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Effect of alloying elements and neutron-irradiation on hydrogen behavior in V alloys

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Abstract

To understand hydrogen behavior in V and V based alloys, static and dynamic hydrogen chargings were carried out for unirradiated and irradiated V and V–4Cr–4Ti. Hydrogen can be trapped by lattice defects, dislocations, vacancies and voids, which are effective up to 500 °C. Unexpected softening occurred at low levels of hydrogen, and hardening occurred at high levels. Alloying elements intensified the hardening, which are seen as general phenomena in V and V based alloys. A significant effect was seen for dynamic charging, which was attributed to fast diffusion and interactions with mobile dislocations.

1. Introduction

Vanadium based ternary alloys, V–Cr–Ti, have been considered as a candidate material for core components in fusion energy systems. Because the alloys can easily absorb hydrogen from the environment of plasma and liquid coolants, hydrogen accumulation, as well as gaseous transmutation during neutron-irradiation [1–4], is an important factor for determining the lifetime and safety of structural materials based on these alloys. Vanadium alloys have extremely high solubility for hydrogen, and are now being considered as candidates for commercial hydrogen storage materials for other uses [1,2]. This behavior suggests that hydrogen isotopes can easily accumulate in vanadium alloys and thus influence the mechanical properties and related microstructural changes [3,4]. Therefore, it is important to understand basics of the hydrogen accumulation process and the mechanisms involved in microstructural changes. The objective of this study is to clarify the behavior of hydrogen in vanadium based alloys, particularly from the point of view of mechanical properties and microstructure, which can aid in the development of advanced vanadium alloys.

2. Experimental procedures

The specimens of vanadium and V–4Vr–4Ti alloys were provided by the National Institute for Fusion Science (NIFS) [5]. Chemical compositions are given in Ref. [5]. The specimens were cold-rolled to a thickness of 0.25 mm with 97.5% reduction and annealed at 900 °C for 1 h. The grain size was approximately 50 μm. Neutron-irradiation was carried out in JMTR to a damage dose of about 0.01 dpa (1×10^{19} n/cm^2) at 290 °C.

Hydrogen charging in the specimens was conducted using two techniques [6,7]; (1) static hydrogen charging prior to tensile testing, and (2) dynamic charging during tensile testing. Static hydrogen charging was performed by electolysis in a solution of 1.0 N H_2SO_4 at a current density of ~6.7 mA/cm^2. Dynamic charging was performed during tensile tasting, and was initiated as soon as yielding occurred. Two methods were used for the dynamic charging. In the intermittent method, the charging was conducted for 5 s at each 5% increase in

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the strain. In the continuous method, the charging was continued until eventual failure. In order to change the dissolved hydrogen level during the dynamic charging, the concentration of H_2SO_4 solution was varied between 0.5 and 1.0 N and the current density was varied between 7 and 33 mA/cm^2. The details of the charging are reported in Ref. [6].

Tensile properties of the specimens were measured using an Instron type machine with a strain rate of 6.7×10^{-5} s^{-1} at room temperature. In order to investigate microstructures as a function of hydrogen charging time, hydride formation and dislocation evolution were examined using a 200 kV TEM (JEM-2010). The samples used for TEM observation were obtained from the specimens after tensile testing.

3. Results and discussion

3.1. Hydrogen-induced hardening in irradiated vanadium alloy

Fig. 1 shows the yield stress as a function of charging time in V–4Cr alloy that was neutron-irradiated to 0.01 dpa at 290 °C in JMTR, and in unirradiated V–4Cr. The unirradiated material showed slight decreasing in yield stress at low charging levels followed by slight increasing at high levels. The overall increase of ~30 MPa is attributed to solution hardening. In the irradiated sample, the neutron-irradiation resulted in a significant increase in the yields stress of 250 MPa, from radiation hardening alone. Hydrogen charging resulted in an additional increase of up to 150 MPa, which was essentially proportional to the charging time.

It has been shown that hydrogen can be trapped by dislocations, vacancies and voids, and is stable up to about 500 °C [6]. It can be assume that this phenomenon

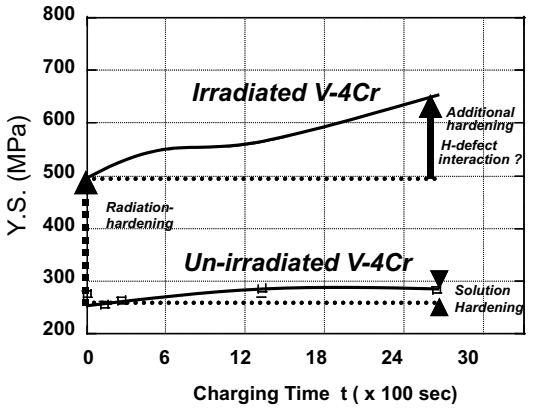

Fig. 1. Yield stress as a function of static charging time in V–4Cr alloy neutron-irradiated to 1×10^{19} n/cm^2 at 290 °C in JMTR.

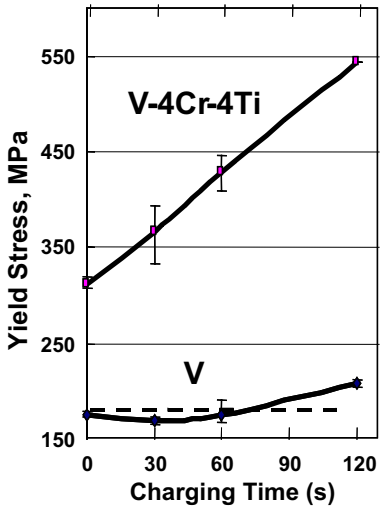

Fig. 2. Yield stress as a function of static charging period in V and V–4Cr–4Ti alloy. Obvious hardening was observed in the alloy, which is the due to the alloying elements.

is based on the interaction between defect-clusters and the hydrogen. When defect-clusters such as dislocation loops trap hydrogen, they can act as an effective barrier for movement of the dislocation during deformation.

3.2. Effect of alloying on mechanical property and hydrogen sensitivity

Fig. 2 shows the relation between yield stress and static charging time for V and V–4Cr–4Ti. Vanadium initially showed a slight softening followed by a slight hardening with increasing hydrogen content (charging time). Details of these results are given in [7]. On the other hand, obvious hardening was seen in V–4Cr–4Ti alloy at similar charging times, which suggests a significant effect from the alloying elements on the hydrogen behavior.

3.3. Dynamic charging effect on mechanical properties

Fig. 3 shows the stress–strain curves during interval dynamic charging for V–4Cr–4Ti with different charging current levels (different H levels). The alloy showed softening and hardening relative to the current, that is similar to that observed in V [8]. Therefore, hydrogen-induced softening and hardening can be seen as general phenomena in V and V based alloys. Fig. 4 shows an expanded section of the stress–strain curve for different charging conditions, during 5 s charging interval. As is evident, there was a response in the stress curve at both the beginning and the end of the charging. At low H levels, the stress dropped quickly and significantly at the start of the cycle, followed by a somewhat slower

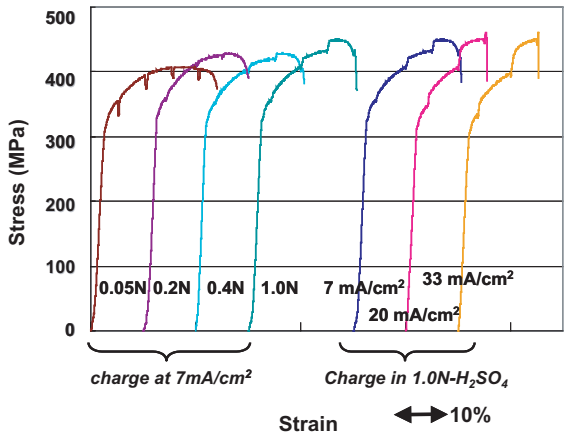

Fig. 3. Stress–strain curves for V–4Cr–4Ti during interval dynamic charging with different current conditions. The alloy showed softening and hardening behavior relative to the current that is similar to that seen in V.

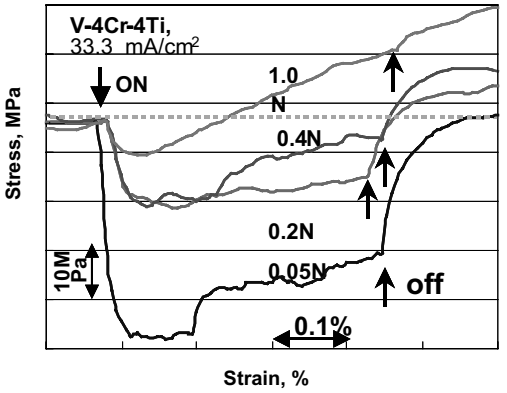

Fig. 4. Dynamic charging during tensile testing of V–4Cr–4Ti. The stress responded rapidly to the on and off of the current (interval charging). At low H levels, fast response and significant stress decrease (softening) are seen, which then recovers to its original level. At high H levels, a smaller loss of stress is seen, followed by an overall increase in the hardening.

asymptotic return to the original level at the end of the cycle. At high H levels, however, the decrease in stress was smaller and somewhat slower at the start of the cycle, followed by an overall increase in the stress at the end of the cycle which was higher than in V. These results indicate that this transient phenomenon is composed of competitive of softening and hardening due to charging.

Fig. 5 shows the stress drop in V and V–4Cr–4Ti as a function of dynamic charging time at different strain levels, where the charging was carried out at 6.7 mA/cm^2 in 0.05 N H_2SO_4. Where, the stress drop values were plotted at the same strain level with every 5%. With

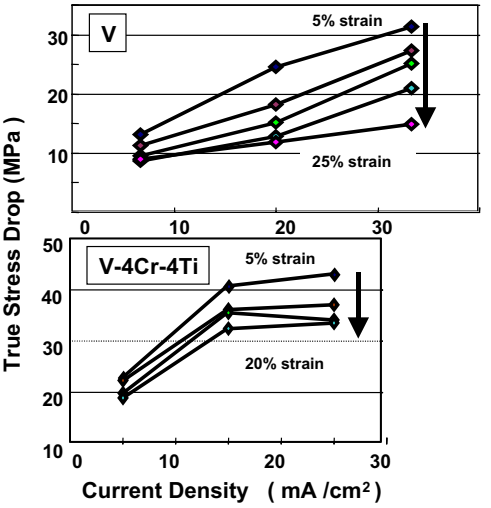

Fig. 5. Stress drop as a function of dynamic charging time at different strain levels. In V–4Cr–4Ti the amount of stress drop (softening) saturated at high H content, which means that alloying elements can suppress the effect of the interaction between H and dislocations.

increasing strain level, the amount of stress drop decreased as shown by the arrows. The drop level was larger in V–4Cr–4Ti than in V, which means the stress softening was much larger. It is also noted that the softening saturated at high H level in the V–4Cr–4Ti. These results suggest that increasing both the H level and the dislocation density may be the cause of the larger stress drop and the saturation.

3.4. Mechanism for hydrogen-induced softening and hardening

Fig. 6 shows a typical stress–strain curve for dynamic charging after reaching the yield point. The charging was performed carefully at 6.7 mA/cm^2 in a solution of 1 N H_2SO_4. Two hardening steps were observed after starting the charging; (A) is the microstructure corresponded to the last phase of the first stage, where only tangled dislocations are observed, and (B) is the microstructure from the last phase of the second stage, where plate-like hydrides and dislocation with high density were developed. The arrows indicate hydride platelets and extra spots in the electron diffraction. In this condition, the hydride formation was delayed as compared with static charging.

Fig. 7 shows the relation between analyzed hydrogen contents and static and dynamic charging times. In the static charging, the content increased with the square root of the static charging time, which suggests this process is being controlled by diffusion. From TEM observations, hydride formation was confirmed above 0.2 wt%; therefore, the solubility limit is about 0.2 wt%

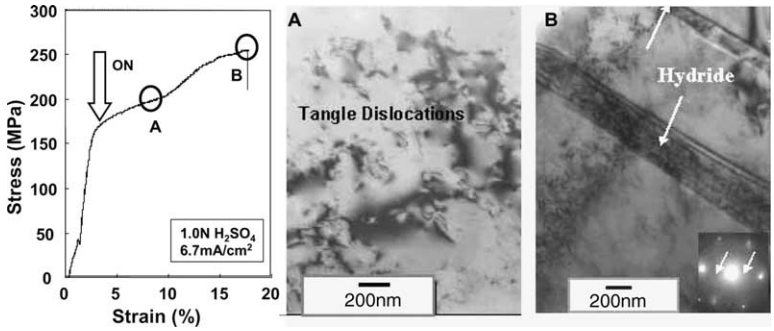

Fig. 6. Two stages of hardening developed during continuous dynamic charging, which correspond to different microstructures; (A) only tangled dislocations, and (B) hydride plates and dislocations at high density, where hydride formation was delayed as compared to static charging.

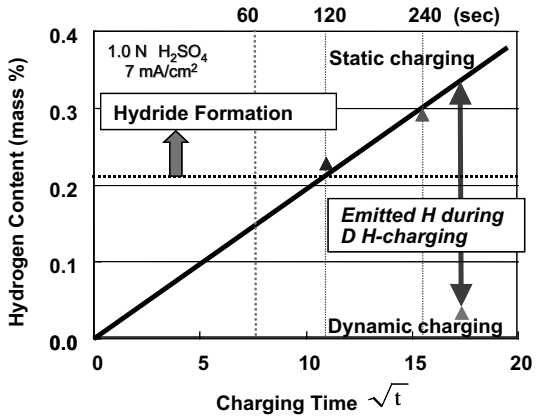

Fig. 7. Hydrogen content as the function of static and dynamic charging time. The content increases with static charging time, but is significantly lower for dynamic charging.

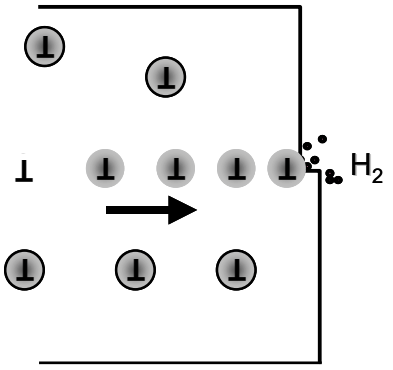

Fig. 8. A schematic diagram of the dynamic interaction between H and dislocations for the softening, hardening and gas emission; (a) dislocation mobility is enhanced by the hydrogen atmosphere, (b) the dislocation gliding with H trapping produces gas emission, and (c) strong trapping and local hydride formation produce hardening.

at room temperature. In the case of dynamic charging, the analyzed hydrogen content was quite low as comparing to static charging. The difference of 0.3 wt% may be caused by the effects of deformation dislocations. This suggests that interactions between the hydrogen and the dislocations resulted in significant hydrogen emission during the dynamic charging.

Fig. 8 shows a schematic diagram of the dynamic interaction between the hydrogen and the dislocations that could explain the softening, hardening, and gas emission. At low hydrogen concentration, (a) the dislocation mobility is enhanced due to the atmosphere; (b) the dislocation gliding with hydrogen induces gas emission from the surface, and (c) at high concentration strong trapping and local hydride formation result in hardening. The actual mechanisms for hydrogen-induced softening and hardening are not completely understood, but it is possible that Piels potential is changed by the trapped hydrogen which may diffuse quickly even at room temperature.

4. Conclusions

To clarify the hydrogen behavior in vanadium and vanadium alloys, static and dynamic chargings were carried out for both unirradiated and irradiated V and V–4Cr–4Ti. The results show that hydrogen can be trapped by lattice defects; dislocations, vacancies and voids, up to 500 °C. With respect to hydrogen-induced softening and hardening, unexpected softening occurred at low hydrogen levels, and hardening developed at high levels. The hydrogen-induced softening and hardening are seen to be general phenomena in V alloys. The addition of Cr and Ti reduced the hydrogen effect on the mechanical properties, such as anomalous softening. A significant effect was seen for dynamic charging, which was attributed to fast diffusion and interactions with mobile dislocations. The results suggest that hydrogen-induced phenomena can be attributed to high hydrogen diffusivity under deformation and the enhanced move-

ment of dislocations, as well as dislocation capture from formed hydrides at high hydrogen concentrations.

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