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Reactions of oxygen with V–Cr–Ti alloys

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Abstract

Fusion reactors have been proposed with a vanadium alloy as the structural/containment material. However, vanadium has a significant affinity for interstitial contamination that could deleteriously affect its mechanical properties. The effects of oxygen pick-up in air and low pressure oxygen environments were investigated at 400–500°C for two V–Cr–Ti alloys. As expected the studies showed that the room temperature tensile ductility is reduced by exposure to air or low pressure oxygen environments. However, the magnitude depends upon processing history and subsequent heat treatment. Possible embrittling mechanisms such as grain boundary weakening or weakening of near-boundary regions are discussed. © 1997 Elsevier Science B.V.

1. Introduction

The present work is part of an ongoing study to assess the effects of both hydrogen and oxygen on the mechanical properties of V–Cr–Ti alloys under conditions relevant to the operation of fusion power reactors. Vanadium alloys are attractive as a first-wall material in fusion reactor blanket applications [1,2] due to their low induced radioactivity, good resistance to neutron radiation damage and good mechanical strength and ductility at the temperatures of interest (400–700°C). Fusion reactor designs have been proposed with liquid lithium as the coolant/tritium-breeding material together with a vanadium alloy as the structural/containment material. However, the attractive mechanical properties of vanadium and vanadium alloys depend strongly upon the concentrations of interstitial elements particularly oxygen, nitrogen and hydrogen [3].

Although the initial objective of this program was to investigate the interaction of V–Cr–Ti alloys with hydrogen, the problem of oxygen contamination occurring in the hydrogen tests spawned the subject investigation, which was aimed at understanding oxygen effects exclusive of hydrogen. Although the oxidation behavior of vanadium and some vanadium alloys has been previously reported [4–7], there have only been a few studies on reaction rates as well as on the effects of interstitial concentration on the mechanical properties of alloys of specific interest for fusion applications, i.e., V–Cr–Ti. Vanadium, like other group V-A metals, has a strong affinity for oxygen, as well as a significant oxygen solubility. For example, using Smith's expression for oxygen solubility [8], the oxygen concentration of alpha-vanadium in equilibrium with the lowest oxide, V_9O, at 500°C is calculated to be 1.1% (by weight). Because oxygen has an even stronger affinity for titanium, oxygen in a V–Ti alloy may preferentially associate with the titanium. If the presence of titanium significantly affects the solubility and distribution of oxygen in the alloy, the mechanical properties of the alloy could be more sensitive to oxygen concentration than unalloyed vanadium. Accordingly, the present studies were aimed at determining the reaction kinetics of air and oxygen with V–Cr–Ti alloys and the effects of oxygen contamination on room temperature tensile properties.

2. Experimental

Two slightly different alloys with the following nominal compositions were investigated: V–5Cr–5Ti and V–

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Table 1
Compositions of V–Cr–Ti alloys

Nominal composition (wt%)	Heat ID	Concentration (wt%)			Concentration (wt ppm)			
		Cr	Ti	Fe	O	N	C	Si
V–5Cr–5Ti	ONRL	4.0	4.0	5.6	0.11	324	204	1100
V–5Cr–5Ti	832394	4.2	4.2	5.4	< 0.045	427	40	< 310
V–4Cr–4Ti	8326	3.1	3.1	4.1	0.022	310	86	780

4Cr–4Ti (concentrations are in wt%). Two heats of V–5Cr–5Ti were tested, whose chemistries are shown in Table 1. The heat identified as 832394 was produced commercially by Teledyne-Wah Chang and the other, identified as ORNL, was a 500 g heat produced at Oak Ridge National Laboratory. The composition of the single V–4Cr–4Ti heat, produced by Teledyne–Wah Chang, is also shown in Table 1. Note that the ORNL heat contains a significantly higher concentration of nitrogen and carbon than the other two heats. The alloys were tested in the form of small tensile specimens, nominally 0.76 mm thick with 1.5 × 7.6 mm long gage sections, that were either machined or stamped from warm-reduced sheet stock. Some of the tensile specimens were also stamped from a 0.76 mm sheet that had been autogenously welded, the welds being positioned transversely at the middle of the gage length. Following fabrication, the specimens were cleaned by acid-etching in a mixture of $HF–HNO_3$.

When exposed to low-pressure oxygen at 10^{-2}–10^{-4} Pa (10^{-4}–10^{-6} Torr), the vanadium alloys were placed in an ultra-high vacuum Sievert's apparatus consisting of a gas supply, an alumina reaction tube coupled to a vacuum system and a high temperature furnace around the reaction tube. High purity gas was admitted to the system through a controllable leak valve while the system was being evacuated by a turbomolecular pump. The pressure at the specimen was determined from the pumping speed, conductance of the system and ion-gage pressure measurements at the entrance and exit of the reaction tube. The temperature of the exposures was in the range 400 to 500°C, with the majority of tests being at 500°C. Exposures to ambient air were generally conducted in horizontal muffle furnaces, with the specimens in open alumina crucibles. In one test series, a V–4Cr–4Ti test specimen was exposed to air in a continuously recording microbalance system. The concentrations of interstitial impurities picked up by the specimens were monitored by weight changes and by selective chemical analyses after the exposures. The oxygen uptakes determined chemically agreed closely with the gravimetric measurements and confirmed the effectiveness of the latter detection method for monitoring the oxygen concentration.

Samples were given various heat treatments before and after exposure to oxygen to evaluate different microstructural features or phases within the alloy. These treatments were conducted in vacuum furnaces at pressures $\leq 10^{-4}$ Pa.

3. Results

3.1. Before-test properties

At the time this program was initiated, the standard pre-test annealing treatment for the V–Cr–Ti alloy was 1 h in vacuum ($< 10^{-4}$ Pa) at 1125°C. However, as the program progressed, the annealing temperature was lowered to 1050°C, based on an improvement in the alloy's fracture toughness properties. The 1125°C annealing temperature produced very different grain morphologies in the two V–5Cr–5Ti alloys. The ORNL heat retained relatively small grains, elongated in the direction of rolling, while heat 832394 developed much coarser, equiaxed grains. The grain morphology after the 1050°C annealing treatment was essentially the same for all heats and was similar to that of the ORNL heat annealed at 1125°C. Irrespective of the prior annealing treatment, the room temperature tensile properties of the alloys were quite similar prior to oxidation. All of the heats showed upper and lower yield points and the tensile elongations were consistently in the range 28–30%. Furthermore, aging the as-annealed V–5Cr–5Ti alloys in vacuum (10^{-6} Pa) at 500°C for times exceeding the exposures to oxygen did not significantly change the room temperature tensile strength or elongation.

3.2. Effects on mechanical properties

3.2.1. Low-pressure oxygen

Controlled amounts of oxygen were added (internally) to the alloys at 500°C by exposing them to pure oxygen gas for periods of 4–24 h at 1.3×10^{-4} and 2.6×10^{-4} Pa, respectively. In the case of the nominal V–5Cr–5Ti alloys, reaction rates with oxygen under these conditions were slightly greater for the ORNL finer-grained heat (7.9×10^{-3} compared with 4–6×10^{-3} mg cm^{-2} h^{-1}); however, the effect of a given oxygen uptake on room temperature ductility was much less for the finer-grained heat (Fig. 1). In samples as-oxidized for 24 h, the oxygen content of the ORNL heat increased by 600–900 ppm (by weight) and the tensile elongation decreased from 29% to

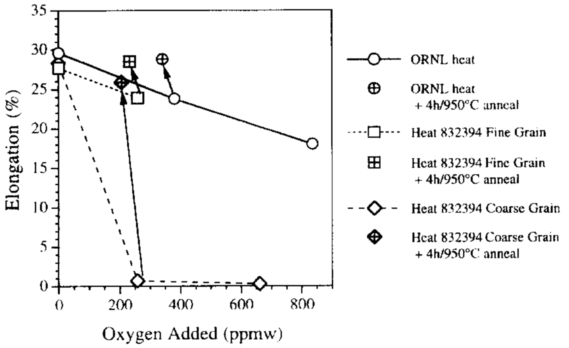

Fig. 1. Room temperature elongation of two nominal V–5Cr–5Ti alloys after oxidation at 10^{-4} Pa/500°C. Samples were heat treated for 100 h in vacuum at 500°C following oxidation.

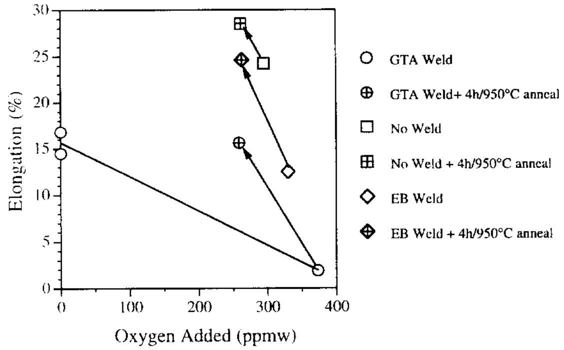

Fig. 2. Room temperature elongation of welded V–5Cr–5Ti (heat 832594) after oxidation at 500°C/10^{-4} Pa. Samples were heat treated for 100 h/500°C in vacuum following oxidation.

around 24%. After further aging for 96 h in vacuum at 500°C, the elongation dropped to 18%. The elongation of the ORNL heat was not affected by the initial 4 h oxidation treatment at 500°C, but further aging for 100 h at 500°C decreased its elongation from 29 to 24%. Under these same conditions, the elongation of heat 832394 with ASTM grain size 5 was reduced from 29 to 7% by the 24 h oxidation treatment and further aging for 96 h at 500°C resulted in fracture with essentially no yielding. The 4 h oxidation treatment at 2.6×10^{-4} Pa reduced its elongation to 16% and further annealing in vacuum for 100 h at 500°C again resulted in brittle fracture. As shown in Fig. 1, when the grain size of heat 832394 was reduced from ASTM 5 to ASTM 6, the decrease in ductility was significantly less for the same uptake of oxygen and was essentially the same as that of the ORNL heat. Similar results were obtained for specimens that were annealed at 1050°C prior to oxygen exposure. The latter specimens showed only a small reduction in ductility for a comparable oxygen pickup following the 100 h anneal at 500°C. Irrespective of the initial annealing treatment or grain size, a final vacuum anneal for 4 h at 950°C restored the tensile elongation of all heats to the as-received level, even for the most embrittling oxidation treatment (Fig. 1).

Effects of oxygen on the room temperature properties of welded specimens of heat 832394 were similarly evaluated. Fig. 2 shows results for specimens that had been welded by the gas–tungsten-arc (GTA) process. The addition of 250 ppm oxygen at 500°C produced a measurable reduction in elongation even in 4 h, but with the additional 100 h anneal at 500°C in vacuum the elongation was reduced as low as 2%. As observed with base metal specimens, further annealing at 950°C completely restored the ductility to its value in the as-welded condition. Similar results were obtained for electron-beam welded specimens, although the ductility decreases were less than those for the GTA-welded specimens (Fig. 2).

In a follow-up oxidation study using the nominal V–4Cr–4Ti heat, 1050°C was adopted as the standard pre-test annealing temperature, which resulted in a grain size close to that of the ORNL V–5Cr–5Ti heat. To assess its susceptibility to oxygen embrittlement, specimens were exposed to oxygen at 1.3×10^{-4} Pa at either 400 or 500°C, with and without a pre-oxidation exposure in air at the same temperature, respectively (Table 2). Exposing the non-preoxidized alloy at 500°C resulted in a pickup of 1375 ppm oxygen, and, after a subsequent vacuum anneal for 100 h at 500°C, the room temperature elongation

Table 2
Effects of pre-oxidation in air on embrittlement of V–4Cr–4Ti by oxygen at low pressure (annealed at 1050°C prior to exposure)

Exposure to air			Exposure to O_2 at 10^{-4} Pa			Vacuum anneal at 500°C	Yield strength (MPa)	Ultimate strength (MPa)	Elongation (%)
time (h)	temp. (°C)	oxygen added (ppm)	time (h)	temp. (°C)	oxygen added (ppm)	time (h)			
24	400	467	–	–	–	100	359	476	25.0
24	400	311	48	400	198	100	363	482	21.1
12	500	2119	–	–	–	–	374	470	24.8
12	500	2151	48	500	< 30	–	358	451	23.3
24	500	2163	48	500	< 30	100	366	460	23.8
–	–	–	48	500	1375	100	353	449	21.5

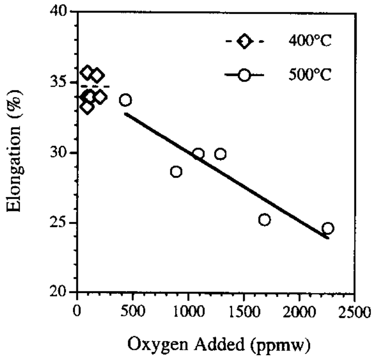

Fig. 3. Effect of low pressure oxidation at 400 and 500°C on the room temperature ductility of nominal V–4Cr–4Ti.

dropped from about 30 to 22%. When initially oxidized in air at 500°C, the alloy picked up 2100–2200 ppm oxygen, but there was essentially no further pickup of oxygen during a subsequent 48 h oxygen exposure at 10^{-4} Pa. Pre-oxidation in air at 400°C was not as effective in limiting oxygen ingress during a subsequent exposure at 400°C to 10^{-4} Pa oxygen (Table 2), probably because the oxide film formed in air at 400°C was not continuous after 24 h. The room temperature elongation after the combined air and oxygen exposures at 400°C (510 ppm oxygen pickup) decreased to 21%.

At reduced oxygen pressures of 10^{-2} and 10^{-3} Pa (Fig. 3), oxide films were not usually visually or microscopically apparent, although the weight changes decreased dramatically after the first 10–25 h. At 400°C, the highest oxygen uptake was only ~ 200 ppm and did not affect room temperature elongation. At 500°C the uptake of oxygen had little effect on ductility up to a level of 1360 ppm; but it caused a slight but measurable drop in ductility (to 25%) at the highest addition of 2260 ppm.

3.2.2. Air exposures

Embrittlement by air was investigated for V–5Cr–5Ti heat 832394 at 400, 450 and 500°C (Table 3). Under these conditions, most of the oxygen remained near the surface and had only a small effect on room temperature tensile elongation. (As observed for essentially all tests in this program, the yield and ultimate strengths were unaffected.) However, a subsequent heat treatment for 100 h at 500°C in high vacuum significantly lowered the elongation. A further heat treatment for 4 h at 950°C in high vacuum recovered the ductility of the specimen oxidized at 400°C that contained ~ 500 ppm, but ductility recovery was less for those oxidized at the higher temperatures containing ~ 1000 and ~ 2000 ppm. In the case of the 450 and 500°C exposures, there was a darkening of the specimen surfaces, indicative of an oxide film, which persisted even after the 100 h vacuum anneal at 500°C.

Table 3
Effect of air oxidation on room temperature properties of V–5Cr–5Ti (heat 832394) (annealed at 1125°C prior to exposure)

Air exposure conditions		Weight change (ppm)	Yield strength (MPa)	Ultimate strength (MPa)	Elongation (%)
time (h)	temp. (°C)				
As-oxidized (no anneals)					
4	400	323	337	482	26.5
24	400	441	363	442	26.2
25	400	647	359	463	28.3
25	450	1131	375	464	24.7
50	450	1391	383	464	16.3
25	500	1854	387	481	21.0
50	500	2901	388	443	5.0
Oxidized + vacuum annealed 100 h at 500°C					
4	400	203	403	459	13.3
24	400	500	400	425	4.0
25	450	1420	401	447	19.7
50	450	1647	400	441	13.5
25	500	1971	401	427	9.4
50	500	2928	387	419	9.4
Oxidized + vacuum annealed 100 h at 500°C and 4 h at 950°C					
4	400	206	327	445	29.6
25	400	500	327	466	27.2
25	450	956	362	494	19.2
50	450	1588	374	454	12.0
25	500	2290	401	428	7.2
50	500	3029	367	474	13.7

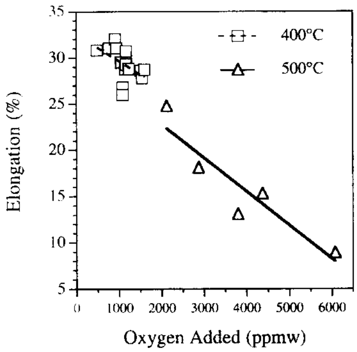

Fig. 4. Effect of oxidation in air at 400 and 500°C on the ductility of V–4Cr–4Ti.

Mechanical properties of the V–4Cr–4Ti alloy were also determined after exposure to ambient air at 400 and 500°C (Fig. 4). Even after 577 h, which increased the oxygen content by 1500 ppm, room temperature tensile properties were essentially unchanged by the 400°C exposures. (Total elongation averaged 29.3% with a standard deviation of only 1.7%). An oxide scale was observed on the surface to a thickness of ~ 2 μm (0.1 mil). The specimens also showed a hardness increase immediately below the scale, an indication of internal oxidation, but the depth of the increase was limited to ~ 10 μm. At 500°C the oxygen increases, shown in Fig. 4, were significantly higher than at 400°C, reaching 6080 ppm after 240 h, with a corresponding scale thickness of 3 μm. Room temperature elongation decreased with increasing exposure time and oxygen pick-up and was 8.9% after 240 h. Obviously, internal oxidation occurs at a much faster rate at 500°C than at 400°C, based on the effect on bulk mechanical properties. This can also be seen in Table 2, where a specimen that picked up 467 ppm of oxygen in air at 400°C shows a slightly lower elongation after subsequent vacuum annealing for 100 h at 500°C than comparable specimens that picked up as much as 1500 ppm oxygen at 400° (Fig. 4).

3.3. Oxidation kinetics

Oxidation rates of the V–4Cr–4Ti alloy in air were determined at 400 and 500°C, respectively. In the 400°C cyclic heating experiments, tensile specimens, annealed at 1050°C, were repeatedly heated to 400°C for 24 h and then cooled to room temperature. In a follow-up experiment, a single specimen was cycled nine times from 400°C to room temperature in air while its weight was continuously monitored in a microbalance system. Weight changes for the combined set of experiments are shown in Fig. 5. The data best fit a logarithmic time dependence:

$$\Delta W\,(\mathrm{mg/cm^2}) = 0.0851 \ln t(h) - 0.1786. \qquad (1)$$

The oxidation rates of V–4Cr–4Ti at 500°C were measured by exposing specimens individually to air for varying periods up to 240 h. The resulting weight changes are shown in Fig. 6. Based on a parabolic rate law, the parabolic rate constant was found to be 5.8×10^{-3} $(\mathrm{mg^2/cm^4 \cdot h})$. The V–5Cr–5Ti heat 832394, annealed at 1125°C, was also exposed to air at 400°C and 500°C (for 25 and 50 h, respectively) and weight changes were essentially the same as for the V–4Cr–4Ti alloy (Figs. 5 and 6).

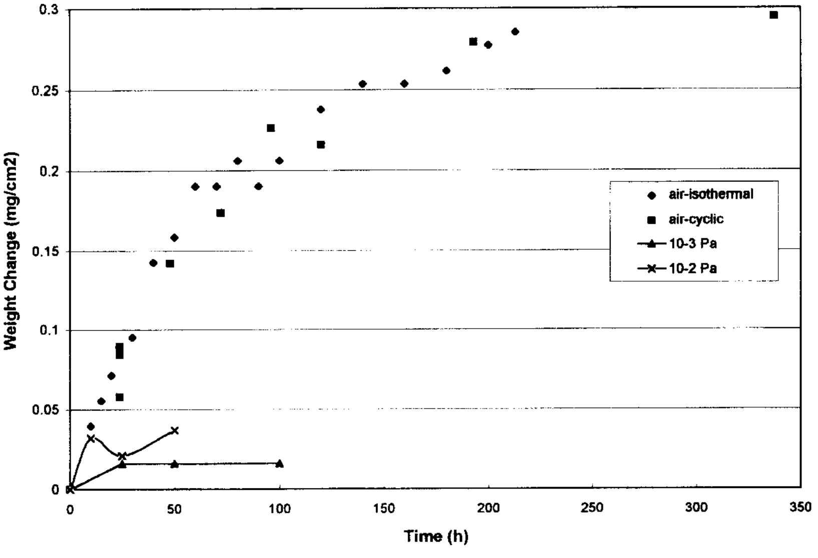

Fig. 5. Oxidation rates of V–4Cr–4Ti exposed to air or low pressure O_2 at 400°C.

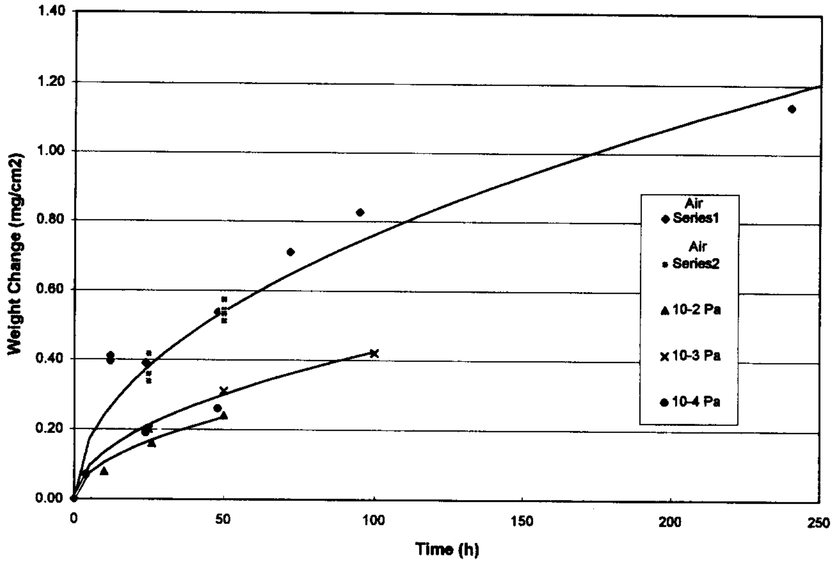

Fig. 6. Oxidation rates of V–4Cr–4Ti exposed to air or low pressure O_2 at 500°C.

The oxidation rates of V–4Cr–4Ti at oxygen pressures of 10^{-2}, 10^{-3} and 10^{-4} Pa were also measured at 500°C. As seen in Fig. 6, the rates at these reduced pressures were significantly lower than in air and were essentially independent of pressure within the lower pressure range itself. The rates decreased with time, indicative of a diffusion-controlled oxidation process. At 400°C the rates determined at pressures of 10^{-2} and 10^{-3} Pa were also much lower than in air, as shown in Fig. 5, and there was no significant change in weight after 10 h.

At 10^{-4} Pa, the weight changes of the ORNL V–5Cr–5Ti heat at 500°C closely matched those of the V–4Cr–4Ti alloy and the weight changes of both of these finer-grained heats were consistently greater than the corresponding weight changes of the coarser-grained V–5Cr–5Ti heat 834394.

4. Discussion

The oxidation kinetics at 400–500°C differed between the air exposures and exposures to low-pressure oxygen ($\leq 10^{-2}$ Pa). In air, exposures at 400 and 500°C produced a darkening of the external surfaces and metallographic examinations revealed thin surface oxide layers, which became more pronounced at the higher temperature. The oxidation rates in air measured over 200–300 h increased logarithmically with exposure time at 400°C and parabolically at 500°C. The logarithmic time dependence is indicative of oxidation controlled by chemisorption of oxygen or electric-field-induced transport of electrons or ions across the relatively thin oxide, while the parabolic dependence is typically seen for the growth of thicker oxide films, controlled by the solid-state diffusion of metal cations outward or oxygen-species inward. In contrast, specimens exposed at lower oxygen pressures remained bright and, based on metallographic examinations, were relatively free of macroscopic oxide films. During exposures for 50–100 h, the weight changes at 400 and 500°C were substantially smaller than those at equivalent times and temperatures in air. However, the oxidation rates at 500°C showed little variation with pressure from 10^{-4} to 10^{-2} Pa and subscribed closely to a parabolic time dependence (Fig. 6). This behavior suggests that internal oxygen diffusion is the primary rate controlling process in this lower pressure regime and that the concentration (activity) of oxygen at the surface does not vary significantly with the pressure. At 400°C the oxidation rate at 10^{-2} and 10^{-3} Pa after 10 h was below detectable limits.

At 500°C, exposure to oxygen for 4–24 h at 10^{-4} Pa resulted in near-surface pickup of oxygen, the specimen interior remaining relatively uncontaminated. Subsequent annealing in vacuum for 96–100 h at 500°C distributed the oxygen more uniformly over the specimen cross-section. In this condition, even the small amount of oxygen picked up in the 4 h exposures (which actually was less than the residual oxygen content of the alloys) substantially affected ductility, particularly in the case of coarse-grained materials. Since there was no hardening of the alloy matrix, i.e., yield strength was essentially unaffected, and the fractures were exclusively intergranular, oxygen penetration at 500°C appears to be primarily along grain boundaries. As reported by Godfrey et al. [9] an atom probe analysis of pure vanadium also showed enhanced concentrations of oxygen (and carbon) on a high angle grain boundary after exposure to air at 200°C. If oxygen is confined to the grain boundary, the local concentration of oxygen in this region will be much larger than the nominal bulk concentration and will increase as the grain boundary surface area decreases, i.e., as the grain size increases. These observations are in keeping with the pronounced effect of small levels of contamination on the tensile ductility of the coarser-grained materials. The higher uptake of oxygen by the finer-grained ORNL heat, with its correspondingly greater grain boundary surface area, is also consistent with grain boundary transport of oxygen. (Furthermore, using the bulk diffusion coefficient for oxygen in pure vanadium at 500°C, the annealing time predicted for oxygen to reach the specimen interior by matrix diffusion is much longer than 100 h.) Although the chemical state of oxygen on the grain boundary has not been defined, the effect on properties indicates that it is different from the residual oxygen in the as-received specimen, which is present as an oxide precipitate. This conclusion was also borne out by subsequently vacuum heat treating the 500°C-aged specimens for 4 h at 950°C. As shown in Fig. 2, the 950°C heat treatment essentially restored the ductility of a coarse-grained specimen of heat 832394, the elongation increasing from 0.7% before heat treatment to 24% after heat treatment. Based on previous oxidation studies of the Nb–1Zr alloy [10], we believe that, at the higher annealing temperature, oxygen was able to react with the titanium in the alloy to form an essentially incoherent precipitate, and its effect on ductility in this form was much less than in the pre-existing state.

The effects of grain size were also borne out in the tests of welded specimens after oxygen doping at 500°C. Since the autogenous welding induced grain coarsening, it is not surprising that the welded specimens showed even greater susceptibility to oxygen embrittlement than the coarse-grained non-welded specimens. Again the fractures of the welded specimens were predominantly intergranular and generally occurred in the heat-affected zone.

Based on these results, grain size will be an important parameter in evaluating the effect of oxygen contamination on candidate vanadium alloys for fusion applications. The current processing conditions for these alloys are designed to produce relatively fine-grained materials, which showed only minor reductions in ductility at the highest contamination levels examined in this study. However, to the extent that welds are used in the fabrication and assembly of reactor components, the resulting grain coarsening can be expected to magnify the embrittling effects of oxygen, if it enters at temperatures around 500°C. Another factor of importance to fusion applications is the operation of the alloys in a low-pressure deuterium/tritium environment. Under conditions where the V–Cr–Ti alloys in this study showed embrittlement by oxygen, subsequent exposure to hydrogen at 10^{-2} to 1 Pa increased the extent of embrittlement even further. Therefore, the synergistic effects of deuterium/tritium in combination with oxygen must be considered in assessing the properties of the reference vanadium alloys, especially for first wall and diverter applications.

The pattern of embrittlement in the low-pressure oxygen tests shows several similarities to that induced by oxygen contamination of the tantalum alloy T-111 (Ta–8%W–2%Hf) at 815°C [11]. T-111 and V–Cr–Ti are similar in that both alloys are based on group V elements with group VI and group IV elements as alloying additions. Both transgranular and intergranular fracture modes were observed in tensile tests of T-111 at lower temperatures, but fractures became increasingly intergranular at higher temperatures (> 1000°C). Embrittlement of T-111 can occur at relatively low oxygen concentrations (≥ 300 ppm) and the embrittlement is alleviated by higher temperature annealing (1300–1400°C). The model advanced by Liu et al. [11] to explain the embrittlement of T-111 by oxygen involved the combined effects of precipitation hardening of the matrix by coherent hafnium–oxygen suboxides and a thin, precipitate-free-zone bordering the grain boundaries. The intergranular fractures were attributed to ductile tearing of the weaker precipitate-free-zone at the grain boundary. Annealing at a higher temperature acted to coarsen the hafnium oxide precipitates and widen the precipitate-free-zone, thus, decreasing the susceptibility to transgranular cleavage and grain boundary tearing.

Other studies of the effects of high temperature aging on the ductility of T-111 may also have relevance to the embrittlement of V–Cr–Ti by oxygen at 500°C. Aging of T-111 in vacuum at 1040°C results in brittle fracture of the alloy in bend tests at −196°C and increases the susceptibility to room temperature embrittlement of the alloy by hydrogen contamination [11]. In examining the microstructure of T-111 after the 1040°C aging treatment, Stephens [12] found a much higher concentration of HfO_2 precipitates at the grain boundaries than in specimens aged at 925 or 1150°C, and he attributed the increased sensitivity to hydrogen and the effect on ductile–brittle transition temperature to this higher volume of precipitates. He proposed that the precipitates were the result of hafnium segregation to the grain boundary at 1040°C and suggested that tungsten increased hafnium grain boundary segregation. The absence of the effect at lower aging temperatures was explained by a slower hafnium diffusion rate, which limited segregation and at higher aging temperatures, by a faster hafnium diffusion rate, which promoted homogenization. There was no evidence of this segregation effect in Ta–W alloys containing 1% or less hafnium or in Ta–2%Hf, suggesting that the presence of tungsten increased the degree of hafnium grain boundary segregation. Although Stephens attributed the aging effects in T-111 to hafnium segregation to the grain boundary, he did not discuss the possibility that the precipitate-free-zone at the grain boundary, reported by Liu et al. [11] could be a related segregation feature.

Unlike the oxygen embrittlement of T-111 at 825°C, which induces a combination of transgranular cleavage and intergranular fracture at room temperature, the oxygen embrittlement of the present V–Cr–Ti alloys at 500°C leads to predominantly intergranular separation. Furthermore, while the tensile strength of the T-111 increases directly as a function of oxygen uptake, that of the V–Cr–Ti alloys remains unchanged. Accordingly, the debilitating effect of oxygen in the V–Cr–Ti alloys appears to be manifested primarily at grain boundaries and there is less effect on the alloy matrix. There are at least two different mechanisms that can be advanced to explain the grain boundary embrittlement of the present V–Cr–Ti alloys. The first is a precipitation of titanium–oxygen clusters or precipitates on the boundary as a result of titanium segregation and oxygen diffusion on the boundary, which weakens the boundary. An alternative mechanism can be modeled after the precipitate-free-zone proposed for the intergranular fracture of T-111 [11]. Although bulk diffusion of oxygen into the matrix appears to be more limited than for T-111, an oxide precipitation zone could nevertheless exist in the immediate vicinity of the boundary, which is fed by oxygen diffusion along the grain boundary. This, combined with a precipitate-free-zone resulting from titanium segregation to the boundary, would provide the same conditions that were postulated to explain grain boundary tearing in T-111. Alternatively, the depletion of titanium near the boundary, of itself, could potentially lead to gain boundary tearing, since titanium is a strong solid-solution strengthener. In the latter case, oxygen rather than aging must be the instrument causing segregation, since there is no effect of annealing the alloy at 500°C in the absence of oxygen. The restoration of specimen ductility by annealing at 950°C is consistent with any of the aforementioned mechanisms. Such an anneal would coarsen any precipitates on the boundary and smooth any titanium concentration gradient bordering the boundary.

It is not clear from the present results whether the embrittlement mechanism operative in the air exposures was the same as that in low-pressure oxygen and in the oxygen-doping experiments. The embrittling effects of oxygen introduced at 10^{-4} Pa was manifested exclusively at grain boundaries and, the smaller the grain boundary surface area, the larger the effect. The oxygen uptake in air was much greater and was proportioned between a thin oxide scale and a hardened zone under the scale. Unfortunately, it is not possible to discern the extent of internal grain boundary oxidation in the air tests from the overall weight changes. However, in other systems (alumina-formers) where catastrophic grain boundary oxidation has been observed at low oxygen pressures, the formation of an oxide film at higher oxygen pressures has suppressed the transport of oxygen on the grain boundary [13]. Some evidence that this may occur in the V–4Cr–4Ti system is seen in the results of specimens that were pre-oxidized in air at 500°C and then oxygen doped by exposure at 10^{-4} Pa. The pre-oxidation completely suppressed the uptake of oxygen at the lower pressure. A similar preoxidation at 400°C was less effective in limiting the ingress of oxygen at 10^{-4} Pa, apparently because the oxide film is much thinner at 400°C. It was also found that the 950°C heat treatment was less effective in restoring the ductility of air-oxidized V–5Cr–5Ti specimens than for oxygen-doped specimens. Whatever the mechanism of the ductility loss in the air tests, the reduction of elongation for the reference test specimen geometry was at least as great as that resulting from internal oxidation at lower oxygen pressures.

5. Summary and conclusions

Two vanadium alloys, nominally V–5Cr–5Ti and V–4Cr–4Ti, were exposed to oxygen-containing environments at 400–500°C in order to measure oxidation rates and effects of oxygen on room temperature tensile properties. The major findings were:

(1) In air at 0.1 MPa (1 atm), oxygen uptake was logarithmically dependent on exposure time at 400°C and parabolically dependent at 500°C. At lower oxygen partial pressures ($\leq 10^{-2}$ Pa), oxygen uptake at 400°C was below measurable limits after the first 10–25 h. At the lower pressures, the rate of uptake at 500°C was also parabolic, but the rate was much lower than in air and did not vary over the pressure range 10^{-2}–10^{-4} Pa.

(2) At 400–500°C the extent of penetration of oxygen into the vanadium alloys was a relatively small fraction of the specimen cross-section after exposure to oxygen at 10^{-4} Pa for up to 24 h and the room temperature ductility loss was minor. However, after subsequent heat treatment in vacuum at 500°C for 100 h, the fracture cross-section of the coarser-grained V–5Cr–5Ti heat became distinctly intergranular, and the elongation dropped to values approaching zero. Further heat treatment at 950°C for 1 h was generally effective in recovering ductility, presumably by the formation of an incoherent titanium oxide precipitate.

(3) The primary effect of oxidation and aging at 500°C on room temperature tensile properties was to reduce ductility. There was little or no effect on yield strength or ultimate tensile strength. In the absence of oxygen, aging at 500°C did not affect the ductility of the alloys.

(4) Loss of ductility was greater in welds or in samples annealed at higher temperature (≥ 1100°C) before oxidation. The ductility loss correlated with the grain size of the specimens.

(5) Possible embrittling mechanisms include grain boundary weakening from oxidation reactions or weakening of the near-boundary regions caused by titanium diffusion to the oxygen-enriched boundary.

As expected, the results of these experiments show that the tensile ductility of the V–Cr–Ti alloys is affected by exposures to oxygen-containing environments. However, the magnitude of the effect depends on the processing history and subsequent heat treatment and is not quantifiable in terms of the initial alloy chemistry. Therefore, the application of vanadium alloys as fusion reactor first wall and diverter components will require consideration of processing parameters (particularly welds) in setting limits on oxygen contamination. These limits are also likely to be lowered by the presence of interstitial protium atoms in the vanadium alloy lattice.

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