing a V-1Ti-0.55O₂ alloy and irradiating it to a fluence of 2.5×10^{22} n/cm² ($E_n > 0.1$ MeV) at 625°C. Void swelling was 1.36%, which led the authors to conclude that oxygen additions enhanced void formation in V-Ti alloys. Interestingly, Carlander, et al., found a few voids in V-20Ti irradiated at 600°C to 6×10^{22} n/cm² ($E_n > 0.1$ MeV). Although these caused negligible swelling, this is the only report of void formation in the V-20Ti alloy. Bentley and Wiffen⁽¹⁹⁾ irradiated V-20Ti in EBR-II at temperatures from 470-780°C to fluences up to 6.1×10^{22} n/cm² ($E_n > 0.1$ MeV) and were unable to detect voids in the micro-structure.

While the mechanism of swelling suppression is not obvious, both Carlander, et al., and Bentley and Wiffen suggest the following possibilities:

- Titanium acts as a gettering agent for interstitial impurities which had been serving as void nucleation sites.

- The formation of a high number density of coherent precipitates accommodates the excess vacancies.
- Enhanced recombination of vacancy-interstitial defects occurs due to the presence of substitutional solute atoms.

Unlike the situation for voids, Ehrlich and Kaletta⁽²⁰⁾ found bubble-related swelling to be as severe in V-20Ti as in unalloyed V after very heavy doses of α -particle irradiations at 625°C.

- Precipitation in Neutron-Irradiated V-Ti Binary Alloys - Carlander, et al.,⁽¹⁷⁾ report a high number density ($\sim 10^{15} \text{ cm}^{-3}$) of small ($\sim 80 \text{ \AA}$) coherent precipitates in V-1Ti irradiated at 525°C to a fluence of $1.1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$). Bentley and Wiffen⁽¹⁹⁾ observed extensive precipitation, up to 1 volume percent, in V-20Ti both before and after irradiation to $6.1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$) at 440 to 580°C; no identification of these precipitates was reported. After irradiation to $5 \times 10^{19} \text{ n/cm}^2$ ($E_n > 1 \text{ MeV}$) at 70°C, Moteff, et al.,⁽⁵²⁾ reported observations of thin ribbon-like precipitates in V-20Ti.

In V-1Ti alloys containing 5500 wppm oxygen Carlander, et al.,⁽¹⁷⁾ reported that irradiation at 525°C to $1.1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$) caused a loss of coherency of planar precipitates which were apparently coherent with the matrix prior to irradiation. In the V-20Ti specimens subjected to very high levels (to 250,000 appm) of α -particle irradiations at 625°C, Ehrlich and Kaletta⁽²⁰⁾ reported large TiO_2 precipitates. These precipitates were present before and after irradiation and were explained on the basis of a high (but unreported) oxygen content.

Semicoherent plates of TiO are reported by Kramer⁽⁵¹⁾ as the normal precipitate in unirradiated V-Ti binary alloys. As the Ti content is increased the number and volume fraction of the precipitates decrease; Kramer interpreted this to indicate that Ti additions increase the solubility of oxygen in the V-Ti alloy matrix. With increased oxygen content in a given alloy, the number and volume fraction of TiO precipitates increases. These observations are consistent with the precipitation reported by Carlander, et al.,⁽¹⁷⁾ and Bentley and Wiffen;⁽¹⁹⁾ hence, it seems likely that TiO was the precipitate observed in each of these investigations.

1.3.3 V-Ti-Cr Alloys

- Voids - V-15Cr-5Ti and V-15Ti-7.5Cr alloys were irradiated near 425°C to a fluence of $2.65 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$)⁽¹⁷⁾ without the formation of voids. Irradiation to a similar fluence at 600°C resulted in a few voids in both alloys, but swelling was completely negligible. Bartlett, et al.,⁽¹⁸⁾ irradiated V-15Cr-5Ti at 450, 550, and 600°C to a fluence of $3.6 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$) and, except for a few isolated voids at 550°C, reported no tendency for void formation or swelling.

- Precipitation Observations - No precipitation phenomena have been reported for any of the V-Ti-Cr alloys irradiated as described above.^(17,18)

1.3.4 Miscellaneous V Alloys

- Voids and Void Swelling - Irradiation of V-10Cr and V-15Cr binary alloys at 525°C to $1.1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$)⁽¹⁷⁾ produced negligible swelling although a large number of tiny voids were seen in the microstructure. Bentley and Wiffen⁽¹⁹⁾ found similar results for V-10Cr irradiated at 496°C and 580°C to $1.5 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$), but reported void swelling values of ~1% for irradiations at 690°C and 805°C to the same fluences. This change was accompanied by significant coarsening of the dislocation substructure and a twenty-fold increase in the average void diameter. Irradiation of the alloy VANSTAR-7 (V-9.1Cr-3.3Fe-1.2Zr-0.05C) at the same conditions produced voids at all irradiation temperatures but swelling was negligible (<0.05% for all conditions).

Low fluence ($5 \times 10^{19} \text{ n/cm}^2$, $E_n > 1 \text{ MeV}$) irradiations at 70°C, produced no evidence of void formation in the alloy VANSTAR-9 (V-6.4Fe-5.3Nb-1.3Zr-0.05C).⁽⁵²⁾

- Precipitation Observations - Carlander, et al.,⁽¹⁷⁾ report a high density of unidentified precipitates in V-10Cr and V-15Cr alloys after irradiation at 525°C to $1.1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$). Similar observations have been made by other investigators for V-10Cr irradiated at 496°C and 580°C, but there was no evidence of a second phase following 690°C or 805°C irradiations;⁽¹⁹⁾ all of these irradiations were for a fluence of $1.5 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$).

Irradiation of VANSTAR-7 (V-9.1Cr-3.3Fe-1.2Zr-0.05C) at temperatures from 496°C to 805°C had no effect on the precipitation present in the starting material.⁽¹⁹⁾ This was primarily a uniform dispersion of spherical ZrC precipitates at a concentration of $\sim 8 \times 10^{11} \text{ cm}^{-3}$. A similar lack of effect of irradiation on the initial precipitate characteristics of VANSTAR-9 have been reported.⁽⁵²⁾ This alloy contains large, incoherent precipitates (mostly ZrC) in the unirradiated condition.

1.3.5 Summary - Void Swelling and Precipitation Due to Neutron Irradiations

- Void Swelling - Void formation and void-related swelling in unalloyed vanadium follows the same general trends as other pure metals, with void concentrations and sizes dependent on both dose and irradiation temperature.

Figures 5 and 6 summarize the data for void related phenomena in unalloyed vanadium and those vanadium alloys where measurable void parameters have been observed. The average void size (Figure 5a) and the void concentration (Figure 6) behave with irradiation temperature in the same manner as most other metals. The trends indicated reflect the competition that obtains between nucleation and growth. At low temperatures the high point defect supersaturations favor nucleation of a high concentration of very small voids. As the temperature increases, void growth is favored by the enhanced vacancy mobility and nucleation plays a lesser role. In Figure 5b, the few observations of void swelling which have been reported for vanadium alloys are included with the data for unalloyed vanadium. All of the data shown in Figures 5 and 6 are for neutron fluences greater than about 10^{22} n/cm^2 ($E_n > 0.1 \text{ MeV}$); in vanadium, this corresponds to about 11 dpa. Peak neutron-induced swelling observed to date for that fluence is about 2% for irradiations at 550-600°C (0.38-0.40 T_m). The influence of interstitial impurities, particularly oxygen, is not completely clear at the present time but it does not appear to be a very large effect.

The most significant result of the neutron-irradiation studies of void formation in vanadium-base alloys conducted to date is the resistance to swelling of the vanadium-titanium binary alloys containing greater than about three wt. percent titanium. While other alloys such as V-Cr, V-Ti-Cr, and the VANSTARS, have not been found to be equally immune to total void formation, void-related swelling

(a)

(b)

Figure 5. The average void size and void volume fraction as a function of irradiation temperature for unalloyed vanadium and selected vanadium alloys.

Figure 6. Void concentration as a function of neutron irradiation temperature in unalloyed vanadium.

observed to date for fluences in the range $1-3 \times 10^{22}$ n/cm² has been negligible. This is encouraging since it implies that there may be compositional or micro-structural variables which can be exploited if the V-Ti binaries prove unacceptable for reasons of mechanical strength or compatibility.

- Precipitation - Precipitation phenomena in unalloyed vanadium do not appear significant and, in any event, are only observed in material containing very high levels of interstitial carbon (and perhaps oxygen although the oxygen solubility is very high in vanadium).

With the exception of the VANSTAR alloys, which contain intentional additions of precipitate-forming elements, precipitation phenomena in the vanadium-base alloys are primarily the products of interactions between interstitial impurities such as oxygen and carbon and the substitutional solutes. Suggestions have been made that the semicoherent or coherent (TiO) precipitation resulting from these interactions may be serving a major role in controlling void swelling. However, such fine-scale precipitation does not appear to occur, or at least does not persist, in V-20Ti and that alloy is unexcelled in resisting void formation.

1.4 MECHANICAL PROPERTIES OF NEUTRON IRRADIATED OR HELIUM INJECTED VANADIUM-BASE ALLOYS

The purpose of this section is to review the limited data base which exists on the mechanical properties of irradiated vanadium and vanadium-base alloys. As will be seen, the relevant experimental investigations have been few. The data and observations which have been reported are, however, encouraging.

Elevated temperature mechanical properties are emphasized here. Several investigations^(2,8,54-56) have been reported which were aimed solely at an evaluation of the effects of neutron radiation on low temperature deformation mechanisms and the relative effects of radiation damage on the thermal (τ^*) and athermal (τ_μ) components of the yield stress. These data are not reviewed here since this information is primarily of interest as it may contribute to our knowledge of the low temperature deformation of the bcc metals, and is of very limited applicability to reactor structural material assessments. The only exception to this would be in the event neutron irradiation caused an increase in the ductile-brittle

transition temperature (DBTT) to near or above room temperature.

Table 3 presents a summary of the elevated temperature mechanical property data which have been reported for vanadium and vanadium-base alloys. Note that there are few data points for time-dependent mechanical properties such as creep-rupture and no data at all regarding the mechanical performance under cyclic loads (fatigue strength or fatigue crack growth rates). Also, with the exceptions of the cyclotron-injected or "tritium trick" doped specimens, there is no information on the effects of helium on the elevated temperature properties.

1.4.1 Vanadium Alloys - Low Temperature Neutron Irradiations

Böhm, et al.,^(22a) irradiated various V-base alloys to a fluence of 1.4×10^{21} n/cm² ($E_n > 0.1$ MeV) at 50⁰-100⁰C and subsequently measured the tensile properties at test temperatures between 20⁰ and 750⁰C.

- V-Ti Binary Alloys - Results for various V-Ti binary alloys are shown in Figure 7. Marked irradiation hardening occurred at room temperature; the yield and ultimate strengths were about equal and the ductility was increased to about 2% elongation. The irradiation damage was annealed out on heating to the 650⁰C test temperature; here, the irradiated properties were the same as those of unirradiated material. In order to depict the temperature dependence, unirradiated data by Yaggee, et al., of ANL on V-20Ti (see Section 2) are also shown in Figure 7. The V-20Ti alloy of Böhm, et al., is stronger than the ANL alloy, presumably because of higher interstitial levels.

- V-Ti-Cr Alloys - Results for V-10Ti-5Cr are shown in Figure 8a.^(22a) These results illustrate a general behavior trend common to all the various V-base alloys irradiated at low temperatures. Marked irradiation hardening occurs at room temperature. Between room temperature and 400⁰C, the irradiated strength decreases significantly but the irradiated ductility remains at a low level (below 5%). Recovery of the irradiation damage begins at a temperature somewhat above 400⁰C and is virtually complete at 650⁰-750⁰C. In his 1973 review paper, Böhm^(22b) showed that the temperature for complete recovery in various V-Ti-base ternary alloys depends on Ti content, being about 650⁰C for more than 10% Ti and about 750⁰C for 5% Ti.

Table 3. Summary of mechanical property investigations of neutron irradiated or helium injected vanadium-base alloys.

Alloy	Experimental Conditions				Starting Material ^(b)					Post-Irradiation Tests				Reference
	Fluence ^(a)	DPA	appm He	T _{irrad.}	C	O	N	H	Heat Treatment	Test(s)	σ_{ys}	$\epsilon_{unif.}$	ϵ_{total}	
V-Ti Binary & Ternary Alloys ^(c)	1.4×10^{21}			50-100°C	700	1000	450		900°C-1 hour	Tensile - RT-750°C	(c)	(c)	(c)	22a
V-3Ti-1Si	1.2×10^{22}			640						Tensile - 650	~40 ksi		~7	22b
V-3Ti-1Si	1.2×10^{22}			640						Tensile - 750	35		~7	22b
V-20Ti	2.6×10^{22}			525						Tensile - 450	82	~11	16	17
V-20Ti	2.6×10^{22}			525						- 550	80	9	22	17
V-20Ti	2.6×10^{22}			525						- 650	66	6	22	17
V-10Cr	1.5×10^{22}	17	3	496	140	77	550		1100°C-1 hour	Tensile - 400	58	4	13	23
V-10Cr	1.5×10^{22}	17	3	690	140	77	550		1100°C-1 hour	- 650	41	4	20	23
VANSTAR-7	1.5×10^{22}	17	3	496	500	760	90		1200°C-1 hour	Tensile - 400	137	2.5	8	23
VANSTAR-7	1.5×10^{22}	17	3	690	500	760	90		1200°C-1 hour	- 650	81	4.6	14	23
V-20Ti	6×10^{22}			370-915	145	575	45		900°C-1 hour	Tensile - 600-750		~5	>9	24
V-20Ti	5.1×10^{21}		~1	650					900°C-1 hour	Tensile - RT	58	14	20	27
V-15Ti-7.5Cr	4.9×10^{21}		~1	610					850°C-1 hour	Tensile - RT	68	14	18	27
V-20Ti	3×10^{22}			600 ± 100					900°C-1 hour	Tensile - 550-650	65-55	>12		28
V-20Ti	5×10^{21}			600 ± 100					900°C-1 hour	Tensile - 400-750	44-72	8-17		28
V-15Ti-7.5Cr	$\sim 5 \times 10^{21}$			600 ± 100					850°C-1 hour	Tensile - 550	87	12		28
V-15Ti-7.5Cr	$\sim 5 \times 10^{21}$			600 ± 100					850°C-1 hour	Tensile - 650	90	10		28
V-20Ti	2×10^{22}			600 ± 100						Creep rupture - 650°C-50 ksi			13.3	28
V-15Ti-7.5Cr	5×10^{21}			600 ± 100						Creep rupture - 650°C-82.5 ksi			10	28
V-20Ti	$1-2 \times 10^{22}$			585						Creep rupture - 650°C-25 to 50 ksi			-	29
V	104 MeV Alpha Part.	10		280					1030°C-1 hour	Tensile - 750-950			8-50	20
V-3Ti-1Si	104 MeV Alpha Part.	1.5		280						Tensile - 750-900			10-40	30
V-20Ti-10Nb	104 MeV Alpha Part.	2		280						Tensile - 750-950			8-2	30
V-15Cr-5Ti	Tritium Trick-Sheet	27	-	-	300	700	200	30	1250°C-1 hour	Tensile - 650	54	10.3	10.3	25
V-15Cr-5Ti	Tritium Trick-Sheet	38	-	-	300	700	200	30	1250°C-1 hour	Tensile - 750	51	3.2	3.2	25
V-15Cr-5Ti	Tritium Trick-Rods	38	-	-	300	700	200	30	1250°C-1 hour	Tensile - 700	53.2	10.6	12.4	25
V-15Cr-5Ti	Tritium Trick-Rods	29	-	-	300	700	200	30	1250°C-1 hour	Tensile - 750	50.7	7.7	10.0	25
V-15Cr-5Ti	44 MeV Alpha Part.	25	-	-	300	700	200	30		Tensile - 700	49.9	12.7	13.2	26
V-15Cr-5Ti	44 MeV Alpha Part.	25	-	-	300	700	200	30		Tensile - 750	49.0	7.4	7.6	26
V-15Cr-5Ti	44 MeV Alpha Part.	25	-	-	300	700	200	30		Tensile - 800	47.5	4.4	4.5	26

(a) Neutron fluences in n/cm^2 for $E_n > 0.1$ MeV

(b) Interstitial analyses in wt. ppm

(c) Specific compositions and data listed in Figures 7-10.

Figure 7. Tensile test results for V-20Ti alloy irradiated at 50°C and tested at the temperatures indicated.

(a)

(b)

Figure 8. Elevated temperature tensile test results for V-Ti-Cr alloys irradiated at 100°C.

Results for three different V-Ti-Cr alloys, including the V-10Ti-5Cr alloy of Figure 8a, are shown in Figure 8b. Whether the differences between the three alloys are significant and due to composition effects per se is moot, but the behavior trend is the same for all three.

- V-Ti-Nb,Mo,Cr Alloys - Results for various V-Ti-base alloys containing Nb, Mo and Cr as third and fourth element additions are shown in Figure 9. The trend of hardening at room temperature and recovery at 650°C is again evident. No sure composition effects are discernible.

1.4.2 V-20Ti Alloy - Elevated Temperature Neutron Irradiations

Carlander, et al.,^(17,27,28) irradiated V-20Ti alloy to fluences of $2-33 \times 10^{21}$ n/cm² ($E_n > 0.1$ MeV) at temperatures of about 500°C-600°C $\pm$ 100°C and subsequently measured the tensile properties at 20°C-750°C. The results are shown in Figure 10. In contrast to the effect of low temperature irradiation, irradiation at these elevated temperatures had little, if any, effect on room temperature properties. Rather significant irradiation strengthening occurred for tests at 400°C-650°C, though ductility was little affected, if any. Variations in grain size from 10 to 35 μ m had no significant effect. The specific dependence of tensile properties on fluence and irradiation temperature is not readily discernible but appears to be small for the range of values studied.

Horak and Wiffen^(24,57) irradiated V-20Ti alloy at 370°C-900°C to a fluence of 6×10^{22} n/cm² ($E_n > 0.1$ MeV). The results of tensile tests at 600°C-750°C are generally consistent with those shown in Figure 10. In a continuing phase of this work, V-20Ti tensile specimens have been injected with two levels of helium (90 and 260 appm) and are being irradiated at 500-800°C in EBR-II. The results of tests on these specimens will be of particular interest when they become available.

Carlander^(28,29) has creep-rupture tested V-20Ti at 650°C at a stress of 50 ksi following irradiation at 600°C $\pm$ 100°C to 2×10^{22} n/cm² ($E_n > 0.1$ MeV). Rupture occurred after 167 hours and an elongation of 13.3%. These results were very similar to those determined for unirradiated specimens of the same alloy. More extensive testing on V-20Ti at 650°C over an applied stress range of

Figure 9. Tensile properties of V-Ti-Nb, Mo, Cr alloys irradiated at 50-100°C.

Figure 10. Tensile properties of V-20Ti alloy irradiated at elevated temperatures.

25-50 ksi resulted in observed minimum creep rates in the range $5 \times 10^{-8} \text{ sec}^{-1}$ to $3 \times 10^{-6} \text{ sec}^{-1}$. These latter tests were on specimens irradiated at 580°C to fluences of $1\text{-}2.1 \times 10^{22}$ ($E_n > 0.1 \text{ MeV}$). The minimum creep rates agree very well with those found for unirradiated V-20Ti under the same test conditions.

1.4.3 V-Ti-Cr Alloys - Elevated Temperature Neutron Irradiations

The same trend noted for V-20Ti alloy is evident for V-15Ti-7.5Cr alloy; experimental data are shown in Figure 11. Thus, elevated temperature irradiation had no effect on room temperature properties but gave irradiation strengthening at $400^{\circ}\text{-}600^{\circ}\text{C}$ with little or no effect on ductility.

A 650°C -82.5 ksi creep rupture test on a V-15Ti-7.5Cr specimen irradiated to $5 \times 10^{21} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$) gave results essentially identical to those for unirradiated specimens tested at the same conditions.⁽²⁸⁾ Rupture life was 9.3 hours compared to 8.9 hours unirradiated, and the elongation at fracture was down from 15% to 10% for the irradiated material.

1.4.4 Other Alloys - Elevated Temperature Neutron Irradiations

Wiffen⁽²³⁾ irradiated V-10Cr alloy and VANSTAR-7 alloy (V-9Cr-3.3Fe-1.3Zr-0.054C) at 496° and 690°C to a fluence of $1.5 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$) and subsequently measured the tensile properties at temperatures in each case below the irradiation temperature. The results are shown in Figures 12 and 13. Significant irradiation strengthening was observed at elevated temperatures and, unlike the elevated temperature irradiation results described in Sections 1.4.2-1.4.3 for V-20Ti and V-15Ti-7.5Cr alloys, at room temperature also, at least for the VANSTAR-7 alloy. Moreover, the temperature for complete recovery of the irradiation damage evidently would be much higher than $650^{\circ}\text{-}750^{\circ}\text{C}$. Irradiation also gave a substantial decrease in ductility.

Böhm^(22b) tested a V-3Ti-1Si alloy which had been irradiated at 640°C to a fluence of $1 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$). The results are shown in Figure 14. Here too, significant irradiation strengthening and reduced ductility were observed at test temperatures up to 900°C . Also, a creep rupture test at 650°C on the irradiated alloy showed a decrease in minimum creep rate by a factor of 10, and a slight increase in rupture life.

Figure 11. Tensile properties of V-15Ti-7.5Cr alloy irradiated at elevated temperatures.

Figure 12. Tensile properties of V-10Cr alloy irradiated at elevated temperatures.

Figure 13. Tensile properties of VANSTAR-7 alloy irradiated at elevated temperatures.

Figure 14. Tensile properties of V-3Ti-1Si alloy irradiated at elevated temperature.

1.4.5 Effects of Helium on Elevated Temperature Mechanical Properties of Vanadium and Vanadium Alloys

The effects of helium on the elevated temperature ductility of vanadium, and the alloys V-3Ti-1Si and V-20Ti-10Nb, have been studied at Karlsruhe by 104 MeV alpha particle injections at 280°C followed by tensile testing at 750-950°C.^(20,30)

The injections were performed by using a beam degrader disc to permit uniform implantation in the 500 µm thick specimens. Unalloyed vanadium containing 10 appm helium displayed no tendency toward reduced ductility for temperatures up to 900-950°C. The V-3Ti-1Si alloy demonstrated identical behavior (900°C maximum test temperature) following injection of 1.5 appm helium. A decrease in ductility to about 2% total elongation was noted for the higher strength V-20Ti-10Nb alloy for specimens containing 2 appm helium when tested above about 750°C. The causes for this were not speculated upon by the authors.

Mattas, et al.,⁽²⁵⁾ have reported the results of investigations of the effects of 25 to 35 appm helium implanted by the "tritium trick" on the 600°-800°C tensile properties of sheet specimens of V-15Cr-5Ti alloys. These results were contrasted with those reported for an earlier study at Argonne which had evaluated the effects of 25 appm helium injected via 44 MeV cyclotron ion irradiations on the same alloy.⁽²⁶⁾ The tensile ductility of both the cyclotron-injected and tritium trick specimens was seen to decrease significantly for high temperature tests. This decrease was noted in the tritium trick specimens beginning at about 650°C, while for the ion bombarded specimens this decrease occurred only above about 700°C.

The effects of tritium trick-doping of cylindrical tensile specimens (0.11 inch diameter) to about 30 appm helium were determined by tensile tests at 700-800°C. These specimens had tensile ductilities approximately equivalent to those of the ion bombarded sheet specimens. The authors conclude this latter observation is a characteristic of the specimen geometry and that, for comparable conditions, the 0.11 inch diameter cylindrical specimens will consistently exhibit greater elongations than the 0.010 inch thick sheet specimens. No conclusions were reached regarding the observed differences in behavior between the ion bombarded and tritium decay sheet specimens although the previously observed tendency of helium introduced via the tritium trick to nucleate preferentially at grain boundaries⁽⁵⁸⁾ may be an important factor.

1.4.6 Discussion and Summary of Mechanical Property Data

There have been essentially no comprehensive or systematic evaluations of the effects of high fluence neutron irradiations on the mechanical properties of vanadium-base alloys. As the data just reviewed indicates, the information base consists of isolated or random investigations of alloys which were, at one time or another, of interest as cladding materials for breeder reactor applications. The closest thing to an exception to this general observation might be the evaluations performed at Karlsruhe by Böhm and his colleagues. Even there, however, much of the early results must be viewed as suspect since irradiations were usually performed at low temperatures and testing was often done at elevated temperatures where purely thermal rearrangements of microstructure could complicate interpretations. The technique used by Wiffen,⁽²³⁾ whereby elevated temperature testing is done at or below the irradiation temperature, is obviously preferred to the oft-used inverse practice.

The dependence of radiation strengthening on radiation temperature is hard to discern from the data because of this factor. While several authors mention a rather low dependence of T_{irr} , Wiffen found a marked dependence in VANSTAR-7, with nearly a 40% greater increase in the 400°C yield strength for 496°C ($0.36 T_m$) irradiation than for 690°C ($0.44 T_m$) irradiation.

For temperatures from about 550°C ($0.38 T_m$) and above, the data of Carlander, et al.,⁽¹⁷⁾ suggest a rather low dependence for irradiation strengthening on fluence variations in the range 0.38 to 5.4×10^{22} n/cm² ($E_n > 0.1$ MeV). This observation seems to be equally valid expressed in terms of both strength increases and tensile ductility changes.

In summary, the response of vanadium-base alloys to moderately high fluences of fast neutrons looks encouraging. The effects of radiation are primarily to increase the short-time mechanical strength. This appears to occur at very little cost in terms of compromising the ductility. Comments on the specific issue of ductility in irradiated vanadium-base alloys are provided in the following subsection.

1.4.7 Comments on Ductility of Irradiated Vanadium-Base Alloys

The results of the experimental investigations reviewed here do not indicate a significant loss of ductility occurs in vanadium or vanadium alloys due to neutron irradiations to temperatures of at least 750°C and for fluences to about $6 \times 10^{22} \text{ n/cm}^2$ ($E_n > 0.1 \text{ MeV}$). This conclusion disagrees somewhat with that reported by several investigators who have interpreted various parts of these data in terms of "severe embrittlement," "extreme loss of ductility," or "gross embrittlement." The highlighted data presented on Table 3 do not support those conclusions, nor were such interpretations possible based on a full review of the literature cited. The only caveat to this conclusion which needs to be noted is the lack of data on the combined influence of high levels of displacement damage and helium.

These data tend to agree with observations on the unirradiated mechanical properties of vanadium-base alloys. Very few observations of intergranular fracture have been reported in the literature. Only a few V-15Cr-5Ti specimens which contained 25-35 appm helium were found to develop intergranular cracking after testing at temperatures above 750°C. For the few tests available, the creep-rupture ductility appears to be essentially unaffected by irradiation to $\sim 10^{22} \text{ n/cm}^2$.

Whether these observations are purely artifacts of the specific test conditions and alloys investigated, and should not be inferred to apply to vanadium-base alloys, in general, is a moot point. They must, however, be considered encouraging. Reservations have to be maintained until important additional testing is performed on the effects of radiation on the mechanical properties under cyclic loads since these will be unavoidable in fusion reactor applications.

1.5 ION IRRADIATION-SIMULATION STUDIES IN VANADIUM AND VANADIUM-BASE ALLOYS

1.5.1 Introduction

Since about 1970, high-energy ion irradiations have been used to simulate the effects of high fluence, elevated temperature neutron damage in metals. The primary advantages offered by these techniques are associated with the high defect production rates which can be achieved. Displacement rates can reach as

high as 10^{-2} or 10^{-1} sec^{-1} , compared to neutron damage rates on the order of 10^{-7} sec^{-1} . Hence, experimental irradiation times can be reduced from years in current test reactors to a matter of a few hours.

The extremely high displacement rate carries a penalty, however, since it necessitates a shift in the "effective" irradiation temperature relative to neutron irradiations. This is because of the greater production rate of vacancies and self-interstitials; compensation for the "extra" supersaturation is achieved by going to a higher temperature where the thermal-equilibrium concentrations of point defects are higher. Irradiating at very high temperatures imposes a particularly difficult problem with a metal as reactive with the environment as vanadium. Another major limitation of ion bombardment techniques is the very short range in metals of most ions which have sufficient mass to be of interest as the damaging species. This factor essentially precludes the use of ion irradiations as a means for studying the effects of high levels of displacement damage on mechanical property specimens.

The choice of ion species for the irradiations can be an important factor since it remains as an "impurity" in the specimen. This has led to the general practice of using self-ions for these experiments; i.e. a vanadium-base alloy is bombarded with vanadium ions. There have been suggestions that even this technique is not satisfactory since many of these may locate in interstitial positions and thereby influence the biasing of the various sinks for point defects. This might alter the resulting void formation and growth in a nontrivial way compared to neutron irradiations.

Post-irradiation examinations are invariably carried out by electron microscopic characterizations of the microstructure. The procedure used for these examinations follows one of two sampling techniques. The differences between these techniques can be explained by reference to Figure 15, where the displacements per atom (dpa) are shown as a function of penetration distance into a vanadium specimen for both 7.5 MeV Ta^{+++} and 46 MeV Ni^{6+} incident ions. (This figure is reproduced from Brimhall's report of the effects of helium on void nucleation in ion bombarded vanadium⁽³²⁾.) The most commonly used technique consists of examining the peak dpa region. Since this is a rather sharp peak, the results depend significantly

Figure 15. Displacement damage vs. penetration for 7.5 MeV Ta⁺⁺⁺ and 46 MeV Ni⁶⁺ bombarded onto vanadium. (Vertical arrows indicate region from which TEM specimens were extracted for analysis in Ref. 32.)

on the accuracy with which the peak can be calculated, and then located during sectioning/polishing procedures. It suffers from the additional problems of rather sharp dpa concentrations within the foil being examined and, since the range of the incident ions is just beyond the displacement peak, may reflect compositional effects which can obscure interpretation efforts. It does offer the important advantage of maximum displacement events and, hence, simulates a greater neutron fluence. The other approach, indicated by the arrows on Figure 15, consists of sectioning and analyzing only the specimen volume within the relatively flat portions of the displacement-distance curves. While minimizing concerns due to "impurity" and dpa gradient effects, this method is restricted to looking at somewhat lower total displacement damage. Both methods have been used in ion irradiation studies on V and its alloys.

Ion irradiation experiments conducted to date on vanadium and vanadium-base alloys have yielded primarily two types of information, void swelling and precipitation reactions. A summary of these experiments is presented in Table 4; investigations have been primarily aimed at establishing the irradiation temperature dependence of void swelling although a few results have been published regarding the dose (damage) dependence as well. Where crystallographic notations are indicated for precipitation phenomena, these refer to the planes or directions of the vanadium matrix. These data are reviewed in the following subsections.

1.5.2 Unalloyed Vanadium-Ion Irradiations

Experiments which will be reviewed in this subsection include those which have looked at vanadium-interstitial alloys such as V-O, V-C or V-N, since these have generally been an extension of the efforts on unalloyed vanadium.

- Void Formation and Swelling - Santhanam and colleagues at ANL^(26,31) have reported on the effects of Ni-ion irradiations in the temperature range 650⁰-850⁰C on void formation in two grades of unalloyed vanadium. Specimens containing 145 wppm total interstitials (C, O, N) and others containing 1220 wppm interstitials (commercial purity) were pre-injected with 10 and 100 appm helium and irradiated at a displacement rate of 4×10^{-3} dpa sec⁻¹. The peak swelling for both materials was ~3% for a total dose of 60 dpa; this occurred at 700⁰C for the higher purity vanadium and at 750⁰C for the commercial purity material. This

Table 4. Summary of ion irradiation studies on vanadium and vanadium-base alloys.

Metal or Alloy	Irradiation Experimental Details						Starting Material ^(d)					Post-Irradiation Characterization		Reference
	Dose/Damage Information				T _{irrad.}	Environment						Peak Swelling	Precipitation, etc.	
	Ions	Ion ^(a) Energy	DPA ^(b)	appm He								ΔV at Temp.		
(HP) V	⁵⁸ Ni ⁺	3.25	60	10-100	650-850°C	Vacuum	120	15	10		1050°C-1 hr.	3% - 700°C	Carbides on void faces	26,31
(CP) V	⁵⁸ Ni ⁺	3.25	60	10-100	650-850	Vacuum	320	600	300		1050°C-1 hr.	~3 - 750	Carbides on void faces	26,31
V	Ni ⁶⁺	46	9	3	750	2 x 10 ⁻⁷					1100°C	0.5 - 750 (w/He)	None reported	32
V	Ta ³⁺	7.5	15-16	-	700-900	2 x 10 ⁻⁶					1100°C	0.7 - 800	None reported	32
(HP) V	⁵¹ V ⁺	3	2-34	-	700	2 x 10 ⁻⁷	120	15	10		1100°C-1 hr.	2 - 700	None reported	33
V-1Ti	⁵¹ V ⁺	3	2-54	-	700	2 x 10 ⁻⁷	150	200	30		1100°C-1 hr.	- -	TiO on {100}	33
(HP) V	⁵¹ V ⁺	3	1-55	-	650	5 x 10 ⁻⁸	120	15	15			0.4 - 650	Unident. Ppts. [{012}]?	34
(HP) V	Cu	18	1-5 ^(c)	-	600-750	~7 x 10 ⁻⁹	50	48	71	3	1050°C-1 hr.	1 - 700	VC(?) Along <110> _v	35
V	⁵¹ V ⁺	3	20	-	650-900	~10 ⁻⁸	125	140	40			2.5 - 720	{012} at T < 650°C	36
V-1 a/o O	⁵¹ V ⁺	3	20	-	550-900	~10 ⁻⁸						~1.0 - 650	{012} at T < 650°C	36
V-10Ti	⁵¹ V ⁺	2.7	5-55	-	650	~5 x 10 ⁻⁸					1300°C-4 hr.	- -	TiO on {100}	37
V-10Ti	⁵¹ V ⁺	2.7	2-60	-	650	~5 x 10 ⁻⁸					1300°C-4 hr.	- -	TiO on {100}	38
V	⁵¹ V ⁺	3	20	-	650-880	~10 ⁻⁸	125	140	40			2.5 - 720	{012} at T < 650°C	39
V-0.1 a/o O	⁵¹ V ⁺	3	20	-	650-880	~10 ⁻⁸						~1 - 760	{012}; {013}	39
V-0.4 a/o C	⁵¹ V ⁺	3	20	-	650-880	~10 ⁻⁸						~1 - 700	{012}; V ₂ C; {013}	39
V-1 a/o O	⁵¹ V ⁺	3	20	-	650-880	~10 ⁻⁸						~1 - 650	{012}	39
V-1 a/o N	⁵¹ V ⁺	3	20	-	650-880	~10 ⁻⁸						<0.4 - 700	No precipitation	39

(a) Ion energy in MeV

(b) DPA calcs. using E_d = 40 eV unless noted

(c) E_d = 26 eV used

(d) Interstitial analyses in wt. ppm

difference was interpreted in terms of an increased concentration of smaller voids in the commercial vanadium due to enhanced nucleation. This merely delays the swelling phenomenon and is consistent with observations in neutron irradiated vanadium.

Voids were cubic in shape with cube perfection increasing with an increase in irradiation temperature. There was no evidence of void ordering. Precipitates were often associated with the voids in these experiments; their appearance coincides with the peak swelling temperature.

Effects of increased helium content from 10 appm to 100 appm were observed only at 750°C where considerably lower void swelling was observed in the vanadium with higher helium content. The authors interpreted this to be due to the very small helium bubbles serving as a very strong sink for point defects, thereby lowering the vacancy supersaturation and resultant swelling.

In a later experiment, Santhanam, et al.,⁽³³⁾ irradiated high purity vanadium with self ions at the peak swelling temperature observed for the Ni ion irradiations (700°C). The results agreed with the swelling observed in the Ni irradiations for equivalent damage levels. There was no evidence, however, of the precipitation-void associations observed in the earlier work. This may indicate the implanted Ni ions are in some way responsible for the precipitation effects. Voids were again cubic in shape and were observed after doses as low as 2.4 dpa.

Agarwal and Taylor⁽³⁴⁾ reported on continued studies at ANL on high purity vanadium irradiated with 3 MeV vanadium self ions at 650°C. The dose dependence of void swelling was studied for the range 1-55 dpa. Maximum swelling (~0.4%) occurred at 13 dpa and decreased for higher doses. This decrease was found to coincide with the appearance of precipitation along the {012} planes of the matrix. The decrease in swelling is suggested to be the result of a reversal of the bias for point defects due to the precipitation; i.e., an excess of vacancies required for the precipitation process could result in the availability of excess interstitials which could shrink the voids.

Brimhall⁽³²⁾ reported on the effects of damage rate and pre-injected helium on void formation in ion bombarded vanadium. The damage rate was varied from $1.2-8 \times 10^{-4}$ dpa/sec. using 46 MeV Ni^{6+} ions to $\sim 10^{-2}$ dpa/sec. with 7.5 MeV Ta^{3+} ions. All of the nickel-ion irradiations were performed at 750°C , with and without pre-injected helium (3 appm); the Ta-ion irradiations were performed over the temperature range $700^{\circ}-900^{\circ}\text{C}$. Comparing the effects of dose rate, at approximately equivalent damage levels (15-16 dpa), indicates very little difference in the void parameters (void size, void concentration, and swelling) for irradiations at $700^{\circ}-800^{\circ}\text{C}$.

Injection with 3 appm helium prior to nickel ion irradiations at 750°C led to increased void formation relative to uninjected vanadium. Quantitative comparisons were not reported.

Weber, et al.,⁽³⁵⁾ irradiated high purity vanadium with 18 MeV Cu ions in the temperature range $600^{\circ}-750^{\circ}\text{C}$. Specimen sectioning and examination was done only in the low damage region (1-5 dpa) to avoid concerns over damage gradients and copper impurity effects. Maximum swelling was approximately 1% and occurred at 700°C . Voids were truncated cubes and were observed for irradiations at all conditions utilized in this study. Despite what appears to be satisfactory vacuum conditions during irradiation (total pressures $< 10^{-8}$ torr; hydrocarbon species partial pressures $\sim 3 \times 10^{-10}$ torr) extensive vanadium carbide precipitation was observed.

The void swelling in unalloyed vanadium and vanadium containing from 1 to 4 at.% oxygen were compared for 3 MeV V^{+} irradiations at $550^{\circ}-900^{\circ}\text{C}$.⁽³⁶⁾ Dose levels of 3, 20 and 35 dpa were achieved with a dose rate of 5.5×10^{-3} dpa. Oxygen additions effected significant reductions in void swelling at all damage levels and caused a slight downward shift in peak swelling temperature (from about 720°C in unalloyed vanadium to 650°C for V-1 a/o O). Voids were not seen in the V-4 a/o O alloy up to the maximum damage level.

In a more extensive survey of the effects of interstitial solutes on void development in self-ion irradiated vanadium,⁽³⁹⁾ irradiations in the temperature range $650^{\circ}-880^{\circ}\text{C}$ indicated nitrogen to be even more effective than oxygen in suppressing

void swelling. A V-1 a/o N alloy exhibited a six-fold reduction in void swelling compared to unalloyed vanadium. Reduction in the void volume fractions by a factor of two to three were found for V-0.1 a/o C, V-0.4 a/o C and V-1 a/o O alloys.

● Precipitation Phenomena - Precipitation has been observed following heavy ion irradiation of both pure (unalloyed) vanadium and vanadium-interstitial solute alloys. The most commonly reported precipitate has a platelet-like morphology aligned on {012} matrix planes with their long axes along $\langle 100 \rangle$ directions. This {012} precipitate has been reported for unalloyed vanadium,^(34,36,39) and in vanadium-oxygen, and vanadium-carbon alloys.^(36,39) Wiffen and Stiegler⁽¹²⁾ and Bressers and Cambini⁽²¹⁾ have also reported finding the {012} precipitate in neutron-irradiated vanadium. Discrete precipitates are not formed; only streaking is observed on the SAD patterns, indicating very thin zones of at most a few atom layers thickness. In both the ion and reactor irradiations, the only observations of {012} precipitation above 650°C have been for ion irradiated V-C alloys.⁽³⁹⁾ Thus, although the evidence is not conclusive, it seems likely that a carbon clustering or pre-precipitation reaction may be responsible. This is also consistent with the fact that the already low carbon solubility decreases to insignificant levels below about 600°C (see Figure 7 in Appendix A).

Vanadium-carbon alloys containing 0.1 a/o C and 0.4 a/o C also develop thin, disc-shaped precipitates which are visible by displacement fringe contrast.⁽³⁹⁾ These appear to have a {013} habit relationship with the matrix and are believed to be a metastable carbide which forms on cooling from the irradiation temperature. They demonstrate a preference for heterogeneous nucleation along dislocations.

Vanadium carbide (V_2C) has been observed to precipitate in V-0.4 a/o C⁽³⁹⁾ and in unalloyed vanadium⁽³⁵⁾ during ion irradiations. In the V-0.4 a/o C alloy, V_2C is the equilibrium precipitate and is not an artifact of the irradiation. In the case where it was seen in unalloyed vanadium it clearly was the result of contamination occurring during annealing and/or irradiation.

An interesting precipitation/segregation reaction was reported by Santhanam, et al.,^(26,31) where very fine (100 Å) precipitates or impurity clusters were

found to be associated with the voids formed in both high purity and commercial purity vanadium irradiated with nickel ions at temperatures of 700°C and higher. A possible mechanism for such an impurity solute redistribution during irradiation was suggested by Okamoto, et al.⁽⁵⁹⁾ This mechanism explained the impurity segregation to void surfaces as occurring due to the migration of vacancy-solute clusters to the voids during the very high dose rate irradiations characteristic of ion experiments. These effects have not been reported in neutron irradiation experiments.

1.5.3 Vanadium-Base Alloys - Ion Irradiations

Ion irradiation experiments have been performed at the Argonne National Laboratory on the V-1Ti⁽³³⁾ and V-10Ti^(37,38) alloys. Irradiation of V-1Ti with 3 MeV V⁺ ions at 700°C resulted in essentially no void formation (at 54 dpa a few isolated voids were observed). Precipitation of TiO on {100} planes of the matrix dominated the microstructure. These precipitates are reported⁽⁵¹⁾ to be the equilibrium precipitate and are not the product of irradiation.

V-10Ti specimens were irradiated at 650°C with 2.7 MeV V⁺ ions to damage levels up to 60 dpa.^(37,38) No voids were observed; again, the microstructure was dominated by TiO precipitation. The orientation relationship was the same as that observed in unirradiated V-Ti alloys; namely,

$$(001)_V \parallel (001)_{TiO}$$

$$[110]_V \parallel [010]_{TiO}$$

Hence, the precipitate is semicoherent, at least during its early stages.

1.5.4 Summary of Ion Irradiation Data

Void swelling results from energetic ion irradiation experiments are generally consistent with those of neutron (reactor) irradiations. The swelling of unalloyed vanadium irradiated with 3.25 MeV nickel ions to 60 dpa is shown in Figure 16a. These curves are plotted from the data of Santhanam, et al.,^(26,31) and typify the reported swelling behavior. The high purity vanadium (HPV) had about 145 wppm total interstitials while the commercial purity material (CPV) contained 1220 wppm. Comparison with the swelling shown in Figure 5b for neutron irradiations indicates

(a)

(b)

Figure 16. The average void size and void concentration as a function of ion irradiation temperature for unalloyed vanadium.

a slightly higher void volume fraction for ion irradiations; this probably reflects the higher damage level of the latter work. Figure 16b shows the trends in void concentration as a function of ion irradiation temperature. The upper range of values are for the 60 dpa Ni ion irradiations of HPV and CPV reported in Figure 16a. The lower range indicated is for unalloyed vanadium irradiated to a damage level of about 20 dpa with 3 MeV self-ions.⁽³⁹⁾ The major cause for the observed shift is believed to be the differences in damage level. The differences in slope may be due to the fact the material irradiated to 60 dpa had been preinjected with helium prior to irradiation. Peak swelling in unalloyed vanadium occurs at about 700°C compared to about 550°C-600°C for neutron-irradiated material; maximum swelling values are about 3%. The effects of helium and impurity content, for very limited data, also appear consistent.

Experiments on V-Ti alloys are in agreement with the neutron irradiation studies in that the addition of titanium essentially eliminates void formation. Precipitation phenomena in both unalloyed vanadium and vanadium alloys are consistent with those observed for neutron irradiated material although the higher temperatures and dynamic atmospheres can lead to special contamination concerns.

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2.0 MECHANICAL PROPERTIES OF VANADIUM AND VANADIUM-BASE ALLOYS

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2.1 INTRODUCTION

The mechanical properties of commercially pure vanadium were studied extensively throughout the 1950's and 1960's.⁽¹⁻³⁸⁾ It was established early that vanadium behaves like other bcc metals and in particular its mechanical properties are markedly influenced by interstitial impurities. As purer metal became available (first calcium reduced, then electrorefined, and iodide vanadium) the specific effects of various interstitial elements were determined. The excellent work on

interstitial effects done at the Bureau of Mines at Reno⁽¹³⁻²²⁾ and at the Ames Laboratory at Iowa State University⁽²³⁻³⁴⁾ are particularly worthy of note.

Vanadium-base alloys were first surveyed in the early 1950's at the Armour Research Foundation of the Illinois Institute of Technology through work sponsored by the Materials Laboratory of the Wright Air Development Center, Ohio. Rostoker, Yamamoto and Riley^(3,4) summarized the early work in 1955. Alloy development work at Armour continued to the late 1950's through support by Argonne National Laboratory. In cooperation with simultaneous work done at ANL, vanadium-base alloys were developed for fuel element cladding in breeder reactors (sodium environment, 650-750°C temperatures). This work was summarized by Smith and Van Thyne in 1959.⁽⁴⁶⁾ Still a third study was conducted at Armour in the late 1950's and early 1960's through support of the Department of the Navy, Bureau of Aeronautics, and Bureau of Naval Weapons. Emphasis in this latter work was on short time strength at temperatures of 650-1300°C, and included attempts to develop dispersion hardened alloys. This work was summarized by Rajala and Van Thyne⁽⁴⁷⁾ and Holtz and Van Thyne.^(48,49) The books by Rostoker⁽⁵⁰⁾ (1958) and Tietz and Wilson⁽⁵¹⁾ (1965) contain some of the results of the above studies.

Two major vanadium alloy development programs were conducted in the mid-to-late 1960's; one was done at Westinghouse, Advanced Reactors Division, under AEC sponsorship, and the other was done at the Nuclear Research Center, Karlsruhe, Germany. Both programs dealt with vanadium alloys for breeder reactor fuel element cladding applications. The work at Westinghouse was summarized by Pollack, et al.⁽⁵²⁾ and by Whitlow, et al.,⁽⁵³⁾ while that at Karlsruhe has been described by Böhm, Mir, Kramer and Schirra.⁽⁵⁴⁻⁶⁰⁾

Today, there is virtually no experimental work in progress on vanadium-base alloys. There is, however, current interest in vanadium alloys for structural components in fusion reactors, particularly the so-called "first wall." The purpose of the present review is to compile, summarize, and interpret the existing mechanical property data on vanadium and vanadium-base alloys as an aid to the further assessment of vanadium alloys for fusion reactor first wall applications. No consideration is given to fabricability, corrosion resistance, or radiation effects; these issues are treated separately in other portions of this document.

2.2 THE ALLOYING ELEMENTS AND BACKGROUND DATA

The various alloying elements which have been studied are shown in Figure 1; they fall into a few common groups as depicted.

- Interstitials - The interstitial elements C, O, N and H are always present as residual impurities. They have a pronounced effect on mechanical properties. Hydrogen is never desirable and fortunately can be reduced to innocuous levels. The others, particularly C and N, may be added intentionally to form precipitates. Boron is not a significant impurity but has been studied and is included in the interstitial group.
- Reactive Metals - The reactive metals, particularly Zr and Hf, may be added in small amounts to react with interstitials to form precipitates. They may also be added in larger amounts as solid solution hardeners, particularly Ti.
- Solid Solution Hardeners - The Group V and Group VI refractory metals (Nb, Ta and Cr, Mo and W) along with Fe and Ni have been studied as solid solution strengtheners.
- Yttrium and Rare Earths - These elements are strong oxygen scavengers and have been studied primarily to assess their effectiveness in removing oxygen from vanadium.
- Miscellaneous - Significant amounts of Al or Si may be retained as residuals in those grades of vanadium where they are used in the reduction process. Evidently it was for this reason that their effects on mechanical properties were evaluated. Numerous other elements are present as trace impurities but thus far none have been identified as detrimental.

2.2.1 Phase Diagrams and Solubilities

The solubility of alloying elements in vanadium is important in alloy development work. Phase diagrams and solubility data are collected in Appendix A.

[illegible]

Interstitials H,B,C,N,O

Substitutional Solutes (Solid Solution Hardeners)

Reactive Metals. Ti, Zr, Hf

Others Fe, Ni

Yttrium and Rare Earths . . . Y,La,Ce,Pr,Nd,Sm

Miscellaneous Al, Si

Figure 1. The alloying elements in vanadium-base alloys. Mechanical property studies have been conducted on vanadium alloyed with the elements indicated.

2.2.2 Diffusion Data

Solute diffusivity is important in the interpretation of mechanical properties; relevant data are collected in Appendix B.

2.2.3 Elastic Properties

Since elastic properties are important in structural analysis and design, the existing data on vanadium and vanadium-base alloys are collected in Appendix C.

2.2.4 Microstructures

Solid solution hardening, precipitation hardening, and to a lesser extent strain hardening, mechanisms have all been used in developing vanadium-base alloys. However, detailed metallographic studies in support of the relative contribution of each mechanism is generally lacking. Most of the substitutional solutes have large solubility in vanadium, many forming a continuous series solid solution, and in the composition range studied should be, and indeed would be, single phase in the pure vanadium-substitutional solute alloys. Yet, many of the nominal solid solution alloys contain precipitates due to the residual interstitials present. At most, the information usually available is whether the alloy is recrystallized, the grain size, and whether precipitates were observed by optical microscopy. Strengthening attributed to solid solution hardening may, unknowingly, contain a contribution due to precipitation. Conversely, strengthening attributed to precipitation, in alloys where a reactive metal such as Zr and interstitials such as C are intentionally added, may actually contain little if any contribution due to second phase precipitates, or the contribution may be indirect, as opposed to direct dislocation-precipitate interactions. Thus, little microstructural information is presented because there is little factual information available.

2.2.5 Experimental Procedures

Some differences in the results of various investigators are inevitable due to differences in experimental procedures--namely, specimen geometry, strain rate, environment, residual impurities (particularly interstitials) and mechanical/thermal processing and associated microstructures. Repeated inclusion of all these details would unduly complicate data presentation; recourse should be made to the original papers.

Mechanical property tests have been run in air, inert gases and vacuum environments. Tensile properties are least sensitive to environment. Creep properties are very sensitive to environment and a separate section is devoted to environmental effects. In tensile tests, variations in strain rate by one or two orders of magnitude are common. In most cases, a factor of ten increase in strain rate will increase strength by only a few per cent (see Section 2.3.11). Similarly, rather large variations in grain size have a relatively small effect on tensile properties (see Section 2.3.12).

2.3 VANADIUM AND INTERSTITIAL EFFECTS

2.3.1 Cold Work, Recovery, Recrystallization and Grain Growth

Cold work, recovery, recrystallization and grain growth behavior of vanadium is shown in Figures 2 and 3. It is sometimes stated that vanadium strain hardens very little, or that rapid strain hardening occurs in the first 5, 10 or 15% cold work and beyond that little further hardening occurs. Curves A-D in Figure 2b support this view. Other data showing continued strain hardening to large deformations is shown in Figure 2a. Annealing behavior is shown in Figure 3. Considerable recovery (softening) occurs prior to recrystallization, Figure 3a. This is typical behavior of Group V refractory metals; Group VI metals, by contrast, typically show little recovery prior to recrystallization. In electrorefined vanadium recovery may begin at temperatures as low as 400°C.⁽¹³⁾ No recrystallization (nucleation and growth) occurs in electrorefined vanadium cold worked less than about 35%; only recovery occurs followed by grain growth above about 900°C. For larger cold reductions normal recrystallization occurs. This explains the wording in the lower part of Figure 2a. Observed recrystallization temperatures are listed in Figure 3c and indicated in Figure 3a. Loria, Ludemann and Rowe⁽¹⁵⁾ found an activation energy of 95 kcal/mole for recrystallization and 75 kcal/mole for grain growth. Though not well defined, impurities, including second phases, are no doubt responsible for the observed variations in recovery, recrystallization and grain growth behavior. O'Brien and Rowe⁽¹⁶⁾ found that yttrium and rare earth additions to vanadium lowered the recrystallization temperature by 50° to 150°C.

(a)

(b)

(c)

Figure 2. Work hardening behavior of vanadium at room temperature.

(c)

Ref.	Recrystallization T, °C		
	Start	Complete	
3	650-800		
1	650-700	<800	
5	750	850-900	
13	700-800	900	No Rx for < 35% CW GG starts at 900
39	860		
15	750-850	950-1000	

Figure 3. Recovery, recrystallization, and grain growth behavior of vanadium.

2.3.2 Tensile Properties of Various Commercial Grades of Vanadium

As illustrated in Figure 4, the stress-strain behavior of vanadium is similar to that of other bcc metals and is characterized by a strong temperature dependence of strength, ductile-brittle transition behavior and mechanical twinning at low temperatures; yield points and strain aging behavior near room temperature; and dynamic strain aging with peaks in tensile and yield strengths around 300° to 500°C. Tensile properties of calcium reduced (least pure), electrorefined and iodide (purest) vanadium are shown as a function of temperature in Figures 5-8. The sources of this data, interstitial analyses and annealing treatments are listed in Table 1.

The large lot-to-lot variation in tensile properties is due primarily to variations in interstitial contents; more specifically, the interstitials in solid solution. "Pure" vanadium would have low strength (lower than the lowest curves in Figures 5 and 6). It would still show a strong temperature dependence below room temperature but no peaks near 400°C and would be quite ductile at low temperatures, probably even at absolute zero except for possible limitations imposed by twinning or plastic instability.

2.3.3 Effect of Carbon

Carbon has relatively low solubility in vanadium. Most lots of vanadium contain carbon in excess of the solubility limit and hence V_2C precipitates. The effect of carbon on tensile properties is therefore dependent on both composition and heat treatment. The effect of carbon on low temperature tensile properties of annealed electrorefined vanadium is shown in Figure 9. The initial increase in strength at low carbon levels is due to carbon in solid solution; at higher carbon levels carbides form, strength decreases and then remains constant with further increase in carbon content. Evidently, the carbide dispersion in this case was not effective as a strengthener and the decrease in strength beyond the peak must reflect a decrease in carbon or other interstitials in solid solution.

The effect of heat treatment on room temperature properties is shown in Figure 10. For the annealed condition (Mathews and Price⁽²⁰⁾) the purest vanadium was single phase; the other four alloys contained carbides as indicated in the lower part of the UTS plot. These four alloys had the same lattice parameter, which was

Figure 4. Schematic of vanadium stress-strain curves and deformation and fracture behavior as a function of temperature.

TABLE 1

SOURCES AND INTERSTITIAL ANALYSES OF DATA SHOWN IN FIGURES 5-8

		PPM				Reference	Anneal
		H	C	O	N		
◇	Calcium	<10 16	940 380	1100 700	600 360	(12) Farrell	900°C/1 hr
□	Calcium	43	470	700	520	(9) Clough & Pavlovic	800°C
▽	Calcium	4	900.	570	700	(7) Pugh	1000°C/1 hr 1600°C
△	Calcium	60	800	~ 200	200	(23) Loomis & Carlson	900°C/5 hr
○	Calcium	-- --	395 930	405 1150	80-200 170-560	(17) Mathews, Keith & Loria	950°C/2 hr
○	Calcium	68	620	850	1100	(2) Brown	Hot Rolled
●	Electrorefined	--	95	345	35	(21) Iverson, Mathews & Winston	900°C/1 hr
■	Electrorefined	--	95 80	345 680	35 95	(17,18) Mathews, Keith & Loria	950°C/2 hr
◆	Electrorefined + EBZR Single Crystals	<10	20	70	< 10	(42) Mitchell, Fields & Smialek	($\sigma = 2\tau$)
◇	Iodide	10	240	~ 100	50	(23) Loomis & Carlson	1100°C/48 hr
□	Iodide	10	150	150	< 5	(24) Eustice & Carlson	1120°C/12 hr
△	Iodide	< 1	150	40	50	(28) Thompson & Carlson	1000°C/1 hr
▽	Iodide	< 1	150	47	< 5	(25) Bradford & Carlson	900°C/4 hr

Figure 5. Ultimate tensile strength of various grades of commercially pure vanadium as a function of temperature. Sources listed in Table 1.

Figure 6. Yield strength of various grades of commercially pure vanadium as a function of temperature. Sources listed in Table 1.

Figure 7. Tensile elongation of various grades of commercially pure vanadium as a function of temperature. Sources listed in Table 1.

Figure 8. Tensile reduction in area of various commercial grades of vanadium as a function of temperature. Sources listed in Table 1.

Figure 9. Effect of carbon on tensile properties of electrorefined vanadium at low temperatures. (20-120 ppm N, 600-1300 ppm O: CW 70%, annealed 950°C/2 hr) Mathews, Keith & Loria (Ref. 17)

Electrorefined V

Mathews & Rowe (Ref. 19)
200 ppm N, 470 ppm O
▲ Annealed 1000°C/1 hr

Mathews & Price (Ref. 20)
10 ppm N, 200 ppm O
● Annealed 900°C/2 hr
■ Solution Treated 1200°C/15 min WQ

Iverson, Mathews and Winston (Ref. 21)
○ □ 20 ppm N, 450 ppm O

Figure 10. Effect of carbon on room temperature tensile properties of electrorefined vanadium for various heat treatments.

smaller than that of the purest vanadium. Hence they contained less carbon in solid solution than the purest vanadium and, therefore, all of the increase in strength with increase in carbon content was due to the carbide dispersion. The solution treated material behaved similarly, though higher carbon contents were retained in solid solution at low carbon levels. Aging the solution treated material produced an effective carbide dispersion but solution treating and aging was effective only at the low carbon level where all the carbon could be retained in solid solution after solution treating.

Tensile properties as a function of temperature for various carbon levels are shown in Figure 11. These results show little effect due to carbon; actually, these data are dominated by the residual oxygen level. The overall magnitude of the strength peak near 400°C , for example, is due to oxygen, not carbon.

In summary, carbon in solid solution is a potent strengthener at low temperatures, but very little carbon can be retained in solid solution (low solubility). Though less potent, carbides are also effective strengtheners at low temperatures provided the proper dispersion is developed, and this requires control of both carbon content and heat treatment. Little is known about the effectiveness of carbides at high temperatures.

2.3.4 Effect of Boron and Boron Plus Carbon

The effects of boron on grain size refinement and on tensile properties were studied by Iverson, Mathews and Winston⁽²¹⁾ and by Keith and Iverson.⁽²²⁾ The solubility of boron in vanadium is low, less than 0.005 wt.% at 950°C , and all the alloys contained second phases. Boron was quite effective in grain refinement, particularly at the higher annealing temperatures of 1000°C - 1100°C , and the separate effects of boron and carbon were additive.

Boron increases strength and decreases ductility, Figures 12 and 13. The effect is relatively small at room temperature and above but is substantial at very low temperatures. Boron does not produce a dynamic strain aging peak (such a peak, if present, should occur around 100°C) nor is it responsive to solution treatment and aging (the solubility is too low).

Figure 11. Effect of carbon on tensile properties of electrorefined vanadium as a function of temperature.

Figure 12. Effect of boron on tensile properties of electrorefined vanadium as a function of temperature. (60-95 ppm C; 15-35 ppm N; 340-500 ppm O: CW 70%, annealed 900°C/1 hr). Iverson, Mathews & Winston (Ref. 21).

Figure 13. Effect of boron on tensile properties of electrorefined vanadium as a function of temperature.

Alloys with boron and carbon respond to heat treatment as shown in Figure 14. The heat treatment response is due to carbon and is similar to that noted in Figure 10. (The ST + Aged data in Figure 10 is the same data given in Figure 14 for zero boron content.)

2.3.5 Effect of Oxygen

Oxygen has a very high solubility in vanadium and is a potent solid solution strengthener; experimental data are shown in Figure 15. Dynamic strain aging dominates behavior at temperatures from about 150° to 500°C. Behavior in this region is characterized by serrated stress-strain curves, broad peaks in strength, minima in ductility, maxima in work hardening exponent and minimal (even negative) strain rate sensitivity. The UTS peaks occur at temperatures between 250°-400°C. Using the yield point return method, Bradford and Carlson⁽²⁵⁾ determined an activation energy of 27.7 kcal/mole. Similarly, Thompson and Carlson⁽²⁷⁾ obtained 27.1 kcal/mole and Edington, Lindley and Smallman⁽³⁷⁾ obtained 25.4 kcal/mole for the activation energy of the diffusing species giving rise to UTS peaks in vanadium of high oxygen content. This activation energy is close to that for diffusion of oxygen and carbon. The observed strain aging behavior is therefore due to either or both oxygen and carbon, but most likely oxygen is the major contributor.

2.3.6 Effect of Nitrogen

Nitrogen, like oxygen, has a high solubility in vanadium and affects mechanical properties in a similar way; experimental data are shown in Figure 16. The intermediate temperature UTS peaks occur at 350°-400°C. Thompson and Carlson^(27,28) determined activation energies of 36.2 kcal/mole by yield point return and 37.3 kcal/mole by strain rate shifts in the temperature of the UTS peak. This identified nitrogen as the diffusing species responsible for the strain aging.

2.3.7 Comparison of Solid Solution Strengthening Due to C, N and O

The relative solid solution strengthening effect of C, N and O has long been of interest. Room temperature results for N and O are shown in Figure 17; they are equally potent. Note that the yield stress for zero % solute (pure V) is about 3 ksi, versus up to 60 ksi for high interstitial content commercial vanadium

Figure 14. Effect of boron and boron plus carbon on room temperature tensile properties of electrorefined vanadium in annealed, solution treated and ST plus aged conditions.

Figure 15. Effect of oxygen on tensile properties of vanadium.

Figure 16. Effect of nitrogen on tensile properties of vanadium.

Figure 17. Solid solution strengthening due to oxygen and nitrogen.

(Figure 6). The data base for C is limited because of the low C solubility but C too is a potent solid solution hardener. Taken literally, the results in Figure 9 indicate that C is about half as potent as N or O. Allowing for the fact that the strain aging peak for N occurs at a higher temperature than for O, the potency of N and O is also about the same at elevated temperatures. Though strength falls to low levels, interstitial strengthening is significant to quite high temperatures, well beyond the strain aging peaks.

2.3.8 Effect of Hydrogen

The effect of hydrogen on the mechanical properties of vanadium has been studied by Roberts and Rogers,⁽⁶⁾ Magnusson and Baldwin,⁽⁸⁾ Eustice and Carlson,⁽²⁴⁾ Van Fossen, Scott and Carlson,⁽³⁰⁾ Owen, Sherman and Scott,⁽³¹⁾ Sherman, Owen and Scott,⁽³²⁾ Owen and Scott⁽³³⁾ and Chen and Arsenault.⁽⁴⁴⁾ Results typical of the effect of hydrogen are shown in Figure 18. Hydrogen induces a pronounced ductile to brittle transition at temperatures from about room temperature down to about -100°C depending on hydrogen content and strain rate; the DBTT increases with increase in hydrogen content (as little as 6 ppm is effective) but decreases with increase in strain rate (the opposite of the usual effect of strain rate on DBTT). The embrittlement persists only over a limited temperature range; below about -75° or -100°C the ductility increases with decreasing temperature and may approach that of zero hydrogen content material. Over the temperature range of minimum ductility the yield strength is increased as indicated in Figure 18. Owen and Scott⁽³³⁾ give a fine review of mechanistic aspects of the hydrogen effect.

The effect of hydrogen on fatigue properties is discussed in Section 2.3.14.

2.3.9 Ductility

- Elevated Temperatures - The tensile ductility of vanadium at elevated temperatures, particularly from room temperature to about 600°C , may be quite high or rather low. Aside from differences due to specimen geometry and testing procedures, and even grain size variations, interstitial content appears to be the important factor. Low interstitial vanadium is quite ductile (see data by Thompson and Carlson^(27,28) in Figure 16 for iodide vanadium). The curves showing low ductility (5-10% elongation) in Figures 11, 13, 15-16 are all for vanadium with high oxygen content (800-1400 ppm). The variations noted in Figure 7 for different lots of

Figure 18. Effect of hydrogen on tensile properties of iodide vanadium. (Eustice and Carlson, Ref. 24)

calcium reduced vanadium probably reflect interstitial effects. The effect of carbon, boron and nitrogen seems to be small, or at least from the available data their effect is masked by that due to oxygen. Ductility minima are observed in the strain aging region (~ 200 - 500°C); the cause of the ductility minimum observed by Pugh⁽⁷⁾ at $\sim 850^{\circ}\text{C}$ (Figure 7) is not known. Only transgranular modes of fracture have been reported in elevated temperature tests.

- Low Temperatures - With decreasing temperature, ductility may decrease gradually while maintaining a ductile mode of fracture or it may decrease sharply to near zero ductility over a narrow temperature range (ductile to brittle transition) with an accompanying change in mode of fracture from ductile, dimple rupture to cleavage. Experimental data from tensile, bend and impact tests are shown in Figure 19.

Tensile Tests. Iodide or electrefined vanadium do not show a tensile DBTT down to -196°C . The apparent DBTT of -110°C reported by Loomis and Carlson⁽²³⁾ and shown in Figures 7 and 8 was probably due to hydrogen. For calcium reduced vanadium the DBTT is below about -150°C . Irrespective of the source of the vanadium the DBTT is determined by the interstitial content; carbon has little or no effect, hydrogen has a potent effect over a narrow temperature range as previously discussed, and nitrogen and oxygen have a strong effect though rather large contents would be required to raise the DBTT to room temperature. The separate effects of interstitials are presumably additive.

Bend Tests. Two widely different sets of results are shown in Figure 19b. Thompson and Carlson⁽²⁹⁾ and Bradford and Carlson⁽²⁶⁾ reported that more than 1500 ppm oxygen or 2000 ppm nitrogen was necessary to induce a DBT at -196°C . Carbon up to 5700 ppm did not cause cleavage fracture though more than 3400 ppm caused intergranular cracking along semicontinuous carbide networks at -196°C . The results by Loomis and Carlson⁽²³⁾ show a similar composition dependence but at a much higher DBTT, or, equivalently, at a much lower interstitial level. In noting this difference, Bradford and Carlson merely stated that the two sets of results would agree if the alloys of Loomis and Carlson contained an additional 1500-2000 ppm oxygen, implying that the solute levels given by Loomis and Carlson are increments added to the base metal and not the total alloy content.

Figure 19. Ductile brittle transition temperature of vanadium as a function of interstitial content for (a) tensile, (b) bend and (c) impact tests.

Impact Tests. The impact test DBTT of calcium reduced vanadium may be above room temperature, Figure 19c. No impact data were found for high purity vanadium.

2.3.10 Cold Worked Vanadium

Tensile properties of cold worked calcium reduced vanadium are shown in Figure 20 as a function of temperature. One of the two sets of cold worked data shows a tensile strength strain aging peak at 400°C and both data sets show considerable recovery (softening) prior to recrystallization, which should occur at around 900°C-1100°C. The two data sets show markedly different ductility; the reason for this is not known.

2.3.11 Strain Hardening Exponent and Strain Rate Sensitivity

The strain hardening exponent and strain rate sensitivity exponent are shown in Figure 21 as a function of temperature and interstitial content. The strain hardening exponent decreases with increasing interstitial content and shows a peak at the temperature where the UTS shows a peak, i.e., where dynamic strain aging is most pronounced. The strain rate sensitivity exponent is essentially independent of interstitial content, at least down to the lowest levels studied; shows a minima in the strain aging range; and is even negative over a portion of this temperature range. The data by Pugh⁽⁷⁾ also shows a minimum at about 825°C, which corresponds to the higher temperature ductility minimum shown in Figure 7.

2.3.12 Grain Size Effects

The effect of grain size on yield stress and associated Petch parameters for vanadium have been studied by Lindley and Smallman,^(35,36) Edington, Lindley and Smallman⁽³⁷⁾ and Loria, Keith and Rowe.⁽¹⁸⁾ Some experimental results are shown in Figure 22. According to custom, the locking term k_y measures the extent of dislocation pinning by interstitial impurities and is proportional to the stress needed to unlock a dislocation from its impurity atmosphere, while the friction stress σ_i gives the sum of the athermal and thermal components of the stress required to move a free, unpinned dislocation across a grain. For vanadium, the grain size method and extrapolation method give the same values for these para-

Figure 20. Effect of cold working on tensile properties of vanadium. Data for recrystallized (Rx) condition from Figures 5 and 6.

$$\sigma = K\epsilon^n$$

$$\sigma = K'\epsilon^m$$

		PPM by Wt.		
Ref.		C	O	N
27*	○	150	10-35	50
	●			580
25*	□	150	47	< 5
	■		955	
7**	◇	900	570	700

*Iodide
**Calcium

Figure 21. Strain hardening and strain rate sensitivity exponents for vanadium as a function of temperature and interstitial content.

Figure 22. Effect of grain size on yield stress and the associated parameters of the Petch equation as a function of temperature.

meters. The bulk of the temperature dependence of yield stress is due to σ_i and the temperature dependence of σ_i is due, presumably, to a Peierls type mechanism; interstitials affect the athermal part of σ_i but not the thermal component. The temperature independence of k_y found by Lindley and Smallman was due to the fact that preexisting dislocations were firmly pinned by precipitates and did not move. Instead, yielding was by the generation of new dislocations at or near grain boundaries. The temperature dependence of k_y observed by Loria, Keith and Rowe suggests some dislocation-interstitial interaction. For N and O, σ_i and k_y increased with increase in interstitial content. For C, σ_i first increased and then decreased while k_y decreased slightly with increase in C content.

2.3.13 Creep Properties

The temperature dependence of steady state or minimum creep rate of vanadium is shown in Figure 23 and the stress dependence is shown in Figure 24. Wheeler⁽³⁸⁾ corrected the apparent activation energies for creep for the modulus effect; the corrected values are shown in parentheses. The activation energy for self diffusion is also shown in Figure 23. Above $0.5 T_m$, the activation energy and stress exponent for creep are generally consistent with a diffusion controlled creep mechanism.

Additional data by Schirra⁽⁶⁰⁾ on creep rate and rupture life are shown in Figures 25 and 26. Note in particular the very large effect of oxygen content. At 650°C , creep rate varies by 4 to 5 orders of magnitude, and similarly for rupture life, as the oxygen content varies from 220 to 750 ppm. Environmental effects on creep of vanadium are discussed in Section 2.4.4.

2.3.14 Fatigue Properties

Stoloff⁽⁴⁰⁾ and Chung, Lee and Stoloff⁽⁴¹⁾ recently conducted fatigue studies on vanadium and hydrided vanadium. Results are shown in Figures 27 and 28. With increasing H content, fatigue life increases in high cycle stress control tests (Figure 27a) but decreases in low cycle strain control tests (Figure 27b). The data in the low cycle range in Figure 27a are the saturation stresses from the strain control tests. In notched bar tests, fatigue life decreased with increase in H content in the low cycle and high cycle ranges. (Note that in Figures 27a and b the 400 ppm H material contained hydrides whereas in Figure 27c, which was

AUTHORS	WT. PPM				ANNEALING TREATMENT			Creep Test
	C	N	O	H	T, °C	Vac., torr	Grain Size	
Wheeler (38)	250	290	570	10	1500	5×10^{-7}	0.25-0.3 mm	10^{-8} - 10^{-9} torr
Yaggee & Gilbert (38)	250	290	570	10	900	4×10^{-6}	0.02 mm	--
Böhm & Schirra (54)	600	400	1000	--	900	"vac."		1×10^{-5} torr

Figure 23. Temperature dependence of minimum creep rate of vanadium.

Figure 24. Stress dependence of minimum creep rate of vanadium. (Symbols same as in Fig. 23)

Figure 25. Stress dependence of minimum creep rate of vanadium with varying oxygen content.

Figure 26. Stress-rupture data for vanadium with varying oxygen content.

Figure 27. Fatigue properties of V and V-H alloys at room temperature. After Stoloff (Ref. 40) and Chung, Lee and Stoloff (Ref. 41). (Stress control at 20 cps; strain control at 0.2-1 cps; both for $R = -1$).

Figure 28. Fatigue properties of V and V-H alloys at room temperature. After Stoloff (Ref. 40) and Chung, Lee and Stoloff (Ref. 41). (Supplement to Fig. 27)

a different batch of material, it was single phase.) Cycles to crack initiation increased with increasing H content, as did the yield stress (Figure 28a). In Figures 28b and c, material with 520 ppm or more hydrogen contained hydrides. The crack growth rate data show no simple monotonic variation with hydrogen content.

The vanadium and V-H alloys all showed cyclic hardening with saturation after 10-100 cycles. The cyclic stress-strain curves showed increasing strength with increasing H content, as did the monotonic curves, but much more rapid strain hardening than the monotonic stress-strain curves.

A pronounced dislocation cell structure developed in vanadium, and to a lesser extent in the V-H solid solutions, but hydrides inhibited development of a cell structure. In vanadium, microcracks formed at slip bands and grain boundary triple points after 30% of life. In V-1000 ppm H, microcracks formed after 20% of life but only at slip bands in hydride plates, and did not propagate into the matrix until 80% of life.

2.4 VANADIUM ALLOYS

Throughout the discussion of vanadium alloys both weight per cent and atom per cent are used to express compositions. Unless atom per cent is explicitly stated, it can be assumed that the composition is in weight per cent. For convenience, certain information on sources of data, interstitial levels, heat treatments, etc. are tabulated in Table 2.

2.4.1 Cold Work, Recovery, Recrystallization and Grain Growth

Cold work, recovery, recrystallization and grain growth behavior of some vanadium base alloys is shown in Figure 29. Work hardening curves for alloys (Figure 29a) are generally similar to those of vanadium (Figure 2); hardening sometimes saturates at low strains, sometimes continues to large strains and sometimes shows a decrease in hardness at very large strains--only the general level of hardness is different, being much higher in the alloys.

Significant recovery occurs prior to the onset of recrystallization, particularly in high Ti alloys. Recrystallization temperatures range from about 800° to

Table 2. Information on material and experimental procedures for selected references*

Reference		Solutes	Interstitials, WPPM			V-Base	Annealed, °C	Grain Size, μm	Strain Rate min^{-1}	Specimen	Environment	Fig. No. in Text
No.	First Author		C	N	O							
4	Rostoker	Ti, Zr, Cr, Mo, Fe, Ni, Al, Si, C	770	860	560	C**	Hot Forged at 1150-1450	-	-	rod	Ar	33, 34, 35, 37, 44, 45, 46, 48, 49, 77
38	Wheeler	Vanadium	250	290	570	UC	1500	250-300	creep	0.06" sheet	$<10^{-8}$ torr	23, 24, 63
38	Yaggee	Vanadium	250	290	570	UC	900	20	creep			23, 24
46	Van Thyne	Ti, Nb, Ta, Mo, Si	470	610	810	EMC**	650-800	-	0.0035	0.25" rod	He	33, 34, 35, 36, 49, 56, 67
47	Rajala	Ti, Nb, Ta, Mo, W	430	370	900	UC**	1000	-	-	0.05" sheet	He	29, 33, 34, 35, 36, 41, 42, 43, 46, 47, 52, 53, 54, 87
48-49	Holtz	Ti, Nb, Ta, Mo, W, Hf, Zr, C	300-500	260-460	400-440	**	1100-1300	-	-	0.05" sheet	coatings	29, 60, 61
52	Pollack	Ti, Nb, Ta, Cr, Mo, W, Fe, Ni, Zr, C	390-3000	200-270	800-1300	-	900-1500		0.05	0.042" sheet	5×10^{-6}	29, 35, 62, 65, 66, 67, 69, 85, 86, 87
53	Whitlow											
54-60	Bohm Schirra	Ti, Nb, Cr, Mo, Zr, Si, Ge, Al	600	400	1000	**	900			0.2" rod	1×10^{-5}	23, 25, 26, 29, 34, 35, 53, 67, 69, 71-77, 80-84, 87
61	Keith	Ti	<10	10-20	400-500	E	825-975	Rx, small	0.04	0.05" sheet	$<10^{-3}$ torr	29, 30, 32, 33
		Ti	290-440	80-150	380-670	C	900-1000	Rx, small	0.04	0.05" sheet	$<10^{-3}$ torr	29, 30, 32, 33
		Mo	<10	10-50	320-900	E	825-975	Rx, small	0.04	0.05" sheet	$<10^{-3}$ torr	29, 45, 46
		Mo	220-420	110-200	360-530	C	900-1000	Rx, small	0.04	0.05" sheet	$<10^{-3}$ torr	29, 45, 46
62	Mathews	W, Cr	270-380	80-140	250-470	C	850-1050	25	0.02	0.06" sheet	RmT	44, 47, 59
63	Keith	Ti, Mo, Ni, Y, Si, C	1000	-	-	C	Rolled at 600	-	0.01	0.05" sheet	10^{-3} - 10^{-5} torr	58
66	Stewart	Ti, Cr	100	90	100	WC	1050	25	0.05	0.04" sheet	Ar	57, 77, 79

Table 2. (Continued) Information on material and experimental procedures for selected references*

Reference		Solutes	Interstitials, WPPM			V-Base	Annealed, °C	Grain Size, μm	Strain Rate min^{-1}	Specimen	Environment	Fig. No. in Text
No.	First Author		C	N	O							
67	Fraser	Ti	270	40	666	C**	850-1077	8-12	0.06	0.015" sheet	Low T	31, 32, 33
68	Yaggee	Ti	(~1200 Total)			**	850-1250	30-50	0.013	0.06" sheet	2×10^{-6}	32, 33, 34, 35, 36, 57, 67, 69, 70
69	Yaggee	Ti	250-390	270-380	360-830	**	Extrude at 1100 or Rx 900	-	0.013	rod & sheet	2×10^{-5}	33, 35, 36, 67
70	Lincoln	Hf	330-870	100-610	-	C	900	-	0.02	0.05" sheet	RmT	37
71	Babitzke	Nb	455	120	450	C**	1500	-	0.05	0.06" sheet	RmT	38, 42
72	Shimomura	Nb	80-190	42-67	270-380	E	1000-1300	40	0.067	0.016" sheet	1×10^{-6}	40, 42
73	Carlson	Cr	-	-	-	-	950	-	0.01 (XHD)	0.125" rod	RmT	44
74	Wiffen	Cr	140	550	77	-	1100	-	0.02	-	He	44
77	Wlodek	Ti, Nb, Si, Al	300-800	200-230	2000-2600	UC	Swaged at 1000	-	0.005	rod	vac.	87
79	Eustice	Nb	100	5	150	I**	1120-1300	500-40	0.008	0.125" rod	Low T	39, 42

*This information is intended as a supplement to the figures in the text. Here the information is general and may not correspond to each specific figure in detail.

** C = Calcium Reduced V

UC = Union Carbide

EMC = Electro Metallurgical Co.

E = Electrorefined

WC = Wah Chang

I = Iodide

The double asterisk ** denotes that the interstitial analysis refers to the vanadium base, otherwise it refers to the V-base alloy.

Ref.	Alloy	RxT or ΔT , °C	Ref.	Alloy	RxT or ΔT , °C
39	< 0.75 a/o		47	V-Ti, Nb, Ta, Mo W Solid Soln.	< 1000°
	Ti, Zr, Hf, Nb, Ta W, Mn, Pd, Re, Pt	Increase by up to +40°		Same + Si or Re	1100°
	Cr, Mo, Fe, Co Ni, Ru, Rh, Os, Ir	Decreased by as much as -30°	63	20Mo-10Ti-0.1C-0.5Y	900°
61	2.5-5 a/o Ti or Mo	+75° to 150°		Same + 0.25-0.5Si	1000°
62	12 w/o Cr 15 w/o W	950° (+100°) 1000° (+150°)	16	Y or Rare Earths	As low as 800° (-1500°)
56	3 Ti 20 Ti	1000° 850°	49	60Nb + Zr + C	1200°
	10-20 Ti	~800°-900°		60Nb + Hf + C	1300°
	15Ti-5 or 7.5Cr	~900°-1000°			
52	VANSTAR-8	1050°			

(d)

Figure 29. Cold work, recovery, recrystallization and grain growth behavior of various vanadium-base alloys.

1300°C, versus about 800° to 1000°C for vanadium. No satisfactory, simple and internally consistent explanation of specific alloying effects is evident; substitutional solute effects are evidently complicated by residual interstitial effects. Possible guidelines might be as follows; V-high Ti alloys recrystallize at about 800°-900°C (recrystallization has been detected at 600°C in V-20Ti cold worked 50%); solutes such as Nb, Ta, Cr, Mo and W retard recovery and raise the recrystallization temperature to about 1000°C; second phases (ZrC or HfC precipitates, for example) refine the grain size, retard grain growth and (perhaps in combination with very high substitutional solute contents) raise the recrystallization temperature to as high as 1200°-1300°C.

Abrahamson⁽³⁹⁾ studied the recrystallization behavior of very dilute (up to a few tenths atom percent solute) vanadium base alloys. The temperature for the onset of recrystallization varied by +40° to -30°C from that for vanadium (860°C). The elements Ti, Zr, Hf, Nb, Ta, W, Mn, Pd, Re and Pt raised and Cr, Mo, Fe, Co, Ni, Ru, Rh, Os and Ir lowered the recrystallization temperature of vanadium. All alloys were reported to be single phase.

O'Brien and Rowe⁽¹⁶⁾ found that Y and rare earth metals decreased the recrystallization temperature from 950°C for electrorefined vanadium to as low as 800°C in the alloys. Alloys which retained more than 0.1 w/o solute contained a second phase precipitate. Keith⁽⁶¹⁾ found that Ti or Mo additions up to about 5 w/o increased the recrystallization temperature by 75° to 150°C. Electrorefined vanadium and its alloys were single phase. Calcium reduced vanadium contained numerous precipitates but the amount of precipitates decreased with increasing additions of Ti or Mo.

2.4.2 Binary Alloys: Tensile Properties

By binary alloys is meant V + substitutional solutes; interstitials are always present and their direct, independent effect or effects due to interstitial-substitutional solute interactions influence mechanical properties.

- Effect of Titanium - The effect of small additions of titanium on low temperature tensile properties is shown in Figures 30 and 31. The strength levels are higher in the calcium reduced than in the electrorefined vanadium base, but the

Figure 30. Effect of titanium (relatively small concentrations) on low temperature tensile properties of electrorefined and calcium reduced vanadium. After Keith, Ref. 61.

Figure 31. Additional data (similar to Fig. 30) on the effect of titanium on low temperature tensile properties of calcium reduced vanadium. After Fraser, and Lund (Ref. 67).

Ti composition dependence is similar. Small Ti additions (0.1-0.5 w/o) increase strength and decrease ductility. With further increase in Ti the strength decreases to a minimum (at ~1-3% Ti, depending on temperature) which may be considerably lower than that of unalloyed vanadium and then increases with still further additions of Ti. Evidently, precipitation, scavenging and solid solution hardening are all involved as discussed in Section 2.4.5.

In order to show the temperature dependence, the above results are replotted in Figure 32 along with other data at higher temperatures and higher Ti contents. At high levels (10-40%) Ti is a potent strengthener. Dynamic strain aging peaks (UTS peak) occur at 10 and 20% Ti but not at 40%. The temperature of the UTS peak shifts to lower temperatures in going from 10 to 20 to 40% Ti. At 10% Ti the peak is at ~600°C versus 400°C for vanadium. The ultimate tensile strength curves for 10, 20 and 40% Ti converge at about 700°C but the yield strength still shows the usual composition dependence at 800°C. The ductility of the vanadium base in these alloys was high and so was the ductility in all the V-Ti alloys. A ductility minimum may occur in the dynamic strain aging temperature range. Heat treatment influences ductility as much or more than variations in Ti content.

The results of various investigations of the effect of Ti on tensile properties at room temperature and above are compared in Figures 33 and 34. On the UTS plot in Figure 33 the lowest curve is for electrorefined vanadium while the other curves are all for calcium reduced vanadium; the upper curve is for as-hot forged material while all the other curves are for recrystallized material. Note in particular the ductility of the hot forged material. The hot forged vanadium itself had low ductility and the addition of 1% Ti reduced it to zero. With further Ti additions the ductility increased markedly and then gradually decreased. As discussed later, this result, along with virtually zero ductility in other hot forged vanadium base binary alloys led to early emphasis on V-Ti alloys; the thought was that Ti was needed to impart ductility. The other results in Figures 33 and 34 show that this is not necessarily true; titanium additions may increase or decrease ductility. A possible behavior trend may be as follows. If the ductility of the vanadium base is very low then Ti additions may markedly increase ductility. If the vanadium base has high ductility then Ti additions

Ref	V Base	Ti %	PPM		
			C	O	N
61	■ Electro.	--	<10	500	20
		0.7	<10	650	<10
		2.6	<10	450	<10
61	▲ Calcium	--	410	670	110
		0.43	300	490	110
		5.5	320	560	80
67	■ Calcium	--	270	660	40
68	◆ Calcium	--	~1200 total		

Figure 32. Effect of titanium on tensile properties of vanadium as a function of temperature. Data of Fig's. 30 and 31 plus additional data of Yaggee (Ref. 68).

Ref	Ti %		Anneal °C
68	40	■	900
		□	1250
	20	▲	900
		△	1000
	10	●	1000
		○	1250

Figure 32. (Continued)

Legend

- Ref. 68
- ▲ Ref. 69
- Ref. 4, 46
- ◆ Ref. 47
- Ref. 61, 67

Figure 33. Comparison of results of various investigators on the effect of titanium on room temperature tensile properties of vanadium.

Figure 34. Results of various investigators on the effect of titanium on tensile properties of vanadium at various elevated temperatures.

have no unusual effects on ductility. Titanium acts as a scavenger. This has two effects; it reduces the interstitial content in solid solution and it alters the morphology and distribution of second phase precipitates. The effect of Ti on ductility may involve both mechanisms.

The composition dependence of strength depends on test temperature (and possibly on microstructure also). At low temperatures, strength increases monotonically with increasing Ti content (beyond perturbations at low Ti levels) though at a decreasing rate at high Ti levels. At high temperatures ultimate strength goes through a maximum at 20 to 30% Ti. The Ti content at the maximum appears to decrease with increasing temperature (Figure 34).

The effects of high Ti additions on tensile and yield strengths are summarized in Figures 35 and 36. The bands for 10, 20 and 40% Ti are drawn to encompass the data points of various investigators. Results on vanadium are superimposed for comparison.

- Effect of Zr and Hf - The effect of Zr and Hf on room temperature tensile properties is shown in Figure 37. Both Zr and Hf have limited solubility in vanadium (less than about 1a/o or so at room temperature). Strength increases with small additions and then decreases, similar to the behavior with Ti. Hafnium decreased the ductility of recrystallized material (1 hr/900°C anneal) while Zr increased the ductility of as-hot forged material. The effect of Zr on ductility is similar to that previously noted for the effect of Ti in hot forged material. The V-Zr alloys were hot-short during fabrication for Zr contents above about 3 w/o and hence were not studied further. The properties shown in Figure 37 are unimpressive; hence, V-Zr and V-Hf binary alloys have not been pursued. However, Zr and Hf, along with carbon, are still of interest in efforts to develop dispersion hardening.

- Effect of Niobium - The effect of Nb on tensile properties is shown in Figures 38-42. Niobium is a potent solid solution strengthener. The results by Babitzke, Asai and Kato⁽⁷¹⁾ shown in Figure 38 depict classical behavior for a solid solution alloy. No explanation is offered for the ductility minima at about 10% solute on both sides of the diagram.

Figure 35. Ultimate tensile strength of vanadium (per Fig. 5) and vanadium-titanium alloys (Refs. 4,46,47,52,54,57,68,69) as a function of temperature. Data bands encompass results of various investigator

Figure 36. Yield strength of vanadium (per Fig. 6) and vanadium-titanium alloys (Refs. 46,47,68,69) as a function of temperature.

Figure 37. Effect of zirconium and hafnium on room temperature tensile properties of vanadium. (V-Zr as-hot forged; V-Hf annealed 900°C/ 1 hr. and <1 a/o solubility.)

Figure 38. Room temperature tensile properties of vanadium-niobium alloys. After Babitzke, Asai and Kato (Ref. 71). (Calcium reduced V: 455 ppm C, 120 ppm N and 450 ppm O)

Figure 39. Tensile properties of vanadium-niobium alloys. After Eustice and Carlson (Ref. 79) (Iodide V: 100 C, 5 N and 150 0 in ppm).

Figure 40. Effect of niobium content and test temperature on the tensile properties of V-Nb alloys. (Shimomura, Kainuma and Watanabe, Ref. 72)

Figure 41. Data of Rajala and VanThyne (Ref. 47) on the effect of niobium content on tensile properties of V-Nb alloys at various temperatures.

Figure 42. Comparison of results of various investigators on the effect of niobium content on the room temperature strength of V-Nb alloys.

Similar results were obtained by Eustice and Carlson⁽⁷⁹⁾ as shown in Figure 39. Twinning occurred at temperatures below -120°C . Thus, the yield stress shown for -196°C corresponds to the twinning stress; it varies only slightly with alloy composition. The alloys were all ductile even at very low temperatures. The alloys of Babitzke, Asai and Kato (calcium reduced V) were slightly stronger (10-15 ksi) than those of Eustice and Carlson (iodide V). The relative strengths of the V and Nb base metal can produce a slight asymmetry in the strength-composition curve, shifting the peak to one side or the other of the 50 a/o composition.

Shimomura, Kainuma and Watanabe⁽⁷²⁾ made a detailed study of V-Nb alloys. Not all of their data was available but that which is shown in Figure 40. Yield strength increased with increasing Nb content up to about 40 w/o. For Nb contents between 40 to 55 w/o, alloy softening (measured by yield strength) was observed below -80°C and the yield strength was constant at any given higher temperature. For any given Nb content the yield strength was approximately constant at temperatures between about 200° and 700°C . Ultimate strength increased continuously with increase in Nb content though the increase was very small above 40 w/o. The temperature of the peak in UTS due to dynamic strain aging increased with increasing Nb content from about 400°C for vanadium to about 600°C for V-50 w/o Nb. Twinning occurred in two different temperature regimes; low and high depending on Nb content. The horizontal line at about 100 ksi in Figure 40 depicts the approximate critical stress for mechanical twinning (assumed to be independent of temperature). Alloys with strengths higher than the twinning stress twin during deformation. At low temperatures the temperature below which twinning occurs increases with increase in Nb content up to 200°C for 55 w/o Nb. For Nb contents above 45 w/o, deformation twinning also occurs after large strains at temperatures of 400° - 600°C ; this is due to dynamic strain aging raising the UTS to above the twinning stress. The high ductility of the high Nb content alloys relative to pure vanadium at -196°C was attributed to twinning in the alloys. With increasing temperature the ductility of the high Nb content alloys gradually decreased and reached a minimum at 900°C .

Other data by Rajala and Van Thyne⁽⁴⁷⁾ are shown in Figure 41; a peak in strength and minimum in ductility occurred at about 50 w/o Nb. A comparison of results at

room temperature from different investigators is given in Figure 42; the spread in UTS is about 25 to 35 ksi. Note also in Figure 40 the very marked difference between the results by Rajala and Van Thyne⁽⁴⁷⁾ and those of Shimomura, et al.⁽⁷²⁾

- Effect of Tantalum - The effect of Ta on tensile properties is shown in Figure 43; strength increases and ductility decreases with increase in Ta content.
- Effect of Chromium - Results of various investigators on the effect of Cr on room temperature tensile properties are shown in Figure 44. The highest UTS curve and lowest ductility curve were for as-hot forged material. The results of Mathews and Iverson⁽⁶²⁾ showed alloy softening with a minimum at about 1% Cr.
- Effect of Molybdenum - The effect of Mo on tensile properties is shown in Figures 45 and 46. The data by Rostoker, Yamamoto and Riley⁽⁴⁾ were for as-hot forged material. The ductility of all these hot forged V-Mo alloys was zero; the composition dependence of UTS is difficult to explain. Keith⁽⁶¹⁾ attributed the small peaks at very low Mo content to inadvertent variations in interstitial content. The temperature of the strain aging peak in vanadium (400°C) appears to be unaffected by Mo (Figure 46), as does the magnitude (UTS at 400°C minus that at 200°C). From room temperature, ductility decreased with both increasing and decreasing temperature; at -196°C the ductility decreased markedly with increasing Mo content.
- Effect of Tungsten - The effect of W on tensile properties is shown in Figure 47. Tungsten is a potent solid solution hardener. Mathews and Iverson⁽⁶²⁾ observed alloy softening at low W contents. No explanation can be offered for the marked difference in ductility between the two sets of data reported.
- Effect of Iron and Nickel - The effects of Fe and Ni on room temperature tensile properties of as-hot forged material are shown in Figure 48. Ductility was zero for all the alloys. Iron and nickel are both rather potent solid solution hardeners. The zero ductility noted should not be taken as characteristic of V-Fe or V-Ni alloys and the peak in UTS curve for Fe (or, better, the drop beyond 4.5 a/o) needs to be substantiated.

Figure 43. Effect of tantalum on tensile properties of V-Ta alloys.
(Rajala and VanThyne, Ref. 47) (6.6 a/o Ta = 20 w/o)

Figure 44. Results of various investigators on the effect of chromium content on the room temperature tensile properties of V-Cr alloys.

Figure 45. Effect of molybdenum content on tensile properties of V-Mo alloys. After Rostoker, et al. (Ref. 4) and Keith (Ref. 61)

Figure 46. Data of Fig. 45 replotted to show temperature dependence of tensile properties of V-Mo alloys. After Keith (Ref. 61), Rostoker, et al. (Ref. 4) and Rajala and VanThyne (Ref. 47).

Figure 47. Effect of tungsten content on tensile properties of V-W alloys. After Rajala and VanThyne (Ref.47) and Mathews and Iverson (Ref.62).

Figure 48. Effect of iron and nickel on room temperature tensile properties of vanadium.

- Effect of Aluminum and Silicon - The effect of Al and Si on tensile properties is shown in Figure 49. No explanation can be offered for the apparent composition dependence of UTS. The extent of strengthening for the first 2 a/o solute is very high. In these tests by Rostoker, et al.⁽⁴⁾ on as-hot forged material, the ductility was zero for all compositions except 1.8 a/o Si where the elongation was 33%. However, tests by Van Thyne⁽⁴⁶⁾ on the same alloy, but annealed at 650°C for 48 hours and water quenched, gave zero ductility and about half the UTS. Carlson, et al.⁽⁸⁰⁾ studied the effect of Si and Al at levels which might exist as residual impurities in Si or Al reduced V₂O₅. Silicon up to 0.08 w/o or Al up to 0.3 w/o increased strength somewhat but had no effect on ductility at room temperature.

- Effect of Yttrium and Rare Earths - O'Brien and Rowe⁽¹⁶⁾ studied the effect of Y and various rare earth metals. The results are shown in Figure 50; similar results were obtained for La, Ce, Pr, Nd and Sm. All of the alloys which retained more than 0.1 w/o solute contained a second phase. The results are consistent with a scavenging effect as indicated by the oxygen contents shown in the figure.

- Summary of Strengthening in Binary Alloys - A number of substitutional solutes have been evaluated. In some cases (e.g. Ti and Nb) the data base is rather extensive, covering wide ranges of solute content and test temperature, and test results of various investigators are available for comparison. In other cases only a few data points are available. Figure 51a depicts the composition trends noted in the actual data; whether the trends indicated are all due to composition per se or some reflect other variables (e.g. microstructure) superimposed is uncertain. Curve types a, b, d and e indicate substitutional-interstitial solute interactions (precipitation, scavenging, alloy softening). Curve types c and g give the expected solution hardening trend. The maximum in curve f at compositions far below the 50-50 atomic per cent value may or may not be real. The spread in results of different investigators for a given solute, curve h, is too large to be due to microstructural differences alone (e.g. grain size), and must reflect interstitial effects. If so, it appears that the interstitial contribution is simply additive to that of the substitutional solute (curves are parallel but shifted up or down the strength axis). The spread in strength for a given nominal binary alloy may be greater than differences due to different substitutional solutes.

Figure 49. Effect of aluminum and silicon on tensile properties of vanadium. After Rostoker, et al. (Ref. 4) and VanThyne (Ref. 46).

Figure 50. Effect of yttrium on room temperature tensile properties of vanadium. The corresponding oxygen content of the various alloys is also shown. Similar results were obtained with various rare earth additions. (O'Brien & Rowe, Ref. 16).

(a) Schematic of strengthening effects in binary alloys

(b) Comparison of the strengthening effect of various solutes in V. Multiple curves indicate a range from various investigators; data from previous figures.

Figure 51. Strengthening effects in vanadium-binary alloys.

Neglecting the perturbations at low solute contents, the relative strengthening effect of different solutes at room temperature is shown in Figure 51b. No attempt is made here to normalize the curves to give the same strength at zero per cent solute (allow for interstitial and microstructural effects) nor has the data been analyzed in terms of solid solution hardening theories. The large differences in strength indicated is more apparent than real; any real difference that exists between the different solutes is clearly much less than that indicated by direct comparison of the curves at a given solute level. The data base is hardly sufficient to adequately define the rate of hardening and saturation effects for all the solutes. All are potent solid solution hardeners and to an approximation are all equally potent. Tantalum looks particularly good, as does Fe and Ni, but the data base is quite limited. Tungsten and Nb look good. Titanium seems to saturate at low levels. Molybdenum never looks best and Cr appears to be least effective.

The relative strengthening effect of different solutes at room temperature is likely to prevail at elevated temperatures also. However, different tendencies toward dynamic strain aging complicate conclusions reached with a limited data base, particularly when ultimate tensile strength is the strength parameter and the temperature dependence is unknown.

2.4.3 Ternary and Higher Order Alloys: Tensile Properties

In the early screening alloy development study by Rostoker, et al.⁽⁴⁾ at Armour, all the binary alloys (V-Cr, Mo, Fe, Ni, Al and Si) were brittle at room temperature except for V-Ti and V-Zr. The V-Zr alloys were hot-short during fabrication for Zr contents above about 3 w/o and hence emphasis was given to the V-Ti alloys. It was reasoned that Ti additions were necessary for ductility. Third and fourth element additions were then made to various V-Ti bases in order to further improve strength. It is now known that low ductility is not characteristic of substitutional solute composition effects per se in vanadium base binary alloys. Even so, the early results on high interstitial content, as-hot forged material influenced subsequent work and most alloy development studies have all but automatically included Ti as an alloy element addition; hence, alloys containing Ti dominate the existing data base.

● V-Ti Base Alloys - The effect of adding third element substitutional solutes to a V-Ti base is shown in Figure 52. The third element solutes increase strength at all temperatures but their effectiveness decreases with increase in Ti content. Alternatively, for a given third element content the effect of Ti content is as shown in Figure 53. For 12 a/o Nb, strength increases somewhat at 25⁰ and 650⁰C with increasing Ti content but at 980⁰C strength goes through a maximum and decreases beyond 5% Ti. Results for Ta, Mo and W are similar; the results at 980⁰C are shown in the figure. These results can be reasonably rationalized in terms of additive solute effects. In binary alloys, hardening saturates at high solute content and may even show a peak at concentrations well below the 50 a/o level (as is, evidently, the case for UTS in V-Ti binaries) and the solute content at peak hardening decreases with increase in temperature. Thus, 5% third element solute ought to produce greater strengthening when added to V-5Ti than when added to V-20Ti. Strength as a function of total solute content (Ti + third element) is shown in Figure 54, along with curves for V-Ti binary alloys for comparison. The ternary alloys are generally somewhat stronger than V-Ti alloys and high Ti content appears to induce early saturation in the ternary alloys at the highest test temperature.

The ductility of these ternary alloys is shown in Figure 55 as a function of Ti content. In many cases the trend is that Ti increases ductility but the number of exceptions evident precludes this being an unqualified composition per se behavior trend.

Other data for additions of small amounts of third elements to V-10Ti are shown in Figure 56.

Data by Yaggee⁽⁶⁸⁾ for V-15Ti-7.5Cr and data by Stewart, LaVake and Christopher⁽⁶⁶⁾ for V-5Ti-15Cr are shown in Figure 57. The marked difference in strength between the two alloys is evidently due primarily to different mechanical/thermal processing treatments, not composition per se. The arrow at 600⁰C denotes the decrease in strength (and ductility) due to increase in annealing temperature. The drop is too large to be due to grain size alone and must reflect effects due to precipitation and/or residual strain hardening.

Figure 52. Effect of third element solutes on tensile properties of V-Ti base alloys. After Rajala and VanThyne (Ref. 47).

Figure 53. Effect of Ti content on tensile properties of various ternary alloys. After Rajala and VanThyne (Ref. 47) and Böhm and Schirra (Ref. 54).

- At.% Solute
- 5-20Ti + 2.7-12Mo
 - ◇ 5-20Ti + 2.7-12Nb
 - ▽ 5-20Ti + 1.5-6.6Ta
 - △ 5-20Ti + 1.5-6.6W

Figure 54. Strength as a function of total substitutional solute content for V-Ti binary and V-Ti base ternary alloys. After Rajala and VanThyne (Ref. 47).

Figure 55. Effect of titanium on ductility of V-Ti base ternary alloys. After Rajala and VanThyne (Ref. 47).

*Prior to anneal at 650°C
†Prior to anneal at 800°C

Figure 56. Effect of small amounts of third element additions on tensile properties of V-10Ti alloys. VanThyne (Ref.46).

Figure 57. Tensile properties of V-Ti-Cr alloys. After Stewart, LaVake and Christopher (Ref. 66) and Yaggee (Ref. 68).

Keith and Winston⁽⁶³⁾ studied V-Ti alloys which contained Mo or Ni as third element additions and Si, Nb and Zr as fourth element additions. The alloys also all contained C and Y additions. In arriving at the optimum composition, Mo was selected over Ni because the alloys with Ni were hot short in fabrication. As fourth element additions, 5 w/o Nb or Zr led to excessive brittleness during fabrication and hence were eliminated. The addition of 0.1 w/o C (plus 0.04 w/o residual in the vanadium stock) had no effect on strength or workability; higher C additions decreased workability. Silicon additions of 0.25 and 0.5 w/o increased strength. Yttrium was added to improve fabricability. The optimum alloy composition selected was V-10Ti-20Mo-0.1C-0.5Y-0.5Si (w/o). The alloy was tested in the warm rolled condition and the results are shown in Figure 58, along with a few results at room temperature on recrystallized material. Data on V-10Ti-20Mo are not available but a few data points for V-10Ti-10Mo in the recrystallized condition are also shown in the figure for comparison. Just how much of the strength differential between the warm rolled alloys of Keith and Winston and the anticipated strength of recrystallized V-10Ti-20Mo is due to composition and how much is due to the wrought microstructure is moot.

- V-W-Cr Alloys - Results by Mathews and Iverson⁽⁶²⁾ on V-W and V-Cr binary alloys were shown previously; their results on V-W-Cr ternary alloys are shown in Figure 59, along with the binary results for comparison. Extrapolation of the curves at high solute content back to zero solute content gives about 28 ksi for the yield stress of vanadium and hardening rates of about 8 ksi/a/o for W and about 3.6 ksi/a/o for Cr. The hardening in the V-W-Cr ternary alloy is given reasonably well by a linear additive mixture of the separate contributions of W and Cr.

- V-Nb Base Alloys - Next to Ti, Nb has been the second most extensively studied alloying element in V base alloys. In the earlier work at Armour, high Nb content alloys were developed with emphasis on strength at very high temperatures. For convenience, the numerous alloys studied are collected herein into three groups. These groups and the room temperature ultimate strengths are shown in Figure 60. Adding small amounts of 3rd, 4th and 5th elements and Hf or Zr and C to the V-Nb base gave strengths which fall generally in the upper part of the band for the simple V-Nb binary alloys. Hence, from these room temperature tests it is

Figure 58. Tensile properties of the alloys developed by Keith and Winston (Ref. 63).

Figure 59. Room temperature tensile properties of V-W, V-Cr and V-W-Cr alloys. After Mathews and Iverson (Ref. 62).

* % Elongation in ().

x Similar alloys + 1-2 w/o Zr or Hf & 0.05-0.1 w/o C.

Figure 60. Strength of various V-Nb base ternary and higher order alloys. After Holtz and VanThyne (Ref. 48).

difficult to establish whether or not the higher order solute additions or Hf/Zr plus carbon additions make any substantial contribution to strength.

Results at high temperatures are shown in Figure 61 along with numerous other results, which makes the figure "busy"; focus first on the results for Groups 1, 2 and 3. The effect of compositional variations within a given group, including Hf/Zr plus C additions, is somewhat moot. Clearly, the alloys are much, much stronger than vanadium. Results for V-20Ti, a familiar reference, are shown for comparison. Since Groups 1, 2 and 3 have high Nb contents, results by Shimomura, et al.⁽⁷²⁾ for V-12 to 40 at/o Nb binary alloys are also shown for comparison. It is uncertain how these latter results should be extrapolated beyond 1000°C, but the Groups 2 and 3 alloys are definitely stronger at 1000°C-1100°C. On the other hand, the results by Rajala and Van Thyne⁽⁴⁷⁾ for V-35 at/o Nb and those by Holtz and Van Thyne⁽⁴⁸⁾ for V-45Nb-1Ti renders assessment of the specific alloying effects in the various alloy groups uncertain. Quite probably the more complex alloys are much stronger than pure V-Nb binaries; the task is to control the composition and microstructure to insure attaining the higher strengths.

- Binary and Ternary Alloys with Zr and C - The effect of various binary and ternary additions of Nb, Ta, Cr, Mo, W and Fe plus additions of Zr and C on ultimate strength at room temperature and 700°C is shown in Figure 62. Superimposed on the figure is the hardening attained in various binary alloys (data from previous figures). These alloys were developed for creep resistance; the three most promising ones are designated VANSTAR-7, -8 and -9. The ultimate strength of these VANSTAR alloys is shown in Figure 61 for comparison purposes.

- Summary of Ternary and Higher Order Alloy Strengthening - Strength increases with increase in total substitutional solute content. There is no discernible evidence of synergistic effects, good or bad. For a given total solute content, strength varies by 20 ksi and more for all results of various investigators and for various alloys. This is a significant variation in strength level but it is not clear that it is due to real differences in solid solution hardening propensity of different solute elements. Specific alloying effects are obscured by simultaneous variations in thermal/mechanical processing (microstructure), interstitial levels and mechanical test parameters. If anything, the potency of

Figure 61. Strength of the three alloy groups noted in Fig. 60 as a function of temperature. Numerous other data are shown for comparison as described in text.

- V
- ★ V-ZrC
- Ti
- Ti-ZrC
- ▲ Nb-ZrC
- ▼ Ta-ZrC
- ◆ Cr-ZrC
- ◇ Cr-ZrC (2.7Zr)
- ◊ Cr-ZrC (4.3Zr)
- ◈ Cr-ZrC (5.3Zr)
- ▶ Mo-ZrC
- ◀ W-ZrC
- Fe-ZrC

- 7• VANSTAR-7 (9Cr-3Fe-ZrC)
- 8• VANSTAR-8 (9Cr-3Ta-ZrC)
- 9• VANSTAR-9 (6Fe-3Nb-ZrC)

- 1x 9Cr-3W-ZrC
- 2x 9Cr-3Mo-ZrC
- 3x 9Cr-3Ti-ZrC
- 4x 6Cr-3Nb-ZrC
- 5x 6Cr-3Ta-ZrC

Figure 62. Tensile strength of various binary and ternary alloys with Zr+C additions. These alloys were developed for creep resistance. After Pollack, et al. (Ref. 52).

specific solutes in ternary alloys is similar to that in binary alloys. Thus, Ta and W look good, as does Nb, while Mo and Cr are perhaps somewhat less effective. However, it is difficult to develop a case for ternary alloys; the same strength level can be achieved in the simpler binary alloys. There is clearly no justification for adding small amounts of 4th and 5th substitutional solute elements to an already single phase solid solution.

Attempts to develop precipitation or dispersion hardening have met with questionable success. However, efforts to date have not been very serious (detailed or thorough). The strength of alloys containing small amounts of Zr or Hf plus C (to give ZrC or HfC) is hardly any greater than that of the binary base, which in most cases has already been stiffened considerably by solid solution hardening. On the one hand, the spread in strength of the solid solution base makes assessment of the dispersed phase contribution difficult; on the other hand, the inadvertent presence of precipitates may be partly responsible for the spread in strength of the solid solution alloy base. The effect of precipitates may be indirect through an effect on recovery and recrystallization. In any event, it has not been established that precipitation hardening makes a really substantial contribution to strength above that attained in the solid solution base.

2.4.4 Creep Properties

- Environmental Effects - Several creep curves for vanadium tested in ultrahigh vacuum are shown in Figure 63. Note the shape of the curve in the 900°C test; the creep rate continuously increases from the origin with no primary or steady state stages. Wheeler⁽³⁸⁾ noted that this type of accelerating creep curve was not observed in ultrahigh vacuum tests at temperatures above 925°C. However, this should not imply that the peculiar curve shape is due to the hard vacuum nor that it is only observed at low temperatures. Accelerating creep curves are far more common than is generally noted. They can be observed in most, if not all, metals and alloys tested in air or vacuum and are most likely to be observed at high temperatures and always at low stresses. The cause of accelerating creep curves is moot; the relative importance of temperature, stress, environment and microstructure (instabilities), and whether it reflects bonafide plastic deformation or microfracturing processes is still being debated. Accelerating creep curves are one reason that minimum creep rates are often reported instead

Figure 63. Creep curves for unalloyed vanadium.

of steady state rates; the other reason, where primary creep is observed, is that the test is discontinued in the primary stage.

The effect of low pressure oxygen or nitrogen atmospheres on creep of vanadium is shown in Figure 64. The creep rate in the oxygen or nitrogen atmospheres is much greater than in high vacuum. Increasing the oxygen content of the vanadium from 130 to 470 ppm prior to testing in vacuum had no effect on creep. At face value, these results suggest that environmental interactions decrease creep strength.

The effect of vacuum pressure on creep of VANSTAR-7 alloy is shown in Figure 65. The results in Figure 65a suggest that environmental interactions increase creep strength. Note that the effect of pressure is quite large. The lower curve in Figure 65a is reproduced in Figure 65b along with a creep curve at 800°C. The extremely high apparent activation energy indicated is most difficult to rationalize in terms of any known mechanism of creep in a microstructurally stable alloy. If it reflects a temperature dependent environmental effect, then either the creep rate at 800°C is increased or that at 700°C is decreased relative to what it would be in the absence of an environmental effect. Creep curves for VANSTAR-9 alloy are shown in Figure 66. The tendency toward accelerating creep at the higher temperature and lower stress is evident.

Environmental effects are only poorly understood. The effects can be very large and complicate assessment of alloying effects, particularly when it is necessary to compare results of different investigators.

- V-Ti Binary Alloys - Stress rupture data of various investigators on V-Ti alloys at 650°C, 700°C and 800°C are shown in Figures 67 and 68. The stress dependence of creep rate is shown in Figure 69. Trends in stress rupture strength parallel those in creep rate, though inversely (increase in rupture strength and decrease in creep rate). At long rupture life (greater than a few hundred hours), creep strength decreases with increase in Ti content and increases with increase in annealing temperature. The effect of annealing temperature on creep of V-20Ti is shown in Figure 70. There are two annealing or grain size regimes; below and above about 900°C. Below 900°C, creep rate increases with decrease in

Figure 64. Effect of interstitials in ambient atmosphere on creep of vanadium. (ORNL data, Ref. 78)

(a)

(b)

Figure 65. Effect of vacuum pressure on creep of VANSTAR-7 alloy.
After Pollack, Whitlow, et al. (Refs. 52,53).

Figure 66. Effect of vacuum pressure on creep of VANSTAR-9. After Pollack, et al. (Ref. 52) and Whitlow, et al. (Ref. 53).

Figure 67. Results of various investigators on stress rupture properties of V-Ti alloys at 650°C.

Figure 68. Stress rupture properties of V-Ti alloys at 700°C-800°C. Symbols same as in Fig. 67.

Figure 69. Stress dependence of minimum creep rate of V-Ti alloys.

Figure 70. Effect of annealing temperature on creep behavior of V-20Ti alloy.

annealing temperature (grain size dependent). Above 900°C creep rate is relatively independent of grain size. Maximum scatter or variability from one investigator to another should be expected for annealing at about 900°C.

The work by Bohm and Schirra⁽⁵⁴⁻⁶⁰⁾ is particularly worthy of note. As shown in Figure 71, tensile strength increases continuously with Ti content while creep strength increases up to about 2-3% Ti and then decreases with further increase in Ti content. The effect of Ti content on the activation energy and stress dependence of creep is also shown in the figure. The interpretation of these results will be discussed later. As part of their mechanistic study, Bohm and Schirra studied the effect of oxygen content on creep of V-Ti alloys; their results are shown in Figure 72. Oxygen had a marked effect at low Ti levels but only a mild effect at 20% Ti. It was reported that C and N had little effect on creep, at least for levels below about 600 ppm. The effect of Ti content on creep ductility is shown in Figure 73. At low Ti contents ductility was little affected by test duration while it increased markedly for 20% Ti. The explanation is found in the effect of Ti content on recovery and recrystallization.

- V-Ti-Nb Alloys - Böhm and Schirra⁽⁵⁴⁻⁶⁰⁾ studied creep in V-Ti-Nb alloys in some detail. The stress rupture results are summarized in Figure 74. The effect of Ti on creep of these ternary alloys is similar to that in the V-Ti binary alloys. The explicit effect of Ti on one thousand hour rupture strength and stress for $10^{-2}\%$ /hr creep rate is shown in Figure 75. The apparent trend of these results can be stated in two ways. Niobium additions to the V-Ti binary alloys increase long time creep strength; significantly at low Ti levels, perhaps less so at 20% Ti. Alternatively, large Ti additions to V-Nb alloys decrease creep strength. The interpretation of this data is discussed later.

The effect of prior cold work on stress rupture strength of V-20Ti-20Nb alloy is shown in Figure 76. Cold working decreased rupture life, increased creep rate and increased rupture ductility. Since recovery was found to be complete after a few hours at 650°C, the effect of cold work after long times was attributed to differences in the recovered microstructure. Creep strength increased with increase in annealing temperature between 700°C and 1100°C following cold work.

Figure 71. Effect of titanium content on creep behavior of V-Ti alloys. (Böhm & Schirra, Ref. 54,56).

Figure 72. Effect of oxygen content on creep properties of V-Ti alloys. After Böhm (Ref. 57).

Figure 73. Creep ductility of V-Ti alloys. After Böhm & Schirra (Ref. 56).

Figure 74. Comparison of stress rupture properties of V-Ti and V-Ti-Nb alloys.

Figure 75. Effect of Ti content on creep properties of V-Ti-Nb alloys.

Figure 76. Effect of cold work on stress-rupture life of a vanadium alloy.

- V-Ti-Cr Alloys - The stress rupture results of various investigators on V-Ti-Cr alloys are shown in Figure 77. Some creep curves are shown in Figure 78 and creep rate data are shown in Figure 79. The variation in creep strength due to heat treatment is nearly as large as that due to composition. The trend is that creep strength increases with increase in annealing temperature, increase in Cr content, and decrease in Ti content.

Additional stress rupture data by Schirra⁽⁶⁰⁾ on V-Ti-Cr alloys are shown in Figures 80 and 81. About 3% Ti is the optimum Ti content in V-Ti-Cr alloys. The one data point for V-13Cr at 700°C (Figure 81) suggests that the 3% Ti addition contributes nothing to creep strength. Whether or not this is true cannot be decided on the basis of one data point but is important in assessing the origin of the strength of these V-Ti-Cr alloys, i.e., the relative contribution of solid solution hardening and dispersion hardening (due possibly to TiO).

- V-Zr-Cr Alloys - Stress rupture data on V-Zr-Cr alloys are also shown in Figures 80 and 81. If it is concluded that 1-3% Ti contributes nothing to the strength of V-Ti-Cr alloys then it must also be concluded that 2-3% Zr markedly decreases the strength of V-Cr binary alloys. In any event, the V-Zr-Cr alloys are much weaker than the V-Ti-Cr alloys. Similarly, a V-3Zr-15Nb alloy (Figure 82) is much weaker than a V-3Ti-15Nb alloy (Figure 74).

- V-Ti-Nb-Cr Alloys - Stress rupture data by Schirra⁽⁶⁰⁾ are shown in Figure 83. Niobium appears to be slightly more effective as a solid solution strengthener than chromium. However, the strength of these V-Ti-Nb-Cr alloys is hardly any different than that of the V-Ti-Nb alloys (Figure 74) or V-Ti-Cr alloys (Figures 80 and 81) for the same total atom per cent solute content.

- V-Ti-Nb-Si Alloys - Adding 1% Si to the V-Ti-Nb alloy gives a very strong alloy at 650°C, Figure 84. However, this strengthening effect is not maintained at temperatures of 750°C and higher. In fact, at these higher temperatures the Si addition appears to be detrimental.

- Binary and Ternary Alloys with Zr and C - The effect of various binary and ternary additions of Nb, Ta, Cr, Mo, W and Fe plus additions of Zr and C on

Figure 77. Stress rupture strength of V-Ti-Cr alloys.

Figure 78. Effect of Ti/Cr ratio and annealing temperature on creep behavior of V-Ti-Cr alloys. After Yaggee (Ref. 75).

Figure 79. Stress dependence of creep rate of V-Ti-Cr alloys.
 [● Data by Stewart, et al. (Ref. 66); ■, ▲, ▼ data by Yaggee (Ref. 75).]

Figure 80. Stress-rupture data for V-Ti-Cr and V-Zr-Cr alloys.

Figure 81. Stress-rupture data for V-Ti-Cr and V-Zr-Cr at 700°C.
Symbols same as in Figure 80.

Figure 82. Stress-rupture data for V-Zr-Nb and V-Ti-Cr alloys.

Figure 83. Stress-rupture data for V-Ti-Nb-Cr alloys.

Figure 84. Stress-rupture data for a V-Ti-Nb-Si alloy for varying oxygen contents.

minimum creep rate at 700°C is shown in Figure 85. Adding Zr-C to V decreases creep rate by more than three orders of magnitude, Figure 85a. Vanadium-10Ti is even stronger, and still stronger yet with Zr-C added. The various binary alloys plus Zr-C give creep rates which are similar within an order of magnitude, Figure 85b,c,d and e. The ternary alloys plus Zr-C designated VANSTAR-7, -8, and -9 were selected as the most promising for creep resistance; they are less than an order of magnitude more creep resistant than the 6-9Ti plus Zr-C alloy, Figure 85f. Results on various alloys in this group at 800°C are shown in Figure 86.

- Miscellaneous Alloys - Stress rupture data on various alloys at 650°-850°C are shown in Figure 87. Included are data on V-3Ti-1Si, V-3Ti-(1-4)Ge, V-5Ti-5Mo and the very limited available stress rupture data on the VANSTAR alloys.

- Summary of Creep Strengthening - Some of the features of alloy creep strengthening in vanadium are depicted schematically in Figure 88a, while experimental stress rupture data for various alloys are compared in Figure 88b. Pure vanadium is quite weak relative to the creep strength which can be attained in vanadium-base alloys. Interstitials affect the creep strength of vanadium and its alloys. The effect can be large, at least for oxygen -- upward of four orders of magnitude in creep rate or rupture life for vanadium and upwards of an order of magnitude in some alloys, e.g., V-3Ti. Environment also affects creep strength. In vacuum, strength decreases the harder the vacuum. This is consistent with the effect of interstitials just mentioned but is inconsistent with limited results showing accelerated creep in low pressure oxygen or nitrogen atmospheres.

There is hardly any creep data on binary alloys (except for V-Ti) upon which to base assessment of specific solute strengthening effects. However, from results on ternary V-Ti base alloys, Nb and Cr are potent solid solution hardeners. Little can be said about Ta, Mo, W, Fe and Ni, though they too are probably potent strengtheners.

The effect of Ti on creep properties of V-Ti alloys is now well known. Strength markedly increases with the first few per cent Ti additions and then gradually decreases with further increase in Ti content. This Ti-effect persists in ternary

Figure 85. Stress dependence of creep rate at 700°C of various binary and ternary alloys containing additions of Zr and C. After Pollack, et al. (Ref. 52) and Whitlow, et al. (Ref. 53).

Figure 85. (Continued)

Figure 85 (Continued)

Figure 86. Stress dependence of creep rate at 800°C of various binary and ternary alloys containing additions of Zr and C. After Pollack, et al. (Ref. 52) and Whitlow, et al. (Ref. 53).

(a)

(b)

Figure 87. Stress-rupture data for V-Ti-Si, V-Ti-Ge and other vanadium-base alloys.

Figure 88. (a) Schematic of various features of alloy creep strengthening effects in vanadium.

Figure 88 (Continued). (b) Comparison of stress-rupture life of various vanadium-base alloys at 650°C.

alloys also. The strengthening effect of small additions of Ti does not occur for small additions of Zr.

In addition to solid solution hardening, precipitation or dispersion hardening quite likely also contributes to the creep strength of most of the vanadium alloys that have been studied. The potential for strengthening by Zr + C additions (via ZrC) is somewhat moot. There is no evidence for strengthening based on nitrides. There is a strong possibility of substantial strengthening by TiO in low titanium content binary and ternary alloys and this is discussed in the following section.

The various vanadium base alloys generally show high creep ductility. Fractures are transgranular. Vanadium-base alloys obey a Monkman-Grant type relationship between creep rate and rupture life. This indicates that alloying affects rupture life by altering creep rate (deformation processes), not fracture processes (third stage creep). It also serves as a guide where data is limited, i.e., the alloy with the lowest creep rate probably also has the longest rupture life.

2.5 MECHANISMS OF DEFORMATION AND FRACTURE

The theoretical literature dealing with low temperature mechanisms of deformation in bcc metals applies to vanadium since vanadium behaves similarly to other bcc metals; for details, see the review by Christian.⁽⁸¹⁾ There are two schools of thought about the rate controlling mechanism of thermally activated deformation at low temperatures. Either an intrinsic, Peierls-type mechanism or an interstitial solid solution hardening mechanism controls the thermal component of the stress, hence the temperature dependence of the flow stress. In their earlier work on vanadium, Arsenault and Pink⁽⁸²⁾ concluded that a Peierls (double kink) mechanism controlled at low interstitial levels (less than a few hundred wppm) but that interstitials (tetragonal distortion) became the controlling short range barriers at high interstitial levels. In a subsequent electron microscopy study, Huang and Arsenault⁽⁸³⁾ observed a preponderance of straight screw dislocations in the deformed vanadium specimens, irrespective of interstitial content. The high density of screw dislocations and absence of edge dislocations in the substructure is inconsistent with the interstitial hardening mechanism but is consistent

with the Peierls mechanism. After further experimental work with emphasis on activation parameters, Crowe and Arsenault⁽⁸⁴⁾ proposed a two-mechanism view of micro- and macroyielding in vanadium; interstitials affect the thermal component of stress in the microstrain region but not in the macrostrain region. In the microstrain region the rate controlling mechanism is thermal activation of edge and non-screw dislocations past randomly dispersed interstitial solutes. Macroflow (which generally includes the 0.2% offset yield stress) is controlled by screw dislocation interactions with the lattice, i.e., the Peierls barrier. The detailed mechanism, according to Crowe and Arsenault, is the double kink nucleation of screw segments whose ends are pinned by dispersed interstitials.

Closely related to the question of the rate controlling mechanism in pure vanadium and the role of interstitials is the question of the mechanism of alloy softening, or so-called solid solution softening, which has been observed in several vanadium-base binary and ternary substitutional solute alloys, e.g., V-Ti,^(61,67) V-W, V-Cr and V-W-Cr.⁽⁶²⁾ Here, too, there are two main schools of thought; either an intrinsic, Peierls-type mechanism or a scavenging (interstitial solution hardening) mechanism is involved. Gibala and Mitchell⁽⁸⁵⁾ argue strongly for a general scavenging mechanism while Pink and Arsenault,⁽⁸⁶⁾ Hasson and Arsenault,^(87,88) and Pink and Stüwe⁽⁸⁹⁾ interpret their experimental work on V-Ti alloys in terms of an intrinsic double kink mechanism. Solute, interstitial and substitutional, are expected to always increase the athermal component of the flow stress; they may increase or decrease the thermal component. Alloy softening only applies to the thermal component.

In their study of V-(1-20)Ti alloys, Arsenault and colleagues found a change in rate controlling mechanism as the temperature increased from absolute zero. At very low temperatures (below about -173°C) the intrinsic double kink mechanism operated and in this regime alloy softening was observed. It was proposed that Ti clusters exert a torque on screw dislocations which lowers the stress required for double kink nucleation; this decreases the thermal component of stress and leads to alloy softening. At higher temperatures solid solution hardening was observed at all Ti levels. These conclusions do not negate scavenging per se, but simply negate scavenging as the mechanism of alloy softening. Clearly, Ti acts as a scavenger for interstitials and this affects the contribution which

interstitials make to the athermal component of the flow stress. Internal friction measurements showed that as little as a few tenths per cent Ti reduces the total interstitial level to <1 wppm (6appm). Keith⁽⁶¹⁾ also showed that about 1% Ti eliminates the O and N Snoek peaks and the strain aging UTS peak (Mo had no such effects). Substitutional-interstitial solute interactions in vanadium have been reviewed by Hasson and Arsenault⁽⁸⁸⁾ and Shikama, Ishino and Mishima.⁽⁹⁰⁾ In terms of vanadium alloys of commercial interest, the latter authors showed that Ti and Al are reactive toward O and N but Fe, Ni and Cr are non-interactive.

The operative slip systems in vanadium, as in other bcc metals, are complicated; the Schmid law of critical resolved shear stress does not always hold. Creten, Bressers and DeMeester⁽⁹¹⁾ discuss anomalous slip in vanadium at -100 to -196°C . Twinning is a common mode of deformation at low temperatures. As expected, the twinning plane is $\{112\}$. The propensity for twinning varies with temperature and purity. For electrorefined vanadium tested in tension, twinning first occurs at temperatures less than about -150°C . At -196°C twinning is profuse but is suppressed by O or N in solution and is completely suppressed by additions of 1500 ppm O or 860 ppm N. Carbon, present as a precipitate, had no effect on twinning.⁽¹⁷⁾ In another investigation on iodide vanadium tested in bending, twinning occurred at temperatures below -110°C with or without N additions up to 6000 ppm but C present as carbides (>300 ppm) suppressed twinning.⁽²⁷⁾ In vanadium containing sufficient impurities to induce ductile-brittle transition behavior, both $\{100\}$ and $\{110\}$ cleavage planes have been identified.^(9,35) In no case has brittle fracture in vanadium (or vanadium-base alloys) been induced by twinning.

Solid solution strengthening raises the twinning transition temperature (temperature below which twinning occurs). It can be raised to well above room temperature e.g. 140°C for V-50 a/o Nb (with addition of sufficient oxygen it can be lowered back to room temperature).⁽⁹²⁾ Twinning may also occur in the dynamic strain aging temperature range.⁽⁷²⁾

Pure vanadium is quite ductile at all temperatures, as are substitutional solid solution alloys. Interstitials determine the actual ductility of vanadium and

its alloys. There is a conspicuous absence of reports on intergranular creep fracture; only transgranular fractures have been reported, even for long time creep tests.

Böhm and Schirra⁽⁵⁴⁻⁶⁰⁾ studied mechanisms of creep in V-Ti and V-Ti-Nb alloys. Experimental results were shown in Figures 71-75. At temperatures above about 700°C the activation energy for creep is about that for self diffusion in vanadium, increasing only slightly with Ti content and independent of Nb content. The stress exponent is low, decreasing to 2-3 at high Ti contents. These results suggest a diffusion controlled creep mechanism, perhaps climb controlled at low Ti content and glide controlled microcreep at high Ti content (lower n values).

Below about 700°C (i.e., at 650°C), creep behavior is more difficult to rationalize. Some of the various facts, observations or deductions invoked by Böhm and Schirra are depicted schematically in Figure 89. The fact that rupture life could be correlated with creep rate via a Monkman-Grant type relationship established that Ti affects rupture strength through its effect on deformation per se and not the fracturing process. The low activation energy at low Ti contents rules out diffusion control due to V, Ti or Nb. The low activation energy at 1-3% Ti is close to that for diffusion of oxygen (and carbon) but interstitial diffusion controlled creep was ruled out on two counts. First, the stress exponent is too high and, secondly, no yield points are observed at low Ti levels in tensile tests, i.e., the interstitial level in solid solution is reduced to too low a level due to Ti gettering (Ti-O clusters). The return of the yield point at high Ti contents could be due to there being sufficient Ti atoms at the core of dislocations that the oxygen clustered with the Ti interacts with the dislocations to induce a yield point. While yield points are not observed for less than 5% Ti, yield points are observed in V-5Ti up to 850°C and in V-20Ti up to 650°C. It would appear that at low Ti levels, creep at 650°C is not diffusion controlled.

The high activation energy at high Ti contents (still at 650°C) is equally difficult to rationalize. The possibility that it is somehow associated with incipient recrystallization was considered. V-20Ti completely recrystallizes during creep at 750°C-800°C (initial 10 μm grain size being refined to 3 μm). With 3-5% Ti, recrystallization during longtime creep occurs at 850°C but very little at 800°C. At 650°C, serrated grain boundaries are observed during creep even at

Figure 89. Top; Summary of observations by Böhm and Schirra on the effect of Ti on the creep strength of V-Ti alloys. Bottom; Schematic of two alternatives for interpreting the Ti-effect; Degradation due to Ti in solid solution or enhancement due to TiO ??

low Ti levels but not in cold worked and annealed material. The serrations are due to strain induced (subgrain formation) grain boundary migration, which is taken to be a precursor of recrystallization. Recrystallization as the cause of the high activation energy was ruled out, however, because in low Ti alloys high activation energies are not observed at higher temperatures where recrystallization does occur. Since only Ti (not Nb or Mo) affects the activation energy it would appear that Ti-interstitial (oxygen)-dislocation interactions are responsible for the observed creep behavior.

Precipitation of TiO occurs at all Ti levels but is a maximum at low Ti content. Here, the precipitate is semicoherent $\{ (001)_M || (001)_{\text{TiO}}; [100]_M || [110]_{\text{TiO}} \}$. The extent of TiO precipitation decreases with increasing Ti content, the precipitate size increases and coherency is lost due to increasing matrix-precipitate mismatch (Ti expands the V lattice). These observations, those related to the yield point, and the observation that an increase in oxygen content increases the extent of TiO precipitation (Hasson and Arsenault⁽⁸⁷⁾ quote the opposite effect of oxygen) suggest that the oxygen solubility is a minimum at low Ti content but increases with increase in Ti. The implication, here, that Ti is less effective as a getterer at high Ti contents was questioned by Hasson and Arsenault⁽⁸⁸⁾ who showed by internal friction measurements as previously mentioned that Ti at all levels getters oxygen.

The convergence of the two curves in Figure 72 at low interstitial level and the associated creep strength relative to that of V suggests that Ti (1 to 20%) in solid solution contributes little to creep strength. The strengthening at low Ti and higher oxygen content (the peak in Figure 89) is, then, due mainly to precipitation of TiO . The contribution of Nb in solid solution is the difference between the curves with Nb and that for the V-Ti binary. Two alternative interpretations of the Ti-effect are depicted in the lower part of Figure 89. One viewpoint is that the V-Nb binary alloy has high creep strength (Point A) and that Ti additions, presumably by some sort of solid solution effect, degrade creep strength (go from A to B). The alternative viewpoint is that the strength of the V-Ti-Nb solid solution (V-Nb binary plus some solid solution strengthening due to Ti) starts at Point B. With decreasing Ti content, strength increases due to TiO precipitation, i.e., the large increase in strength due to TiO outweighs the small decrease in Ti solid solution hardening.

According to the latter viewpoint, then, it would be fundamentally incorrect to say that Ti decreases the creep strength of V-Nb solid solution alloys. Rather, the effect is that too large an addition of Ti negates the potent contribution of TiO precipitation at low Ti levels. In addition to the electron microscopy work by Kramer,⁽⁵⁹⁾ support for this viewpoint also comes from noting that the creep strength of the V-(1-3)Ti-Nb alloys appears to be too high relative to the ultimate tensile strength of V-Nb binary alloys to be due solely to Nb solid solution hardening. No creep data on the V-Nb binary alloy is available to check this. The correct explanation of the Ti-effect is more important than mere academic interest. The two alternative viewpoints suggested have importantly different implications to future alloy development.

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3.0 CORROSION AND COMPATIBILITY IN LIQUID ALKALI METALS

CONTENTS

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3.1 INTRODUCTION

The feasibility of vanadium alloys as containment or structural materials for the first wall and/or blanket hardware of fusion reactors will depend greatly on their compatibility with the coolants and breeding materials included in the blanket system. Conceptual fusion reactor designs to date have employed both liquid alkali metals and high pressure helium as the coolant. Of the liquid alkali metals, lithium offers the dual advantage of being an excellent neutronic breeder of tritium as well as an excellent heat transfer fluid. The use of a single working fluid to achieve both the cooling and breeding functions of the blanket has obvious advantages.

In addition to lithium, the alkali liquid metal sodium has also been suggested for the blanket coolant. The major advantages of sodium over lithium are related to its corrosion properties, although most of this advantage applies more to the austenitic stainless steels or nickel-base alloys than to the refractory metals. The relatively high solubility of nickel in lithium has been a major cause of concern for high temperature systems design; this has led to the suggestion of the possible use of sodium as the coolant, coupled with a

semi-stagnant tritium-breeding lithium stream, for high temperature stainless steel/nickel-base alloy containment systems.

High pressure helium gas has also been suggested as a blanket coolant. While this gas is nominally inert, trace concentrations of active impurities, which are always present and essentially impossible to monitor and control, will react unfavorably with vanadium alloys at the temperatures of interest (to 650°C). It is generally recognized that blanket/first wall designs of systems employing high pressure helium will not be designed with refractory metal alloys. Hence, no review or discussion of these compatibility concerns is provided here.

The literature dealing with liquid alkali metal corrosion of vanadium and its alloys is reviewed in the following subsections. Attention is given to both lithium and sodium data. Preceding this review, a brief outline of the current state of understanding of liquid metal corrosion mechanisms is provided.

3.2 GENERAL REVIEW OF LIQUID METAL CORROSION MECHANISMS

The use of vanadium alloys in a D-T fueled CTR system employing liquid lithium as a tritium breeding agent and lithium or sodium as a heat transfer medium will depend, among other things, on the compatibility of the vanadium alloy with the liquid metal coolant. Compatibility can be defined as an acceptable amount of interaction between the liquid metal and the structural containment material under the intended service conditions. The interaction limits are a function of the system design. The interactions usually referred to as corrosion are simply the result of the system moving toward chemical equilibrium as facilitated by the system temperature. The movement toward equilibrium can occur by a number of mechanisms. In order to provide a basis for understanding the various corrosion mechanisms which operate in liquid metal systems employing refractory metals, the corrosion mechanisms are classified and described in general terms in the following discussion. Classification of the corrosion mechanisms considered is as follows:

- Dissolutive corrosion
 - Dissolution of solid metal by liquid metal
 - Dissimilar metal mass transfer
 - Temperature-gradient mass transfer

- Impurity reaction
 - Liquid metal impurities
 - Solid metal impurities
 - Partitioning of impurities between solid and liquid metals

3.2.1 Dissolutive Corrosion

- Dissolution of Solid Metal by Liquid Metal - Dissolutive corrosion involves a simple solubility relationship between the liquid metal and the elements which make up the solid containment material. The solubility relationship for a given element "A" can be represented by the following reaction:

The dissolution process proceeds until the chemical potential of A is equivalent in both phases. The rate of solution is dependent on temperature, flow velocity, surface area to volume ratio, and surface condition of the metallic phase. The dissolution rate of polycrystalline metal is generally more rapid in high energy regions such as grain boundaries and twinned regions. The dissolving process and the variables which affect it have been discussed in considerable detail in a number of publications. (1-6)

- Dissimilar Metal Mass Transfer - When two or more solid metals or alloys are placed in contact with a common liquid metal, extensive interalloying can take place between the solid metals even when the solubility limits in the liquid metal of the various elements involved are very small. The driving force for this process is the thermodynamic requirement that the chemical potential of each element be equivalent in all phases that are in contact. Kinetic considerations usually limit the extent of alloying and, as would be expected, this corrosion process becomes increasingly more important as the system temperatures increase.
- Temperature Gradient Mass Transfer - Temperature gradient mass transfer occurs in solid metal-liquid metal systems as a result of the temperature dependence of solubility of the solid metal in the liquid metal. A coolant circulating in a heat-exchange system tends to dissolve the container metal in the hot zone and to transfer it to cooler zones where it may deposit and plug the circuit.

Although kinetic factors such as diffusivities, rates of dissolution, and rates of crystal nucleation and growth have an important effect on the rate of mass transfer it is recognized that the basic driving force for this process lies in the variation of solubility of both the solid metal and liquid metal with temperature.

Since the solubility of a solid metal in liquid metal nearly always increases with temperature, temperature gradient mass transfer must be considered as a serious compatibility problem in high-temperature heat-transfer systems. The most important effect of temperature gradient mass transfer in relatively compatible systems is generally not the removal of metal (although interstitial loss/gain may be critical) from the hot regions but the subsequent crystal deposition in the cooler regions of the systems. These deposits increase the pressure drop in circulating systems and can eventually restrict flow completely.

3.2.2 Impurity Reactions

The interstitial elements, oxygen, nitrogen, carbon, and hydrogen have been found to be the major impurities which have the greatest influence on corrosion in many liquid metal systems.^(2,7-12) The corrosion mechanisms are complex and in many cases not completely understood. The initial location of the highest impurity concentrations, solid containment material versus the liquid metal, and their redistribution or partitioning on reaching operating temperature, also have a profound affect on corrosion behavior. Examples and explanation of some experimentally observed phenomena are given in the following discussions.

- Liquid Metal Impurities - Impurities in liquid metals, oxygen in particular, have been found to increase the corrosion rate of some metals presumably through the formation of soluble or loosely adherent compounds. A classic example is the iron-sodium system where oxygen in the sodium leads to an increase in the amount of temperature gradient mass transfer. It is postulated, and strong evidence exists, that oxygen in the sodium reacts with iron to form the complex compound $\text{FeO} \cdot (\text{Na}_2\text{O})_2$.^(13,14) The complex oxide is thermodynamically more stable with respect to oxygen dissolved in sodium at high than at low temperatures. The successive formation and reduction of $\text{FeO} \cdot (\text{Na}_2\text{O})_2$ in the hot and cold zones, respectively, is responsible for the enhanced mass transfer of iron. It has been

noted that niobium, vanadium, and tantalum also form complex oxides with sodium oxide.^(13,15,16)

● Solid Metal Impurities - The presence of oxygen, carbon, and nitrogen in the solid metal has also been found to cause corrosion. The phenomenon commonly referred to as liquid metal penetration has been observed to occur when the solid metal contains greater than a certain threshold impurity concentration.^(1,17,18) This concentration depends on the metal, the alkali metal, and the temperature. The liquid metal penetrates along grain boundaries and certain crystallographic planes. Penetration is rapid; for example, a 0.040 inch specimen of tantalum containing 600 ppm oxygen was completely penetrated by lithium after exposure for 0.5 hour at 600°C.⁽¹⁸⁾ The penetration phenomenon was encountered in niobium and tantalum exposed to lithium, but has also been found to occur when these metals are exposed to sodium, potassium and sodium-potassium eutectic.^(12,18-20) Early work with pure iron indicated resistance to attack by lithium; however, iron containing small amounts of carbon was penetrated intergranularly by lithium at certain temperatures.^(1,21) Corrosion was attributed to the reaction of lithium with carbon in the grain boundaries.⁽¹⁾

The problem of grain boundary penetration was circumvented for niobium and tantalum by the development of more corrosion resistant alloys, i.e. through the addition of minor amounts of the reactive metals zirconium or hafnium; however, the mechanism by which penetration occurs is still not clear. Penetration models involving diffusion⁽²²⁾ and a wedging mechanism have been proposed.⁽¹⁸⁾ There are conflicting reports in the literature regarding the susceptibility of unalloyed vanadium to the penetration phenomenon.^(1,22,23) This matter will be addressed in more detail later.

● Partitioning of Impurities - The extent to which oxygen, nitrogen, and carbon will undergo reactions within refractory metal-liquid metal systems can be assessed by examining the partitioning of the interstitial elements. When the interstitial element concentrations in both the refractory metal and liquid metal are below saturation, i.e., single phase, the partitioning of these elements can be represented by the equilibrium distribution coefficient, which is the ratio of the impurity element concentration in the solid metal to that in the liquid metal.

From a knowledge of the distribution coefficients and the initial concentrations of interstitial elements in both the solid metal and liquid metal, the tendency for interstitial transfer can be assessed. The type of interstitial-element interactions that are likely to occur in each liquid metal system can be evaluated. For example, the severe grain-boundary penetration phenomenon, which has been observed after exposure of some metals to lithium, occurs in systems with distribution coefficients much less than unity.^(8,17,24) Reduced strength of the refractory metal as a result of loss of interstitial elements to lithium may also be important in systems with distribution coefficients much less than unity.^(25,26) Conversely, embrittlement of the material as a result of interstitial transfer from the liquid metal may be important in systems with distribution coefficients substantially greater than unity. If a sufficient amount of impurity element is present in the liquid metal, enough impurity may be transferred to saturate the surface of the container material and form a compound, e.g., an oxide, nitride, or carbide, on the surface. Substantially different corrosion kinetics and mechanical behavior of materials can result when compound formation occurs.

The derivation of the distribution coefficient is reported in detail in a number of publications.^(8,27-29) The distribution coefficient is calculated from basic thermodynamic data for the binary systems, viz, solubility of the impurity in the solid metal and liquid metal, and free energies of formation of the most stable compounds formed by the impurities under consideration. These data are used in the Nernst equation. As a first order calculation, it is assumed that the solid metals and the liquid metals are mutually insoluble and that dilute solutions of the interstitial elements in the solid metals and liquid metals obey Henry's law. The distribution coefficient K_T can be represented by:

$$K_T = \frac{C_M}{C_{LM}} = \frac{(C_M)_s}{(C_{LM})_s} \exp \left[\frac{\Delta F_{LM}^0 - \Delta F_M^0}{RT} \right]$$

where C_M and C_{LM} are the concentrations (atomic fractions) of the interstitial element in the solid metal and liquid metal, respectively; the subscript s on the C's represents the saturation concentrations; and ΔF_{LM}^0 and ΔF_M^0 are the free energies of formation of the stable compounds of the interstitial with the liquid

metal and the solid metal, respectively. Solubility and free energy of formation data are derived from the open literature.

3.3 VANADIUM AND VANADIUM ALLOY/LITHIUM COMPATIBILITY

3.3.1 Literature Survey

The amount of experimental work reported in the open literature involving the compatibility of vanadium and vanadium base alloys with lithium is sparse. The paucity of data can be attributed to the fact that vanadium alloys were never a prime structural candidate for a major system involving lithium. Thus, a systematic investigation to obtain compatibility data for vanadium alloys with lithium has never been carried out.

The first significant data involving vanadium/lithium compatibility was reported by Hoffman.⁽¹⁾ Unalloyed vanadium containing 0.15O₂, 0.14C, 0.04N₂ and 0.0001H₂ (weight percent) was exposed under static and dynamic (rocking capsule) test conditions at 816°C for 100 hours. The lithium contained 200 to 600 ppm nitrogen and 100 to 400 ppm oxygen. In the static test, which was conducted under isothermal conditions for 100 hours, the vanadium gained 8.4 mg/in². In the rocking tests, which operated with a hot zone at 816°C and a cold zone at 482°C for the same period of time, the hot zone lost 1.3 mg/in² while no change was reported for the cold zone. Hoffman, however, did note a shallow subsurface void formation ~0.001 inch deep in the hot zone material. Freed, et al.,⁽³⁰⁾ reported the results of a monometallic forced flow loop which operated between 871°C and 651°C for 1194 hours at a flow rate of 13 fps. Results were reported qualitatively as nil attack in the hot zone and nil deposition in the cold zone.

DiStefano reported compatibility results for unalloyed vanadium/lithium tests carried out in isothermal capsules for 100 hours at 816°C.⁽⁸⁾ The tests were carried out in capsules made from the same material as the test specimens. Additions of oxygen, up to 2200 ppm, were made to some vanadium samples prior to lithium exposure. The samples were charged with oxygen and given a homogenization anneal. Hardness traverses were taken to check homogeneity. The vanadium samples were not penetrated by the lithium regardless of oxygen content. All samples experienced a loss of oxygen as a result of the lithium exposure. Oxygen content in a sample which contained 2200 ppm initially was reduced to 180 ppm.

Partition coefficients for oxygen distribution were not calculated. In later work reported by DeVan, unalloyed vanadium encapsulated in V capsules and V-20Ti sample encapsulated in molybdenum⁽³¹⁾ were exposed at temperatures from 608° to 1000°C. In all cases, oxygen was removed from the vanadium and V-20Ti alloy regardless of the initial oxygen content of the lithium. There was no evidence of lithium penetration. Initial oxygen levels were 1336 ppm for the unalloyed vanadium and 940 ppm for the V-20Ti alloy. At temperatures of 700°C and above, the final oxygen level of the unalloyed vanadium was < 15 ppm. Vanadium containing as high as 2200 ppm oxygen was not penetrated by lithium. The V-20Ti alloy was deoxidized by lithium at 800 and 1000°C. The deoxidation process was more sluggish than in the case of unalloyed vanadium. Evidence of dissimilar metal mass transfer was noted for V-20Ti alloy samples encapsulated in molybdenum and exposed at 1000°C. DeVan suggested that removal of oxygen might result in degradation of mechanical properties for alloys that derive strength from oxygen in solution or from second-phase oxide particles in the matrix.

Borgstedt⁽²³⁾ reported results for the exposure of unalloyed vanadium and V-3Ti-15Nb alloy to lithium at 700°C for 310 and 500 hours. Samples of the unalloyed vanadium and the V-3Ti-15Nb alloy were encapsulated in stainless steel equivalent to AISI 316. The unalloyed vanadium had an initial oxygen content of 1450 ppm; this was reduced to 570 ppm after 300 hours and 275 ppm after 500 hours. Carbon level, however, increased as a result of the test exposure from 800 to 1300 ppm. The unalloyed vanadium exhibited evidence of grain boundary penetration in a zone 100 μm wide near the surface. The V-3Ti-15Nb alloy did not experience a change in oxygen level as a result of the test exposure. Initial and final oxygen level was reported as 1100 ppm. No evidence of grain boundary penetration of the V-3Ti-15Nb alloy was noted. Carbon, as in the case of unalloyed vanadium, increased from a level of 480 to 1055 ppm. Examination of the inner surface of the stainless steel capsule revealed evidence of decarburization.

In subsequent work involving a V-5Ti-2Cr alloy, samples were exposed for 500 hours at 700°C in lithium contained in both type 316 stainless steel and type 321 stainless steel.^(32,33) Borgstedt reported essentially no change in oxygen level in the vanadium alloy regardless of containment material. Carbon levels, however, doubled in the sample encapsulated in unstabilized type 316 stainless steel. The vanadium alloy sample thermally exposed to lithium in the stabilized type 321 stainless steel

exhibited virtually no change in bulk carbon concentration. Hardness traverses indicated a gross increase in hardness in the first 0.05 mm near the surface of the sample exposed in unstabilized stainless steel, while only a slight increase in hardness was noted near the surface, <0.02 mm, for the sample exposed in the stabilized type 321 stainless steel. Borgstedt also reported results involving a V-4Ti-5Nb-10Cr alloy which had been exposed to lithium at 700°C for 1000 hours. Nitrogen concentration increased from ~200 ppm to 3100 ppm after 500 hours and to 4300 ppm after 1000 hours. The sample exhibited a significant increase in hardness at each exposed surface; the increased hardness zone extended half way to the mid-plane of the specimen.

Smith has conducted an extensive analysis of the thermodynamics of interstitial interactions with a number of refractory metal/lithium systems.^(25,34) The interactions were analyzed in terms of the equilibrium distribution coefficient. The interstitial element concentrations required in lithium for the formation of stable oxides, nitrides, or carbides were also determined. The results of these analyses are presented in Figures 1-5. In Figure 1, the distribution coefficient for oxygen in vanadium is seen to be much less than unity. This low value indicates that oxygen should transfer from the vanadium to the lithium; this is consistent with the limited experimental data discussed above.

The other elements for which distribution coefficients are shown in Figure 1, zirconium, titanium, niobium, chromium, and molybdenum, are frequently used as alloying additions to vanadium. Chromium, molybdenum, and niobium have distribution coefficients which are equal to or even less than that of vanadium indicating that even large additions of these elements should have no effect on the movement of oxygen from the solid metal to the lithium. Titanium additions to vanadium should tend to stabilize oxygen; however, since titanium oxide ($\delta\text{-Ti}_3\text{O}_2$) is unstable (according to Smith) in lithium, internal oxidation of vanadium-titanium alloys in contact with lithium is not predicted. This has also been discussed by DeVan.⁽³¹⁾ Zirconium, which has a coefficient of ~2 in the temperature range of interest, would not be expected to have a significant effect on oxygen retention in vanadium when present at levels of a few percent. Higher levels of zirconium, however, may influence the partitioning of oxygen, or at least the kinetics of the partitioning process.

Figure 1. Temperature dependence of the equilibrium distribution coefficients for oxygen between selected refractory metals and lithium. (Refs. 25, 34)

Figure 2. Temperature dependence of the equilibrium distribution coefficients for nitrogen between selected refractory metals and lithium. (Refs. 25;34)

Figure 3. Temperature dependence of the equilibrium distribution coefficients for carbon between selected refractory metals and lithium. (Refs. 25,34)

Figure 4. Temperature dependence of the nitrogen concentrations in lithium at which selected refractory metal nitrides are stable. (Refs. 25,34)

Figure 5. Temperature dependence of the carbon concentrations in lithium at which selected refractory metal carbides are stable. (Refs. 25,34)

In Figures 2 and 3, the distribution coefficients for lithium-nitrogen-refractory metals and lithium-carbon-refractory metals are plotted. In each case, the elements zirconium, titanium, niobium, and vanadium have distribution coefficients much greater than unity. Thus, these elements would tend to getter nitrogen and carbon from lithium. Chromium and molybdenum, even at high concentrations, would not be expected to affect nitrogen and carbon distribution in vanadium alloy/lithium systems.

In Figures 4 and 5, the results of nitride and carbide stability determinations are plotted as a function of nitrogen and carbon concentration in lithium with temperature. Included in each figure is the expected nitrogen and carbon level that could be maintained by cold trapping. The levels were determined by Smith from solubility data for nitrogen and carbon in lithium at the melting point, 180°C. Included also in Figure 5 is a reference carbon activity of 10^{-3} with respect to graphite. This activity level for carbon was found to be typical for a large sodium system--EBR II--that utilizes type 304 stainless steel for containment.

The results shown in Figures 2 and 4 indicate that nitrogen transfer from lithium to vanadium and its alloys is likely to occur. This is particularly true for vanadium alloys which contain niobium, titanium, and zirconium. Embrittlement of vanadium by nitrogen and by nitride formation is very possible. Smith suggested that the nitrogen level in a system could be controlled to satisfactory levels by hot trapping with one or more of the strong nitride formers, titanium and/or zirconium.

The situation with carbon is similar to that of nitrogen. The results in Figures 3 and 5 indicate that low carbon levels, <1 ppm in lithium are required to avoid carbide formation. Zirconium, titanium, and niobium along with vanadium are indicated to be strong stable carbide formers even at very low carbon levels in lithium. As in the case with nitrogen, additions of molybdenum to vanadium should reduce the tendency for carbide formation at temperatures below 700°C. At the indicated carbon cold trapped level, a tendency for chromium carbide to stabilize is shown. Thus, some level of chromium should be tolerable in vanadium. Titanium, zirconium, and niobium should, as in the case with nitrogen, be excellent hot trap getters for controlling carbon level in lithium.

It should be pointed out that C and N have considerably lower solubilities in vanadium than does oxygen. Thus, one can anticipate the formation of carbides and nitrides for most practical C and N levels in Li (certainly in cases where conventional alloys are in contact with the vanadium).

3.3.2 Discussion

As indicated in the literature survey, little experimental data concerning the compatibility of vanadium alloys with lithium have been reported. The most profound effects on the corrosion behavior of vanadium and vanadium alloys that have been revealed experimentally are attributed to interstitial element interactions. These results have come primarily from experiments which utilized small capsules with tests conducted for relatively short times; <1000 hours. Only one forced convection loop experiment has been reported. This loop operated for ~1200 hours, and was evaluated in a qualitative manner. Little or no material was removed from the hot zone or deposited in the cold leg of the system. Many questions regarding the effects of interstitial impurities in a vanadium alloy/lithium system operating for an extended time, on the order of several years, at a peak temperature of 650°C remain to be answered.

The extremely small distribution coefficient for oxygen/vanadium and the other refractory and reactive metals indicates that oxygen enhanced corrosion most likely will not occur in these systems. The removal of oxygen from the base metal containment materials is not without potential hazard. Most vanadium alloys contain from 500 to 1500 ppm oxygen as an impurity. This is due to the fact that the best commercially available vanadium melt stock, until recently, contained between 1000 to 2000 ppm oxygen. Vanadium with lesser amounts of oxygen, <200 ppm, is available in small quantities at premium prices. Thus, all mechanical property data are derived from alloys with fairly large concentrations of impurity oxygen. The experiments of DeVan and others indicate that within several hundred hours the residual oxygen in a lithium/vanadium alloy system could be well below 1 ppm. Binary alloys that rely on secondary oxide particles to pin grain boundaries may be prone to massive grain growth as a result of lithium deoxidation. Vanadium alloy development programs aimed at CTR applications involving lithium must consider this aspect and include it in the evaluation process. It has also been shown that alloy bases such as niobium and tantalum are susceptible to lithium penetration when the oxygen impurity

level is above some threshold level. The penetration phenomenon is rapid and occurs before the oxygen can vacate the base metal for the lithium. DeVan has shown that unalloyed vanadium containing 2200 ppm oxygen and tested in a mono-metallic system is apparently not susceptible to lithium penetration. Borgstedt, on the other hand, reports that unalloyed vanadium with 1450 ppm tested in a type 316 capsule is vulnerable to lithium penetration. The cause for this seemingly contradictory behavior must be determined. The conditions which foster its occurrence must be well defined. The opportunities for oxygen contamination during welding of large structural components are great. Harrison⁽¹⁹⁾ has reported incidents of lithium penetration of niobium and tantalum alloys which had been welded in impure atmospheres. The alloys contained small levels of zirconium and hafnium additions which were effective in preventing lithium penetration by reducing the oxygen activity in the base metal. The weld metal, however, contained sufficient oxygen in solution to promote lithium penetration. Lithium penetration can undoubtedly adversely affect mechanical behavior when the penetrated area represents a significant portion of the material cross section.

While there is little experimental data to confirm predictions drawn from the nitrogen and carbon equilibrium distribution coefficient data, the presence of these impurity elements in vanadium/lithium systems may be cause for more concern than that of oxygen. The indicated strong tendency for vanadium, niobium, zirconium, and titanium to form embrittling nitrides and carbides must be confirmed. A single reported test result by Borgstedt⁽²³⁾ indicates a rapid uptake of carbon by a vanadium alloy when tested in a stainless steel container. The presence of a large graphite shield in a CTR can provide an infinite source of carbon to the lithium coolant unless similarly contained. The kinetics and mechanisms of interstitial mass transfer must be determined and means to control carbon and nitrogen impurities in the lithium must be developed. Cold trapping of the lithium appears to be impractical due to the high solubility of nitrogen and carbon in lithium at its melting point. This thermodynamic prediction must also be confirmed.

In addition to the effects of interstitial impurities, dissolution type corrosion mechanisms must also be investigated. In particular, dissimilar metal mass transfer must be considered for designs involving a multimetallic system. This type of investigation is best conducted in forced convection loops which have

appropriate surface area ratios of the various containment materials involved, at temperatures anticipated in the actual system. In these systems, interstitial impurity levels must be monitored and controlled. Reliable continuous monitoring equipment must be developed for this purpose. There is also a definite need to experimentally determine the behavior of V alloys in Ti and Nb stabilized stainless steel systems.

3.4 VANADIUM AND VANADIUM ALLOY/SODIUM COMPATIBILITY

3.4.1 Literature Survey

Vanadium and vanadium alloys behave quite differently in sodium at elevated temperatures than in lithium. An indication of this difference in behavior is illustrated in Figure 6.⁽³⁵⁾ As is the case with lithium, interstitial element impurities such as oxygen have a significant effect on corrosion/compatibility. The free energy of formation of lithium oxide is significantly more negative than that of sodium oxides over the entire temperature range of interest. The stability of sodium oxide as a function of various oxygen activities in sodium graphically illustrates the role of oxygen in the vanadium/sodium system. A simplistic interpretation of the free energy curves indicates that vanadium, niobium, and titanium will tend to getter oxygen from sodium, even at concentrations as low as 10 ppm, whereas lithium will remove oxygen from these same elements. It can also be concluded from the thermodynamic data that molybdenum and chromium additions to vanadium should not have a deleterious effect on vanadium with respect to oxygen pick up from sodium and that zirconium and titanium additions should accentuate the oxygen pick up in vanadium alloys. These aspects will be discussed in light of published experimental results.

Smith has calculated the equilibrium distribution coefficient for the vanadium-sodium-oxygen system.⁽³⁶⁾ The results of these calculations are reproduced in Figure 7 along with values determined from experimental data. The coefficient is large and positive over the entire temperature range, decreasing with increasing temperature. Inserting solubility values for oxygen in vanadium into the expression which describes the curve in Figure 7, produces the oxygen concentrations in sodium required for the $V_{(O \text{ sat.})} - O_{(Na)} - V_5O$ phase equilibrium as a function of temperature. Smith has experimentally determined the oxygen concentration required in sodium to produce oxide films on small diameter vanadium wires.⁽³⁶⁾ The minimum oxygen concentration in sodium which produces a V_5O film on vanadium is shown in Figure 8 as a function of temperature. Unalloyed vanadium which is exposed to

Figure 6. Free energy of oxygen in Na and Li as a function of oxygen concentration compared with the free energy formation of oxides of V, Cr, Al, Ti, Nb and Zr. (Ref. 35)

Figure 7. Calculated and experimentally measured distribution coefficients for oxygen in the V-O-Na system.

Figure 8. Temperature dependence of the $V(\underline{o} \text{ sat.}) - \underline{O}_{\text{Na}} - V_5O$ equilibrium. (Ref. 36)

sodium containing oxygen will take the oxygen into solution when the oxygen level and temperature are below the phase boundary. Above the boundary, an oxide layer forms on the surface of the vanadium which can be removed by abrasion in flowing systems. In the former case, the corrosion behavior is characterized by weight gain as oxygen is taken into solution. In the latter case, a weight loss situation is produced by any action that removes the loosely adherent oxide layer. Alloying additions would be expected to shift the phase boundary to higher or lower oxygen values depending on the concentration present and the value of the equilibrium distribution coefficient for the element with respect to the oxygen-sodium system. This relationship, along with the difficulty in accurately measuring the oxygen content in sodium in the very low ppm range, may account for the variety of corrosion behavior that has been reported in the literature for various alloys. (In a continuation of the work published in Reference 36, Smith has examined the effects of chromium additions to vanadium, and titanium additions to V-Cr binaries, on the amount of oxygen picked up during exposure to sodium at 550°-700°C. The results of these experiments indicate titanium may reduce the kinetics of oxygen transport in V alloys to an extent where, even in Li systems, loss of oxygen may occur at insignificant rates).

Unlike the vanadium/lithium system, a great deal of experimental work has been conducted to investigate the compatibility of vanadium alloys with sodium. The impetus for this work was provided when it was discovered that vanadium was not susceptible to gross fast neutron damage and possessed relatively good strength at elevated temperatures. These prerequisites made vanadium a prime alloy base candidate for fuel clad applications in the liquid metal fast breeder reactor (LMFBR) program. Vanadium alloys were considered as a fuel containment material with an expected life in the reactor of 3 years or approximately 24,000 hours.⁽³⁷⁾ Thus compatibility with sodium was based on maintaining adequate end-of-life mechanical and structural integrity for this time period. The three year fuel cycle of the LMFBR reference design represents only a fraction of a desired CTR blanket system life. It is recognized that the first wall may be replaced several times during the life of the plant. Other components not subject to the neutronic environment of the first wall will no doubt have a target life equivalent to that of the total plant for economic reasons. The published sodium/vanadium alloy

compatibility data must be interpreted in light of these two quite different system requirements, CTR and LMFBFR.

When it became apparent that vanadium alloys were the leading alternative to stainless steels for use as fuel cladding in the LMFBFR system, a number of alloy development programs were initiated at various facilities around the world. The majority of vanadium alloy/sodium compatibility work in the U.S. has taken place at Argonne National Laboratory, Oak Ridge National Laboratory, and at Westinghouse. Significant experimental work has also been conducted at Karlsruhe, West Germany, the National Research Institute for Metals in Japan, and at the Center for Nuclear Studies, Saclay, France.

The first work concerning the compatibility of vanadium and vanadium alloys with sodium at temperatures up to 650°C conducted in this country took place at Argonne National Laboratory. As a result of screening test programs involving niobium and vanadium alloys, the superiority of vanadium alloys over niobium alloys was demonstrated with respect to corrosion resistance in sodium at 650°C.⁽³⁸⁾

In subsequent test programs at Argonne, a large number of binary and ternary vanadium base alloys were investigated in static and flowing sodium.^(39,40) V-20Ti alloy was selected as a reference alloy to provide a basis for comparison.

Binary alloys containing titanium, aluminum, copper, chromium, iron, nickel and silicon were evaluated. Ternary alloys of vanadium-titanium-chromium, titanium-molybdenum, titanium-tantalum, titanium-niobium, and chromium-aluminum were also evaluated for compatibility with sodium at temperatures up to 650°C, under static and dynamic conditions with oxygen levels in the 2-6 ppm range and in the 10-16 ppm range. It was determined that corrosion behavior was particularly sensitive to oxygen concentration in the sodium. In the static systems at low oxygen levels, the alloys gained weight in a protective manner, and above about 10 ppm, the alloys lost weight proportional to exposure time. Under low oxygen conditions for times up to 475 hours, and over the temperature range 550 to 750°C, most of the experimental results can be expressed in terms of the parabolic rate law, $(\Delta W/A)^2 = k_p t$. The observed weight gains are attributed to the solution of oxygen in the metal rather than to the formation of surface oxides. The variation of the parabolic rate constant with temperature follows an Arrhenius-type

relationship. Microhardness traverses indicated that in many cases a subsurface hardened zone was formed as a result of diffusion into the alloy.

In a dynamic system (velocity 6.1 m/s) at 650°C and oxygen levels of 10 ppm in the sodium, protective kinetics were observed.⁽³⁹⁾ After a 139 day (3336 hr) exposure, the weight gain was described by the empirical equation $\Delta W = 0.26t^{0.24}$ (ΔW in mg/cm² and t in days). The quantitative differences in the rate laws observed in the two experiments were not explained. As a result of the Argonne evaluation, the alloys, V-5Cr, V-10Cr, V-15Cr-5Ti, V-15Ti-7.5Cr and V-20Ti were recommended for further development as core clad alloys for the LMFBR provided that oxygen levels in sodium could be maintained below 10 ppm. The effects of long term exposure to sodium under these conditions on mechanical properties were not determined for these alloys.

Early work reported by Champeix, et al.,⁽⁴¹⁾ involved the study of the corrosion behavior of vanadium and the binary alloys, V-20Ti, V-10Al, V-6Nb, V-1.5Zr, and V-0.8Si, in flowing sodium (2 m/s) at 600°C for times up to 1000 hours. When the sodium was hot trapped, negligible weight changes were noted, ~0.1 mg/mo. No change in structure or hardness was noted. A slight surface hardening was observed in the case of titanium and zirconium alloys. When cold trapped sodium was utilized, linear weight loss behavior occurred as a result of erosion of oxidation products from the surface by the flowing sodium. With regard to the alloy additions, titanium and zirconium were not recommended. Aluminum and molybdenum produced increases in weight. However, considerable surface hardening was associated with the vanadium-aluminum alloy, whereas hardness increases were observed in the core of the vanadium-molybdenum alloy. On the basis of weight loss data, silicon, niobium, and chromium were considered to be beneficial since they apparently reduced the susceptibility of vanadium to oxidation by a factor of 3. It was noted, however, that these additions caused considerable case hardening. Chromium was considered the most valuable addition since it formed a relatively adherent oxide layer on the alloy which could result in long-term reduction of corrosion kinetics. The mechanical property behavior of the reported alloys was not investigated.

Westinghouse, under contract to the AEC, developed a number of vanadium alloys specifically designed for use in the LMFBR.^(42,43) The alloys were developed

with long term creep resistance, compatibility with the nuclear fuel, and sodium compatibility as major objectives. The most promising alloys were designated VANSTAR-7 (V-9Cr-3Fe-1.3Zr-0.05C), VANSTAR-8 (V-10Ta-8Cr-1.3Zr-0.05C) and VANSTAR-9 (V-6Fe-5Nb-1.3Zr-0.05C). These alloys were exposed along with V-20Ti in flowing sodium (1.5 m/s) containing < 10 ppm oxygen maintained by a cold trap.⁽⁴⁴⁾ Samples were exposed from 500 to 1500 hours in the temperature range 675 to 800°C. The loop was constructed of stainless steel with a stainless/vanadium ratio of 7.7/1. Samples were inspected after 500 and 1500 hours exposure. In all cases, weight gains were observed. The weight gain of the VANSTAR alloys was one-third as great as the weight gain of the V-20Ti. The results appear to fit the parabolic rate law, $\Delta W^2 = k_p t$ and the weight gains were due to the transport and solution of nitrogen, carbon and oxygen. The variation of the parabolic constant with temperature followed an Arrhenius-type relationship. All the alloys experienced surface hardness increases due to interstitial absorption, and in the case of the VANSTAR alloys, considerable hardening was observed away from the surface regions. The bend ductile-brittle transition temperatures were increased and considerable reductions were noted in room temperature tensile ductility. Ductility was retained at temperatures above 150°C. In VANSTAR-9, exposed 1500 hours at 790°C, interstitial pick up was determined, at a depth of about 0.001 inch, to be:

<u>Interstitial</u>	<u>Wt. PPM</u>	
	<u>Initial</u>	<u>After Exposure</u>
Nitrogen	79	22,000
Carbon	570	6,500
Oxygen	640	5,800

Analyses of the stainless steel adjacent to the specimen holder revealed that the average nitrogen, carbon, and oxygen content had decreased by 200, 250 and 120 ppm, respectively. It is clear that transport of interstitials from the stainless steel through the sodium to the vanadium alloy had occurred. The use of stabilized stainless steel, i.e. 321 vs 316, produced little difference in elevated temperature tensile properties.⁽⁴⁵⁾ Interstitial pickup could not be compared since the ratio of stainless steel/vanadium alloy area was reduced to near unity for the stabilized stainless steel system.

Work at the Institute for Materials and Solid State Research in Karlsruhe by Borgstedt has produced results similar to those previously discussed.⁽⁴⁶⁻⁴⁸⁾ Alloy systems which were investigated included the following:⁽⁴⁶⁾

V-(3-20)Ti-(0-20)Nb

V-(0-4)Zr-(0-16)Cr

V-3Zr-(10-15)Mo

It was demonstrated that Ca in the sodium, at levels greater than 10 ppm, accelerates corrosion through the formation of complex metallic-calcium oxides which promote spalling. V-3Ti-15Nb, V-3Ti-12Cr, V-2Zr-15Cr, V-1Ti-15Cr have been evaluated in the temperature range 500 to 600°C in flowing sodium containing 0.05-8 ppm oxygen (hot and cold trapped). The corrosion phenomena and kinetics are strongly influenced by the oxygen content of the sodium; with less than 1.0 ppm oxygen in the sodium, the weight gain of the alloy is governed by a parabolic rate law and the formation of oxide layers are not observed. At higher oxygen activities (1 to 10 ppm), oxide layers are formed on the alloys and the specimens suffer linear weight losses.

At low oxygen concentrations, the oxygen dissolved in the alloys is related to the oxygen concentration in the sodium. At 600°C, the saturated oxygen content of the alloys was 4000 to 5000 ppm. At oxygen concentrations in the sodium higher than necessary to saturate the alloys, oxide layers are formed that are removed by the flowing sodium. The pick up of carbon for this group of alloys was considered less important than the oxygen exchange, and the reactions are influenced by alloy composition, especially by the titanium content.

DeVan at Oak Ridge National Laboratory has studied the effect of oxygen in static sodium on vanadium alloys that internally oxidize and those that do not internally oxidize.^(49,50) The alloys which oxidize internally contained titanium and zirconium. The non-internally oxidizing alloys evaluated contained chromium and molybdenum. The vanadium alloy samples were exposed for 600 hours at 600 to 800°C in sodium containing 2000 ppm oxygen. Unalloyed vanadium was also investigated in stainless steel and molybdenum capsules which contained sodium with oxygen concentrations which ranged from 50 to 4000 ppm. An equilibrium distribution coefficient of greater than 10^4 was verified for unalloyed vanadium in contact with sodium at 600°C. For unalloyed vanadium, V-5Cr, V-10Cr, V-15Cr and V-20Mo,

oxygen dissolves in the matrix to form a solid solution. Both chromium and molybdenum lower the equilibrium distribution coefficient by lowering the apparent oxygen solubility in vanadium.

In the case of the vanadium alloys which internally oxidize, the following alloys were exposed to sodium containing 2000 ppm oxygen at 600°C; V-20Ti, V-15Cr-5Ti V-1.3Zr, V-5Zr, VANSTAR-7, VANSTAR-8 and VANSTAR-9. Oxygen content of the alloys was measured as a function of exposure time and compared with the oxygen content of unalloyed vanadium samples exposed in the same capsule. Hardness traverses and metallographic inspections of the microstructure were also conducted on samples removed at 100 hour intervals. The hardness data indicated that equilibrium distribution of oxygen in these alloys had not occurred within the 600 hour time period. Major conclusions drawn by DeVan from this work include:

- Cr, Mo, Fe, Ta and Nb lower the solubility of oxygen in vanadium
- Alloys that contain either titanium or zirconium (and thus form an internal oxide) getter more oxygen than the same alloys without titanium or zirconium. After internal oxidation, the oxygen is present in two forms; oxygen in the precipitated oxide and oxygen dissolved in the alloy matrix. The concentration of dissolved oxygen probably approaches the equilibrium solubility for the same alloy without the internal oxidation component (titanium and zirconium)
- Internal oxide precipitates harden the lattice and thus embrittle the material
- It follows from the above that vanadium alloys that contain titanium or zirconium are inferior to alloys without titanium or zirconium for use in sodium systems.

Suzuki has recently reported mechanical property data for three vanadium alloys exposed to hot trapped sodium containing ~1.0 and ≤ 0.6 ppm oxygen.^(51,52) The alloys investigated were V-20Nb-10Mo, V-20Nb-5Cr, and V-20Ti. Corrosion and tensile specimens were exposed for 500 hours at 700°C. All alloys increased in oxygen content as a result of the exposure. The V-20Nb-5Cr gained the least. Oxygen in the alloy increased from ~400 ppm to over 4000 ppm for exposure to sodium containing ~1.0 ppm. For the lower oxygen level sodium, the increase was up to 1800 ppm. The V-20Nb-10Mo increased to 5600 ppm from ~400 ppm in the ~1.0 ppm oxygen sodium. In the 0.6 ppm oxygen level sodium, the V-20Nb-10Mo alloy increased to 2400 ppm. Oxygen in the V-20 Ti alloy increased to 24,000 and 15,000 ppm, respectively, after exposure to the ~1.0 and ≤ 0.6 ppm oxygen sodium. These increases in oxygen levels,

influenced mechanical behavior, particularly properties at room temperature. Ductility, as measured by elongation, was nil for the exposed specimens. The ultimate and yield strength values were identical in most cases and below the values for unexposed material.

Litton⁽⁵³⁾ of the Los Alamos Scientific Laboratory has reported the results of an investigation of the corrosion behavior of vanadium-titanium binary alloys containing from 10 to 40 wt. percent titanium and the ternary alloys V-5Ti-15Cr and V-15Ti-7.5Cr exposed to hot trapped sodium. Exposure temperatures ranged from 450 to 750°C and exposure times ranged from 500 to 4000 hours. The sodium analysis during the test ranged from 1.7 to 8.7 ppm oxygen. The samples were exposed in a small recirculating loop constructed of stabilized 321 stainless steel. At temperatures up to 650°C, the maximum weight change varied from a weight loss of 0.45 mg/cm²-day for vanadium to a weight gain of 0.46 mg/cm²-day for the V-40Ti alloy. Oxygen analysis of the samples indicated a sensitivity to the oxygen content of the sodium. Weight changes for all the alloys and vanadium was insignificant at temperatures below 650°C. Oxygen was desorbed from unalloyed vanadium over the entire temperature range. Alloys which contained >10% titanium experienced significant increases in oxygen at 650°C and above. The oxygen level of the V-5Ti-15Cr alloy remained constant with increasing temperatures. All of the vanadium alloys increased in carbon and, in some cases, nitrogen content. The absorption of the interstitial elements resulted in the precipitation of complex titanium compounds; microprobe analysis revealed titanium carbide as a surface film. Hardness data indicated that titanium bearing alloys exhibited a hardened zone only after exposure to sodium containing 8.7 ppm oxygen at temperatures above 550°C. No other mechanical property data were reported.

3.4.2 Discussion

Although much work has been done, the compatibility of vanadium alloys with circulating sodium in the temperature range 500 to 600°C has not been established. Interstitial pick up in response to the thermodynamic relationships is a major source of concern. Oxygen transport has been examined to a greater extent than nitrogen and carbon; however, it has been shown experimentally that these elements cannot be ignored. Advocates who supported the use of vanadium alloys in systems

such as the LMFBFR, claimed that vanadium would prove satisfactory provided the oxygen level in the system sodium was maintained at levels below 10 ppm. Such levels are achievable by cold trapping. Experimental results reported in the literature indicate that a more realistic level may be on the order of 1 ppm or even lower. The equilibrium distribution coefficient determined from thermodynamic considerations predicts that a 1 ppm oxygen level in sodium at 650°C requires about 5000 ppm oxygen in vanadium to maintain chemical equilibrium. This prediction has been verified in work reported by Smith,⁽³⁴⁾ DeVan,⁽⁴⁹⁾ and Suzuki.⁽⁵¹⁾ Distribution coefficients calculated from experimental work reported by Litton⁽⁵³⁾ are two order of magnitude lower and approach unity. Litton reported the removal of oxygen from unalloyed vanadium by hot trapped sodium containing <5.0 ppm oxygen. The discrepancy may be explained by the possibility that the oxygen level in the sodium may have been significantly lower than indicated by chemical analysis.

Oxygen can react with vanadium alloys in a number of ways depending on temperature and oxygen level in the sodium. If the rate of arrival of oxygen at the surface of the vanadium is lower than the rate at which oxygen diffuses into the matrix of the alloy, no scale is formed on the surface. If the oxygen level in the sodium is such that the arrival rate is higher than the inward diffusion rate, then an oxide scale forms on the surface. In the first case, weight gains are noted in samples exposed to sodium as a function of time and the weight increase follows the parabolic rate law. In the second case, the oxide film spalls or is removed by erosion in a flowing sodium system, and a weight loss is experienced which is linear with time. Alloying additions can shift and modify this behavior significantly. Titanium, zirconium, and aluminum additions to vanadium have been shown to increase the rate and level of oxygen up take by vanadium. In addition, these elements can produce a subsurface hardened zone in which the hardness can be increased by as much as an order of magnitude. The embrittled zone thickness has been shown to be a function of time and temperature. This zone can drastically affect mechanical properties, particularly ambient temperature tensile ductility. The level of the oxygen gettering elements that can be tolerated in an alloy has not been determined. Elements such as chromium, molybdenum, iron, tantalum and niobium have been shown to lower the apparent solubility of oxygen in vanadium. Oxygen, whether in solution or precipitated as an oxide phase in an embrittled or hardened zone near the surface, has an adverse effect on the mechan-

ical behavior of vanadium. This adverse behavior has been demonstrated in material which has been exposed to hot and cold trapped sodium for time periods of several thousand hours or less. Experimental work which was reviewed involved vanadium/sodium compatibility which was aimed at fuel cladding applications in the LMFBFR. In a projected three year fueling cycle for the LMFBFR, the cladding must retain integrity for approximately 24,000 hours. A CTR central station power plant would undoubtedly require structural components to operate for a much longer time period, >240,000 hours. Thus, allowable degradation of material properties due to corrosion must be assessed in light of the longer expected system life. The effect of transient excursions, in which oxygen levels in the system sodium attain high levels for short periods of time must also be evaluated. Reactions involving interstitial elements under transient conditions are for the most part irreversible and would tend to accumulate with each occurrence.

The amount of experimental work conducted using hot trapped sodium with a controlled oxygen level of 1.0 ppm or less to evaluate the behavior of vanadium alloys has been minimal. Analytical methods for detecting and controlling oxygen at this level are difficult. However, until more experimental work is conducted in this area, the question of the viability of vanadium alloy/sodium systems for CTR applications will remain unanswered. The introduction of a multimetallic system, i.e. stainless steel/vanadium extends the question to the other interstitial elements, nitrogen and carbon.

Based on unreported experimental research at ORNL, DeVan⁽⁵⁴⁾ feels C and N transport will not be a problem at 650°C or lower for SS/V/Na systems. This judgment is based on considerable experience with refractory metal/Na forced convection, bimetallic loops operated for times up to 10,000 hours at 700°C.

3.5 CONCLUSIONS

Interstitial mass transfer is the dominant mechanism of corrosion or incompatibility in vanadium-base alloy/liquid alkali metal systems. Other mechanisms, e.g., dissolution, might also be important but are of secondary concern at 500°-650°C in the simultaneous presence of interstitial mass transfer problems. The equilibrium distribution coefficient provides a basis for predicting the direction of interstitial solute transfer between vanadium or vanadium-base alloys and the

liquid metal (Li or Na) with which they are in contact. Based on calculations and experimental data, predictions for V/Li and V/Na couples are shown in Figure 9; the effects expected for various substitutional solute elements are also shown.

Vanadium loses oxygen but absorbs carbon and nitrogen when in contact with lithium. In contact with sodium, however, vanadium absorbs all three interstitials. Substitutional solutes (at the concentrations likely to exist in vanadium-base alloys) do not change the direction of interstitial mass transfer, but may alter the rate of transfer, the interstitial solute distribution (solid solution or precipitate), and features of grain boundary penetration, formation of surface layers of interstitial compounds, and spalling.

Specific effects of substitutional solutes are not sufficiently well defined to permit a clear choice of individual elements, particularly with regard to transfer of all three interstitial impurities. Although the goal of an alloy development effort should be to suppress completely all interstitial impurity element transfer, this will be difficult to attain in practice. A reasonable approach, therefore, might be to design the alloy on the basis that a loss of interstitials to the liquid metal is preferred over absorption from the liquid metal. Depletion of the alloy matrix in interstitial content would lead only to a loss of strength without negative impact on ductility whereas continued accumulation of interstitials by the vanadium alloys must inevitably produce an embrittled structure.

A dominant element affecting the overall compatibility of structural alloys within liquid metal systems which is not visible in Figure 9 is the choice of materials for the balance of the coolant-heat exchange subsystem. The selection of materials and components, including the hot or cold trapping methods and other features of the heat exchange subsystem, will ultimately control the level and identity of interstitial impurities present in the recirculating liquid metal. Therefore, even if substantial progress can be realized in modifications of the primary structural alloy, the ultimate success of these efforts will require attention to the system as a whole.

*Could reverse at large concentrations

Figure 9. Schematic of interstitial mass transfer in vanadium/liquid alkali metal systems.

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4.0 GAS-METAL REACTIONS IN VANADIUM AND VANADIUM-BASE ALLOYS

CONTENTS

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4.1 INTRODUCTION

Gas-metal reactions must be understood to completely evaluate the performance of a metal in a given environment, and conversely, the effect of the metal on the environment. A gas-metal reaction will affect the environment in one of three ways:

- A gaseous product will be formed
- A gaseous reactant will be removed
- A gaseous reactant will be exchanged for a new gaseous product

A gas-metal reaction will affect the metal in several ways:

- Cause metal loss by volatilization of reaction products
- Change mechanical properties as a result of oxygen, nitrogen, carbon and hydrogen pickup by either going into solution or by forming internal oxides, nitrides, carbides and/or hydrides
- Change the mechanical properties by removing alloying strengtheners such as carbon by selective oxidation
- Change mechanical properties via grain boundary reactions

To determine the conditions under which metals take up or lose gases, information on the following processes and properties must be known:

- Solubility of gases in the metal
- Diffusivity of gases in the metal
- Degassing characteristics of the metal
- Absorption interaction of gases with the metal surfaces

This section will deal with the solubility, diffusion, permeation, and reaction of vanadium with the gases oxygen, nitrogen, and hydrogen, and with carbon. The effects of these interstitial impurities on mechanical properties are also described. This section will show the extent of available data which can be used to understand how the impurity was added to or removed from the metal, how fast it moves through the metal, and what factors affect its solubility, diffusivity, and/or permeability.

4.2 VANADIUM-OXYGEN SYSTEM

The α -solid solution range of the V-O system is of interest. The solubility limit of oxygen in vanadium has been recently measured by Fromm and Kirchheim^(1,2) and Steckel and Altstetter⁽³⁾ using emf techniques. These studies investigated the temperature ranges of 600 to 1100°C and 700 to 1200°C, respectively. Henry, et al.,⁽⁴⁾ has studied the high vanadium region of the vanadium-oxygen system using X-ray, metallographic, and differential thermal analysis techniques over the temperature range 250 to 1200°C. Alexander and Carlson⁽⁵⁾ also studied the V-VO phase system using melting point determination, DTA, metallographic and X-ray techniques. These results are summarized on Figure 1. The solid line phase boundaries are those of Henry, et al.⁽⁴⁾ The published results⁽¹⁻⁵⁾ of the $\alpha/\alpha+\beta$ phase boundary region are plotted for comparison.

Smith⁽⁶⁾ added oxygen to vanadium between 450° and 750°C using V-O-Na distribution techniques; he then used internal friction techniques to determine the V-VO phase boundary between 200° and 400°C. Inert gas fusion was used to determine oxygen concentration and X-ray techniques were used to identify the oxide phase. This work was done on vanadium wire containing < 500 ppm metallic impurities. This data does not agree with the other data and no explanation for the discrepancy is currently available.

Figure 1. Solubility limits of oxygen in α -vanadium.

Alexander and Carlson⁽⁵⁾ have reviewed the V-O phase diagram proposed by Stringer⁽⁷⁾ in 1965. They have updated the phase diagrams and have presented a comprehensive review of their results concerning the V-O system up to ~50 at % oxygen.

Equations describing the oxygen solubility equilibrium relationship and the free energy of formation of the β -phase as a function of temperature are listed in Table 1.

4.2.1 Diffusion of O in V

Schmidt and Warner⁽⁸⁾ have examined the diffusion data of Powers and Doyle⁽⁹⁾ and have determined that the diffusion coefficient of oxygen in vanadium follows the equation

$$D_{\text{O}}^{\text{V}} = (0.0246 \pm 0.0031) \exp[(29,495 \pm 110)/RT] \quad \text{cm}^2/\text{sec}$$

This data is based on the assumption that ΔH is constant over the entire temperature range from room temperature to 1825°C.

4.2.2 Rate of Reactivity at Low Pressures

All of the data for the V-O system presented thus far are equilibrium data describing the phase relationships and solubility as a function of pressure and temperature. Vanadium forms several oxides, each of which is stable over a certain range of composition. V_2O_5 melts at 675°C and is relatively volatile. Gulbransen and Andrews⁽¹¹⁾ have investigated the oxidation kinetics for vanadium between 400 and 600°C and report nearly parabolic behavior following the equation

$$k_p = (1.3 \times 10^{-3}) \exp(-30,700/RT) \quad \text{g}^2/\text{cm}^4\text{sec}$$

for oxygen pressures of 0.1 atm and for times up to 2 hours. McAdams and Geil⁽¹²⁾ have obtained oxidation rates which agree with Gulbransen and Andrews. Although V_2O_5 was the only oxide identified, the experimental techniques precluded the identification of the higher oxide expected to be in equilibrium under these conditions.

TABLE 1
EQUATIONS DESCRIBING THE SOLUBILITY LIMIT
FOR OXYGEN IN VANADIUM

- Equilibrium Pressure for Oxygen in Vanadium (in Pascals)
(Ref. 3)

$$(1) P_{O_2,V} = 1.01 \times 10^5 (\gamma X)^2 \exp\left(\frac{2}{R}\right) \left[14.6 \pm 0.6 - \frac{100,720 \pm 330}{T}\right]$$

and

$$(2) \ln \gamma = \left[(0.20 - \frac{964.70}{T})X + 12.00 - \frac{50,770}{T}\right](1 - 0.01X)^2 - 11.96 + \frac{50,690}{T}$$

where X = concentration (at.%)

γ = activity coefficient (Eqn. (2) is applicable at oxygen compositions above 3 at.% since Henry's Law is obeyed at the lower concentrations. Above 3 at.% a positive deviation from Henry's Law is observed.)

- Equilibrium Pressure for Oxygen in Vanadium
(Refs. 1 and 2)

$$C = 5.64 \times 10^{-4} \sqrt{P_{O_2}} \exp[101,000/RT]$$

where P_{O_2} is the oxygen partial pressure in atmospheres

C is the concentration in atom %

- Concentration-Pressure Relationship for Oxygen in Vanadium
(Ref. 10)

$$\log P_{O_2} = 2 \log C_0 + 9.4 - 44,100/T$$

where P_{O_2} is the oxygen partial pressure in Torr

C_0 is the concentration in atom %

- Equations for the Free Energy of Formation of the β -Phase

$$\Delta G^0 = -103,000 + 21.1T \text{ (cal/mole}^\circ\text{K)} \quad (\text{Refs. 1, 2})$$

$$\Delta G^0 = -100,900 + 24.1T \text{ (cal/mole}^\circ\text{K)} \quad (\text{Ref. 10})$$

The rate of reaction at low oxygen partial pressures was studied by Svedberg⁽¹³⁾ on unalloyed vanadium, V-10.5Cr, V-9.5Mo, and V-9Cr-3Fe-1.3Zr-0.05C (VANSTAR-7 alloy).^{*} At low partial pressures it is possible for a reactive metal like vanadium to take oxygen, hydrogen, nitrogen, and carbon into solution directly from the ambient environment without forming a reaction product on the surface of the metal. The rate at which this occurs is always some fraction of the rate at which the atoms impinge on the surface of the sample. A sticking coefficient is calculated to determine the rate of reactivity of the gaseous environment with the metal surface. The sticking probability or coefficient is the ratio of atoms of oxygen which are reacted into the metal surface to the actual rate of impingement of the gas molecules on the surface. A sticking coefficient of 0.18 ± 0.04 was measured for O on vanadium and the alloys and the rate of oxygen pickup was calculated to be

$$k = (6.7 \times 10^3) \cdot P_{O_2} \text{ mg/cm}^2/\text{hr}$$

within the oxygen partial pressure range of 10^{-5} to 10^{-7} torr. The sticking coefficient for oxygen was found to be independent of composition.

The pressure-concentration isotherms for the V-V₂O₅ system are shown in Figure 2.

4.3 VANADIUM-NITROGEN SYSTEM

Figure 3 summarizes the most recent data describing the solid solubility limit of nitrogen in vanadium. The recent work of Hörz⁽¹⁴⁾ utilized the concentration dependence of resistivity, X-ray diffraction lattice parameter measurements, and hardness measurements to determine the nitrogen solubility limits between 500 and 1500°C. Monroe and Cost⁽¹⁵⁾ used the height of internal friction peaks to determine the solubility limits of nitrogen in vanadium between 275 and 575°C. Henry, et al.,⁽¹⁶⁾ used X-ray and metallographic techniques to determine the nitrogen solid solubility limits in the temperature range between 600 and 1200°C. Table 2 lists the concentration as a function of temperature and illustrates the close agreement between the work of Henry, et al.,⁽¹⁶⁾

^{*}All compositions are in wt%.

Figure 2. Pressure-concentration isotherms in the V-V₀ system. (Ref.2)

Figure 3. Solubility limits of nitrogen in α -vanadium.

TABLE 2
SOLUBILITY EQUATIONS FOR THE VANADIUM-NITROGEN SYSTEM

Solid Solubility Limit (atom percent)	Temperature Range ($^{\circ}\text{C}$)	Reference
$C = 50 \exp(-5500/RT)$	275-575	15
$C = 33 \exp(-3700/RT)$	600-1200	16
$C = 31.5 \exp(-3800/RT)$	500-1500	14

TABLE 3
LATTICE PARAMETER VALUES OF VANADIUM AS A FUNCTION OF
NITROGEN CONCENTRATION AT ROOM TEMPERATURE

Expression	Reference
$a(\text{\AA}) = 3.0255 + 0.0048[\text{at.\%N}]$	14
$a(\text{\AA}) = 3.0261 + 0.0141[\text{wt.\%N}]$	15

and Hörz⁽¹⁴⁾ for the heat of solution of β -nitride V_3N in the α solid solution. The heat of solution is smaller than that reported by Monroe and Cost⁽¹⁵⁾ and is ascribed to the fact that for temperatures below 500°C a different nitride phase is in equilibrium with the α solid solution, probably a $V_{16}N$ compound as described by Potter and Altstetter.⁽¹⁷⁾ This phase is described as an interstitially ordered nitride phase in which the vanadium exhibits a body-centered tetragonal structure with a c/a ratio of 1.03 at 400°C. The precipitation of this phase at 300°C causes hardening.

Table 3 lists the equations describing the dependence of the room temperature lattice parameter on nitrogen concentration.

There is little data describing the nitrogen pressure in equilibrium with the vanadium/nitrogen solid solutions or on the decomposition pressures of V_3N . Hörz⁽¹⁴⁾ indicates that the equilibrium pressures are low. For example, during annealing of α -vanadium-nitrogen solid solutions at 1400°C and 10^{-6} torr, no nitrogen was liberated to the gas phase. However, at 1400°C and a nitrogen pressure of 10^{-3} torr, the β -nitride phase was formed. These results are inconsistent with the values of decomposition pressure of the β -phase of 0.1 torr at 1300°C and 1.0 torr at 1600°C reported in an earlier work by Brauer and Schnell.⁽¹⁸⁾

Schmidt and Warner⁽⁸⁾ have reported the diffusion of nitrogen in vanadium as described by the equation

$$D_{\frac{V}{N}} = (0.0417 \pm 0.0034) \exp[(35,459 \pm 111)/RT] \quad \text{cm}^2/\text{sec}$$

4.3.1 Kinetics of Vanadium-Nitrogen Reactions

Gulbransen and Andrews⁽¹¹⁾ exposed vanadium to nitrogen gas between 873 and 1173 K for 2 hours at pressures of 1.01×10^4 Pa (76 torr). At 1173 K they also nitrided samples at pressures of 2.0×10^2 and 1.01×10^3 Pa (1.5 and 7.6 torr). The rate of weight gain followed parabolic behavior except during the initial stages of the reaction. The reaction was not sensitive to pressure, indicating

that a nitride layer formed on the surface. They reported an activation energy of 131 kJ/mole (31.4 kcal/mole) for the reaction, compared to the activation energy of 148 kJ/mole (35.5 kcal/mole) for the diffusion of nitrogen in vanadium.

Verkhoglyadova, Dubovik, and Samsonov⁽¹⁹⁾ exposed vanadium powder to nitrogen gas at 1 atm for up to 4 hours in the temperature range of 773 to 1773 K. Above 1073°K they reported parabolic kinetics and identified V_3N (hcp) and VN (fcc) phases.

Muije, Horton, and Duran⁽²⁰⁾ have determined the kinetics of reactions between 99.83 pct vanadium and purified nitrogen gas in the temperature range 1173 to 1723°K at pressures of 9.3×10^4 to 9.3 Pa (700 to 6×10^{-2} torr) for times up to 160 hours. At high temperatures and near atmospheric pressures the reaction kinetics changed from parabolic to cubic at longer times. At the lowest pressures, the preparabolic kinetics were linear. The parabolic weight gains are described by the equation

$$\left(\frac{\Delta W}{A}\right)^2 = 3.2 \times 10^{-4} T (e^{-162,000/RT})_t \quad (\text{kg/m}^2)^2/\text{s}.$$

The cubic kinetics were related to the formation of an outer layer of VN over an intermediate layer of V_3N and a core of saturated solution of nitrogen in vanadium. The weight gain for the cubic kinetics can be described by the equation

$$\left(\frac{\Delta W}{A}\right)^2 = 1.24 \times 10^{-3} T (e^{-208,000/RT})_t \quad (\text{kg/m}^2)^3/\text{s}$$

where ΔH is in kJ/mole.

Svedberg⁽¹³⁾ studied the kinetics of reaction of low pressure nitrogen with unalloyed vanadium and the alloys V-10.5 Cr, V-9.5 Mo, and VANSTAR-7 at temperatures between 600 and 800°C (873 and 1073°K) and at nitrogen partial pressures of 1.33×10^{-2} to 1.33×10^{-4} Pa (10^{-4} to 10^{-6} torr). Unlike the sticking probability of oxygen on these alloys, which was independent of alloying addition, the sticking coefficient for nitrogen was found to be

composition dependent, with the VANSTAR-7 and V-10.5 Cr alloys exhibiting the lowest sticking coefficient. During reaction with nitrogen, some oxygen pickup was observed indicating again that oxygen is much more reactive with vanadium than nitrogen.

4.4 VANADIUM-HYDROGEN SYSTEM

Vanadium forms a wide range of solid solutions with hydrogen as does palladium and the Group V transition metals, niobium and tantalum. At lower temperatures these solid solutions are interrupted by miscibility gaps. Veleckis and Edwards⁽²¹⁾ and Kofstad and Wallace⁽²²⁾ have studied the V-H system in the range of 246-554°C and 165 to 456°C, respectively.

Figure 4 shows the P-C-T isotherms measured for the vanadium-hydrogen system.⁽²¹⁾ It is evident that with increasing temperatures and the consequent lower solubilities of hydrogen in the metal, the isotherms progressively approach linearity as is expected according to Sievert's Law. Using the assumption that the hydrogen atoms form solutions by entering interstitial positions within a perfect metal lattice, Veleckis and Edwards⁽²¹⁾ calculated the critical constants of the V-H system and constructed the phase diagram describing the miscibility gap portion of the phase diagram shown in Figure 5. The results are in excellent agreement for the Nb-H system for which accurate phase boundary measurements have been made,⁽²³⁾ indicating the validity of these techniques.

Marêché, et al.,⁽²⁴⁾ have measured the solubility of both H₂ and D₂ in vanadium over the temperature range of 400 to 800°C. Their results agree with those reported by Veleckis and Edwards.⁽²¹⁾ In addition, there is no isotope effect for D₂ in vanadium. D₂ and H₂ exhibit the same solubility as a function of pressure and temperature. In addition, they report that the solubility-pressure relationship does not follow Sievert's Law.

Cantelli, et al.,⁽²⁵⁾ have studied the diffusion of hydrogen and deuterium in vanadium by investigating the Gorsky effect (long range diffusion) over the

Figure 4. Pressure isotherms for the V-H system: open symbols, absorption measurements; solid symbols, desorption measurements. (Ref. 21)

Figure 5. Phase diagrams and isobars for the V-H system.
Dashed curve, Ref. 26. Solid curve calculated,
Ref. 21.

temperature range from 110 to 930°K. The diffusion of hydrogen and deuterium can be described by the following equations:

$$D_H^0 = (4.4 \pm 1.5) \times 10^{-4} \text{ cm}^2/\text{sec}$$

$$D_D^0 = (3.1 \pm 0.8) \times 10^{-4} \text{ cm}^2/\text{sec}$$

$$W_H = (0.059 \pm 0.007) \text{ eV}$$

$$W_D = (0.073 \pm 0.006) \text{ eV}$$

At 327°C the diffusion coefficient for H in vanadium is $1.5 \times 10^{-4} \text{ cm}^2/\text{sec}$ and at room temperature the diffusion coefficient is about $5 \times 10^{-5} \text{ cm}^2/\text{sec}$.

4.5 VANADIUM-CARBON SYSTEM

Based on the phase diagram⁽²⁷⁾ for the vanadium carbon system, there appears to be very limited solubility of carbon in α vanadium at temperatures below 1200°C. Generally carbon is introduced into vanadium via reaction with CH_4 at elevated temperatures.

Schmidt and Warner⁽⁸⁾ report the diffusion of carbon in vanadium to follow the equation:

$$D_C^V = (0.0088 \pm 0.0018) \exp[(27,792 \pm 180)/RT] \text{ cm}^2/\text{sec}$$

4.6 VANADIUM-MIXED GAS INTERACTIONS

The kinetics of decomposition of water vapor at the surface of vanadium at temperatures of 1100 to 1700°C and water vapor pressures between 5×10^{-5} and 5×10^{-3} torr have been investigated by Jehn and Hörz.⁽²⁸⁾ The reaction of water vapor with vanadium forms oxygen solid solutions with the metal. For vanadium the rate of oxygen dissolution is independent of the reaction time. The initial rate is proportional to the water vapor pressure and depends only slightly on temperature.

The experimental relationship between the water vapor pressure, temperature, and oxygen reaction rate is given by

$$V_o = (3.06 \times 10^2) p_{H_2O} [\exp(-4400/RT)]$$

where V_o = reaction rate (mg O/cm²·min)

p_{H_2O} = pressure in torr

T = Temperature (Kelvin)

This is then directly compared to the rate of oxygen solubility in pure vanadium given by the equation:

$$V_o = \frac{1.16 \times 10^3 \cdot p_{O_2}}{1 + (1.85 \times 10^{-3}) \exp(17,600/RT)}$$

For comparison, the rate of oxygen uptake in 10^{-5} torr water vapor at 1100°C is 6.099×10^{-4} mg O/cm²·min while the rate of oxygen uptake in oxygen at 10^{-5} torr at 1100°C is 5.341×10^{-3} mg O/cm²·min.

Kohl⁽²⁹⁾ has measured the rate of oxygen uptake in helium-oxygen gas mixtures with an oxygen partial pressure equal to 0.75 torr, in varying system total pressures. In experiments with the helium partial pressure at 68 ± 2 torr for short reaction times (less than 30 seconds) the rate of reaction decreased as the temperature increased. At 20 seconds, $32 \mu\text{gO/cm}^2$ was picked up by the vanadium at 700°C, $27 \mu\text{gO/cm}^2$ at 800°C, and $23 \mu\text{gO/cm}^2$ at 900°C. In addition to the reaction rate decreasing with increasing temperature, Kohl found that the reaction rate of oxygen with vanadium was proportional to $1/p_{He}^{2/3}$. In the temperature range 600-900°C Kohl describes the reaction rate of oxygen using the following equation:

$$v = (5.14 \times 10^{-6}) \exp(4030/RT) (p_{O_2} / p_{He}^{2/3})$$

where v = reaction rate (gO/cm²·sec)

p_{O_2} and p_{He} in torr

The presence of inert gases mixed with oxygen at a constant partial pressure decreases the rate of reaction as the total gas pressure is increased.

4.7 EFFECT OF ENVIRONMENT ON THE PROPERTIES OF VANADIUM AND VANADIUM ALLOYS

Vanadium and vanadium alloys, similar to the other Group V elements niobium and tantalum, are susceptible to contamination by the interstitial elements carbon, oxygen, nitrogen and hydrogen. Because of the chemical reactivity of vanadium and vanadium alloys, pickup of the so-called interstitial contaminants occurs during exposure at elevated temperature to gaseous atmospheres containing measurable quantities of these elements. A consequence of interstitial contamination is to alter the mechanical properties and flow and fracture behavior of vanadium and vanadium alloys. The most significant amount of information is reported on the low temperature behavior, i.e., $<0.2 T_m$ ($\sim 300^\circ\text{F}$) a region below which there is established a significant temperature dependence of the yield strength. As a result of interstitial contamination, the low temperature ductility of vanadium and vanadium alloys can be significantly impaired. Thus the ductile brittle transition temperature, which for pure vanadium is below -196°C , can be raised to near or above room temperature.

Contamination of vanadium and vanadium alloys occurs generally during consolidation and processing to a desired final form and subsequent elevated temperature testing. Elevated temperature exposure of vanadium and vanadium alloys occurs during:

- a. Melting
- b. Primary and secondary working operations
- c. In-process and final heat treatment operations under reduced pressures
- d. Mechanical property testing.

Generally, the most significant changes in the interstitial level of vanadium and vanadium alloys occur during (c) and (d). These operations are carried out in what is generally accepted to be a minimally reactive environment. Most high temperature working operations are carried out on thick sections using protective claddings and where time at temperature is relatively short.

To illustrate the influence of section size, the potential or maximum rate of contamination of a specimen exposed in a given vacuum environment, was determined using the following expression:

$$\gamma = 3.513 \times 10^{22} P / \sqrt{MT}$$

where γ = impingement frequency, number of molecules/cm²·sec
 P = pressure in torr
 M = molecular weight
 T = temperature, °K

Thus for a sample 1 cm x 1 cm x thickness exposed at a pressure of 1×10^{-6} torr for one hour at 1400°K, (a temperature in the general range used for in-process annealing or recrystallization of cold worked vanadium) and assuming all the residual gas pressure is oxygen and the sticking coefficient is unity, the oxygen pickup in one hour for a specimen thickness of 1 cm, 0.1 cm and 0.01 cm, is 32, 128 and 1090 weight ppm, respectively. Thus, to avoid contamination during final annealing treatments or during long time thermal exposure (i.e. creep testing) where metal thickness is generally on the order of 0.01-0.1 cm, the necessity for maintaining partial pressures of the reactive gases below 1×10^{-8} torr is apparent. However, most commercial vacuum annealing and elevated temperature test equipment are unbaked, use polymer seals and vapor pumping and generally operate in the 10^{-5} torr pressure range. A technique used to minimize contamination during heat treatment or elevated temperature testing is to wrap the specimen with a refractory or reactive metal foil barrier layer.⁽³⁰⁾

4.7.1 Unalloyed Vanadium

The effect of carbon, oxygen, nitrogen, and hydrogen on the hardness, strength, and ductility of high purity vanadium has been studied in some detail.⁽³¹⁻³⁵⁾ Adding nitrogen and oxygen to vanadium increases the room temperature hardness quite rapidly as illustrated in Figure 6. Vanadium containing 0.005% oxygen, 0.0005% nitrogen and 0.015% carbon exhibited a room temperature hardness of 50 DPH. Increasing the oxygen and nitrogen content to 0.3%, the hardness increased to 205 and 270 DPH, respectively. A comparable amount of carbon only increased the room temperature hardness to approximately 62 DPH and most of the increase occurred up to 0.03%, the solubility limit reported for carbon at room temperature. The bend ductile-brittle transition temperature remained below room temperature (see Figure 7). Thompson and Carlson⁽³²⁾ did not see evidence of a cleavage failure in vanadium containing 0.57% carbon. Eustice and Carlson⁽³³⁾

Figure 6. Effect of carbon, oxygen and nitrogen on the room temperature hardness of iodide vanadium. (Refs. 31, 32)

Figure 7. Effect of oxygen and nitrogen on the bend ductile-brittle transition temperature of iodide vanadium. (Refs. 31,32)

report that as little as 10 weight ppm hydrogen causes vanadium to exhibit brittle fracture at -100°C while 800 ppm hydrogen causes brittle fracture near room temperature. The transition to brittle fracture in hydrogenated vanadium is dependent on hydrogen concentration and strain rate.⁽³³⁾ As the testing temperature was lowered, the ductility underwent a minimum and then increased. This behavior was noted for material containing 10-100 ppm hydrogen.⁽³³⁾ Hörz⁽³⁴⁾ reports that hydrogen additions to vanadium of up to 1.5 atom % (~ 300 weight ppm) increases the ductile brittle transition temperature to slightly below room temperature.

Whitlow, et al.⁽³⁶⁾ reported the bend ductile-brittle transition temperature for vanadium containing 0.0130, 0.0050, and 0.001N as $< -196^{\circ}\text{C}$. By exposure to a 10^{-6} torr oxygen partial pressure at $600-800^{\circ}\text{C}$ until 1600 ppm of oxygen were absorbed, the DBTT was raised to near room temperature; absorbing 850 ppm N raised the DBTT to $+150^{\circ}\text{C}$. This is not in agreement with the data of Thompson and Carlson⁽³²⁾ and is attributable to concentration gradients existing in the sheet specimens.⁽³⁶⁾ The temperature of exposure was not sufficiently high to homogenize the nitrogen throughout the vanadium specimen thickness.

There is a paucity of data on the influence of carbon, oxygen, nitrogen and for hydrogen on either the time dependent or time independent deformation and strength properties of unalloyed vanadium at elevated temperature.

4.7.2 Vanadium Alloys

V-9.5 Mo, V-10.5 Cr, and VANSTAR-7 were exposed to low (10^{-7} to 10^{-5} torr) oxygen and nitrogen partial pressures at 600°C .⁽³⁶⁾ A significant increase in room temperature tensile strength with a corresponding decrease in elongation were reported.⁽³⁶⁾ The data is difficult to interpret since significant concentration gradients existed throughout the specimen thickness. However, VANSTAR-7 absorbed 2800 ppm O_2 before the room temperature elongation became nil.

Whitlow, et al.⁽³⁶⁾ exposed VANSTAR-7, VANSTAR-8, VANSTAR-9 and V-20 Ti to flowing sodium for 1500 hours. Depending on the temperature of exposure, carbon, oxygen and nitrogen were picked up via transport from the stainless steel containment to the vanadium alloy test specimens. Substantial concentration gradients with surface nitrogen and carbon contents of up to 15,000 ppm were reported. Even

with these high interstitial pick-ups, the vanadium alloys exhibited substantial ductility in tensile testing at 150°C and 600°C, i.e., >20% tensile elongation. However, at room temperature, tensile elongation was less than 2% for all compositions.

Very little systematic work has been reported on the influence of test environment on the creep properties of vanadium alloys. Begley, et al.,⁽³⁷⁾ report that the creep rupture properties of VANSTAR-7 are significantly affected by the test pressure (see Figure 8). The reason for this behavior was not explained. It was not determined whether the high pressure (10^{-6} torr) caused strengthening by picking up additional interstitials or the low pressure (10^{-9} torr) caused weakening by removal of interstitials or is representative of the actual strength of the material.

Nitriding studies on VANSTAR-8 were reported by investigators at UCLA.⁽³⁸⁾ The data shown in Figure 9 indicate a substantial increase in room temperature strength as the nitrogen content was increased to 0.2%. The nitriding conditions would have resulted in a substantial concentration gradient based on the data of Whitlow, et al.⁽³⁶⁾ This may explain the low ductility exhibited by the VANSTAR-8 in the as nitrided condition. However, after a homogenization anneal, a tensile elongation of 12.6% was reported with a tensile ultimate near 200 ksi.

Figure 8. Creep behavior of VANSTAR-7 (V-9Cr-3Fe-1.3Zr-0.05C) at 700°C and 40,000 psi. (Ref. 37)

As Received
1200°C Anneal
for 1/2 hr

Y.S. 60 ksi
U.T.S. 82 ksi
Elong. 30%

After Nitriding
at 830°C for 2 hr
(0.2% N₂)

Y.S. 82 ksi
U.T.S. 82 ksi
Elong. 0.2%

After Nitriding and
Homogenization at
1300°C for 1 hr

Y.S. 176 ksi
U.T.S. 196 ksi
Elong. 12.6%

Figure 9. Tensile properties of VANSTAR-8 as-received and following nitriding treatments. (Ref. 38)

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5.0 CONSOLIDATION AND FABRICATION OF VANADIUM AND VANADIUM-BASE ALLOYS

CONTENTS

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5.1 PREPARATION OF VANADIUM METAL

A number of methods have been employed to prepare a variety of grades of vanadium metal. A study by Joly⁽¹⁾ revealed that those methods that could be extended to large scale industrial processes could be categorized as follows:

- Reduction of the oxide with a reactive metal such as aluminum or calcium, or with carbon under vacuum
- Reduction of vanadium halides with hydrogen, magnesium or sodium

The metallothermic reduction of the oxide has shown the greater promise and is the technique that was used to produce commercial quantities of vanadium metal. Attempts to produce vanadium metal by carbon reduction of the oxide have been hampered by lack of a suitable inert crucible material to contain the molten vanadium.⁽²⁾ Wilhelm⁽²⁾ has demonstrated the production of vanadium metal by carbon reduction of the oxide, but at the time this work was reported in 1969, interest in vanadium was waning.

The aluminothermic reduction of V_2O_5 results in an aluminum content in the reduced vanadium derby of 10-16%.⁽⁹⁾ High purity V_2O_5 (<170 ppm Si, 100 ppm N) was used as feed stock since neither silicon or nitrogen are removed in subsequent electron beam refining. At this writing, there is not a vanadium technology of any consequence in the USA.^(13,14) The primary demands are ferro-vanadium for the steel industry and the vanadium used as an alloying addition to titanium alloys.

The latter is from aluminothermic reduction of the pentoxide and generally has the composition 15Al-85V with major impurities of 0.3Fe and 0.3Si.⁽¹²⁾

5.2 PURIFICATION

Vanadium metal produced by calcium or aluminothermic reduction has been purified by electron beam melting in combination with vacuum arc melting.^(3,9)

Sullivan, et al.⁽⁴⁾ also demonstrated that by repeated electrorefining, vanadium with a purity of 99.95% could be produced.

Reed⁽¹¹⁾ by electron beam float zone melting produced 99.99% vanadium. However, the technique is only suited for laboratory purposes. Electrorefining, as developed by Sullivan⁽⁴⁾ has been scaled up to pilot plant size at Oregon Metallurgical Corporation.^(10,14) Electrorefining has the advantage that all impurities can be reduced to a very low level. Comparative analyses of vanadium metal produced by various methods are listed in Table 1. The feed stock for the electrorefining or electron beam purification was produced by either calcium or aluminothermic reduction of V_2O_5 .

One of the constraints in producing high purity vanadium via electron beam refining is that the V_2O_5 must be low in nitrogen and silicon, since these two impurities are not removed during the electron beam melting stage.⁽⁹⁾ This is not the case with electrorefining since all impurity elements can be reduced to a very low level.⁽¹⁰⁾ However, the oxygen content of the electrorefined crystals was strongly influenced by the final crystallite size. From Table 1, the oxygen content for vanadium crystallites -1/4 inch + 80 mesh, the size normally produced,⁽¹⁰⁾ analyzed approximately 800 ppm oxygen. Larger crystals deposited at slower rates, and typical of those grown under laboratory conditions,⁽⁴⁾ analyzed approximately <220 ppm oxygen. The -1/4 inch + 80 mesh was the base material used for the fuel cladding alloy development program sponsored by the AEC.^(7,8)

With the termination of the vanadium fuel cladding development program in the late 1960's, the development of technology for producing high purity vanadium essentially ceased.^(13,14)

TABLE 1
CHEMICAL ANALYSIS OF VANADIUM METAL

Type of Purification	Analysis, Weight Percent						Ref.
	C	O	N	Si	Al	Fe	
1. Electrorefined -1/4 inch + 80 mesh	0.008	0.078	0.018	<0.02	<0.01	<0.02	8
2. Electrorefined +1/4 inch XTAL	0.002	0.022	0.003	0.0037	N.R.	0.009	8
3. E. B. Refined	0.008	0.019	0.009	0.015	0.009	0.0055	9
4. Electrorefined -1/4 inch + 80 mesh	0.01	0.06	0.01	N.R.	N.R.	0.04	10
5. Vacuum Arc Melted	0.06	0.02	0.05	0.50	0.20	0.10	3
6. E. B. Float Zone	0.003	0.003	0.001	0.001	0.0001	0.0001	11

At this writing, there are no existing commercial facilities producing high purity vanadium metal. Teledyne Wah Chang has indicated that they could be in production within 6-8 months if the need existed.⁽¹³⁾ Wah Chang has produced relatively high purity vanadium metal by electron beam refining aluminum bomb reduced V_2O_5 .

5.3 ALLOY MELTING

The consolidation techniques for producing vanadium alloys do not differ greatly from those used to produce other refractory metal alloy compositions and generally follow the schedule shown in Figure 1. This schedule has been followed in producing alloy ingots up to 6 inches in diameter. Not indicated on Figure 1 is the use of nonconsumable electrode melting which is generally used in the preparation of small ingots (≤ 200 grams) for screening alloy compositional investigations. As with all Group V refractory metals, maintaining atmosphere purity during processing is necessary to avoid extraneous contamination of the product.

Preparation of the V-20Ti alloy has been accomplished by a combination of electron beam melting and/or consumable electrode arc melting.^(5,7,8) Alloys containing high vapor pressure elements such as chromium present composition control problems during electron beam melting. Thus, alloys containing high vapor pressure elements are generally processed by consumable electrode arc melting.⁽⁶⁻⁹⁾ Melting at the commercial scale is normally accomplished using straight polarity dc power with the consumable electrode negative.⁽⁹⁾ Developmental and pilot scale melting (up to 3-4 inch diameter ingots) has been done using either dc or ac power.⁽⁵⁻⁸⁾ Melting is generally accomplished under a static partial pressure of argon⁽⁵⁻⁹⁾ or under dynamic vacuum.⁽⁹⁾

The utilization of electrorefined vanadium as a starting base has certain advantages. Being available as granules ($-1/4$ in + 80 mesh), this form is readily adaptable to briquetting techniques and facilitates the introduction of alloying additions such as Ti, Cr, Zr, Fe which are all available as sponge or flake. The only disadvantage of the electrorefined vanadium crystals is their high oxygen content (>600 ppm). Briquetting is the technique generally used for fabricating first melt vanadium alloy electrodes.⁽⁵⁻⁹⁾ Even when high purity vanadium metal

Figure 1 . Schedule for producing vanadium alloys.

has been produced as electron beam refined ingot, the ingot has been converted to chips by machining to furnish starting material for fabricating the first melt electrodes of a V-15Cr-5Ti alloy.⁽⁹⁾

The capacity currently existing in the USA for melting of pure vanadium and/or vanadium alloys is 11-1/2 inch diameter x 9 feet long ingot by electron beam melting or up to 23 inch diameter x 9 feet long ingot by consumable electrode vacuum arc melting.^(13,15) This represents ingot weights based on the density of pure vanadium (0.22 lb/in^3) of approximately 2500 and 9,900 lb, respectively.

5.4 PRIMARY WORKING

As with the other Group V alloys, the breakdown of the as-cast ingot structure of the vanadium alloys is accomplished by extrusion and/or forging at temperatures of $1000-1200^\circ\text{C}$. Atmospheric contamination of the extrusion or forging billet is avoided by encapsulating the billet in an evacuated and weld sealed 304 stainless steel container.⁽⁵⁻⁹⁾ Suitable protection should be provided during all working operations at temperatures above 700°C since V_2O_5 melts at 690°C and molten V_2O_5 is corrosive to steel tooling.⁽¹³⁾

5.5 SECONDARY WORKING

Secondary working operations such as rolling, swaging, and tube drawing are carried out over the temperature range of room temperature to 500°C .⁽⁵⁻⁹⁾

Intermediate and final annealing treatments are carried out under vacuum ($< 5 \times 10^{-5}$ torr) at $800-1200^\circ\text{C}$. All common mill forms of vanadium alloys such as strip, sheet, rod, bar and tubing have been produced. The alloys which have been scaled up to four inch diameter include V-15Cr-5Ti, V-20Ti, V-15Ti-7.5Cr, VANSTAR-7, VANSTAR-8, and VANSTAR-9; V-15Cr-5Ti and the V-20Ti have been melted and fabricated from the six inch diameter size.^(5,9) By stringent control of melting technique a sound ingot of V-15Cr-5Ti was cast and, following controlled primary and secondary working schedules, 0.04 inch thick sheet was produced.

Vacuum annealing capacity typically available in the U.S. today, and totally dedicated to refractory metal heat treating, is on the order of 42-54 inch diameter x 106-120 inches long with temperatures and pressure capability of up to 1600°C and $\leq 5 \times 10^{-5}$ torr, respectively.^(13,15) Although there exists some large

vacuum furnace capacity, these units are generally used for brazing, coating, and/or heat treatment of iron and nickel base alloys, and these are not suitable for heat treating refractory metals. To prevent deleterious contamination of refractory metals it is of extreme importance to use melting and heat treating facilities that are totally dedicated to processing refractory metals.

5.6 WELDING

There is very limited information on the weldability characteristics of vanadium alloys. Kramer, et al.,⁽⁶⁾ have reported satisfactory GTA (gas-tungsten arc) and electron beam (EB) welding behavior for the V-15Ti-7.5Cr alloy based on metallographic observation of plug-to-tube GTA welds and bead-on-plate or butt EB welds in sheet. Tensile testing of the EB butt welds with the weld bead perpendicular to the tension axis produced failures outside the weld bead zones.⁽⁶⁾ Thus this test was more a measure of the load bearing ability of the weldment rather than a measure of the ductility of the weld. Pollack, et al.,⁽⁷⁾ investigated the GTA weldability of unalloyed vanadium and various experimental vanadium alloys including the V-10Ti and V-20Ti alloys. The influence of GTA welding on the low temperature ductility was evaluated by observing the change in the bend ductile-to-brittle transition temperature (BDBTT); the more pertinent data are summarized in Table 2. Pure vanadium containing ~1600 ppm C, O, and N exhibited a BDBTT of -102°C and was not altered by GTA welding. However, GTA welding of the V-20Ti alloy increased the BDBTT from $<-196^{\circ}\text{C}$ to -25°C . A series of alloys containing the reactive metal zirconium with intentional additions of approximately 500 ppm C and containing approximately 6-12 a/o substitutional solute additions (Nb, Cr, Fe, W, and/or Ta) exhibited base metal BDBTT's of $<-196^{\circ}\text{C}$ which was increased to above room temperature for as-GTA welded material. Post weld annealing of as-GTA welded material reduced the BDBTT to or below room-temperature.⁽⁷⁾ Thus the increase in the BDBTT for the vanadium alloys can be attributed in part to solutioning of the interstitial elements (C, O, and N) during the welding thermal transient. Similar behavior has been observed for niobium and tantalum-base alloys.⁽¹⁶⁻¹⁸⁾

Although significant increases in the strength of vanadium can be achieved by addition of substitutional solutes, the permissible level of solute addition should be limited by their effect on the low temperature ductility, a most attractive

TABLE 2

INFLUENCE OF GTA WELDING ON BEND DUCTILE TO BRITTLE TRANSITION
TEMPERATURES (BDBTT) OF VANADIUM AND VANADIUM ALLOYS⁽⁷⁾

Alloy Composition (wt. percent)	BDBTT*, °C	
	Base Metal	As-GTA Welded
V-0.046C-0.090 ₂ -0.02N	-102	-102
V-10Ti-0.048C-0.0860 ₂ -0.02N	<-144	- 72
V-20Ti-0.04C-0.10 ₂ -0.023N	<-196	- 25
V-10.4Cb-1.27Zr-0.06C-0.0950 ₂ -0.026N	<-196	> RT
V-6.5Fe-1.32Zr-0.06C-0.0940 ₂ -0.025N	<-196	> RT
V-12.3Cr-2.40Zr-0.16C-0.120 ₂ -0.024N	<-196	RT
V-8.5Cr-10W-1.24Zr-0.065C-0.110 ₂ -0.024N	<-196	> RT
V-9.11Cr-3.3Fe-1.3Zr-0.064C-0.110 ₂ -0.024N	<-196	> RT
V-8.5Cr-9.8Ta-1.24Zr-0.06C-0.10 ₂ -0.023N	<-196	> 11

*0.042 inch thick, weld bead tension side of bend. Specimens bent at 1t radius.

characteristic of vanadium. Experience in niobium and tantalum alloy development has shown that changes in the bend ductile-to-brittle transition temperature (BDBTT) caused by inert gas-tungsten-arc (GTA) welding provides a reliable index of alloy fabricability. That is, alloy compositions having good as-GTA-welded bend ductility generally will be highly fabricable and can be melted as large diameter ingot and processed to variety of mill shapes (sheet, plate, bar) under a relatively broad range of processing conditions.⁽¹⁶⁾

It has been generally observed that tantalum and niobium base alloys containing less than ~10-12 atom percent Group VI solute elements (Mo,W) exhibit minimal changes in the BDBTT after GTA welding. Also, it was further observed that intentional interstitial additions of carbon and/or nitrogen above approximately ~0.35 atom percent to alloys containing ~10 a/o substitutional solute resulted in increasing as-GTA welded BDBTT to near or above room temperature.⁽¹⁶⁻¹⁸⁾

No systematic investigations have been reported on the welding characteristics and behavior of vanadium alloys. Information such as optimum welding parameters and the effect of composition and section size on low temperature ductility is missing. This information is considered vital since proposed first wall structures would be fabricated from relatively thick sections (>1/8 inch) of wide plate.

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APPENDIX A: PHASE DIAGRAMS FOR VANADIUM-BASE ALLOYS

These phase diagrams are collected here for convenience in qualitative assessment of the nature of the various vanadium-base alloy systems. For the most part they were taken from standard references. No extensive search was made for more recent or more accurate data, nor has an effort been made to critique comparative results of different investigators. The phase diagrams are arranged in the following order:

<u>Fig.</u>	<u>System</u>	<u>Reference</u>	<u>Fig.</u>	<u>System</u>	<u>Reference</u>
A-1	V-H	Elliott	A-12	V-Ti	Hansen
A-2	V-H	Owen & Scott	A-13	V-Zr	Hansen
A-3	V-B	Elliott	A-14	V-Hf	Rudy & Windisch
A-4	V-Al	Hansen	A-15	V-Y	Lundin & Klodt
A-5	V-Si	Hansen	A-16	V-Nb	Hansen
A-6	V-C	Hansen	A-17	V-Ta	Carlson, et al.
A-7	V-C	Mathews & Rowe	A-18	V-Cr	Carlson, et al.
A-8	V-N	Horz; Monroe & Cost; Henry, et al.	A-18	V-Mo	Elliott
A-9	V-O	Hansen	A-18	V-W	Elliott
A-10	V-O	Stringer/Carlson, et al.	A-19	V-Fe	Hansen
A-11	V-O	Steckel & Altstetter	A-20	V-Ni	Carlson, et al.

Figure A-1.

Figure A-2.

Figure A-3.

Figure A-4.

Figure A-5.

Figure A-6.

Figure A-7.

Figure A-8.

Figure A-9.

Figure A-10.

Figure A-11.

Figure A-12.

Figure A-13.

Figure A-14.

Figure A-15.

Figure A-16.

Figure A-17.

Figure A-18.

Figure A-19.

Figure A-20.

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APPENDIX B: DIFFUSION DATA FOR VANADIUM AND VANADIUM-BASE ALLOYS

Diffusion data for diffusion of interstitials in vanadium are listed in Table B-1. Since internal friction measurements are widely used to determine the activation energy for interstitial diffusion and in the study of substitutional solute - interstitial solute interactions, the temperatures of the Snoek peaks due to interstitials in vanadium are listed in Table B-2 for general reference purposes.

Vanadium self diffusion data are shown in Figure B-1. Vanadium is one of a small group of metals which shows anomalous diffusion behavior. In the data by Peart, for example, there is a change in slope at 1356°C with significantly different activation energies above and below this temperature.

The chemical interdiffusion coefficient for V-Ti alloys is shown in Figure B-2 as a function of composition and temperature. Data for $\tilde{Q}$ and $\tilde{D}_0$ for V-Ti interdiffusion are shown in Figure B-3. The composition dependence of the interdiffusivity and intrinsic diffusion coefficients for Ti and V in Ti-V alloys are shown in Figure B-4. Note that at the lower Ti contents the Ti atoms move about 4 times faster than V.

Diffusion data for V-Nb alloys are shown in Figure B-5.

TABLE B-1
DIFFUSION DATA FOR INTERSTITIAL DIFFUSION
IN VANADIUM

Interstitial	D_0	Q	Reference
	cm ² /sec	kcal/mole	
C	0.0047	27.3	Powers & Doyle (1958)
O	0.019	29.3	Powers & Doyle (1958)
O	---	29.6	Powers & Doyle (1959)
O	---	28.6	Powers
O	0.003	28.2	Stanley & Wert
O	---	27.9	Tichelaar, et al.
N	---	34.6	Powers & Doyle (1959)
N	---	34.1	Powers
N	0.018	35.1	Stanley & Wert
N	---	36.7	Tichelaar, et al.
H	0.00035- 0.00044	1.15-1.45	Schaumann, et al.* Cantelli, et al.*
D	0.00031- 0.00048	1.68-1.9	Boes & Zuechner* *in D&DD, <u>13</u>

TABLE B-2
TEMPERATURE OF SNOEK INTERNAL FRICTION PEAKS
DUE TO INTERSTITIALS IN VANADIUM

Interstitial	Peak T, °C	f, cps	Reference
C	162	0.55	Powers and Doyle(1958)
O	186	1	Powers
N	272	1	Stanley and Wert

Figure B-1. Self diffusion data for vanadium.

Figure B-2. Chemical interdiffusion data for V-Ti alloys.

Figure B-3. Activation energy $\bar{Q}$ and preexponential factor $\bar{D}_0$ for V-Ti interdiffusion.

Figure B-4. Interdiffusion ($\bar{D}$) and intrinsic diffusion (D_{Ti} and D_V) coefficients for V-Ti alloys.

Figure B-5. Diffusion data for V-Nb alloys.

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APPENDIX C: ELASTIC PROPERTIES OF VANADIUM AND VANADIUM-BASE ALLOYS

Vanadium in single crystal form is elastically anisotropic. Indeed, most metals are; W and Al being familiar exceptions. Low temperature values for the three independent elastic constants are shown in Figure C-1. Smith and Bolef interpret the anomalous temperature dependence at very low temperatures as an effect due to hydrogen. The elastic properties of polycrystalline V, V-20Ti and V-15Ti-7.5Cr are shown in Figure C-2. The range of values for V-15Ti-7.5Cr is due to variations in heat treatment. The effect of Ti and Hf content on Young's modulus is shown in Figure C-3. For V-Ti alloys, Yaggee stated that at 25°C the modulus showed a peak at 10% Ti, similar to the 600°C curve in Figure C-3, but at 200°C and 400°C the modulus decreased for all Ti contents up to 40%.

Figure C-1. Dynamic elastic constants of single crystal vanadium.

Figure C-2. Elastic properties of vanadium and several vanadium-base alloys. (Dynamic Measurements)

Figure C-3. Effect of Ti and Hf on Young's modulus of vanadium.

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