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Journal of Nuclear Materials 307–311 (2002) 625–629

journal of nuclear materials

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Hydride formation and fracture of vanadium alloys

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Abstract

The effects of hydrogen in vanadium, V–5Cr and V–5Ti have been evaluated by the change in surface and in microstructure and by the aspect of fractured surfaces. Hydrogen accumulation promotes local concentration of hydrides and assists the generation of stacking faults. Under increased stress, crack propagation occurs by the successive formation of crack fronts.

1. Introduction

The perspective of using vanadium alloys as a component of the blanket of fusion reactors has motivated significant research in the last decades. Detrimental effects of hydrogen remain as a main concern and have been widely documented [1–7]. Common sources of hydrogen include neutron induced transmutation of vanadium alloys, intake from primary fuel components, coolants and byproducts of corrosion reactions. In evaluating the effects of hydrogen particular attention has been given to the characteristics and formation of hydrides [8–14] and to its influence in the embrittlement process. Theoretical models, however, tend to imply assumptions and restrictions, which sometimes limit their reach and often lead to overemphasized abstractions. Back to the roots of research on embrittlement lies the direct observation of fractured surfaces, which is worthy to revisit and reconsider in the search of new ideas and clues and as a pivotal point in the application of theoretical models. The present study approaches the embrittlement process from a direct observation of damaged surfaces using SEM and TEM techniques, and considers the effects of sample preparation as an intrinsic part of the results.

2. Experimental procedure

Vanadium, V–5Cr and V–5Ti alloys were prepared from 99.9% pure vanadium by arc melting in an argon atmosphere. The ingots were cold-rolled and punched into tensile specimens for in situ straining experiment with a gauge size of 2×7 mm^2 and 0.1 mm in thickness. 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-pressured oven at 450 °C with hydrogen pressures of 0.5 and 0.8 MPa. Hydrogen levels, which can be controlled by temperature and gas pressure, were estimated according to charging conditions to be in the range of the metal/hydrogen ratio $H/M = 0.15–0.24$. Specimens for in situ straining experiment were electro-polished and tested in a 1300 kV HVTEM at room temperature. The fracture surface observation was carried out in a 200 kV SEM.

3. Results and discussion

3.1. Surface changes

The first visible evidence of the effect of hydrogen in the samples comes from early examination during sample preparation. In the electro-polishing process, an acid solution is projected from both sides of the sample making progressively thinner the material in the center until a hole is formed. Fig. 1 compares the final shape of

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PII: S0022-3115(02)01217-5

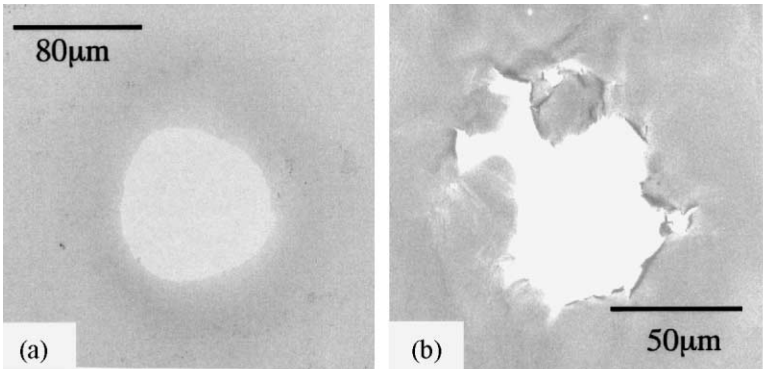

Fig. 1. Electro-polished hole in (a) non-hydrogenated V–5Ti and (b) hydrogenated V–5Ti with a H/M ratio of 0.24.

the electro-polished hole of non-hydrogenated V–5Ti with the same alloy charged with a metal/hydrogen ratio of 0.24. In the first case the hole has an almost perfect circular shape and is surrounded by a quite smooth surface as a consequence of the regular removal of material during chemical attack. Hydrogen additions, on the other hand, turned the samples extremely brittle and this condition is reflected in the irregular shape of the electro-polished hole caused by the premature breaking of thin surfaces. The hydrogen distribution is not uniform, there are zones of higher concentration in which hydride formation is promoted and once thinned enough are more prone to fail.

3.2. Change in microstructure

High concentrations of hydrogen produced a quite complicated arrangement of dislocations which usually are distributed by sectors in the sample in an unorganized way, but sometimes, rather organized patterns can be identified. Fig. 2 presents the microstructure of V–5Ti and V–5Cr hydrogenated with a H/M ratio of 0.21. Parallel bands extend across the sample as a consequence of stacking faults produced by the extension of zones rich in hydride from the grain boundaries towards the matrix. This behavior resembles the anomalous slip observed also in niobium, tantalum and molybdenum and documented as special case of plastic deformation of bcc metals [15]. There are three main theories to explain this effect on the basis of the mobility of dislocations. The first considers anomalous slip as an effect of the mobility ratio between screw and non-screw dislocations. A second theory establishes that anomalous slip occurs as a response to the mutual interaction of two sets of screw dislocations, and a third possible mechanism includes a cross slipping of the screws after mutual blocking of the leading dislocation as a cause.

In bcc metals there is a tendency for the slip to occur in an asymmetrical way, that is, the shear stress to move a dislocation lying in a slip plane in one direction is not the same as the shear stress required to move it in the opposite direction in the same plane. Hydride formation involves localized hardness in the matrix of the sample and dilatational changes in lattice parameters, which eventually produce alterations in stress distribution and can contribute to block the screw dislocation movement in a specific direction. Sets of extended stacking faults bounded by dislocations and lying in parallel slip planes can eventually coincide and promote the formation of the parallel fringe patterns shown in Fig. 2.

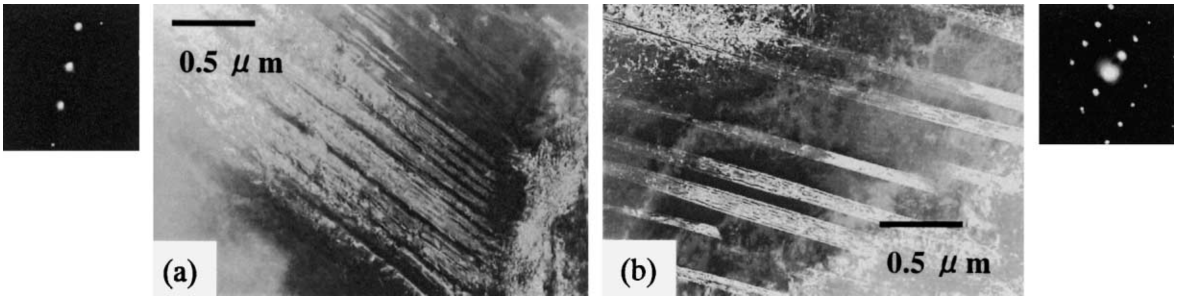

Fig. 2. Parallel fringes in (a) V–5Ti and (b) V–5Cr with a H/M ratio of 0.21.

3.3. Fractography

Non-hydrogenated samples failed by ductile fracture characterized by a thin edge formed along the whole fractured surface due to the almost unaltered flow of material. Fig. 3 presents two different aspects of such kind of failure in non-hydrogenated vanadium. The general aspect of the thin edge formed during tensile test is shown in Fig. 3(a). There is a significant reduction of thickness before failing as a consequence of the high elongation and this condition prevails along the whole length of the failed surface. The flow of material however presents subtle fluctuations in the form of hills and valleys and the edge itself reflects such variations in the failure line as can be seen in Fig. 3(b).

High hydrogen contents, on the other hand, turned the samples extremely brittle. The surface surrounded the electro-polished hole was so damaged that it was quite difficult to follow the evolution of the cracks in the in situ straining experiments, first, because of the multiple appearance of microcracks and potential crack generation points and second because once generated, the crack proceeded so quickly that it was almost impossible to monitor its evolution. This suggests that the crack propagated following the simultaneous formation of microcracks in the severely damaged material. Fig. 4 presents different aspects of the fractured surfaces of vanadium hydrogenated with a H/M ratio of 0.15 and 0.21. In Fig. 4(a) load direction is normal to the page plane, and crack proceeded from left to right. There is no indication of activated slip planes, and the fractured surface appears very rough. Evidence exists that the crack growth was blocked and as a consequence changes in its morphology emerged. The fractured surface can be considered as divided in two main parts as indicated by the section 1, 2. The left side of the fractograph can be again considered as divided in two parts, the upper part labeled A shows a clear resistance of the sample to be fractured as indicated by the presence of new formed edges orientated perpendicular to the direction of the crack. In the lower region, labeled B, the tendency of the new formed edges is to follow the direction of propagation of the crack although with a minor normal component. When the crack front reaches the section 1, 2, a pronounced change occurs, the main component of new formed edges in the upper part tend to follow the direction of crack propagation with a small component in the normal direction, and those in the lower part tend to change to a normal position. The changes in the evolution of the crack occurred rather suddenly from A to C, but a high increase in stress was necessary in changing from B to C as evidenced by the displacement of the section 1, 2 to the right side and by the severely deformed region separating B and C. The presence of hydride in the sample contributes to increase the stress required for crack propagation. When additional stress is supplied the crack can find new barriers requiring additional stress or find regions where less stress for fracture is required; in such case the crack will propagate extraordinarily fast.

A different response to the movement of the crack front is presented in Fig. 4(b) in which a cleavage kind of fracture is more evident. In this case crack proceeded from right to left. The condition presented in region A of Fig. 4(a) prevails across the whole surface until the barrier A, B is reached, in such case there is an additional requirement of stress to overcome it and once supplied, the strong interaction with the barrier produces a shift in the general plane of the direction of the crack front.

Fig. 4(c) shows the fractured surface of a severely damaged sample of vanadium hydrogenated with an H/M ratio of 0.21. Load direction is normal to the plane of the page and crack proceeds from right to left. There is a general tendency of the directional components of the crack to try to coincide with the central line of the crack

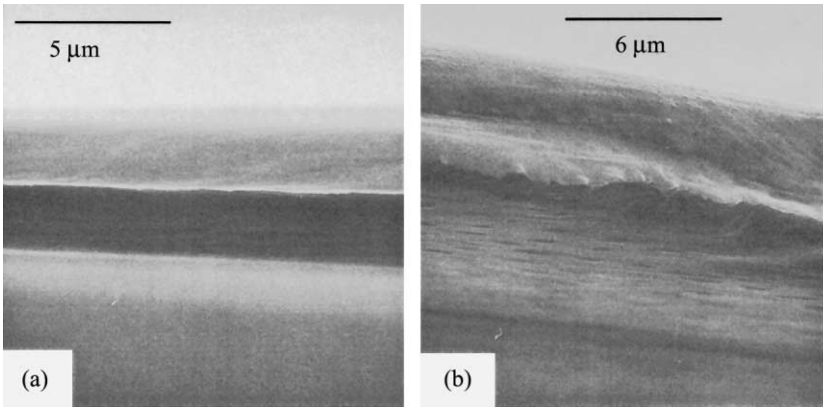

Fig. 3. Fracture surface of non-hydrogenated vanadium (a) failure edge and (b) irregularities in the failure line.

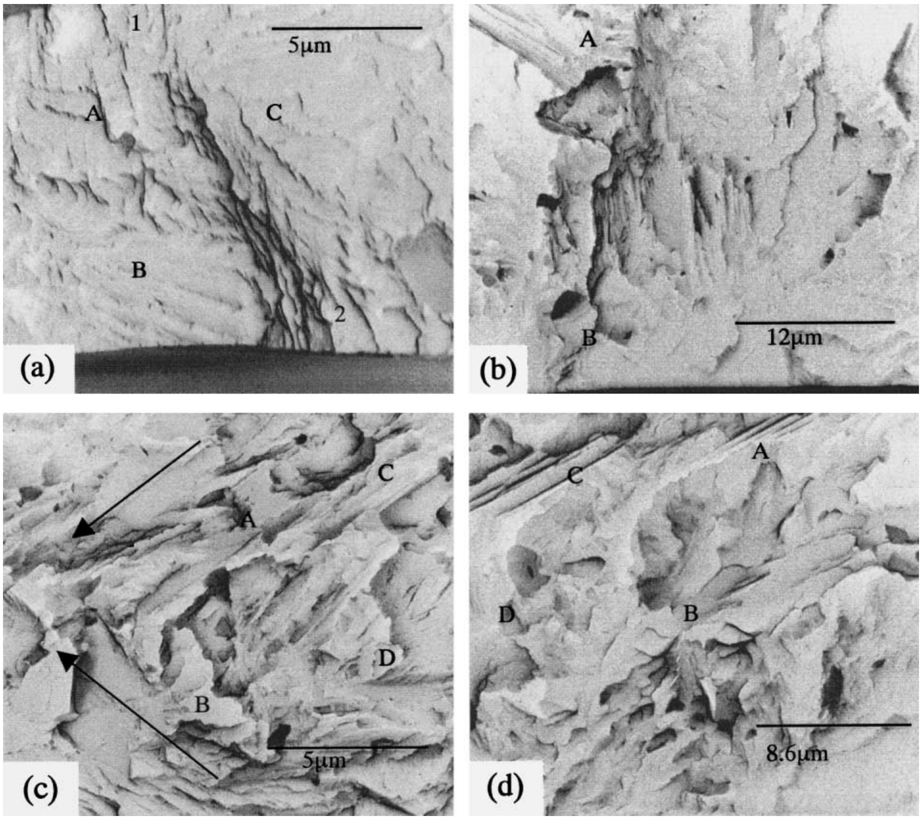

Fig. 4. Fractured surface of vanadium hydrogenated with a H/M ratio of (a,b) 0.15 and (c,d) 0.21.

front as indicated by the arrows. The term crack growth should be understood here in its relative meaning. In Fig. 4(c), crack evolves by the successive breaking of surfaces which exposes the craters limited by the edges A, B and C, D, indicating that failure occurred not by the coalescence of microcracks but as a result of the simultaneous breaking of susceptible surfaces. In both cases craters appear which suggest that very hard material was taken off from them and can be considered as additional evidence for the local concentration of hydrides.

The same coexistence of craters and cavities can be observed in Fig. 4(d). In this case cavities are concentrated mainly in the severely damaged surface below point B. Crater line C, D is interrupted by a small crater which holds a cavity indicating that small and disperse regions rich in hydride have an effect also as stress concentration points. Indeed the radial disposition of fractured material below B is evidence for the same effect for a local concentration of cavities.

In order to get a better understanding of the crack evolution from the interpretation of fractured surfaces the conventional two-dimensional description of a crack was extended to a three-dimensional one in which the concept of the crack tip is replaced by the crack front, this is, a line instead of a point. The notorious irregularities in the breaking surfaces of Fig. 4 suggest that the crack proceeded by successive stages involving the formation of new fronts which implies multidirectional variations in the stress field leading to the sudden breakout of brittle regions and not by the coalescence of microcracks ahead a main crack. In situ straining experiments showed that the predominant type of fracture in hydrogenated samples was transgranular. The change in orientation of slip steps and the breaking edges shown in Fig. 4 are caused by a local stress concentration which is altered by the dilatational effects of hydride formation and promotes velocity gradients of the crack as general stress increases.

4. Conclusions

The hydrogen distribution in the samples is not uniform. Regions rich in hydrogen are prone to form the hydride, which makes some regions more brittle than others altering stress distributions and promoting the failure of susceptible regions. In zones where hydrogen is accumulated, stacking faults bounded by dislocations are promoted. The main characteristic of fracture in hydrogenated samples is the formation of barriers that block the free movement of dislocations. The increased stress required to overtake such barriers is a potential generator of microcracks with quite different orientation which can affect locally the speed of propagation of the crack. As a consequence of fluctuations in stress gradients, it is inferred that the crack proceeds not by coalescence of microcracks ahead of the crack tip but by the successive formation of new crack fronts.

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