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~~APPENDIX II~~

AN INVESTIGATION OF METHODS OF PREPARING
HIGH PURITY VANADIUM

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An Investigation of Methods of Preparing
High Purity Vanadium^{*†}

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Abstract

High purity vanadium single crystals (resistance ratios in excess of 600) have been grown in an electron beam float zone refiner. Numerous parameters have been varied and their effects on the purification process studied. Also hydrogen and ammonia gases were introduced during the first molten zone pass and pumped back out on subsequent molten zone passes. Most experiments were performed twice, once with, and then without, pedestal rod rotation.

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Introduction

In recent years there has been a significant and somewhat concerted effort by a growing number of investigators to produce high purity single crystals of the body-centered cubic refractory metals. The reasons for investigating methods of producing high purity vanadium are basically the same reasons that have led various other investigators to produce high purity single crystals of other b.c.c. refractory metals. However, in the case of vanadium, there is an additional reason for producing crystals of high purity. The radioactive isotopes of vanadium have very short half lives and hence the radioactivity caused by irradiation decays rapidly. Therefore vanadium can be studied in conventional surroundings.

Investigations of methods of producing high purity vanadium single crystals are almost non-existent. The calcium reduction technique^(1,2) presents the drawback of severely contaminating the vanadium with the material of the crucible and so eliminates the possibility of doing irradiation studies. A possible reason for the subsequent lack of interest in attempting to produce high purity vanadium could be the theoretical work of Brewer and Rosenblatt⁽³⁾ which indicated it was at least two orders of magnitude more difficult to purify vanadium than niobium. Also Stringer⁽⁴⁾ has calculated that an oxygen partial pressure of

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less than 10^{-13} torr is required to reduce VO.

High vacuum electron beam zone melting has proven to be an efficient method of purifying some of the b.c.c. metals⁽⁵⁾. However, the literature concerning the high vacuum electron beam zone melting of vanadium is very vague,⁽⁶⁾ and most conclude it is not a practical means of purification⁽⁷⁻⁹⁾. The principal reason for the interest in the removal of oxygen is due to the large tetragonal strain associated with interstitial oxygen. The strain due to oxygen is four times larger than the strain produced by a nitrogen interstitial⁽¹⁰⁾ and could be at least three times larger than a carbon interstitial in the vanadium lattice.⁽¹¹⁾

There are reasons for assuming that if oxygen could be removed, the remaining interstitial impurities would not be difficult to remove. The stable nitride of vanadium, VN, should decompose above 900°C in vacua,⁽¹²⁾ and it has been stated that nitrogen follows Sievert's law in vanadium.⁽⁸⁾ Therefore nitrogen should be readily removed by high vacuum annealing above 900°C. The case of carbon is not as clear, but Powers and Doyle⁽¹³⁾ state that the addition of carbon to vanadium was difficult to accomplish.

The purpose of this investigation was to consider various techniques of high vacuum electron beam zone melting as a means of producing vanadium with a low interstitial concentration.

Experimental Procedure

The starting material was obtained from the U. S. Bureau of Mines, Boulder, Colorado, in the form of dendritic crystalline powder. The initial analyses of the powder are shown in Table I. The aggregate purity of the dendritic crystals was also checked by determining the value of the ratio of the resistance at room temperature to the resistance at 4.2°K.

The experimental equipment consisted principally of a modified arc melter, which has been described elsewhere⁽¹¹⁾, and an ultra-high vacuum electron beam float zone refiner. The zone refiner is shown diagrammatically in Fig. 1. Several features make the system quite unique. First, the system incorporates internal heaters. Long strip heaters are strapped to the scanner assembly, making it possible to bake the entire scanner to temperatures in excess of 425°C. Second, a special split mantle is so designed that, in conjunction with the placement of external heaters, it is possible to bake most of the surface area of the 12 in. dia. stainless steel bell jar to 325°C, the viewing ports to 300°C, and the electrical feed-throughs, with their ceramic insulators, to 225°C. This non-uniform temperature distribution greatly increases the life of the electrical feed-throughs and has an insignificant effect on the value of the working vacuum. After baking the system, this mantle can be easily removed since it is split. Third, the variable leak valve, which is not thermally insulated, is preceded by a bakeable valve. The bakeable valve is baked to 200°C but the precision leak valve does not reach temperatures in excess of 75°C. This has greatly increased the life of the sapphire valve seat in the precision valve without affecting the value of the working vacuum. Fourth, the system is equipped with a turbomolecular pump which is usually the only active high vacuum pump during the baking period. The advantage is that the solid state pumps may be baked while being inoperative. In addition, there is a large valve preceding the turbomolecular pump, so that this pump may be closed off the system when pressure is below 1×10^{-8} torr. This eliminates the possibility of backstreaming of oil or hydrogen through the pump. Fifth, the

stainless steel bell jar is equipped with a cooling jacket. The jacket covers approximately 80% of the external surface area of the bell jar. A mixture of pure ethylene glycol and water is used as the coolant and during an experiment, it is possible to maintain the temperature of the coolant at -10°C . Sixth, the system is equipped with four pressure measuring gauges. The first is included in the VacIon pump and is reasonably reliable only to 1×10^{-9} torr. The second is actually a monopole residual gas analyzer. This unit is reliable only to 1×10^{-10} torr in the total pressure mode, so a Keithley Model 610C electrometer is used to facilitate measurements at lower pressures. The substitute electrometer is also used on occasion to help resolve the residual gases. The third is a nude ion gauge located at the base, but in front of the scanner. The fourth is also a nude ion gauge located at the base of the scanner, but this one is located behind. At no time is this last gauge in a direct line to the molten zone. With no filament power and a pressure in excess of 1×10^{-9} , all the gauges usually agree to within a factor of 3x. When a molten zone has been established, the gauge in front of the scanner indicates the highest pressure, the gauge behind indicates lower, the monopole analyzer indicates lower still, and the gauge in the pump indicates the lowest pressure. In a normal experiment however the monopole analyzer is usually maintained in the partial pressure mode. The reason for this is that the emission current for the gauge filament is different for the two modes of operation and it takes considerable time to achieve equilibrium with respect to the temperature of the tube. The value of the total pressure within the system is taken as that indicated by the gauge located behind the scanner. Since all pressure determinations from ion gauges are usually accepted with suspicion, the values quoted herein as true total gas pressures are therefore conservative in this regard. Unfortunately the stainless steel bell jar is equipped with only two viewing ports and there is a dead space between these ports. When the electron gun is moving in this dead space, it is impossible to view the heat zone. By observing the pressure indicated by the gauge located in front of the scanner, it is still possible to

determine if a molten zone exists. Seventh, the motion of the electron gun or filament is by direct drive. The reason for going to direct drive was to make a first attempt to eliminate the banded structures which other investigators⁽¹⁴⁾ have found. This also makes the mechanism simpler, a laudable feature for any mechanism used in ultra-high vacuum work. Eighth, the system incorporates the ability to rotate the pedestal rod, again by direct drive. The traverse motion of the block which holds the pedestal rod is also by direct drive. However, if the pedestal block is moved over 4 inches from bottom, the pedestal rod rotation mechanism uncouples.

Many of the experiments to be described have certain initial steps in common and where deviations occur, they will be noted. First, an ingot, prepared in various ways to be described, is swaged to the desired diameter. The rod is etched in a mixture of HF and HNO₃ before each reduction. The rod is next cut to length, etched again, and installed in the zone melter. The pedestal rod is a seed crystal and all crystals grown during this series of experiments had the same orientation to eliminate a variable. The orientation chosen was approximately 14° from the (110) and 5° from the (110)-(111) symmetry line of a standard stereographic triangle. The chamber is closed and evacuated to approximately 1×10^{-5} torr. If a gas is to be introduced during the experiment, the leak valves are opened to the gas source and the necessary lines are purged with that gas. The precision leak valve is then closed and the entire system is put into the baking cycle. After baking for approximately 16 hours, with the temperature distribution noted earlier, the pressure is typically 2×10^{-6} torr. At this time the system elements are taken off bake out in a programmed manner. Just prior to bringing the last element, the bell jar, off bake out the pressure is 3×10^{-7} torr. When the pressure drops below 1×10^{-8} , the turbomolecular pump is valved off the system. The system is usually allowed to cool until the surface of the bell jar not covered by the cooling jacket is fairly close to ambient temperature, at which time the pressure is typically 2×10^{-10} torr, with the principal residual gas being hydrogen.

The filaments are usually hand-wound from 0.025 in dia. tungsten wire with the filament diameter being approximately 1.25 in. The diameter of the rods to be zone melted are typically 0.250 in. The next step in the process is to energize the filament without turning on the high voltage. The filament is then made to traverse the length of the rod. It is found that the pressure within the system will rise as much as two orders of magnitude during this operation with about 85% of this difference due to hydrogen. In this mode of operation, the temperature of the rod does not exceed 400°C since the heating is obviously by radiation only. Such a low temperature of course prohibits any significant amount of diffusion within the rod, even of hydrogen.⁽¹⁵⁾ Therefore the hydrogen and other minor gases must be coming from the surface of the rod.

If a gas is to be introduced during the first molten zone pass, the next step is to weld the rod and the pedestal rod together and then shut down all power. The solid state pumps are shut down, the valve to the turbomolecular pump is opened, and the system is allowed to equilibriate. The appropriate gas is introduced to near the desired pressure, a molten zone is established about 3 in. above the position of the original weld and a zone pass is made. No sputtering, i.e., the molten zone spewing gas and, if violent enough, metal particles out of itself, occurs when the first molten zone pass is made at these higher pressures. The rod is then pulled apart while a molten zone is present and the entire system is put back into the bakeout cycle. The experiment proceeds further from this point almost as if the introduction of the gas had not transpired. For the gases used, the ammonia was commercial grade while the hydrogen was high purity and was passed through a palladium diffusion purification apparatus prior to its introduction into the system. The maximum pressure for which electron beam zone melting is possible was found to be roughly in agreement with other investigators,⁽⁷⁾ but once a fluctuation in the system caused a plasma to develop during a hydrogen experiment and all later experiments were conducted at a slightly lower pressure.

If no gas was to be introduced, a second "light" degassing pass

is made in the opposite direction. Pressure during this second pass is usually an order of magnitude lower than for the first pass, but the principal contaminant is still hydrogen. At the conclusion of this pass, the rod and pedestal rod are welded together and then a beam power degassing pass is made. The power used is approximately 60% of that required for the welding process. The temperature at the outside center of the heat zone is probably in the range of 700 to 1300°C. Pressure during this pass is usually in the same range as for the second light degassing pass, but the residual gas composition is now more divided, though hydrogen is still dominant. In the case that a gas had previously been introduced, the pressure is usually one to two orders of magnitude higher and the major contaminant, for the experiments involving hydrogen or ammonia, is by far hydrogen. Also in the case that a gas had previously been introduced, the next operation is a molten zone pass, otherwise a second beam power degassing pass is made.

If no gas had previously been introduced, the initial molten zone pass is always made in the upward direction, starting just below the weld. A single crystal always seems to result, irrespective of the zone speeds used during the experiments. The growth of crystals of the same orientation at this point will always have the same surfaces exposed to the vacuum atmosphere. The purpose for this is that some investigators⁽¹⁶⁾ believe that the hot portions of the rod above and below the molten zone react readily with the residual gases within the chamber. Hence after the first pass the reactive surfaces exposed were always the same.

If a gas had previously been introduced, the next molten zone pass is always made in a downward direction, since it is not desirable to contaminate the seed. The result of the third molten zone pass has the proper orientation.

The number of molten zone passes for a specific experiment is determined either by previous, similar experiments or by experimental conditions, i.e., the pedestal rotation comes uncoupled as mentioned earlier, the viewing ports become too coated with condensed

metallic vapor to allow observation of the experiment (even though a rotating window cover is used) or it becomes seemingly impossible to maintain a molten zone.

For resistivity ratio determinations, the methods of cutting the crystals and welding the leads has been described elsewhere.⁽¹¹⁾ The circuit used is shown in Fig. 2. All connections are made within a grounded aluminum box which also contains the standard resistors, to avoid thermal effects. For measurements at room temperature and at 77°K, the currents used never exceed 0.6 amp to avoid heating the sample. For measurements at 4.2°K, currents as high as 6 amps are used. A simple switch allows reversing the flow of current for each current value so that thermal emf's may be eliminated in a very straight-forward manner. Measurements at 4.2°K are of course made in the presence of a magnetic field. Data is taken as a function of the field values and extrapolated to zero field.

The internal friction apparatus was designed here and was designed to have a much lower background Q^{-1} than other torsional pendulum systems mentioned in the literature.^(6,13) Temperature is controlled by a thermocouple located adjacent to but not touching the middle of the sample and two temperatures are recorded during an experiment, one from a thermocouple in contact with the stationary lower specimen grip and the other from a thermocouple hanging free near the top of the specimen. The temperature is varied in a programmed manner and data points are observed every 15 min, since it has been verified that equilibrium has been reasonably well established within this interval of time. The system can be evacuated to a pressure of 3μ , but the tests are conducted in a dynamic helium atmosphere of approximately 27μ . All the specimen tested had a 0.050 in. dia. and were tested at a frequency of 4 Hz. The method of specimen preparation has been described elsewhere.⁽¹¹⁾

Experimental Results

The starting material for this series of experiments was obtained from the U. S. Bureau of Mines, Boulder, Colorado, in the form of dendritic crystalline powder. The initial analyses of the powder are shown in Table I. The resistance ratio of two of the largest dendrites in Lot A was determined to be approximately 1000.*

A summary of the first or vacuum series of experiments is shown in Table II. The starting rod for these experiments was obtained by arc melting compacted powder, and then cold swaging the ingot to a 0.250 in. diameter. The most significant result is the reduction in the oxygen concentration. However, the variation in the total pressure during the last molten zone pass results in no consistent variation in the resistance ratio, provided the total pressure was below 4×10^{-9} torr.

The rotation of the pedestal rod appears to result in a contamination of the crystal, i.e., the resistance ratio of the rotation zoned crystal is, in general, less than that of a non-rotated sample. However, increasing the number of zone passes does result in a significant increase in the resistance ratio. The number of molten zone passes was generally limited to four, because in some cases the zone became unstable, i.e., the surface tension decreased and it was seemingly impossible to continue. However, by swaging a four zone pass crystal bar to a 0.187 in. diameter rod it was possible to increase the number of molten zone passes to a total of eight. Once a problem with the surface tension decreasing occurs, all subsequent passes are made in the upward direction, where as prior to that, the direction is alternated for each successive pass. This was done since the expected method of purification was vacuum distillation. The resistance ratio of the 8 pass crystal was 360 where as the 4 pass crystal had a resistance ratio of 193, and both crystals were zoned at the same total pressure.

From a partial pressure analysis during the last molten zone pass, hydrogen was always found to be the dominant residual gas, with

* As determined separately by Dr. R. E. Reed of the Oak Ridge National Laboratory and Dr. D. R. Anderson of the Department of Physics, University of Maryland.

the others being quite varied. If the Orb-Ion pump was shut-off, the total pressure was lower. Hydrogen was still the principal residual gas, but, of the others, CO and CO₂ were more dominant. Interestingly, the resistance ratio was smaller than in experiments where the Orb-Ion pump was used.

A second series of investigations, or the gas addition series, is presented in Tables III and IV. The technique of the addition of a third component to remove a second component and result in a more pure first component is a well known technique for zone melting.⁽¹⁷⁾ Hydrogen was chosen because previous investigations⁽¹²⁾ have shown that hydrogen reduces some of the oxides of vanadium. Hydrogen was also chosen because it exhibits a reasonable attempt to follow Sievert's law in vanadium at low temperatures⁽¹⁸⁾ and at higher temperatures⁽¹⁹⁾. Further, the hydride is not stable at the temperature of molten vanadium.⁽¹⁵⁾ Also, some of the mechanical properties of hydrogenated vanadium have been investigated⁽²⁰⁾ for possible later comparisons. Ammonia was chosen because it should have all the benefit of hydrogen and also nitrogen. Nitrogen is supposed to follow Sievert's law in vanadium.⁽⁸⁾ Other investigators have noted that ammonia reacts more favorably to reduce the oxides of vanadium than does hydrogen.⁽¹²⁾ However, their work was done at low temperatures. Also the solubility of nitrogen in fairly pure vanadium has just recently been investigated.⁽⁶⁾ In the low temperature investigation, it was also noted that carbon was reduced from the vanadium with the production of HCN gas and it was hoped that the same reaction would prevail at higher temperatures. The zone speed during the introduction of the various gases was always 20 cm/hr.

The addition of hydrogen or ammonia during the first molten zone pass did not improve the resistance ratio or decrease the oxygen content of the as-zoned crystals. In fact the resistance ratio is lower than that of the crystals grown without hydrogen or ammonia additions and the oxygen concentration is greater.

Again, similar to the results obtained from the high vacuum series of investigations, rotation of the pedestal rod results in even smaller resistance ratios and larger oxygen concentrations than

without rotation.

At the completion of the molten zone passes for the hydrogen experiment without rotation, an attempt was made to anneal the crystal bar, in situ. However, the total pressure within the system began to increase significantly and the experiment was consequently terminated. The system total pressure after the power was shut down was 6×10^{-11} torr, which is typical, so the problem was apparently not a vacuum leak.

At a later date, the samples for resistance ratio measurements from experiments 8, 10, and 12 were given a short duration, low temperature anneal as a check on the behaviour of experiment 7. The crystals were annealed in the EBFZR by placing them in molybdenum wire baskets and heating with the electron beam. The system total pressure increased two orders of magnitude as each of the crystals, in turn, were heated to approximately 800°C ($\pm 150^{\circ}\text{C}$). The dominant contaminants were hydrogen and carbon monoxide and, to a lesser extent, carbon dioxide. New leads were welded (the original leads had been etched away prior to annealing) and the resistance ratios measured. The low temperature anneal resulted in a significant increase in the resistance ratio of the hydrogen rotation zoned sample, had no effect on the ammonia rotation zoned sample, as shown in Table IV, but, the resistance ratio of the ammonia without rotation sample decreased noticeably.

For all the experiments involving ammonia, no problem with the surface tension decreasing occurred. Part of the problem may have been due to the relative impurity of the gas used. During the third molten zone pass, the presence of helium and argon was still detectible in all cases. These gases are never detected after the second "light degassing" pass on the other experiments. Also, all the vacuum pumps on the system were found to pump ammonia gas in a very sluggish manner. In the hydrogen addition case, problems with the surface tension decreasing occurred during the third pass of one experiment but did not reoccur on the fourth pass.

A summary of the third or powder series of experiments appears in Table V. The arc-melted ingot was obtained by directly melting the dendritic crystalline powder, without previously compacting it.

The oxygen and nitrogen contents of the arc-melted ingot are comparable to those obtained when a compact is arc-melted. However, there appears to be a greater reduction of the oxygen content during zone melting when the arc-melted ingot is not made from compacted powder. Again, increasing the number of molten zone passes, even though the pressure does not decrease, results in lower oxygen concentrations. A high temperature ($1600^{\circ}\text{C} \pm 150^{\circ}\text{C}$) anneal at high vacuum resulted in an increase in the oxygen concentration and a decrease in the resistance ratio.

The fourth or zoned compact series of experiments is summarized in Table VI. Here, the compacted dendritic powder was placed directly in the EBFZR. The diameter of the compact was 0.75 in., and no focussing plates with such a large aperture were available, so a nude filament was used. The height of a completely molten zone would have been prohibitive under such conditions, so only the surface of the ingot was melted. The technique used involved getting the surface molten, letting it solidify, translating the filament, and then repeating the process. It was however, possible to melt the compact through its entire cross-section at two places along the length, using this technique. The result was a vanadium compact within a vanadium tube. This ingot, which had a 0.5 in. dia., approximately, was swaged to furnish a 0.250 in. diameter rod.

Again the oxygen concentration decreased with an increased number of zone passes. However, the most significant observation is the high value of the resistance ratio of the annealed crystal, 655, and it should be recalled that annealing at high temperatures and at a high vacuum results in an increase in the oxygen concentration and a decrease in resistance ratio. Further, it should be noted that the last three of the five zone passes were in the upward direction. The sample from the bottom of the crystal bar had the ratio of 655 whereas the sample with the ratio of 232 came from the top.

The internal friction results are shown in Fig. 3. The first sample was taken from a swaged rod and was annealed for 75 minutes at 700°C and at a pressure of 7.0×10^{-9} torr. The sample was

analyzed and was found to contain 118 wt. ppm. oxygen and 127 wt. ppm. carbon. The second sample was taken from a zone melted crystal bar, reduced to the proper size for the internal friction experiment in a manner identical to the first sample. It was then annealed for 45 minutes at 700°C and at a pressure of 2×10^{-9} torr. This sample was analyzed and was found to contain 46 wt. ppm. oxygen and 30 wt. ppm. carbon. The value of the room temperature damping which is taken as the background Q^{-1} was less than 0.00015 in both cases. A half-width analysis shows that both curves may be composed of more than one relaxation process, i.e., the activation energy so determined (24 kcal/mole) is less than that for either carbon or oxygen.⁽¹³⁾

Since the spectrum of values exists in the literature for the value of the resistivity of vanadium at room temperature⁽²¹⁻²⁶⁾, this was measured on the sample used for the resistance ratio determination for experiment #1. The value calculated for the resistivity at 296°K is $22.8 \mu\Omega - \text{cm} \pm 0.3\%$, where the error is principally in the measurement of the lead spacing.

Discussion

This extensive investigation indicates several major points which are contrary to the existing literature concerning vanadium and supports some of the conclusions which have resulted from the investigations of others.

The first major point which is contrary to the literature, is that it is possible to improve the purity of vanadium by ultra-high vacuum electron beam zone melting techniques.^(3,4,7-9) In Fig. 3, it is shown that the zone melting operation removes free interstitial oxygen, as well as free interstitial carbon. However, it is to be noted that the analysis values deviate significantly from the internal friction results. Oliver and Garofalo⁽²⁷⁾ noted similar behaviour for carbon and oxygen in iron, but for much lower concentrations. The absence of nitrogen for the case of the sample from the arc-melted and swaged rod is in keeping with the usually low concentration of nitrogen in vanadium from the arc-melter, the fact that the swaging operation has no tendency to

introduce nitrogen, and that the sample was annealed at a total pressure of 7×10^{-9} torr. The large carbon contamination occurring during the arc-melting operation could be due to the vaporization of the vacuum grease used in the sliding members inside the arc-melter.

The vacuum series of investigations did prove that it is possible to reduce the oxygen concentration by zone melting at total pressures of 10^{-9} to 10^{-10} torr. However, variation in the pressure from 10^{-9} to 10^{-10} torr did not result in a corresponding variation in the oxygen concentration. Also, high vacuum annealing (10^{-10} torr) at $1600^\circ\text{C} \pm 150^\circ\text{C}$ resulted in an increase in the oxygen concentration. It was previously proposed⁽¹¹⁾ that the reduction in the oxygen concentration which occurs during zone melting and not during annealing was the result of the envelope of metallic vapor which surrounds the molten zone.^(16,28) This vapor envelope effectively reduces the partial pressure of oxygen below 10^{-13} torr so that oxygen removal can occur.⁽⁴⁾

A second point which is contrary to the existing literature on zone refining concerns the rotation of the pedestal rod. The results of this investigation clearly indicates that pedestal rod rotation does not result in greater purification as has been found in iron.⁽²⁷⁾ Pedestal rod rotation here results in higher oxygen concentrations and lower resistance ratios. The significance of the increase in the oxygen concentration will be considered along with the subsequent discussion of the gas additions.

A significant point concerning high purity vanadium is that there is not necessarily a correlation between the oxygen concentration and the resistance ratio. Comparing the results in Tables II and V, for approximately the same oxygen concentration, the resistance ratio varies from 193 to 392. This large difference in resistance ratio is probably due to another impurity, which could be carbon. The internal friction results support such an assumption. This observation is again contrary to the literature⁽¹³⁾, where it has been stated that adding carbon to vanadium was difficult.

The gas addition series of experiments (Tables III and IV) is

very interesting. The first conclusion here is that the addition of either hydrogen or ammonia at the melting point is harmful, i.e., results in a higher interstitial concentration in comparison to the vacuum series of experiments, though ammonia is not as harmful initially as hydrogen.

The second point is that the rotation of the pedestal rod is again harmful. The hydrogen series and also the ammonia series indicates that, for a constant number of zone passes, rotation is worse, irrespective of the final value of the pressure.

An explanation of the detrimental effects of the gas additions could be based upon the impurities existing as gases. However, if this were the case, then the ammonia experiments should have resulted as the poorer case, but just the opposite was observed. Therefore it must be concluded that the gases themselves have a detrimental effect in terms of purifying vanadium. This conclusion is further substantiated by considering the results in Table IV. A short duration, low temperature anneal caused significant changes which ideally should not have taken place. The resistance ratio almost doubled for the hydrogenated sample. Earlier it was noted from the literature^(18,19) that hydrogen is supposed to follow Sievert's law in vanadium. If this were absolutely the case, then very little should have happened during the anneal where the hydrogen partial pressure was almost two orders of magnitude higher than during zone melting. The only reasonable explanation for such behaviour is that hydrogen must exhibit retrograde solubility in vanadium. However, the high temperature investigation⁽¹⁹⁾ was limited to temperatures below 1300°C, and therefore this phenomena was not observed.

In the case of nitrogen (ammonia), there was a significant decrease in the resistance ratio compared to the other experiments. This clearly indicates that high vacuum (10^{-10} torr) does not result in a reduction in nitrogen concentration, which is again contrary to the existing literature^(8,12) which states that nitrogen follows Sievert's law in vanadium.

The harmful effects of pedestal rod rotation cannot be easily explained. The usual reason for the use of pedestal rod rotation is to improve mixing within the molten zone. However, before con-

sidering the mixing within the molten zone, it is necessary to consider the diffusion of oxygen, carbon, nitrogen, and hydrogen in vanadium.

Powers and Doyle⁽¹⁰⁾ have tabulated the appropriate values for oxygen, carbon, and nitrogen in vanadium at low temperatures from their internal friction and elastic after-effect investigations. Schmidt and Warner⁽²⁹⁾, in their electromigration studies, have determined the same quantities at high temperatures. Their results indicate a similar activation energy in all cases, but their values for the diffusivities of carbon and nitrogen are greater by a factor of two, which is not uncommon for b.c.c. materials.⁽³⁰⁾ It is more interesting to note that oxygen does not behave in a similar manner.

Butera and Kofstad,⁽¹⁵⁾ in their investigation of the internal friction behaviour of hydrogen in vanadium, list the activation energy for diffusion. Further, they note enough information to allow the calculation of the diffusivity. Their results indicate

$$D_{H-V} = 1.21 \times 10^{-4} \exp \left(\frac{9,050}{RT} \right)$$

where the symbols have their usual significance. If this equation, which is valid at the temperature of the measurements (195°K), is used at higher temperatures, then the appropriate information for both hydrogen and nitrogen in vanadium is known. Using the classical $x^2 = 4Dt$, taking for D the value just below t_{mp} , and t the average time that a given section of crystal bar is molten, then the value of x obtained is greater than the radius of the crystal bar being zoned. Therefore, conventional diffusion of a single free interstitial atom cannot account for the difference between rotation and non-rotation. In addition, the usual approximation is to increase the value of D by at least an order of magnitude for diffusion in the liquid, which is particularly applicable for zone melting due to the minor turbulence which is always present.^(14,31) However, this even further weakens the case for conventional diffusion. The need for pedestal rod rotation to improve mixing in vanadium is of dubious advantage. The question remains, though, as to why the

rotation results in harmful effects.

The mixing which does occur must be harmful. If the assumption is valid that the reduction of the oxygen concentration occurs by the decomposition of the oxides at the surface of the molten zone, then it is possible that the oxides are mixed into the molten zone, where their decomposition would not readily occur.

The effect of rotation during the hydrogenation experiments can be readily explained by noting that the results are basically similar to those of the vacuum series of experiments. There is no appreciable difference between the resistance ratios of rotated and non-rotated samples in the vacuum series and the rotated and non-rotated hydrogen series of experiments.

The difference between the rotated and non-rotated nitrogen (ammonia) series of investigations is somewhat more difficult to explain. The compounding difficulty is to explain why the low temperature anneal resulted in the reduced resistance ratio of the non-rotated sample and the resistance ratio of the rotated sample remained the same. If the nitrogen enters the vanadium interstitially, then, from consideration of the diffusion process, rotation vs. non-rotation should have little effect. If the nitrogen reacts with the vanadium to form a known nitride, then the nitride could become mixed into the molten zone. However, the known nitrides of vanadium are supposed to decompose for temperatures above 800°C in vacua.⁽¹²⁾ Therefore if the nitride formed on the solid surface of the rod, then it should decompose as the molten zone approaches. Nitrogen complexes have been identified in Ta⁽³²⁾ and in Ta-Re alloys.⁽³³⁾ It is conceivable that such may also be the case for nitrogen in vanadium. The existence of complexes in vanadium is not new to the literature as evidenced by the investigations of Edington and Smallman,⁽³⁴⁾ but they attributed the complex to be an oxide, even though they could neither identify nor isolate it. Problematically though, the diffusion characteristics, again indicate an anomaly. The explanation of the greater impurity content with rotation requires the value of the diffusivity to be low, and to explain the significant decrease in the resistance ratio upon a short duration, low temperature anneal,

a higher value for the diffusivity is required.

Other anomalous behaviour of nitrogen in vanadium has been noted in the literature. If the nitrogen content is high, it may be removed, obeying Sievert's law very nicely.⁽⁸⁾ Further, again for high concentrations, it will move during electromigration experiments.⁽²⁹⁾ The data of Stanley and Wert⁽³⁵⁾ indicates that as the concentration is reduced, nitrogen ceases to move during electromigration and fails to obey Sievert's law. Horz has verified both cases^(36,37) and other investigators generally agree.^(13,36)

The only seemingly plausible explanation for the results of the present investigation is that at low temperatures the nitrogen is present as an uncombined interstitial. A complex, either with other interstitials or with the vanadium, must exist at higher temperatures. To account for this, the free energy of formation of the complex must change quite drastically with temperature, to allow the stability of the low temperature free interstitial. It should also be noted that the same behaviour is found in the experiment was present in the investigation of Stanley and Wert, but no conclusions seem to have been drawn from it.

The highest purity vanadium, as determined by the largest resistance ratio, was obtained by electron beam melting a compacted rod. The carbon content was low due to the fact that there was no possible exposure to vacuum grease. The total pressures during zoning were higher than the previously mentioned experiments. This implies that for low pressures, the metallic vapor envelope surrounding the molten zone does afford complete protection^(16,28) and also may have the effect of locally reducing the partial pressure of oxygen below 1×10^{-13} torr which is needed to remove oxygen from molten vanadium. However, annealing in the same atmosphere as zoning contaminates the specimen, giving additional strength to the above conclusion, i.e., that the oxygen reduction occurs only as a result of the metallic vapor envelope surrounding the molten zone.

The reason for the increased resistance ratios which result from an increased number of zone passes is not clear. A plausible

explanation is that a true zone refining effect is occurring since there is a decrease in the resistance ratio when going from the bottom to the top of a crystal bar, i.e., the direction of zone traversal.

Finally, the present value determined for the room temperature resistivity is in good agreement with White and Woods.⁽²⁵⁾ That this agreement occurs inspite of the difference in the resistance ratios (280 vs. 7.4) is in keeping with the Debye temperature of vanadium.⁽³⁸⁾

Summary

This investigation demonstrates that it is possible to consistently electron beam zone melt vanadium at total pressures within the 10^{-10} torr range. One of the principal features of the system which makes this possible is the ability to bake the electrostatic pumps and the major part of the system at pressures below 10^{-6} by using the turbomolecular pump.

The experimental results presented are in general contrary to the existing literature concerning interstitial impurities in vanadium. The results clearly indicate that it is possible to reduce the oxygen concentration in vanadium by high vacuum electron beam zone melting. However, changing the total pressure during zone melting from 4×10^{-9} to 2×10^{-10} torr does not result in a corresponding decrease in the oxygen concentration.

A second major experimental finding which again is contrary to the existing literature is that rotation of the pedestal rod here results in an increase in the oxygen concentration and a decrease in the resistance ratio. The literature indicates that pedestal rod rotation should result in greater purification.

Yet another experimental finding which is contrary to the literature is that hydrogen or ammonia gas additions do not aid in purification. They actually result in a contamination of the crystal.

High temperature, high vacuum annealing in general results in an increase in the oxygen concentration and a decrease in the resistance ratio. It is therefore concluded that the removal of

oxygen occurs by the decomposition of vanadium oxides at the surface of the molten zone, i.e., a metallic vapor envelope surrounds the molten zone and affectively reduces the partial pressure of oxygen below 1×10^{-13} torr. Since there is no ready correlation between the resistance ratios and oxygen contents of the various samples tested, it must be concluded that other impurities are present within the crystals. Carbon is the most likely suspect because the internal friction results indicate that carbon is present in the samples. The presence of carbon indicates, again contrary to the literature, vanadium will become easily contaminated with carbon.

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Figure Captions

- Fig. 1. Diagram of the electron beam floating zone refining system.
- Fig. 2. Circuit used for resistance ratio measurements.
- Fig. 3. Comparison of internal friction results for high vacuum zone melted vanadium and vanadium which had been only arc-melted and swaged.

(1) Orb-Ion Pump; (2) Chamber; (3) Rod to be zoned; (4) Filament travel block; (5) Pedestal rod travel block with rotation capability; (6) Wheeler flange on bell jar; (7) Bottom of bell jar (sump); (8) Ports for electrical feed-throughs, ion gauges, and monopole residual gas analyzer; (9) Bakeable valve; (10) Precision leak valve; (11) Turbomolecular Pump; (12) Valve; (13) Vac Ion Pump; (14) Valve; (15) Valve to atmosphere; (16) Magnetic rotary feed-throughs for direct drive of filament travel block, pedestal rod travel block, and rotation; (17) Mechanical roughing pump.

Fig. 1. Diagram of the electron beam floating zone refining system.

A, B Standard Resistors, 5a @ 50 ma
 C Circuit protection resistor
 D Switch for putting standard resistors in parallel or series

E Switch for by-passing standard resistors
 F Switches to reverse polarity of current and potentiometer
 G Sample

Fig. 3. Comparison of internal friction results for high vacuum zone melted vanadium and vanadium which had been only arc-melted and swaged.

Table I

Analyses of Vanadium Dendritic Crystalline Powder
Supplied by U. S. Bureau of Mines

	Lot A*	Lot B**	Lot C**
Oxygen	110 ⁺	28	18
Nitrogen	10		1
Carbon	20	10	12
Hydrogen	10	43	40
Chromium	<6	16	14
Silicon	<15	24	17
Magnesium	3		<3
Aluminum		36	7
Copper		<5	<5
Manganese		<5	5
Nickel			<3
Lithium	Chlorides		
Sodium			
Potassium			
	~200	~200	~200

* Oxygen and hydrogen were determined by vacuum fusion analysis and nitrogen by the Kjeldahl method on an arc-melted button of the vanadium.

** Oxygen, hydrogen, and nitrogen were determined by vacuum fusion analysis on the dendritic crystals.

+ All figures in wt. ppm.

Table II
Vacuum Series

Experiment No.	1	2	3	4	5	6
Compacting Pressure (kpsi)	24	30	30	30	30	
Analysis of Arc-melted ingot						
Oxygen	175	141	141	141	141	153
Nitrogen	14	8	8	8	8	6
Pressure in EBFZR during 1st molten zone pass (torr)	6.0×10^{-8}	4.0×10^{-9}	4.0×10^{-9}	7.0×10^{-9}	7.0×10^{-9}	1.4×10^{-9}
Pedestal rod rotation speed (rpm)	0	0	0	45	45	0
No. of molten zone passes	4	4	4	4	8	3
Pressure in EBFZR during last molten zone pass (torr)	4.0×10^{-9}	3.4×10^{-10}	2.2×10^{-10}	5.5×10^{-10}	6.8×10^{-10}	7.0×10^{-10}
Crystal growth rate (cm/hr)	10	20	20	20	30	10
Analysis of zoned crystal						
Oxygen	46			46		35
Nitrogen						14
Carbon	30					43
Resistivity ratio as-zoned crystals	280	150	86	193	360	

Table III

Experiments No.	Gas Addition Series					
	7	8	9	10	11	12
Compacting Pressure (kpsi)	24	30	30	30	30	30
Analysis of Acr-melted ingot						
Oxygen	175	141	141	141	141	141
Nitrogen	14	8	8	8	8	8
Gas added during 1st pass	H ₂	NH ₃	NH ₃	H ₂	H ₂	NH ₃
Base pressure of system before introducing gas (torr)	6.0x10 ⁻⁸	8.0x10 ⁻⁹	8.0x10 ⁻⁹	1.5x10 ⁻⁹	1.5x10 ⁻⁹	8.0x10 ⁻⁹
Pressure during 1st molten zone pass (torr)*	1.4x10 ⁻³	8.0x10 ⁻⁵	8.0x10 ⁻⁵	1.4x10 ⁻³	6.0x10 ⁻⁵	8.0x10 ⁻⁵
Pedestal rod rotation speed (rpm)	0	0	0	30	30	45
Pressure during Beam power degassing	2.0x10 ⁻⁷	9.7x10 ⁻⁹	9.4x10 ⁻⁹	6.0x10 ⁻⁸	8.0x10 ⁻⁹	2.0x10 ⁻⁸
No. of further zone passes	3	3	1	3	3	3
Pressure in EBFZR during last zone pass (torr)	6.0x10 ⁻¹⁰	1.6x10 ⁻¹⁰	1.0x10 ⁻⁹	6.0x10 ⁻¹⁰	7.2x10 ⁻¹⁰	6.5x10 ⁻¹⁰
Crystal growth rate (cm/hr)	8	8	20	20	20	20
Analysis of zoned crystal						
Oxygen	49			68		
Nitrogen						
Resistivity ratio of as-zoned crystals	111	190	86	86	66	80

* Hydrogen pressures shown have been corrected for the ionization constant of the gauge.

Table IV

Annealing Results — Gas Addition Series

Experiment No.	8	10	12
Cold system total pressure before annealing (torr)	6.0×10^{-11}	3.8×10^{-10}	4.2×10^{-10}
Maximum pressure during annealing (torr)	8.0×10^{-9}	9.5×10^{-9}	9.0×10^{-9}
Total annealing time (hr)	2	1.25	1.5
Final total pressure (torr)	3.4×10^{-9}	1.0×10^{-9}	1.8×10^{-9}
Resistivity ratio of annealed crystals	125	160	80

Table V

Arc-melted Powder Series

Experiment No.	13	14	15
Analysis of Arc-melted ingot			
Oxygen	153	153	153
Nitrogen	6	6	6
Pressure in EBFZR during 1st molten zone pass (torr)	1.8×10^{-9}	1.7×10^{-8}	1.8×10^{-9}
No. of molten zone passes	3	3	6
Pressure in EBFZR during last molten zone pass (torr)	$<1.0 \times 10^{-9}$	$<1.0 \times 10^{-9}$	$<1.0 \times 10^{-9}$
Crystal growth rate (cm/hr)	10	10	10
Analysis of zoned crystals			
Oxygen	33	18	16
Nitrogen	4	250	
Resistivity ratio of as- zoned crystal		135	
Total annealing time (hr)	33	51	39
Pressure during annealing (torr)	2.5×10^{-9}	3.4×10^{-10}	3.4×10^{-10}
Analysis of annealed crystals			
Oxygen		58	48
Resistivity ratio of annealed crystals	149	100	392

Table VI
Zoned Compact Series

Experiments No.	16	17	18
Compacting Pressure (kpsi)	3.8	3.8	3.8
Pressure in EBFZR	5.5×10^{-8}	5.5×10^{-8}	5.5×10^{-8}
Analysis of Ingot			
Oxygen	89	89	89
Nitrogen			
Pressure in EBFZR during 1st molten zone pass (torr)	2.8×10^{-9}	9.0×10^{-9}	9.0×10^{-9}
No. of molten zone passes	2	5	5
Pressure in EBFZR during last molten zone pass (torr)	2.3×10^{-9}	1.3×10^{-9}	1.3×10^{-9}
Crystal growth rate (cm/hr)	16	13	13
Analysis of as-zoned crystals			
Oxygen	55		
Resistivity ratio of as-zoned crystals			
Total annealing time (hr)	0.75	15	15
Pressure during annealing (torr)	2.0×10^{-10}	2.7×10^{-10}	2.7×10^{-10}
Analysis of annealed crystals			
Oxygen		31	
Resistivity ratio of annealed crystals	342	655	232*

* Value determined by Dr. R. E. Reed of the Oak Ridge National Laboratory.