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J. Wanagel, S. L. Sass and B. W. Batterman

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Department of Materials Science and Engineering

Cornell University

Ithaca, New York 14850

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LOW TEMPERATURE PHASE TRANSFORMATION IN THE
VANADIUM-HYDROGEN SYSTEM[†]

J. Wanagel, S. L. Sass and B. W. Batterman
Department of Materials Science and Engineering
Cornell University
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ABSTRACT

Electron microscope specimens containing β -vanadium hydride showed evidence for the occurrence of a low temperature phase transformation. Upon cooling to a specific temperature in the range from 170-200°K additional $\frac{1}{3}$ order reflections appeared which were shown to come from different regions than the β hydride domains. The $\frac{1}{3}$ order reflections are consistent with $(10\bar{1})_{\text{b.c.t.}}$ planes of hydrogen atoms spaced $3d_{10\bar{1}}$ apart.

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INTRODUCTION

A partial phase diagram for the V-H system was determined by Maeland⁽¹⁾ and extended to VH_2 by Reilly and Wiswall⁽²⁾. The α -phase is an interstitial solid solution of hydrogen in b.c.c. V; the β -hydride phase is an ordered monoclinic structure, with the V atoms in a b.c.t. arrangement and the γ -hydride phase is an ordered f.c.c. structure.

Wanagel, Sass and Batterman⁽³⁾ observed half order reflections from the β -hydride which were shown to be due to the ordering of hydrogen atoms and used electron diffraction to determine the reciprocal lattice of a single domain. The ordered structure with composition V_2H was shown to be monoclinic and the hydrogen atoms were arranged in alternate $(10\bar{1})_{\text{b.c.t.}}$ planes.

Several studies have suggested the presence of low temperature transformations in the β -vanadium hydride or deuteride phase field. Roberts⁽⁴⁾, using neutrons, reported an order-disorder transformation in V_4D_3 at $207 \pm 10^\circ\text{K}$. A resistivity study by Westlake⁽⁵⁾ indicated that β -vanadium hydride undergoes a transformation below 224°K . X-ray and neutron studies by Westlake and Mueller⁽⁶⁾ on β -hydrides and deuterides provided further evidence for such transformations.

In this paper electron microscope observations are reported on a new low temperature phase transformation occurring in the β -vanadium hydride phase field.

EXPERIMENTAL PROCEDURE

250 μm thick sections were cut from V single crystals containing a few atomic percent hydrogen, and then ground down to 75 μm with wet 600 grit silicon carbide powder on glass. These

specimens were chemically polished in a cooled solution ($<10^{\circ}\text{C}$) of 2 parts HF and one part HNO_3 which is known to considerably increase the hydrogen content of V^(7,8). All observations were made at 100 kV on an AEI EM6G electron microscope equipped with a two axis 25° tilt cold stage capable of reaching 110°K.

EXPERIMENTAL RESULTS

At room temperature the electron diffraction patterns show half order reflections characteristic of the monoclinic $\beta\text{-V}_2\text{H}$ reported previously (Fig. 1a). The pattern in Fig. 1a is the $[131]^*$ b.c.t. reciprocal lattice section which contains half order reflections from two β domains. Upon cooling additional reflections appear at a specific temperature in the range from 170-200°K depending upon the specimen. Fig. 1b, taken at 165°K, shows the presence, along the $10\bar{1}$ reciprocal lattice direction, of half order reflections characteristic of $\beta\text{-V}_2\text{H}$ as well as $\frac{1}{3}$ and $\frac{2}{3}$ order reflections from a new phase which will be called δ . Further cooling to 110°K strengthens the $\frac{1}{3}$ and $\frac{2}{3}$ order reflections and weakens the $\frac{1}{2}$ order reflections. Often, as in Fig. 1b, the $\frac{1}{3}$ and $\frac{2}{3}$ order reflections are elongated along the $10\bar{1}$ reciprocal lattice direction indicating that the δ phase is forming in thin platelets parallel to $(10\bar{1})$ planes, in agreement with the dark field image in Fig. 1c made using a $\frac{2}{3}0\frac{2}{3}$ spot. Dark field microscopy shows that the half order reflections come from different regions than the $\frac{1}{3}$ order reflections and that all the $\frac{1}{3}$ order reflections come from the same region. To a first approximation

* The symbol $[131]$ represents the reciprocal plane perpendicular to the $[131]$ direction. For convenience the reciprocal lattice planes and directions are indexed in terms of the b.c.t. arrangement of V atoms.

the positions of the full order reflections are unchanged during the formation of the δ phase indicating that the positions of the V atoms are substantially unchanged by the transformation.

Attempts were made to map out the reciprocal lattice of a single δ domain as done for $\beta\text{-V}_2\text{H}^{(3)}$, but this could not be accomplished because of the limited range of tilt available with the cold stage. Thus it was not possible to determine the crystal system of the δ structure. Fig. 2a,b,c shows several reciprocal lattice sections obtained by tilting about the $10\bar{1}$ axis and for this case the δ reflections are not elongated. Note that in Fig. 2a all the $\frac{1}{3}$ order reflections lying along $10\bar{1}$ directions belong to a single domain while the remaining $\frac{1}{3}$ order spots come from a different domain.

DISCUSSION

From the sequence of diffraction patterns shown in Fig. 1a,b it is apparent that there are additional two phase and one phase regions present within the β phase field. While there is insufficient information available at present for even determining the crystal system of the δ hydride preliminary comments can be made about the δ structure. Since the V atom positions are unchanged by the transformation, the $\frac{1}{3}$ order reflections would appear to result from H atom rearrangement to form a super-structure. Since the $\frac{1}{2}$ order reflections observed from the β hydride could be related⁽³⁾ to $(10\bar{1})$ planes of hydrogen atoms spaced $2d_{10\bar{1}}$ apart it is reasonable to suggest that the $\frac{1}{3}$ order reflections are related to $(10\bar{1})$ planes of hydrogen atoms spaced $3d_{10\bar{1}}$ apart.

Roberts was able to index the reflections from V_4D_3 at 77°K

observed using neutrons on the basis of a primitive cubic unit cell with a_0 equal to $6.30\text{\AA}$, or twice the b.c.c. lattice parameter determined by x-rays. Since $3d_{10\bar{1}} \approx 2.1 a_0$, it might have been possible that Roberts' pattern was also from the δ structure.

As usual, in the case of observations of phase transformations in thin foils, it remains to be demonstrated that the same transformation occurs in the bulk.

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FIGURE CAPTIONS

- Fig. 1: (a) $[131]$ reciprocal lattice plane from β -vanadium hydride at 298°K . $\frac{1}{2}$ order reflections are present along the $10\bar{1}$ and $\bar{2}1\bar{1}$ directions; each set lying along a particular direction comes from a different domain.
- (b) The same region as in (a) at 165°K , showing $\frac{1}{2}$ and additional $\frac{1}{3}$ order reflections along the $10\bar{1}$ direction.
- (c) Dark field micrograph made using the $\frac{2}{3}0\frac{2}{3}$ reflection indicated in (b). Striations are present running perpendicularly to the $10\bar{1}$ direction. The micrograph is oriented relative to the diffraction pattern in (b).

Fig. 2: Reciprocal lattice sections containing $\frac{1}{3}$ order reflections obtained by tilting about the $10\bar{1}$ direction.

Temperature of observation is 160°K .

- (a) $[0\bar{1}0]$ plane. Dark field microscopy shows that all the $\frac{1}{3}$ order reflections lying along the $10\bar{1}$ direction come from one domain, while the $\frac{1}{3}$ order reflections lying along the $\bar{1}0\bar{1}$ direction come from another domain.
- (b) $[\bar{1}\bar{5}\bar{1}]$ plane. The $\frac{1}{3}$ order reflections lying along the $10\bar{1}$ direction come from one domain while the $\frac{1}{3}$ order reflections lying along the $\bar{2}1\bar{3}$ direction come from another domain.
- (c) $[\bar{1}\bar{3}\bar{1}]$ plane.

(a)

(b)

(c)

Figure 1

(a)

(b)

(c)

Figure 2