Performance of V–Cr–Ti alloys in a hydrogen environment

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Abstract

A systematic study is underway at Argonne National Laboratory to evaluate the mechanical properties of several V–Cr–Ti alloys after exposure to environments containing hydrogen at various partial pressures (pH_2). The goal is to correlate the chemistry of the exposure environment with hydrogen uptake by the samples and with the resulting influence on microstructures and tensile properties of the alloys. Other variables examined are specimen cooling rate and synergistic effects, if any, of oxygen and hydrogen on tensile behavior of the alloys. Experiments were conducted to evaluate the effect of pH_2 in the range of 3×10^{-6} and 1 Torr on tensile properties of two V–Cr–Ti alloys. Up to pH_2 of 0.05 Torr, negligible effect of H was observed on either maximum engineering stress or uniform and total elongation. However, uniform and total elongation decreased substantially when the alloys were exposed at 500°C to 1.0 Torr of H_2 pressure. Preliminary data from sequential exposures of the materials to low-pO_2 and several low-pH_2 environments did not reveal adverse effects on the maximum engineering stress or on uniform and total elongation when the alloy contained ≈ 2000 wppm O and 16 wppm H. Furthermore, tests in H_2-exposed specimens, initially annealed at various temperatures, showed that grain-size variation by a factor of ≈ 2 had little or no effect on tensile properties. Also, specimen cooling rate had a small effect, if any, on the tensile properties of the alloy. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Vanadium-base alloys nominally containing 4–5 wt% chromium and 4–5 wt% titanium have been identified as the most viable materials for fusion reactor applications because they have lower long-term activation, lower irradiation afterheat, lower biological hazard potential and thermal stress factor, better creep resistance, compatibility with coolants such as liquid alkali metals, and better mechanical formability than other structural alloys. A primary deterrent to the use of V-base alloys at elevated temperatures is their relatively high affinity for interstitial impurities, i.e., O, N, H, and C. The purpose of this study is to identify the key variables and establish performance envelopes for V-base alloys for service in H_2 environments. By analogy, the information can be used to assess the behavior of alloys in environments containing other H isotopes.

This paper examines the influence of H uptake of V–Cr–Ti alloys, specimen cooling rate, and grain size on the tensile properties of the alloys at room temperature [1–3]. Furthermore, the effects of simultaneous presence of O and H and their interactions on the tensile properties of the alloys are examined.

2. Experimental procedure

The nominal compositions of the heats of V alloys selected for the study were V–4 wt% Cr–4 wt% Ti (identified as 44) and V–5 wt% Cr–5 wt% Ti (identified as 55). Chemical analyses of these heats are given in Table 1. The alloys were obtained as 1-mm-thick cold-rolled sheets. Samples with dimensions of about $1 \times 10 \times 20$ mm³ were cut from each alloy. Before any further treatment or testing, all samples were annealed for 1 h at 1000°C in a vaccum of $\approx 10^{-6}$ Torr. The samples were wrapped in Ti foil to protect them from contamination during annealing. Samples of Alloys 44 and 55 were exposed for 100 h at 200–500°C in pure H_2

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Table 1
Compositions of V–Cr–Ti alloys used in hydrogen studies

Alloy	Heat #	Composition					
		Cr (wt%)	Ti (wt%)	Si (wppm)	O (wppm)	N (wppm)	C (wppm)
44	832665	3.8	3.9	783	310	85	80
55	832394	4.6	5.1	310	440	28	73

gas environments with pressures in a range of 3×10^{-6} to 1 Torr.

Furthermore, for a given pH_2 in the exposure environment, the H concentration in the V-base alloy increases as the temperature is lowered; this seems to indicate that the H concentration determined at room temperature will be influenced by the specimen cooling rate and that to obtain the value corresponding to that expected at the higher exposure temperature, fast cooling or quenching of the specimens may be needed. Experiments were conducted in which specimens were equilibrated at 350°C or 500°C and cooled at a faster rate by pulling the specimens from the hot zone of the furnace into a flowing high-purity He atmosphere and using dry ice to cool the specimen. A cooling rate of 100 times that of normal rate is obtained by this approach.

Tensile specimens of several of the alloys were fabricated according to ASTM Standard E8-69 specifications and had a gauge length of $\approx$19 mm and a gauge width of $\approx$4.5 mm. Specimens were annealed for 1 h at 1000°C before H_2 exposure and tensile testing. Tensile specimens were exposed for 100 h to environments containing H_2 at various partial pressures and at 200°C, 350°C, and 500°C. The H-exposed specimens were tensile-tested at a strain rate of 1.8×10^{-4} s^{-1} at room temperature in air. Total elongation was measured with a vernier caliper and by using load/elongation chart records. The fracture surfaces and longitudinal and axial cross-sections of tested specimens were examined by scanning electron microscopy (SEM). Several of the tested specimens were thinned in an acid solution and their microstructures were analyzed by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Hydrogen uptake

Data on the solubility of H in Ti and V as a function of temperature showed that at a given temperature, the H concentration in Ti is much lower than in V for precipitation of their respective hydrides. However, because the Ti concentration in the V alloys of interest is in the range of 4–5 wt%, pH_2 needed to precipitate TiH in the alloys will be much higher and probably closer to that for precipitation of VH. Furthermore, the H concentration in the alloy must exceed $\approx$100 wppm for VH to precipitate in the alloy at temperatures above $\approx$150°C. Exposure of specimens of Alloys 44 and 55 for 100 h at 200–500°C in H environments with pressures of 3×10^{-6} to 1 Torr yielded H concentrations in the specimens in a range of 6–360 wppm. Furthermore, a grain size increase by a factor of 2 ($\approx$35 and 55 μm for large-grain specimens of Alloys 44 and 55 obtained by annealing at 1200°C, versus 18 and 30 μm in specimens of the same alloys annealed at 1000°C) did not have a significant effect on H uptake of the alloys.

3.2. Effect of cooling rate

As discussed earlier, cooling rates can have an effect on the H uptake of the alloys because the H concentration in the alloy increases as the temperature decreases at a given pH_2 in the environment. Therefore, H can transfer to the alloy, depending on the length of time the alloy is exposed to the higher pH_2 at lower temperatures. Fig. 1 shows the temperature versus time plots for normal cooling rate from 500°C and fast cooling rates from 500°C and 350°C. The rates in the normal and fast cooling were $\approx$0.04 and 4.5°C/s and the total time to reach $\approx$50°C in the fast cooling was <100 s. Table 2 shows the tensile properties for Alloy 44 exposed at a nominal pH_2 of $\approx 10^{-6}$ Torr at 500°C and 350°C and cooled at various rates. Results indicate that the cooling rate has very little effect on the tensile properties of
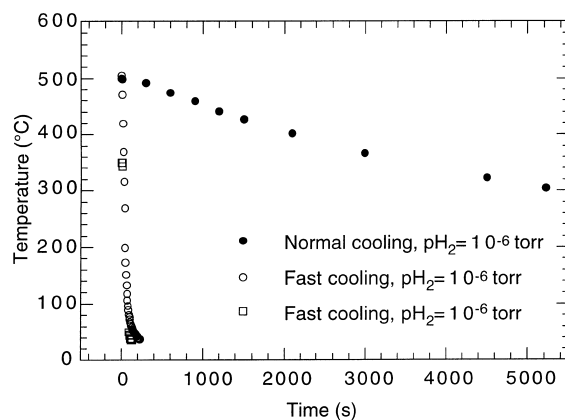

Fig. 1. Temperature-time curves for normal and fast cooling of specimens from H_2 exposure temperature.

Table 2
Effect of cooling rate on room temperature tensile properties of Alloy 44

Exposure temperature (°C)	pH$_2$ (Torr) in exposure environment	Cooling rate (°C/s)	Maximum engineering stress (MPa)	Uniform elongation	Total elongation
500	3×10^{-6}	0.04	440	0.174	0.263
	1×10^{-6}	4.5	433	0.164	0.301
350	1×10^{-6}	0.04	434	0.133	0.184
	1×10^{-6}	4.5	418	0.182	0.331

specimens exposed at 500°C. At 350°C, the fast-cooled specimen exhibited some decrease in maximum engineering stress and some increase in uniform and total elongation, compared with those for normal-cooled specimens.

3.3. Effect of H concentration on tensile behavior

Fig. 2 shows the engineering stress/engineering strain plots at room temperature for Alloys 44 and 55 in as-annealed condition and after exposure at 500°C in pH$_2$ levels of 3×10^{-6} and 0.01 Torr. Table 3 lists the tensile data obtained on Alloy 44 after exposure at various temperatures and H$_2$ pressures. Results showed that in the pH$_2$ range of this study, Alloy 44 exhibited a small decrease in uniform and total elongation after exposure to H$_2$ at 500°C. Furthermore, tensile test data generated at 200–500°C after exposure to pH$_2$ levels in the range of 1×10^{-6}–5×10^{-2} Torr showed little or no effect on the maximum engineering stress for Alloy 44. Fig. 3 shows the plots of uniform and total elongation values as a function of H concentration for the alloy exposed at 200°C, 350°C, and 500°C and tested at room temperature. Uniform and total elongation values for the alloy ranged between 0.14–0.20 and 0.18–0.31, respectively, at 200°C and 500°C and in pH$_2$ < 0.05 Torr. Only at a pH$_2$ of 1 Torr and at 500°C did the uniform elongation for

the alloy decrease to 0.002. This corresponded to a H concentration of $\approx$360 wppm in the alloy, indicating that this H level may be the threshold for embrittlement of the alloy. DiStefano et al. [4] based on their studies, concluded that >500 wppm H is needed for embrittlement of Alloy 44.

To examine the effect of initial grain size on subsequent H uptake and tensile properties, specimens of Alloys 44 and 55 were annealed for 2 h at 1200°C, which increased the grain size of the alloys by at least a factor of 2 over those annealed for 1 h at 1000°C. With the increased grain size, both alloys exhibited some increase in strength and some decrease in elongation (see Table 4). Similar effects were observed when the specimens were exposed for 100 h at 500°C to a pH$_2$ of 3×10^{-6} Torr.

3.4. Synergistic effect of O and H on tensile properties

To examine the synergistic effect, if any, of O and H in the alloy on the tensile behavior of V–Cr–Ti alloys, specimens of the Alloys 44 and 55 were pre-treated in several low-pO$_2$ environments for 100 h at 500°C. Subsequently, the exposure gas was changed from O$_2$ to H$_2$ at the same temperature, and specimen exposure was continued for another 100 h. Pre-exposure of the specimens to the low-pO$_2$ environments resulted in different
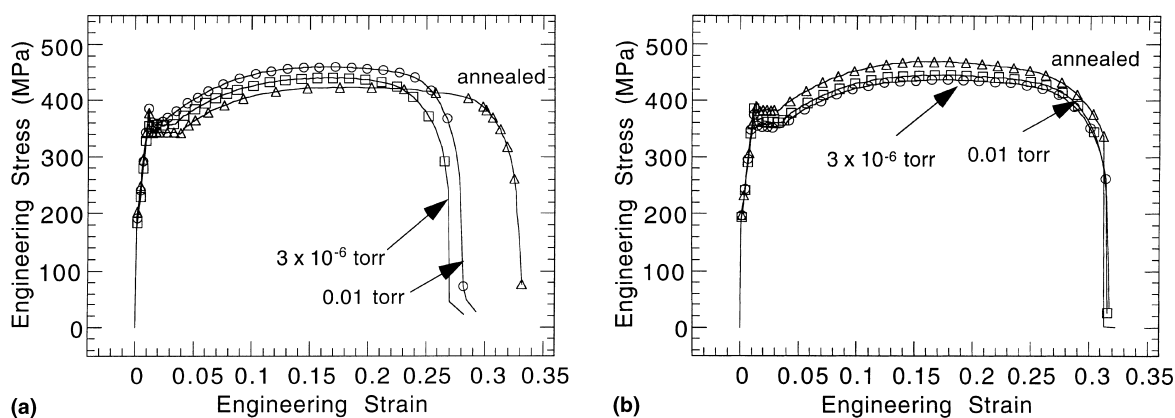

Fig. 2. Engineering stress/engineering strain plots for Alloys (a) 44 and (b) 55 in as-annealed condition and after 100-h exposure at 500°C to various pH$_2$ levels and normal cooling rate.

Table 3
Effect of 100-h H exposure on room-temperature tensile properties of Alloy 44

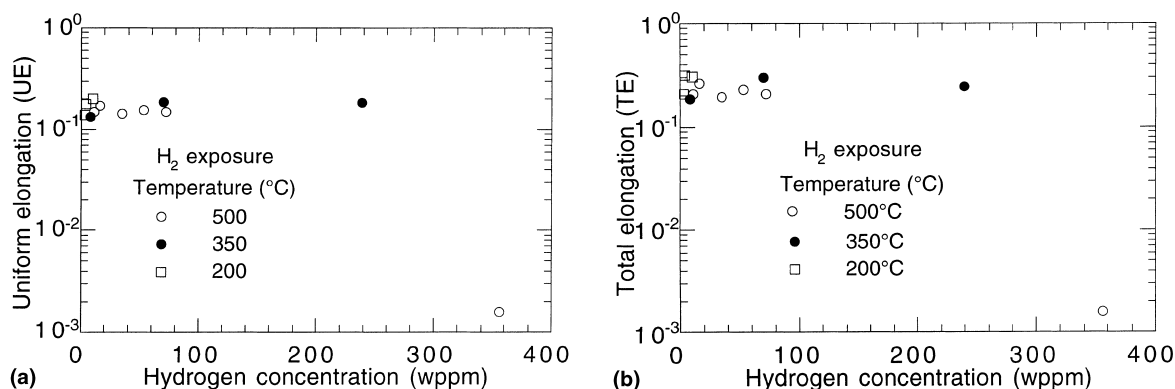| Exposure temperature (°C)	pH_2 in exposure environment (Torr)	Maximum engineering stress (MPa)	Uniform elongation	Total elongation
200	3×10^{-6}	421	0.199	0.302
	1×10^{-4}	420	0.178	0.313
	5×10^{-2}	419	0.138	0.207
350	3×10^{-6}	434	0.133	0.184
	1×10^{-4}	525	0.182	0.242
	5×10^{-2}	460	0.183	0.294
500	–	424	0.186	0.322
	3×10^{-6}	440	0.174	0.263
	1×10^{-4}	467	0.154	0.227
	1×10^{-4a}	491	0.148	0.206
	1×10^{-2}	459	0.169	0.263
	5×10^{-2}	477	0.142	0.191
	1	468	0.0016	0.0016

[a] Repeat.

Fig. 3. (a) Uniform and (b) total elongation as a function of H concentration for V–4Cr–4Ti alloy tested at room temperature.

Table 4
Effects of 100 h H exposure at 500°C on room-temperature tensile properties of enlarged-grain V–Cr–Ti alloys

pH_2 in exposure environment (Torr)	Maximum engineering stress		Uniform elongation		Total elongation	
	55	44	55	44	55	44
3×10^{-6}	515	472	0.144	0.159	0.250	0.225
1×10^{-2}	524	479	0.160	0.153	0.244	0.227

concentrations of O in the alloys, which were subsequently exposed to various H_2 pressures. The specimens exposed to the dual treatment were analyzed for O and H by vacuum fusion. Table 5 lists the O and H concentrations for specimens with different treatments. The O concentrations ranged between 550 and 2230 wppm, while the H concentration range was 6–16 wppm. It should be noted that the diffusion coefficient for O is a few orders of magnitude lower than that for H in these

alloys; as a result, after the 100-h exposures, the measured H concentration will be uniformly distributed over the entire 1-mm-thick section of the specimens, while the O concentration will be confined to a depth of ≈ 50 μm from the surface [5,6].

The pre-treated and H-exposed specimens were tensile-tested at a strain rate of $1.8 \times 10^{-4} \, s^{-1}$ in room-temperature air. Engineering stress/engineering strain curves from various tests were analyzed to evaluate the

Table 5
Concentrations of O and H in pretreated tensile specimens[a]

| pO_2 in exposure environment (Torr) | pH_2 in exposure environment (Torr) | Concentration (wppm) | | | |
| | | Oxygen | | Hydrogen | |
		55	44	55	44
–	3×10^{-6}	550	670	12	11
3×10^{-7}	1×10^{-6}	625	620	16	16
1×10^{-6}	1×10^{-6}	730	1030	6	7
1×10^{-4}	3×10^{-6}	2230	2000	15	12

[a] Pre-exposure in O_2 was 100 h at 500°C, and subsequent exposure in H_2 was 100 h at 500°C.

Table 6
Effects of dual O/H treatment[a] at 500°C on room temperature tensile properties of V–Cr–Ti alloys

| pO_2 in exposure environment (Torr) | pH_2 in exposure environment (Torr) | Maximum engineering stress (MPa) | | Uniform elongation | | Total elongation | |
		55	44	55	44	55	44
–	–	469	424	0.165	0.186	0.303	0.322
–	3×10^{-6}	437	440	0.189	0.174	0.313	0.263
3×10^{-7}	1×10^{-6}	452	453	0.173	0.162	0.297	0.266
1×10^{-6}	1×10^{-6}	507	475	0.165	0.146	0.268	0.228
1×10^{-4}	3×10^{-6}	484	451	0.132	0.136	0.184	0.177

[a] Pre-exposure in O_2 was 100 h at 500°C and subsequent exposure in H_2 was 100 h at 500°C.

effect of dual treatment on the tensile properties for the alloys. Table 6 shows the values for maximum engineering stress and uniform and total elongation for the two materials after the dual treatments. Figs. 4 and 5 show the maximum engineering stress and the uniform and total elongation as a function of O concentration for both the alloys. It is evident that O concentration up to ≈2300 wppm, even though confined to the surface regions of the specimens, has a negligible effect on tensile properties; no synergistic effect of O and H on the properties is observed when the H concentration in the alloy was in the range of 6–16 wppm, based on the

present study. However, DiStefano et al. [4] reported embrittlement of the alloy at room temperature after pre-oxidation at 500°C to obtain 800 wppm O and with subsequent H uptake of 100 wppm. Results developed in both these studies indicate that the interaction between O and H in the V-base alloys may be more complex and needs significant additional effort to clarify whether a synergistic effect of O and H is present and to assess the magnitude of this effect on the mechanical properties of the alloys.
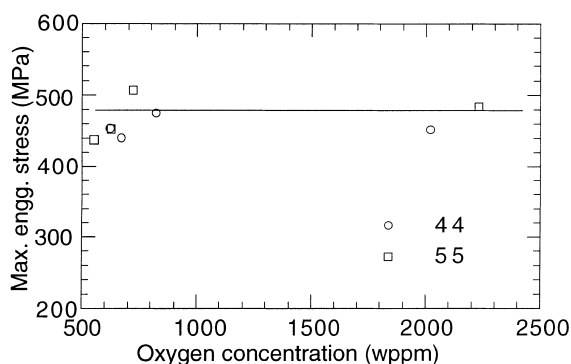

Fig. 4. Maximum engineering stress as a function of O uptake during preoxidation and subsequent H_2 exposure for Alloys 44 and 55 tested at room temperature.
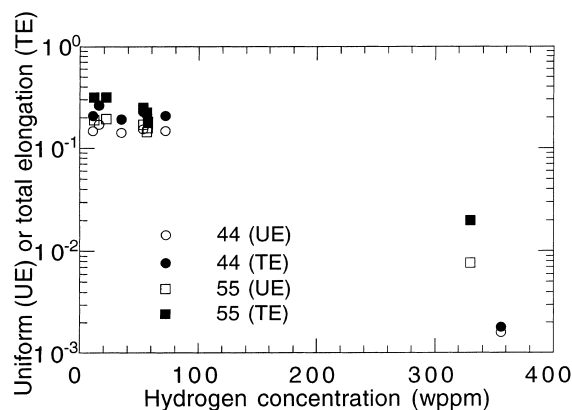

Fig. 5. Uniform and total elongation as a function of O uptake during preoxidation and subsequent H_2 exposure for Alloys 44 and 55 tested at room temperature.

3.5. Microstructural observations

Microstructures of specimens from various tensile tests without and with pre-treatment of O were examined by TEM, and preliminary observations are reported below [7]. Alloy 44 specimen after exposure to pH_2 of 3×10^{-6} Torr at 500°C contained 11 wppm H and exhibited clean grain boundaries with no hydride precipitates, as expected. Even with 35 wppm H in the specimen, alloy grain boundaries and grain interiors were devoid of precipitates, indicating no preferential segregation of H or hydrides in the specimen.

Alloy 44 specimen that was pre-treated for 100 h in 3×10^{-6} Torr pO_2 at 500°C and subsequently exposed for 100 h in pH_2 of 3×10^{-6} Torr at 500°C contained O, N, and H concentrations of 1030, 100, and 7 wppm, respectively. The specimen exhibited uniform and total elongation values of 0.15 and 0.23, respectively. TEM analysis showed precipitates predominantly along the grain boundaries, which can be attributed to the pre-treatment in the low-pO_2 environment. Grain boundaries in the alloy exhibited precipitates of ≈ 100–200 Å in size.

The Alloy 44 specimen that was pre-treated for 100 h in 1×10^{-4} Torr pO_2 at 500°C was subsequently exposed for 100 h in pH_2 of 3×10^{-6} Torr at 500°C contained O, N, and H concentrations of 2020, 110, and 13 wppm, respectively. TEM analysis showed extensive continuous precipitation along the grain boundaries and some preferential precipitation within some grains but not in others. We plan to analyze the precipitates in these specimens and also to examine specimens from several other experiments to evaluate the effect of increased H concentration and O/H interactions on the microstructures and tensile properties of the alloy.

4. Summary

We have evaluated the effect of H uptake of Alloys 44 and 55 in pH_2 in the range of 3×10^{-6} to 1 Torr on tensile properties of the alloys. The effect of pH_2 in the range of 3×10^{-6} to 5×10^{-2} Torr on tensile properties is minimal; at a pH_2 of 1 Torr, the maximum engineering stress is unaffected but the tensile elongation decreased significantly. The H concentration corresponding to this condition is ≈ 360 wppm. Effect of H on the tensile properties of Alloys 44 and 55 with enlarged (by a factor of 2) grain sizes was negligible. Pre-oxidation (resulting in an O concentration of ≈ 2000 wppm) and subsequent H_2 exposure (resulting in 16 wppm H) did not affect the tensile properties of the alloy at room temperature. TEM analysis of specimens exposed to low-pH_2 atmosphere exhibited neither segregation of H in the grain boundaries nor any precipitates of hydrides. Specimens with oxygen concentrations of 1030 and 2000 wppm (present due to low-pressure O_2 pre-treatment) exhibited significant precipitation of, presumably, oxides along the grain boundaries and within some of the grains in the alloy.

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