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Effect of hydrogen accumulation on mechanical property and microstructure of V–Cr–Ti alloys

K. Aoyagi, E.P. Torres *, T. Suda, S. Ohnuki

Graduate School of Engineering, Hokkaido University, Kita-ku, Kita-13, Nishi-8, Sapporo 060-8628, Japan

Abstract

Pure vanadium, V–5Cr, V–5Ti and V–5Cr–5Ti alloys doped with different amounts of hydrogen were tested under tension and observed under TEM in order to clarify the interaction between hydrogen and vanadium. Hydrogenated samples tested under tension showed a typical hydrogen-embrittlement behavior. TEM observation suggests that the embrittlement is caused by hydrogen diffusion at the triple point of grain boundaries, hydride formation and the subsequent generation of dislocations and micro-cracks.

1. Introduction

Vanadium-based ternary alloys, V–Cr–Ti, have been considered as candidate materials for core components in fusion energy systems [1]. Hydrogen accumulation, as well as gaseous transmutation during neutron irradiation, might be an important factor in deciding the lifetime and safety of the structural materials because the alloys can easily absorb hydrogen from the environment of plasma and liquid coolants. Vanadium alloys have extremely high interaction with hydrogen and are now being considered as candidates for commercial hydrogen storage materials for other uses. This behavior suggests the possibility that hydrogen or its isotope can easily accumulate and influence the mechanical properties and related microstructural changes [1–8]. Therefore, it is important to understand the basics of the hydrogen accumulation process and the mechanisms involved in embrittlement [9–12]. The objective of this study is to clarify hydrogen behavior in vanadium-based alloys, especially from the point of view of mechanical properties and microstructure, which can lead to the development of advanced vanadium alloys.

* Tel.: +81-11 706 6771; fax: +81-11 706 6772.

E-mail address: p-torres@loam-ms.eng.hokudai.ac.jp (E.P. Torres).

2. Experimental procedure

V, V–5Cr, V–5Ti and V–5Cr–5Ti alloys were prepared from 99.9% pure dendritic vanadium by arc melting in an argon atmosphere. The ingots were cold rolled to 0.2 mm and punched into tensile specimens with a gauge size of 1×6 mm^2 and TEM disks 3 mm in diameter. The samples were evacuated in a quartz tube and annealed in vacuum at 1000°C for 1 h. Hydrogen was doped into the samples in a high-pressure oven at 250°C, 350°C and 450°C. Hydrogen levels, which can be controlled by temperature and gas pressure, were estimated in the range 4–12%. A tensile test was performed at room temperature with a strain rate of 4.1×10^{-4} s^{-1}. The disks were electro-polished and observed in a 200 kV TEM.

3. Results and discussion

3.1. Hydrogen content

Fig. 1 shows the hydrogen level in V, V–5Cr, V–5Ti, and V–5Cr–5Ti at different doping temperatures as determined by the difference in gas pressure measured before and after hydrogenation. The hydrogen level increased with doping temperature; the highest values were observed in pure vanadium hydrogenated at 723 K. In general, the actual doping process is controlled by diffusion and surface reaction, which means that

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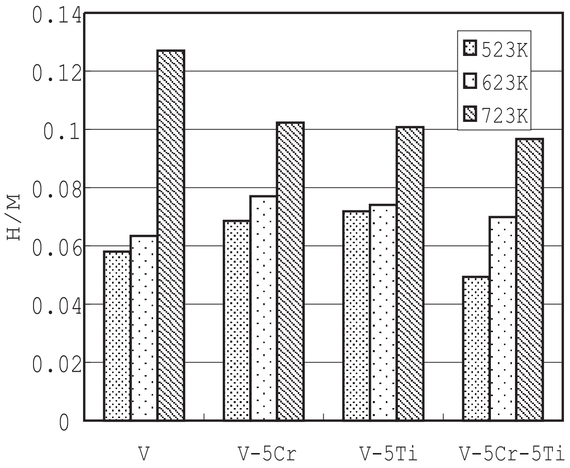

Fig. 1. Doped hydrogen level for pure vanadium and its alloys at different temperatures.

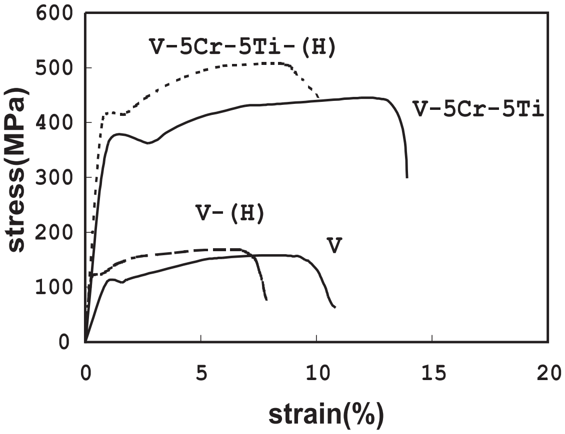

Fig. 2. Stress–strain curves for pure vanadium and V–5Cr–5Ti before and after hydrogen-doping.

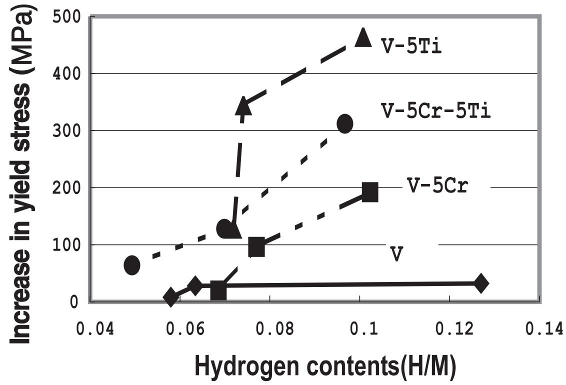

Fig. 3. Change in yield strength for vanadium and its alloys after hydrogen-doping.

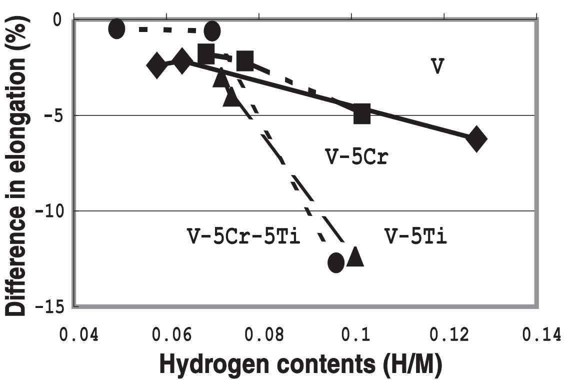

Fig. 4. Reduction in total elongation due to hydrogen-doping.

hydrogen intake and migration into the alloys are enhanced by activation and decomposition of the oxide layer at high temperature [2,3].

Hydrogen absorption was more or less the same in all alloys; in such cases the presence of alloying elements can reduce the mobility of hydrogen atoms. The doping process was more sensitive to temperature in V–5Cr–5Ti than in the other alloys. It is believed that titanium solute can decrease the diffusion coefficient of hydrogen [1], but such an influence was not so apparent in this case.

3.2. Effect of hydrogen on mechanical properties

Fig. 2 shows two sets of stress–strain curves for V and V–5Cr–5Ti before and after hdrogenation at 623 K, tested at room temperature. There is an obvious increase in the elastic constant and a decrease in ε_T due to hydrogen doping. The hydrogenation caused higher $\sigma_{0.2}$ and σ_{UTS} for both V and V–5Cr–5Ti; this behavior is typical of hydrogen embrittlement.

Fig. 3 shows the relation between hydrogen content and increment of yield stress, which was defined from the difference in stress before and after doping. In V, there is some saturation in the hydrogen effect on the yield stress at relatively low concentrations. V–5Cr and V–5Cr–5Ti showed a linear increase, which suggests no saturation with inrease in concentration, but V–5Ti showed the most sensitive behavior and an obvious increase from the concentration of 0.07.

Hydrogen charging had obvious effects: the loss of total elongation and a gain in strength, Fig. 4. The reduction of the elongation in both V and V–5Cr showed almost the same tendency with small values. In the case of V–5Ti and V–5Cr–5Ti, there was a step decrease in elongation from the concentration of 0.07 confirming that embrittlement is drastically enhanced by hydrogen content.

3.3. Effect of hydrogen on microstructure

To clarify the mechanisms of hydride formation, hydrogenated samples were observed under the TEM. Figs. 5 and 6 show micrographs of V and V–5Cr–5Ti doped with different hydrogen contents. Hydride formed preferentially at the triple point of the grain boundaries, and it was identified as a VH structure, Fig. 5. At the same time, some small cracks and dislocations were initiated from the triple boundaries, as indicated in Fig. 6. Small amounts of hydrogen cause no clear changes, which means it is in solution. Because all hydrides, cracks, and dislocations formed suddenly when the solubility limit was just exceeded, it is implied that triple grain boundaries are the most convenient zones for hydride formation and crack initiation. With increasing hydrogen level, hydride developed in the matrix and generated dislocations with high density.

3.4. Hydride formation process

The development of hydrogen-induced cracks depends on a critical hydrogen content below which no embrittlement occurs.

The most propitious sites for hydrogen accumulation are the grain boundaries, particularly the triple points, where hydride formation is promoted. The difference in ductility between the hydride and the matrix makes dislocations converge to non-slip planes and generate a shear stress field, which opposes the stress field of slipped dislocations, promoting the formation of microcracks.

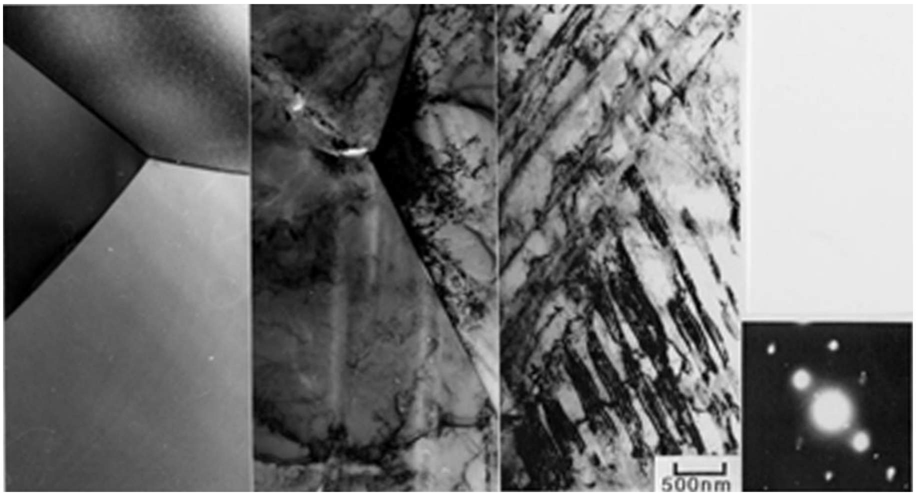

Fig. 5. Hydride formation in vanadium at different hydrogen levels.

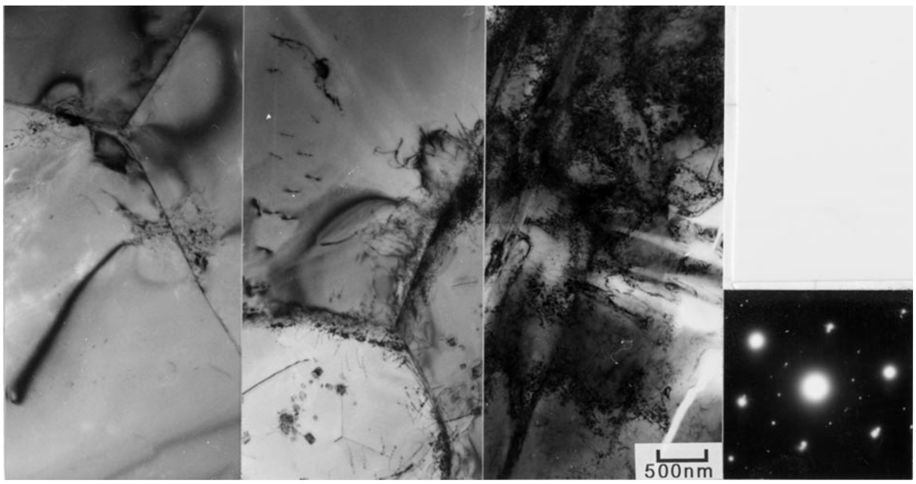

Fig. 6. Hydride formation in V–5Cr–5Ti at different hydrogen levels.

4. Conclusions

Tensile tests and TEM observations were performed on V, V–5Cr, V–5Ti and V–5Cr–5Ti in order to determine the change in mechanical properties and microstructures produced by hydrogen doping. Vanadium alloys are susceptible to hydrogen absorption and have extensive ability to form hydrides even at low hydrogen content. Hydrogen-doped alloys showed high strength and low elongation. This is a typical behavior in the hydrogen-embrittlement process, which can be explained as the formation of hydride at the triple point of grain boundaries and a subsequent generation of dislocation and cracks. An increment in hydrogen content makes hydride and dislocation extend to the matrix, increasing dislocation density and the probability of crack formation.

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