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Section 6.2. Vanadium alloys

Effect of hydrogen and oxygen on the tensile properties of V–4Cr–4Ti

H.D. Röhrig [a,*], J.R. DiStefano [b], L.D. Chitwood [b]

[a] *Projektleitung Kernfusion, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe, Germany*
[b] *Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge. TN 37831-6157, USA*

Abstract

Flat subsized tensile specimens of the vanadium alloy V–4Cr–4Ti were loaded with different amounts of pure hydrogen in order to study its effect on room temperature tensile properties. It was found that, apart from a slight influence of pretreatment, hydrogen can be tolerated up to about 2.5 at.%, whereas higher hydrogen contents lead to catastrophic failure. It is suggested that this behavior is attributed to coexistence of dissolved hydrogen and brittle hydride at room temperature. In addition, some measurements were made with specimens that had been loaded with about 850 wppm oxygen from a low oxygen partial pressure at 500°C (773 K), prior to hydrogen exposure. In this case room temperature ductility, starting from a decreased level, suffered severe deterioration by hydrogen concentrations of much less than 1 at.%. Apparently, in this case, embrittlement is concentrated at the near-surface grain boundaries, and stresses can no longer be absorbed if the matrix gets hardened by the addition of hydrogen. Thus, under the given conditions, oxygen and hydrogen show a strong synergistic effect on the tensile properties of this material.

1. Introduction

Vanadium alloys are prospective structural materials for future fusion reactors because of their favorable thermophysical and mechanical properties [1] and their potentially low long-term radioactivation. V–4Cr–4Ti is a candidate material for further investigation and qualification. A concern is its high affinity for reactive gases like hydrogen and oxygen.

Hydrogen, mostly in its isotopic form of protium, is not only existent to a certain degree in any technical material. But, due to the fusion neutron spectrum with energies up to 14 MeV, hydrogen is also produced by various nuclear reaction paths [2]. Any contact with a coolant medium containing hydrogen isotopes would also lead to hydrogen uptake. Deuterium and tritium are abundant in a fusion reactor, and there could be many ways for them to migrate into vanadium alloy structures where they would be readily absorbed. In the same way oxygen (or its chemical compounds) as an almost unavoidable impurity content in cooling media like, e.g. helium would be trapped in vanadium alloys.

The present work was, therefore, carried out to study what effect hydrogen would have on the tensile properties of the candidate material among the wide range of vanadium alloys under consideration, and how this behavior might change under the influence of additional oxygen. Only the room temperature mechanical properties were investigated.

2. Experimental techniques

For all tests described in this paper small flat tensile specimens with 7.62 mm gauge length and 0.76 mm thickness [3] were stamped or machined from V–4Cr–4Ti sheet material produced at ORNL. Prior to testing, the specimens were wrapped in zirconium and annealed for 1 h under high vacuum. Three sets of specimens of different grain size were produced depending on the annealing temperature of 1050°C, 1150°C or 1200°C (or 1323, 1423 and 1473 K respectively). All specimens were

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[*] Corresponding author. Tel.: +49 7244 82 5463; fax: +49 7247 82 5467; e-mail: roehrig@pkf.fzk.de.

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carefully weighed on a microbalance to monitor interstitial impurity uptake.

For the hydrogen loading, an ultra-high vacuum (UHV) system with a heated furnace tube and an attached hydrogen supply was used (Fig. 1). The furnace tube essentially is a UHV-tight alumina retort attached to a metallic header. One pump train is for evacuation of the system to a base pressure of less than 10^{-8} mbar (10^{-6} Pa) prior to hydrogen inlet. The other pump train, together with an orifice, maintains the pressure in an attached quadrupole residual gas analyzer (QMS) in the proper working range. Ultra-high purity (UHP) hydrogen is derived from the gas flow out of a commercial pressurized hydrogen tank by means of a palladium membrane diffuser, and then manually metered into the retort via an adjustable control valve. The hydrogen supply pressure then results from the effective pumping speeds though the orifice and/or the UHV-valve, and is measured by means of an absolute pressure gauge with an optimum reading in the milliTorr range. Tensile specimens are suspended from the top flange with a molybdenum wire, and they can be extracted from the heated zone by pulling the wire up through a vacuum feedthrough.

The test procedure usually comprised careful evacuation of the system combined with bake-out until both the absolute pressure and the mass spectra showed that residual water and nitrogen/carbon monoxide were down to the detection limits (in this case the orifice was by-passed by a high conductance connection). The bake-out was then stopped, furnace heating of the specimens was started and the Pd-diffuser was made operational. Then the by-pass at the orifice and the UHV-valve were closed, and the metering valve was opened so as to admit hydrogen into the specimens at the desired pressure and temperature. Once the desired hydrogen flow, and hence pressure, had been attained there was excellent stability over many hours.

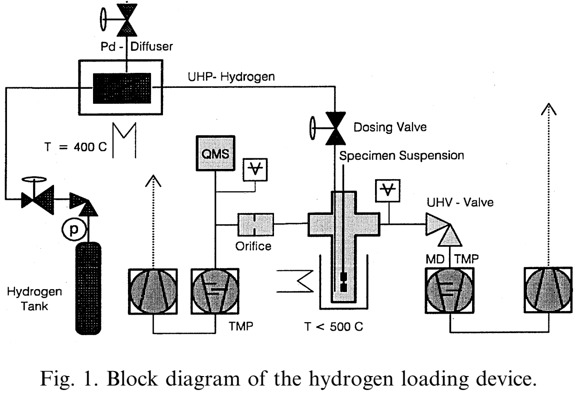

Fig. 1. Block diagram of the hydrogen loading device.

For the final phase of each test there was a choice between fast cool-down by pulling the specimens out of the hot zone, either under full hydrogen pressure or under vacuum, or slow cool-down with the specimens maintained in their position in the furnace retort. These conditions had to be modified as will be discussed later. After ambient temperature had been reached, the specimens were removed, weighed again and then tensile-tested at room temperature. Fragments were either used for chemical analysis or for fractography; however, the results of the latter will be discussed on another occasion [4].

For the tests with oxidized specimens, the vacuum-annealed samples, after weighing, were assembled in another UHV-device which allowed for a defined oxygen partial pressure at a chosen temperature. According to experience from other investigations [5] the oxygen exposure conditions were adjusted to 500°C (773 K) with a pressure of 10^{-5} Torr for a duration of 24 h in order to produce an uptake of about 1000 wt. ppm. An additional vacuum treatment for 25 h at 800°C (1073 K) was meant to distribute the oxygen evenly over the full thickness of the specimen, however it was found to be only partly successful.

As to the tensile tests, they were all made at ambient temperature with a strain-controlled Instron machine at a rate of 0.02 in. (0.5 mm) per min and recorded on a chart recorder. Evaluations of uniform and total elongation, and of 0.2% yield and ultimate tensile stress (UTS) were made from the load–extension curves according to established standards [6].

3. Results and discussion

The first tests in which hydrogen was added at 450°C (723 K) and 0.1 Torr already gave cause to a number of important conclusions. First, the weight gain was so small that it could solely be attributed to the uptake of hydrogen without parasitic oxygen; chemical analysis later confirmed the validity of this hypothesis. Secondly, the hydrogen content was consistent with the solubility data for pure vanadium as given in the literature [7]. Thirdly, the effect of this quantity of hydrogen on tensile properties was within the range of variability of a virgin sample.

Starting from these findings most of the subsequent exposure tests were conducted at a temperature of only 325°C (598 K) and with a variation of pressure up to nearly 2 Torr which was at the very limits of the test facility in the present configuration. With these conditions it was possible to cover the hydrogen concentration range until about 400 wt. ppm, and to attain uptakes above ca. 700 wt. ppm. The intermediate range seemed for some initially unknown reason “forbidden”. The tensile results for the higher hydrogen concentrations, in contrast to those for the lower concentration range, indicated complete embrittlement. This suggested that formation of an unstable hydride was involved when cooling down to room temperature, the composition of which could only be fixed if the pressure of the surrounding hydrogen was lowered at the same pace as the temperature decreased during a relatively fast cooldown, until the sluggishness of kinetics at ambient temperature prevented any further change. This metastable condition, far from thermodynamic equilibrium, is then thought to be frozen by the formation of a passivation layer when the specimens had again contact with air.

Fig. 2 shows the relationship between the hydrogen concentration in the V–4Cr–4Ti specimens and exposure pressure at 325°C (598 K), compared with the first measurement obtained at 450°C (723 K). The agreement with two isotherms derived from [7] for the V–H system not only demonstrates that Sieverts' law applies, but also that the vanadium alloy seems to behave like pure vanadium in this respect.

In Fig. 3 the pressure vs. concentration isotherms have been drawn once more on a much smaller scale in order to elucidate our interpretation of what happens if one tries to approach the hydrogen concentration range around 500 wt. ppm. The (p, c)-isotherms according to Ref. [8] for the V–H system have been extrapolated into the low temperature/low pressure range, and by conversion of the literature data on solubility limit vs. $1/T$ [9] and two-phase equilibrium pressure vs. $1/T$ [10] into isotherms the horizontal lines have been generated. In practical terms they depict the hydride phase in coexistence with dissolved hydrogen. Their extension to larger

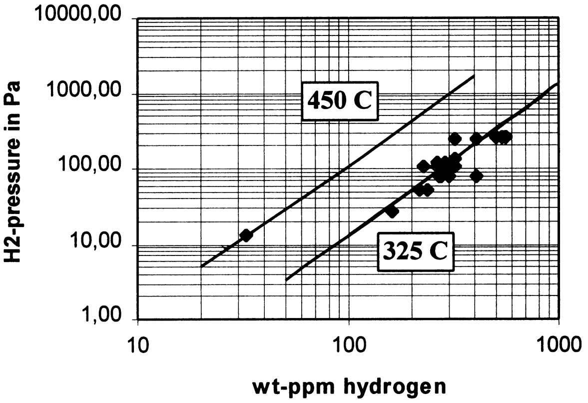

Fig. 2. H_2 content vs. exposure pressure.

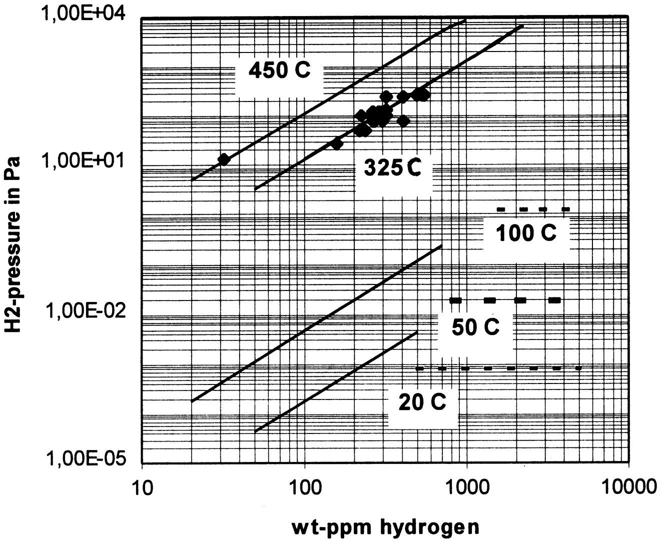

Fig. 3. H_2 content vs. exposure pressure, V–H phase data added.

concentrations is not known, but does not play a role here. For the "normal" solubility isotherms the lower limits of validity as given by Ref. [8] have clearly been exceeded, based on the assumption that deviations from the Arrhenius straight lines as often reported are not real and can be attributed to experimental deficiencies. This has led to the curves as given for 80°C (353 K) and 50°C (323 K) with a gap in the unknown transition area. It can be seen that the same amount of hydrogen in solution in the higher temperature range leads to the two-phase regime when the specimen is cooled down below 50°C without changing its concentration. This is, as already pointed out, an extremely unstable condition: either the hydride fraction decomposes if the outside pressure is reduced to zero at the end of the experiment, and the surplus hydrogen escapes from the specimen due to fast diffusion kinetics, or more hydrogen is taken up if the pressure that was valid at 325°C (598 K) is maintained until the temperature is reduced to ambient conditions. This may explain why we were at first not successful in producing hydrogen concentrations in the range between ca. 450 and 650 wt. ppm. Only by applying the already mentioned sophisticated cool-down / pressure reduction strategy were we able to obtain at least a few points in the most interesting region as discussed in Figs. 4–6.

Fig. 4 gives the results of total elongation, initially considered to be the most critical parameter, vs. hydrogen concentration, for all specimens that were exposed to hydrogen only. Not withstanding the paucity of data in the ductility transition region and large error margins, two effects can clearly be seen: one is a moderate decrease with increased hydrogen content, until there is a fast drop to zero; and the other is a slight, but visible, inverse dependency on grain size (or its corresponding annealing temperature), in line with many observations on various materials. In order to guide the eye, purely empirical curves have been inserted in the graph, but there are good reasons why the drop of elongation should be rather sharp when the region where dissolved hydrogen coexists with brittle hydride is reached.

Fig. 5 concentrates on all four quantities usually derived from strain-controlled tensile tests, namely uniform and total elongation, 0.2% yield and ultimate tensile stress. Only the results for the 1050°C (1323 K)-annealed material are presented because most of the measurements were made with this grain size. One can derive that in contrast to total elongation, uniform elongation is not affected by the presence of hydrogen – as long as the transition regime to coexisting hydride is not reached in which case the two quantities cannot be differentiated. Yield and UTS, however, clearly show an increase from the very beginning of hydrogen introduction. It can be concluded that the effect of hydrogen on tensile properties is, matrix hardening ending up in complete embrittlement when the hydride phase is formed.

Fig. 6 now shows the results for the hydrogen-exposed samples that were previously doped with ca. 850 wppm oxygen. The properties of the oxidized specimen without hydrogen (outer left points) were similar to an unoxidized sample with ca 500 wt. ppm of hydrogen (cf. Fig. 5); only uniform elongation of the oxygen-doped sample seems more affected. Although ductility of the oxidized specimen decreases sharply with a hydrogen concentration as low as 90 wt. ppm, and approaches zero at 230 wt. ppm, the amount of additional hydrogen leading to total embrittlement is in both cases the same. This is a remarkable result, but difficult to explain, because the effect of oxygen is thought to take place at the grain boundaries [5] under the specific processing con-

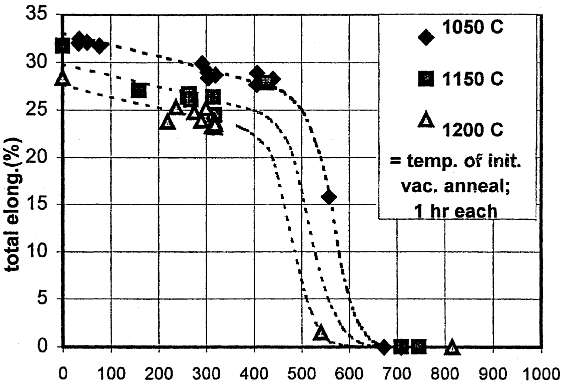

Fig. 4. Room temperature total elongation vs. H_2 content.

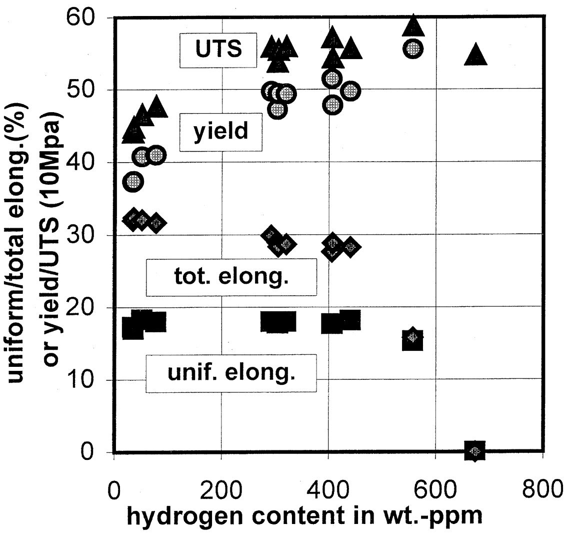

Fig. 5. Tensile data of unoxidized V–4Cr–4Ti vs. H_2 content.

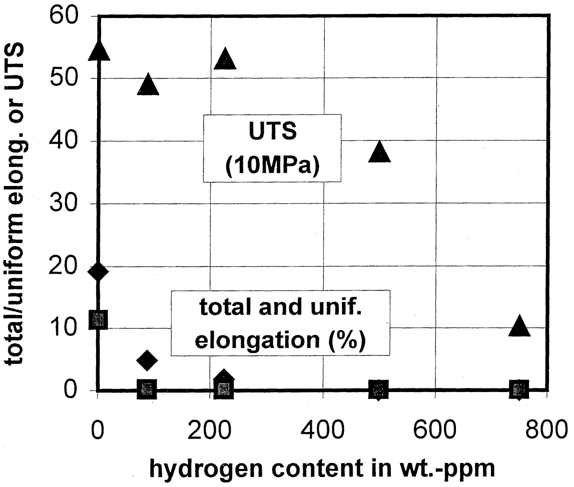

Fig. 6. Tensile data of oxidized V–4Cr–4Ti vs. H_2 content.

ditions of treating the samples with a low oxygen partial pressure at 500°C (773 K). It might be that this hydrogen, although moderate in its quantity, adds so much internal stress to an already affected structure, that cracks starting along grain boundaries can proceed as cleavage through a still ductile core. In this sense, synergism between the action of oxygen and hydrogen can be seen as an additive effect.

4. Conclusions

Special care has been taken to investigate the influence of pure hydrogen on the tensile properties of V–4Cr–4Ti without uncontrolled pick-up of other reactive gases. Under this condition hydrogen solubility was determined in most experiments by the V–H phase diagram comprising the applicability of Sieverts' law. Room temperature tensile behavior then revealed matrix hardening and a slight effect of grain size on total elongation up to about 2.2 at.% hydrogen in the alloy. Above this value brittle behavior rapidly developed, which can be attributed to the appearance of a hydride phase when reaching room temperature. If specimens were pre-exposed to oxygen in a way that there was accumulation at grain boundaries, the tensile behavior was strongly affected, which is assumed to be caused by embrittlement along the grain boundaries or weakening of the adjacent matrix. The catastrophic effect of an only moderate addition of hydrogen is believed to provoke additional internal stresses which cannot be absorbed. The conditions under which this takes place, could be quite typical for a V-alloy structure in contact with a technical grade inert gas at the most interesting fusion reactor operation temperature.

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References

[1] H. Matsui, K. Fukumoto, D.L. Smith, H.M. Chung, W. Van Witzenburg, S.N. Votinov, J. Nucl. Mater. 233–237 (1996) 92–99.
[2] E. Daum, Report KfK 5230, Forschungszentrum Karlsruhe (1993).
[3] R.L. Klueh, Nucl. Eng. Design/Fusion 2 (1985) 407.
[4] M.L. Grossbeck, H.D. Röhrig, J.R. DiStefano, J.H. DeVan, B.A. Pint, Effects of Oxygen and Hydrogen on Fracture Mechanisms in V–4Cr–Ti, to be submitted to ASTM Conference, Seattle, 15–17 June 1998.
[5] J.R. DiStefano, J.H. DeVan, these Proceedings.
[6] ASTM Standard E8-89 b, Am. Soc. for Testing and Mat., Philadelphia, PA.
[7] E. Fromm, E. Gebhardt (Eds.), Gase und Kohlenstoff in Metallen, Springer, Berlin, 1976, p. 441, V–H data; p.451, fig.3: (*p*,*c*)-isotherms.
[8] J.C. Huang, K. Fujita, Tokai-University, Tokyo, private communication to E. Fromm, mentioned in [7].
[9] D.G. Westlake, Trans. AIME 239 (1967) 1341.
[10] R. Griffiths, J.A. Pride, A. Righini-Brand, Trans. Faraday Soc. 68 (1972) 2344.