**REACTIONS OF HYDROGEN WITH V-Cr-Ti ALLOYS** — J. R. DiStefano, J. H. DeVan, L. D. Chitwood (Oak Ridge National Laboratory), and D. H. Röhrig (Projektleitung Kernfusion, Forschungszentrum Karlsruhe)

## OBJECTIVE

The objective of this task is to assess the effects of hydrogen on the mechanical properties of V-Cr-Ti alloys.

## SUMMARY

In the absence of increases in oxygen concentration, additions of up to 400 ppm hydrogen to V-4 Cr-4 Ti did not result in significant embrittlement as determined by room temperature tensile tests. However, when hydrogen approached 700 ppm after exposure at 325°C, rapid embrittlement occurred. In this latter case, hydride formation ins the presumed embrittlement cause. When oxygen was added during or prior to hydrogen exposure, synergistic effects led to significant embrittlement by 100 ppm hydrogen.

## PROGRESS AND STATUS

<u>Experimental Program</u>

Two alloys, V-5 Cr-5 Ti and V-4 Cr-4 Ti, were exposed to hy vironments. Samples were given various heat treatments before and after exposure to to evaluate their effects on hydrogen embrittlement. The alloys were exposed to hydro apparatus consisting of a gas supply, an alumina reaction tube coupled to an ultra high ystem, and a high temperature furnace around the reaction tube. High purity hy as (99.9999%) was admitted through a controllable leak valve while the system w vacuated by the vacuum system. Temperatures of exposure were in the range 325 to some cases specimens were rapidly cooled after exposure by withdrawing them to a cold zone above the furnace, while other specimens remained in the furnace zone as it was cooled to room temperature. Hydrogen flow was maintained during cool down. The amounts of hydrogen picked up were monitored by weight changes and selective chemical analyses. Room temperature tensile tests were used to determine the effect of hydrogen on the mechanical properties of the two vanadium alloys.

Initially, tests in hydrogen were conducted on two heats of V-5 Cr-5 Ti (Table 1) at 450-500°C. Specimens were generally vacuum-annealed at 1125°C prior to hydrogen exposure. Hydrogen pressures were in the range $10^{-2}$ to 10 Pa ($10^{-4}$ to $10^{-1}$ torr) and exposures were for 24 or 100 h. Subsequently, hydrogen uptake by V-4 Cr-4 Ti (Table 1) was determined at 10 Pa (~$10^{-1}$ torr) and 450°C or at 325°C between 25-250 Pa (0.2-2 torr). In the latter tests on V-4 Cr-4 Ti, the gas supply system was modified by the addition of a hydrogen gas purifier that contained a Pd-Ag membrane to exclude oxygen and water vapor from the system, and the pre-test annealing temperature was lowered to 1050°C.

Table 1. Compositions of V-Cr-Ti Alloys

| Nominal composition (wt %) | Heat ID | Concentration (wt %) | | | Concentration (wppm) | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Ti | Fe | O | N | C | Si |
| V-5Cr-5Ti | ORNL | 4.0 | 5.6 | 0.11 | 324 | 512 | 204 | 1100 |
| V-5Cr-5Ti | 832394 | 4.2 | 5.4 | <0.045 | 427 | 52 | 40 | <310 |
| V-4Cr-4Ti | 8326 | 3.1 | 4.1 | 0.022 | 310 | 85 | 86 | 780 |

Results and Discussion

In the initial tests on the two heats of V-5 Cr-5 Ti, exposures at $10^{-2}$-$10^{-1}$ Pa resulted in only minor hydrogen uptake and weight change, with minimal effects on mechanical properties. However, at hydrogen pressures of 1-10 Pa, weight gains generally exceeded those attributable to hydrogen alone, and selected chemical analyses indicated a concomitant increase in oxygen content. For any given exposure condition, the uptake of hydrogen was similar for the two heats. However, as shown in Fig. 1, specimen furnace (slowly) cooled under the hydrogen exposure pressure showed higher hydrogen concentrations than companion specimens moved quickly to a relatively cool region of the furnace. Some effect of grain size on tensile ductility was noted as indicated in Fig. 2. (Numbers refer to oxygen concentration associated with hydrogen concentration.) The heat of V-5 Cr-5 Ti identified as 832394 exhibited a larger grain size for a given annealing temperature and, in general, was more susceptible to hydrogen (plus oxygen) embrittlement. Hydrogen concentrations <50 wppm seriously embrittled this heat, while 70-80 wppm hydrogen resulted in only slight embrittlement of the finer-grained ORNL heat. Post-exposure heat treating the V-5 Cr-5 Ti alloys in vacuum for 100 h at 500°C was effective in removing hydrogen, as shown in Table 2. Although this treatment recovered most of the ductility in the finer-grained ORNL heat, heat 832394 remained brittle, an indication that oxygen contamination was a significant factor in the embrittlement of the latter heat.

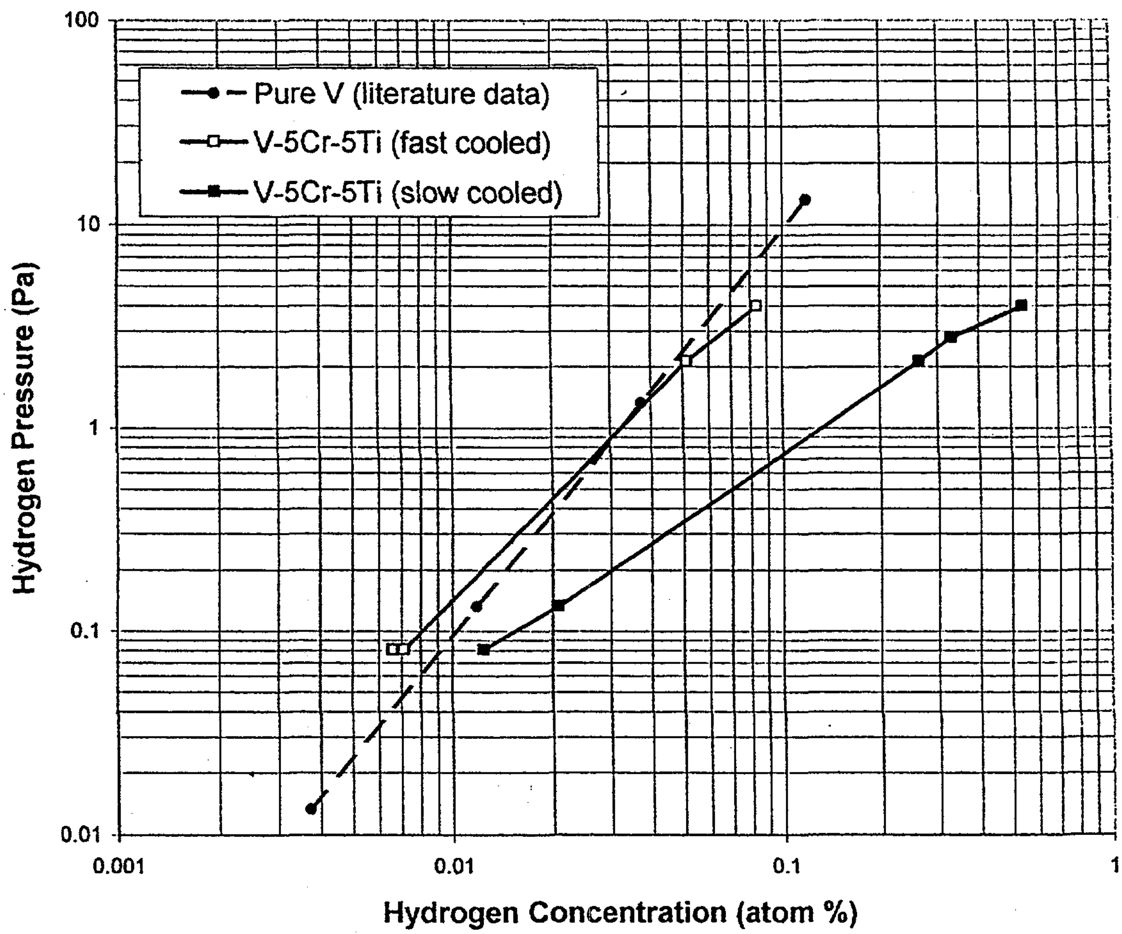


Fig. 1. Hydrogen concentrations in V-5 Cr-5 Ti and unalloyed vanadium [9,10] after exposure to low-pressure hydrogen at 500°C.

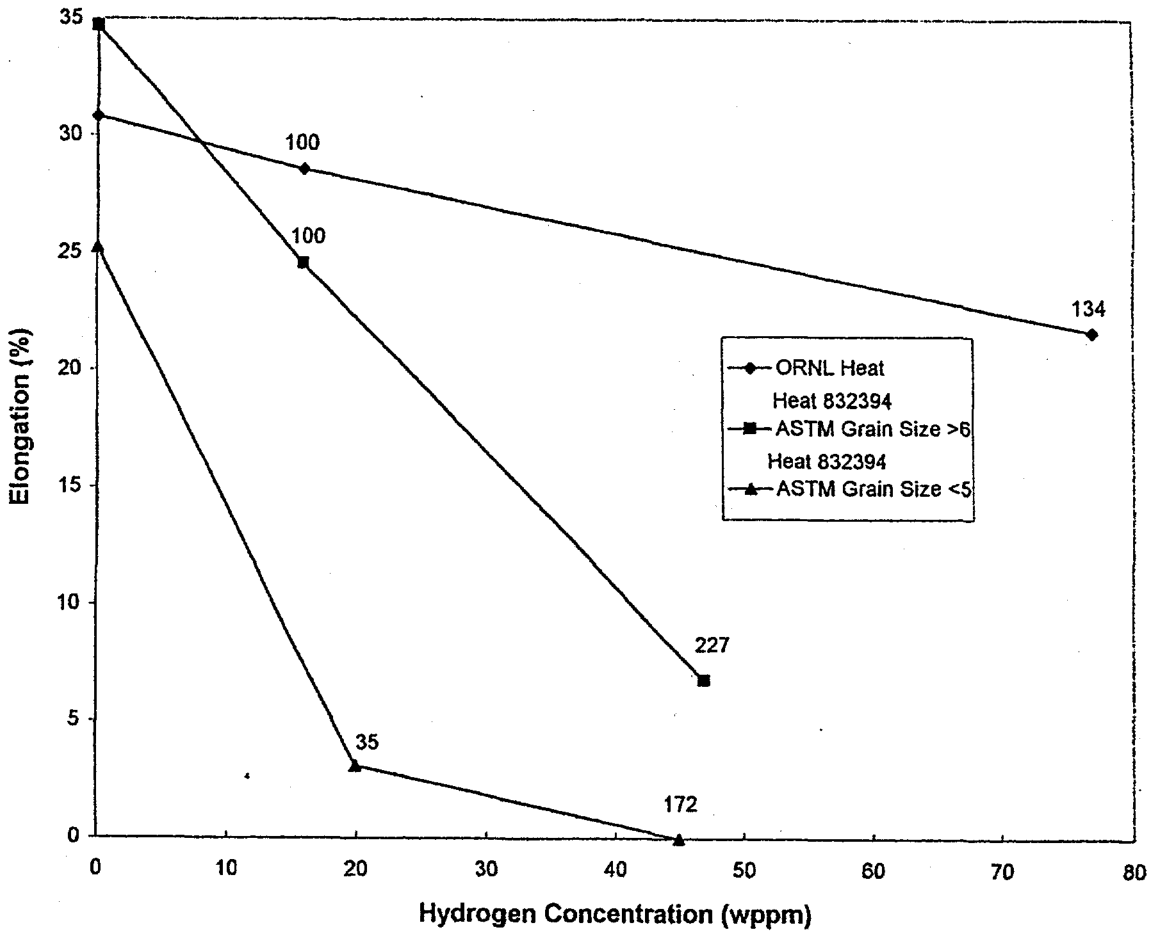


**Fig. 2. Room temperature elongation (a) and yield strength (b) of two heats of V-5 Cr-5 Ti annealed at 1125°C prior to exposure to high purity hydrogen gas at 500°C. Numbers above data points show increases in oxygen concentration (ppm) accompanying hydrogen exposures.**

Table 2. Effect of hydrogen exposure at 3 x $10^{-2}$ torr on V-5Cr-5Ti at 500C before and after vacuum heat treating at 500C[a]
(Exposure and heat treating times were 100 h, respectively)

| Heat | Cooling rate in hydrogen | Vacuum heat treat | Concentration (ppm) | | Yield strength (MPa) | Ultimate strength (MPa) | Elongation (%) |
|---|---|---|---|---|---|---|---|
| | | | Hydrogen | Oxygen | | | |
| 832394 | Fast | No | 45 | 172 | FBY[b] | FBY[b] | 0.0 |
| 832394 | Slow | No | 107 | 245 | FBY[b] | FBY[b] | 0.0 |
| 832394 | Slow | Yes | 2.4 | 185 | 506 | 515 | 0.3 |
| ORNL | Fast | No | 59 | 284 | 476 | 515 | 18.0 |
| ORNL | Slow | No | 150 | 332 | 493 | 533 | 7.0 |
| ORNL | Slow | Yes | 0.8 | 246 | 453 | 561 | 22.6 |

[a]Samples annealed at 1125C prior to exposure to hydrogen.
[b]Failed before yield.

To avoid the complexity of oxygen contamination effects, the test system was modified by the addition of a hydrogen purifier. The Pd-Ag alloy membrane in the purifier permitted only hydrogen to pass through, effectively eliminating oxygen as an impurity. This was verified by a residual gas analyzer which indicated that, except for a small amount of residual water vapor, hydrogen was the only gas that could be detected in the system.

Hydrogen uptake by V-4 Cr-4 Ti was then determined as shown in Fig. 3. The data in Fig. 3 for hydrogen concentration in V-4 Cr-4 Ti as a function of pressure at 325°C can be described by a Sievert's law relation and correlate with the data for fast-cooled V-5 Cr-5 Ti at 500°C, shown in Fig. 1. The agreement of the present data (shown as individual points in Fig. 3) with isotherms (lines in Fig. 3) derived from the literature for the V-H system,[1,2] demonstrates that V-Cr-Ti behaves similarly to pure vanadium with respect to hydrogen uptake at a given hydrogen pressure and temperature.

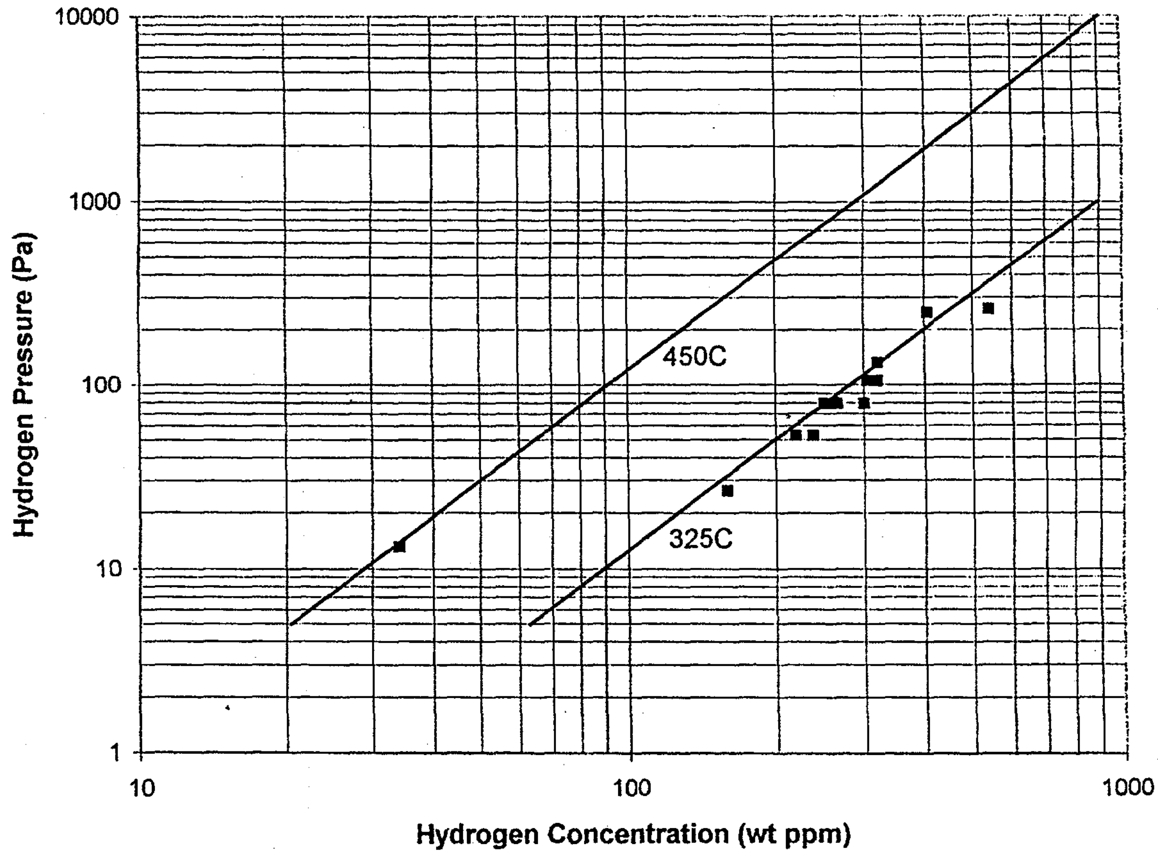


Fig. 3. Comparison of hydrogen concentrations in V-4 Cr-4 Ti with calculated concentrations in unalloyed vanadium at 450 and 300°C [9,10].

Results of room temperature tensile tests on V-4 Cr-4 Ti after exposure to hydrogen at 325°C are shown in Fig. 4. When oxygen was excluded, the addition of up to 400 ppm hydrogen increased the room temperature tensile strength slightly with only a small decrease in tensile elongation (Fig. 4). The fractures tended to be the cup/cone type, similar to that of the as-received alloys. However, a further increase in hydrogen concentration to 700 ppm resulted in complete embrittlement (Fig. 4). As shown in Fig. 5, this hydrogen concentration corresponds to the solubility threshold for hydride formation in pure vanadium below 80°C and is indicative that the ductile-brittle transition for specimens containing more than 400 ppm hydrogen is most likely associated with hydride formation.

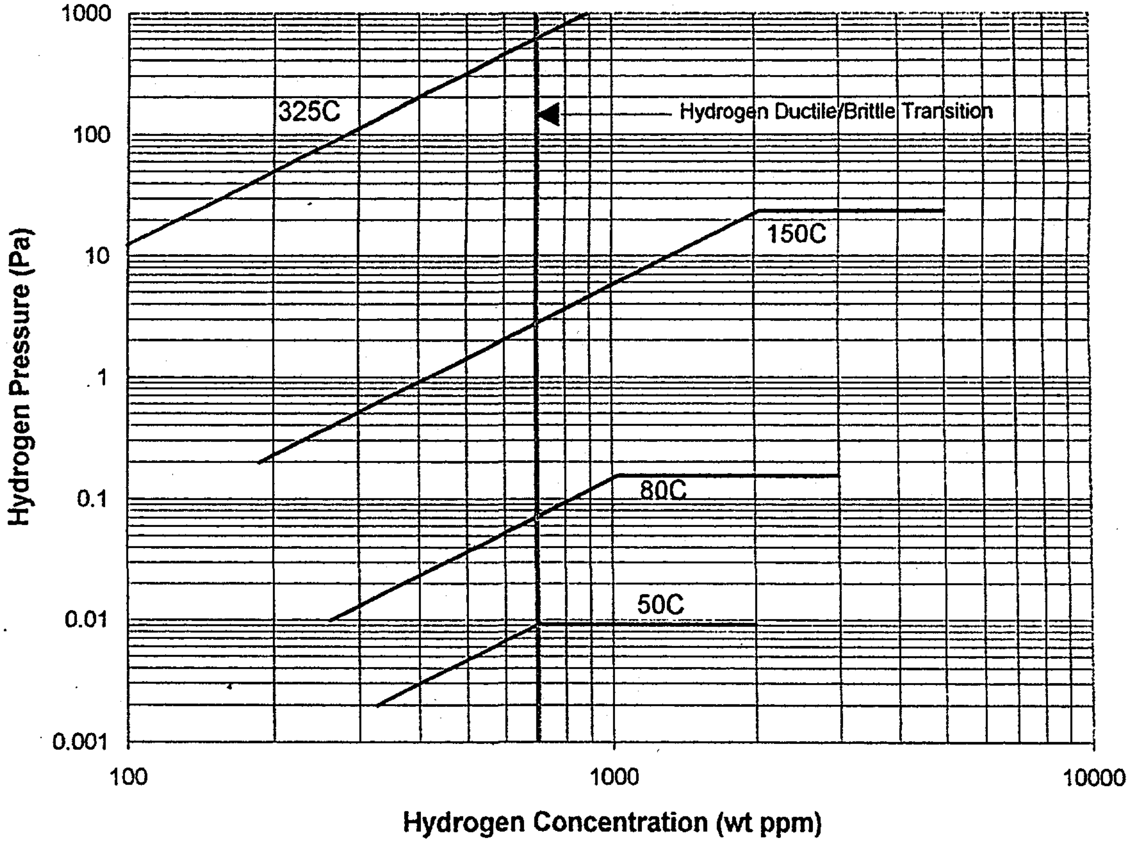


Fig. 4. Effect of hydrogen on room temperature elongation of V-4 Cr-4 Ti.

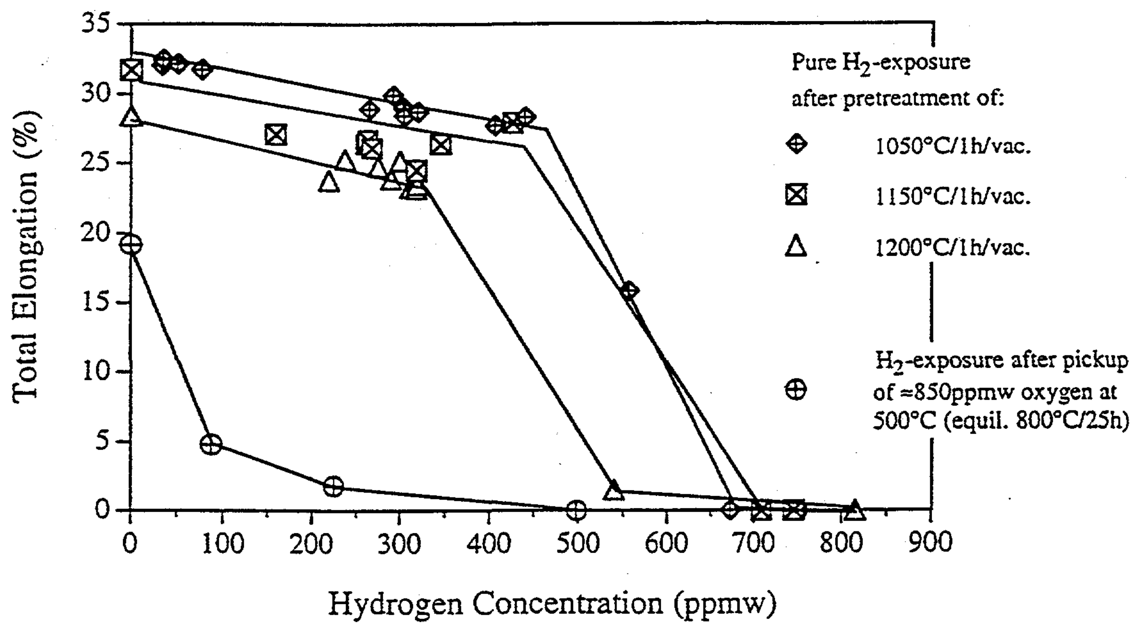


Fig. 5. Hydrogen concentrations in unalloyed vanadium at 50-325°C [10]. Horizontal portions represent two-phase regions (hydride + solid solution).

The synergistic effect of oxygen in combination with hydrogen was determined for V-4 Cr-4 Ti by first exposing the specimens to oxygen at 500°C, heat treating in vacuum at 800°C and then exposing the oxygenated specimens to hydrogen (Fig. 4). The initial addition of ~850 wppm oxygen reduced room temperature elongation from approximately 30 to 20%. However, subsequent exposure of a similar specimen to hydrogen drastically reduced its elongation to 5% after only 100 wppm hydrogen was added, whereas, in the absence of oxygen, >500 ppm hydrogen was generally required before room temperature ductility fell precipitously. Fracture cross sections indicated that the oxygen-doped specimens retained a relatively ductile core until the hydrogen concentration approached its solubility limit (Fig. 6). Oxygen was confined to a fixed depth below the surface, and embrittlement appeared to be associated with the combined effects of oxygen and hydrogen in this outer case. However, initiation of cracks in the outer case could also affect the fracture toughness of the hydrogen strengthened, ductile core, thereby further reducing the ductility.

Where embrittlement is due to the combined effects of oxygen and hydrogen, desorbing hydrogen by vacuum heat treating will generally improve the ductility, although embrittlement induced by oxygen is not reversed by heat treatments in the range normally used to remove hydrogen (<500°C). In fact, embrittlement by oxygen is exacerbated by heat treating in the 400-500°C temperature range,[3] and the desorption of hydrogen advisedly should be conducted above or below this range. The heat treatment needed to counter embrittlement by oxygen, when it is absorbed at 400-500°C, was shown to be in the range of 950°C and higher,[3] where the oxygen is precipitated from the matrix in the form of $TiO_2$.

Based on the present results, serious embrittlement of the reference V-Cr-Ti alloys by hydrogen isotopes would not be expected under nominal fusion reactor operating conditions, providing that oxygen pickup is carefully controlled. Given present estimates of plasma leakage to the first wall, our calculations of the deuterium-tritium pressures behind the currently proposed light element coatings (i.e., in cracks or crevices) show them to be on the order of $10^{-1}$ Pa ($10^{-3}$ torr). At this pressure, as shown by the present results and those of Natesan,[4] hydrogen concentrations in V-Cr-Ti alloys are well within the solid solution range, and the principal mechanical property effect would be limited to slight hardening. One caveat is a possible additive effect with radiation damage, where protium produced in the alloys by transmutation reactions and radiation hardening may lead to an increase in the ductile-to-brittle transition temperature. Also, depending on design, hydrogen isotopes could affect the properties of V-Cr-Ti alloys if used for components on which plasma directly impinges, such as the divertor.

One of the major concerns in the application of V-Cr-Ti alloys to fusion reactors will be oxygen pickup, particularly in welds during reactor construction and during system bake-out prior to operation. As shown earlier,[3,5] oxidation that occurs internally at lower temperatures (e.g., 500°C) can of itself cause serious embrittlement, and, as shown here, the uptake of relatively small concentrations of hydrogen further increases the degree of embrittlement for a given level of oxygen. Accordingly, the permissible level of oxygen contamination will be strongly impacted by the uptake of hydrogen isotopes expected during reactor operation.

## REFERENCES

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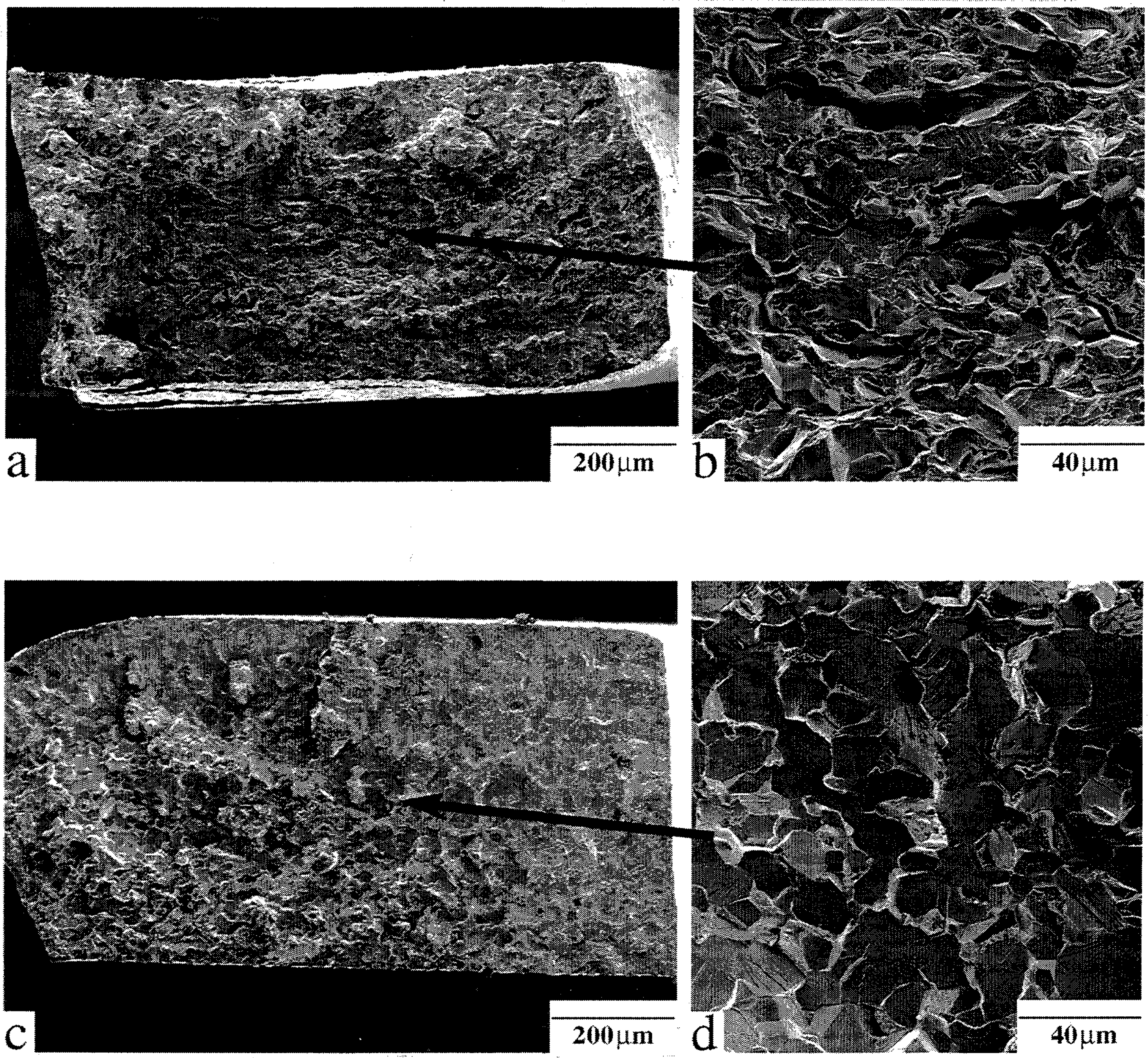


Fig. 6. SEM secondary electron images of V-4 Cr-4 Ti tensile fracture sections. Specimens were pre-exposed to oxygen (≈850 ppm) and aged at 800°C prior to hydrogen exposure at 325°C. The region of brittle cleavage and intergranular cracking increased in depth as H concentration increased from (a,b) 900 ppm to (c,d) 500 ppm.