Effects of Implanted Helium on the Mechanical Properties of Vanadium-Based Binary Alloys

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Effects of helium on the mechanical properties of vanadium base binary alloys have been studied using tritium trick technique. Emphasis was placed on the effect of atomic size factor of solute atoms. Substantial reduction of ductility was observed by tensile tests at room temperature by helium charging. Strong correlation was observed between apparent solid solution hardening, ductility reduction and atomic size factor of solutes. It is concluded that under-sized solutes strongly trap helium atoms. The distribution and the state of helium obtained by tritium trick technique has been suggested to be very much different from that anticipated for fusion neutron irradiation. Although tritium trick technique offers a unique and interesting way to study the effects of helium, the results should be taken with caution.

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I. Introduction

Fusion reactor materials are expected to be irradiated by 14 MeV neutrons produced by D-T fusion nuclear reaction. The nuclear cross section for (n, α) reaction increases rapidly for neutrons above about 5 MeV. This results in helium generation rate for fusion neutron much greater than that for fission neutron irradiation. Helium is virtually insoluble in metals and tends to form clusters and promotes bubble nucleation or segregates to grain boundaries and induces so-called helium embrittlement. Helium embrittlement is an important process which casts an upper limit for materials for operation. Therefore the study of helium embrittlement is very important for successful development of materials suitable for fusion reactor applications. Materials systems consist of vanadium alloys and liquid lithium coolant/breeder is very attractive for commercial fusion reactors, because of the low induced activity, high operational temperatures, favorable thermal stress factor, etc. Since the high operational temperature is one of the most advantageous point for vanadium alloys, to raise the lower bound of the design window due to helium embrittlement is an issue with a very high priority.

Helium embrittlement of vanadium alloys has been studied fairly extensively in the past. Study of helium effects usually involves ion implantation[19],[20], boron-10 technique[3], tritium trick technique[36], etc.; each of these has its merits and demerits. Ion implantation is generally favorable when implantation or damage rate is unimportant. Boron-10 technique enables fairly uniform helium distribution in bulky specimens suitable for mechanical testing, while the microscopic distribution is often very inhomogeneous and lithium production accompanied with helium production is very troublesome for the interpretation of experimental results. Tritium trick is an experimental technique utilizing tritium decay into helium-3; vanadium alloys is particularly suited for this technique since the solid solubility of hydrogen isotopes in vanadium is very large, so that uniform helium generation within the specimen is expected.

Helium introduced into vanadium alloys by tritium trick is believed to be located in interstitial sites, at least just after the decay process. Interstitial helium has generally high mobility and will migrate quickly until it is trapped by lattice defects, e.g. dislocations, grain boundaries, vacancies, and solute atoms, etc. If the trapping strength is large enough, helium will stay in the matrix and may be detected through changes in mechanical properties, i.e. yield stress, etc. Strong binding of some solutes with helium can be utilized to inhibit helium migration to grain boundaries, and thus mitigate helium embrittlement. It is interesting, therefore, to study mechanical property change by helium in alloys with various kinds of solutes.

In the present paper, the result of mechanical testing of vanadium alloys which is doped with helium by using tritium trick technique is presented. Emphasis is on the effect of atomic size factor on the interaction of helium with those solute atoms.

II. Experimental

The alloys prepared are: V-1 at%Si, V-5 at%Ti, V-5 at%Cr, V-5 at%Fe, V-5 at%Nb and V-5 at%Mo. These alloys have been selected to cover a wide range of atomic size factor of solutes in vanadium. The starting material was 99.9% pure Chinese vanadium and was electron beam melted for further purification. The materials for alloying have been purchased from several sources; the
Table 1 Measured helium concentration in the alloys.

<table>
<thead>
<tr>
<th>Alloy type</th>
<th>He concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure V</td>
<td>363</td>
</tr>
<tr>
<td>V-1 at%Si</td>
<td>307</td>
</tr>
<tr>
<td>V-5 at%Ti</td>
<td>688</td>
</tr>
<tr>
<td>V-5 at%Cr</td>
<td>269</td>
</tr>
<tr>
<td>V-5 at%Fe</td>
<td>154</td>
</tr>
<tr>
<td>V-5 at%Nb</td>
<td>405</td>
</tr>
<tr>
<td>V-5 at%Mo</td>
<td>267</td>
</tr>
</tbody>
</table>

Purity levels of these materials ranged from 99.99 to 99.999%. The alloy ingots were obtained by argon arc melting. These ingots were cold rolled to approximately 0.25 mm thick sheets. TEM disks and small tensile specimens with gage part of 5 mm × 1.2 mm × 0.25 mm were punched from sheet specimens. They were doubly wrapped with tantalum and zirconium foils and sealed in evacuated quartz tubes. The recrystallization annealing was done at 1100°C for 2 h.

Tritium trick was conducted at 400°C at a tritium pressure of 54.7 kPa. Tritium was extracted after decay period of 1.44 Ms (400 h); the specimen chamber was evacuated and the temperature of the specimens was increased up to 700°C. Some release of helium and/or change in the state of helium are expected during this extraction treatment. Since all the alloys have been treated at the same pressure and temperature, the helium concentration is different in different alloys through the difference in equilibrium tritium solubility. Concentration of helium determined by vacuum extraction method is given in Table 1. Tensile tests were done at room temperature at a constant crosshead speed, which corresponded to a strain rate of 4.7 × 10⁻⁴/s.

### III. Results

#### 1. Mechanical properties

Figure 1 shows stress-strain curves of the alloys with and without helium doping. It is seen from this figure that remarkable reduction in tensile elongation occurred by helium doping. The degree of embrittlement is dependent on the alloy type and/or helium concentration. In V-5 at%Ti alloy with 688 ppm He shows maximum reduction in elongation; the helium-doped specimen shows completely brittle failure. In Fig. 2 are shown SEM micrographs of the fractured surface. The fracture occurred completely along grain boundaries in this V-5 at%Ti specimen. The V-5 at%Fe specimen, on the other hand, shows only little embrittlement by 154 ppm helium. The fracture surface is almost entirely transgranular as shown in this figure. V-5 at%Mo alloy shows intermediate behavior. The fracture surface consists of mainly intergranular surface, while considerable part of the surface shows ductile dimple-like rupture feature.

Increase in yield strength is also noted by helium doping in Fig. 1. Helium in the specimens is believed to be not in solution but in some form of clusters, so that the hardening observed here should not be termed as solid solution hardening. Let us tentatively refer to this hardening as "apparent solid solution hardening". The apparent solid solution hardening determined from the change in the yield strength caused by helium of unit concentration is plotted in Fig. 3 as a function of atomic size factor of solute atoms. Here, atomic size factor is defined as lattice parameter change, determined by X-ray diffraction, caused by addition of unit concentration of solute terms.

The data point for silicon is multiplied by a factor of five in order to take into account that this alloy only contains 1 at% rather than 5 at% of solute as all the other alloys studied; this compensation is probably not justified rigorously and will be discussed below in discussion section. A remarkable correlation is found in this figure between atomic size factor and the apparent solution hardening. Alloys with strongly under-sized solutes, i.e., iron, silicon and chromium, shows large solution hardening. Solution hardening is small for pure vanadium, and for over-sized solutes molybdenum and titanium, and relatively large for strongly over-sized niobium solute.

In Fig. 3 is also plotted ductility reduction by helium expressed as the ratio of tensile elongation of helium-doped specimens to that of control specimens; the scale of the ductility reduction is indicated on the right hand side of Fig. 3. Here again the data for silicon have been multiplied by a factor of five in order to compensate the different solute concentration by the same factor. The dependence of ductility reduction by helium on atomic size factor is remarkably similar to that of the apparent solid solution hardening by helium. Alloys with undersized solutes, as well as with strongly over-sized solute, i.e., niobium, are less susceptible to helium embrittlement; pure vanadium and alloys with relatively weakly oversized solutes show maximum embrittlement by helium.

#### 2. Electron microscopy

Figure 4 shows dislocation microstructures of vanadium alloys after helium doping by tritium trick method. Microstructure in control specimens, not shown, is featureless except for grain boundaries and occasional appearance of dislocation segments. Dislocation loops and segments are observed in all the micrographs in Fig. 4. Dislocation loops are pronounced especially in V-5%Fe and V-5%Cr alloy. It is also noted that some of the dislocations in pure vanadium are accompanied by stacking fault-like fringes. It is believed that these fringe contrast is caused by some segregation of impurity atoms to these dislocations. Dislocation loop density was determined from this figure and is plotted against atomic size factor in Fig. 5. The data point for V-5%Nb alloy is missing because of the difficulty in specimen preparation for TEM in this particular type of alloy. There is a systematic change in the loop density with atomic size factor; the alloys with strongly undersized solutes, i.e., Fe, Si and Cr give high density of dislocation loops, while it shows minimum for pure vanadium. The tendency is quite similar to that of apparent solid solution hardening as
shown in Fig. 3.

In the vicinity of grain boundaries, there is a denuded zone in which few dislocation loops or segments are observed as shown in Fig. 6. The width of this denuded zone is typically of the order of one μm and is dependent on the type of solutes. In the V-5%Ti alloy, the width of this zone is much smaller than those found in the other alloys.

Figure 7 shows cavity microstructure, where micrographs were taken with none of the diffracted beams being strongly excited. In all the alloys studied, bubbles are observed by helium doping. Bubble size is relatively small in alloys with under-sized solute. In V-5%Mo and V-5%Ti alloys, bubbles tend to align along some line, presumably they have been formed on dislocations. The electron micrographs in Fig. 7 for these two alloys are somewhat atypical; average bubble density is lower than in this figure. In V-5%Ti alloy, dislocation tangling is observed around such bubble clusters. This may have been caused by tritide precipitation during tritium trick treatment.

Figure 8 shows bubble microstructure in the grain boundary region. In all the alloys studied, grain boundaries are more or less covered with bubbles. There is,
however, certain systematic difference in the size distribution of bubbles. In V-5%Fe, the atomic size factor is the smallest, and the bubble size is the smallest, while the bubbles in pure vanadium and in oversize-type alloys are larger and the coverage of grain boundary area by bubbles is greater in the latter type of specimens.

**IV. Discussion**

Helium embrittlement is caused by the segregation of helium to grain boundaries which is weakened either by atomic helium or by helium bubbles. Therefore, helium transport towards grain boundaries must occur before embrittlement manifests itself, so that the embrittlement is generally recognized to be a high temperature phenomenon. There are several possible mechanisms for helium transport: (1) bulk diffusion via interstitial mechanism, (2) bulk diffusion via vacancy mechanism, (3) dissociative mechanism, (4) pop-out mechanism where a helium atom trapped within a vacancy is ejected when a self-interstitial atom is captured by the vacancy, (5) diffusion along grain boundaries or along disloca-
Fig. 5 Dislocation loop density determined from electron micrographs as shown in Fig. 4 plotted as a function of atomic size factor.

Grain boundary denuded zone

V-5%Fe
500nm

V-5%Cr
500nm

V-1%Si
500nm

pure V
500nm

V-5%Mo
500nm

V-5%Ti
500nm

Fig. 6 Dislocation microstructure in the vicinity of grain boundaries.

Cavity image

V-5%Fe
200nm

V-5%Cr
200nm

V-1%Si
200nm

pure V
100nm

V-5%Mo
500nm

V-5%Ti
100nm

Fig. 7 Cavity microstructure in the matrix of vanadium alloys.

Grain boundary bubbles

V-5%Fe
200nm

V-5%Cr
100nm

V-1%Si
200nm

pure V
100nm

V-5%Mo
100nm

V-5%Ti
100nm

Fig. 8 Cavity microstructure on grain boundaries.

tions, and (6) transport swept by moving dislocations. All these transport mechanisms, except for (1) require high temperatures, therefore the embrittlement observed in the present study is somewhat atypical to the helium embrittlement observed in the past. Similar embrittlement has also been reported by Braski[6], where helium was doped by tritium trick technique in exactly the same procedure employed in the present study. The peculiarity of the state of helium introduced into metals by this technique will be discussed first.

In tritium trick technique, tritium resides in interstitial sites before it decays into helium. Helium is then in-
roduced on an interstitial site by the decay. The kinetic energy released in the decay process is less than 18.6 keV\(^{19}\) and most of the energy is carried by the \(\beta\)-particle, so that atomic displacement during this decay process is unlikely. Thus, helium is introduced with He/dpa, the ratio of the rate of helium generation (apm) to that of displacement damage, virtually infinity. What follows then is rapid migration of interstitial helium and trapping of them by dislocations or grain boundaries. The bubbles observed along grain boundaries as shown in Fig. 8 are believed to be created by helium atoms trapped by grain boundaries. It has often been argued that tritium segregation to grain boundaries may be the cause of the grain boundary bubble formation. This is probably not very likely in vanadium alloys by the following consideration.

The segregation tendency is roughly inversely proportional to the solid solubility\(^{16}\), and the solid solubility of hydrogen isotope is very large at the temperature of the tritium decay treatment of 400°C\(^{11}\); this temperature is above the miscibility gap in the vanadium-hydrogen system, where the system forms a continuous solid solution. Therefore, the significant segregation of tritium is not very likely at the temperature of tritium decay and helium is believed to be generated uniformly within the grain interior. The number of helium atoms contained in grain boundary bubbles as estimated below is also much too high if only those helium atoms generated from tritium segregated in the grain boundary were contained in the grain boundary bubbles. The bubble radius \(r_b\) is of the order of 5 nm as shown in Fig. 8. By assuming that the bubbles are equilibrium ones, the pressure \(p\) is obtained from \(p = 2\gamma / r_b\), to be 800 MPa, where \(\gamma\) is the surface energy and is set equal to 2 J/m\(^2\). The number of helium atoms contained in such a bubble may be obtained by using a gas equation of state given by Mills, Liebenberg and Bronson\(^{22}\) to be 17000 at 973 K, at which de-tritiation is conducted. On the other hand, the number of helium atoms in the grain boundary area per bubble is less than 2000 by assuming mono-layer coverage of grain boundary area by helium. Mono-layer coverage is the upper limit estimate of equilibrium tritium segregation. Thus, helium must be transported from the bulk to grain boundaries in order to account for the number of helium contained in the grain boundary bubbles.

The temperature range in which migration of helium to grain boundaries took place will be discussed here. For interstitial helium, the mobility at 400°C is by orders of magnitude larger than that required for helium to reach grain boundaries\(^{13}\). Chen et al.\(^{14}\) have reported that significant helium migration started above 340 K in niobium. They interpret this temperature to be the one at which the migration of single or small clusters of interstitial helium takes place. If the scaling with homologous temperature holds, this process will occur in vanadium at a still lower temperature. The decay treatment temperature of 400°C is again much higher than their helium migration temperature, so that it is likely that a significant fraction of helium migrated to grain boundaries during the decay treatment at 400°C.

The stability of helium cluster is substantially increased when it contains vacancies. It has been suggested that helium forms clusters containing vacancies even when no displacement damage occurs\(^{15}\); agglomeration of helium atoms may result in ejection of self interstitial atoms by generating vacancies, and these vacancies are built into the helium cluster for further stabilization of the cluster. The self interstitial atoms generated in this process will form dislocation loops. The loops shown in Fig. 4 are probably formed by this mechanism so that it is very likely that helium clusters are stabilized by vacancies. Similar observation of loop formation has also been reported by Jäger et al.\(^{16}\) in tritium-charged vanadium. Helium must first be detrapped from helium clusters before migrating to grain boundaries. The dissociation of a helium atom from a vacancy occurs about 1200 K in molybdenum\(^{17}\) and 1500 K in tungsten\(^{18}\). If the helium-vacancy dissociation in vanadium occurs at the same homologous temperature as in molybdenum and tungsten, dissociation in vanadium will occur above 900 K. As the cluster size increases, it is further stabilized by so-called "trap mutation". The evaporation of helium then takes place at temperatures several hundreds K above the dissociation temperature of single helium from a vacancy. Helium migration to grain boundaries in this case is then not expected to occur below 700°C. Thus, the grain boundary bubbles observed in the present study are concluded to be formed with helium atoms migrating as small interstitial type clusters to grain boundaries. The migration probably occurred during the decay treatment at 400°C.

It must be pointed out here, that the state of helium is probably very much different from that anticipated fusion neutron irradiation condition. In tritium trick technique, He/dpa is virtually infinity, while in fusion condition, He/dpa is about 5 to 7; generated helium can easily be trapped by vacancies and will lose its high mobility. Therefore, helium embrittlement is unlikely for room temperature tests, since segregation of helium to grain boundary is very difficult at room temperature. Thus, it should be kept in mind that the ductility reduction at room temperature observed in this study is probably absent after irradiation in fusion reactor environments.

**Mechanical properties**

The increase in yield strength by helium charging observed in the present study may have a few possible origins. The dislocation loops as shown in Fig. 4 certainly contribute to the hardening. The increase in yield stress has been calculated based on the observed dislocation loop density as shown in Fig. 5, and is plotted as a function of atomic size factor in Fig. 9. Here, the increase in tensile yield stress \(\Delta\sigma\) is taken as twice the shear stress increase, i.e. \(2\Delta\tau\). The latter is given as \(2\Delta\tau = 2\alpha u b \sqrt{\rho}\), where \(\alpha\), \(\mu\), \(b\), and \(\rho\) are the obstacle strength parameter, the shear modulus, the Burgers vector and the dislocation density, respectively. The \(\alpha\) value is set equal to a rather high value of 0.5 in order to obtain an upper limit estimate. In Fig. 9 are also plotted the ob-
observed increase in yield stress and it is clear from this figure that the calculated stress is only a small fraction of the observed increase in yield stress. It follows that there are sources for the yield stress increase other than the observed dislocation loops.

Bubbles observed in the matrix as shown in Fig. 7 also contribute to the yield stress increase. The density, however, is too low to account for significant increase in the yield stress. The presence of dislocation loops as shown in Fig. 4 indicates the presence of helium clusters in the matrix. In the absence of other possible source of hardening, these helium clusters are considered to be the major source of the observed hardening. The correlation of atomic size factor with the hardening implies that the same correlation holds with the concentration of helium clusters. In other words, solutes with small atomic size has strong binding with helium resulting in high cluster density. For over-sized solutes, the binding is not large except for extremely over-sized solute of niobium.

The correlation of ductility loss by helium with atomic size factor is remarkably similar to the correlation of yield stress increase as shown in Fig. 3. The ductility loss reflects the grain boundary coverage by helium bubbles. For solutes with strong binding with helium atoms, the fraction of helium in the matrix increases and the helium population at grain boundaries decreases. Thus, it is quite straightforward to understand the two correlations, i.e. hardening and ductility loss by helium charging with the atomic size factor of solute atoms. Undersized solutes, i.e. iron, silicon and chromium and extremely oversized solute niobium have strong binding with helium, and enhance cluster formation in the bulk. The fraction of helium reaching grain boundaries is small for alloys with these solutes. The cluster in the bulk contributes to the hardening and helium reached grain boundaries causes reduction in ductility.

In the figures showing correlation with atomic size factor, the values for V-1%Si has been multiplied by a factor of five in order to take into account that only this alloy has solute concentration of 1 at% rather than 5 at% in other alloys. This procedure may be justified if helium cluster formation depends linearly on the solute concentration. The number of helium atoms reaching grain boundaries would also be reduced by a factor of five, and the ductility reduction would be mitigated accordingly. The amount of ductility reduction caused by helium at grain boundary, however, is difficult to estimate quantitatively.

V. Conclusions

(1) Helium embrittlement was observed by tensile tests at room temperature after helium charging by tritium trick technique.

(2) The distribution and the state of helium obtained by tritium trick technique is probably very much different from that anticipated for fusion neutron irradiation. The effects of helium on the mechanical properties studied using this technique should be examined with caution.

(3) Strong correlation was observed between apparent solid solution hardening, ductility reduction and atomic size factor of solutes. It is concluded that undersized solutes strongly trap helium atoms.

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REFERENCES


