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Effect of hydrogen on the low-temperature mechanical properties of V–5 at % Ti alloys

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The effects of grain size and hydrogen in solid solution or as hydrides on the strength and ductility of V–5 at % Ti was studied over the temperature range 15–448 K. Comparison of the strength and ductility characteristics of hydrogenated alloys where hydrides were not observed down to 78 K (1.8 and 1.9 at % H alloys) or where hydrides were observed to form near 230 K (3.8 and 3.9 at % H alloys) indicated that the presence of hydride precipitates had no apparent influence on the strength or ductility characteristics. It appears that the main consequence of hydride precipitation is that hydrogen is removed from solid solution making strengthening less effective than expected based on the total hydrogen content. Decreasing grain size from 31 μm to 8 μm had no apparent effect on ductility in the nonhydrogenated alloys (< 0.05 at % H) but it did increase the strength over most of the temperature range and especially at 15 K. In the hydrogenated alloys this decrease in grain size lowered the transition temperature about 10 K and it appreciably increased the degree of ductility return at 78 K and below. The ductility return below 78 K peaked near 50 K before decreasing below 30 K with the improvement in ductility being greatest in the alloys with the lower hydrogen contents.

1. Introduction

Refractory metal alloys offer great promise as potential materials for fusion reactor first wall applications and vanadium alloys appear to offer more promise than other refractory metal alloys [1, 2]. Of the different possible vanadium alloys, V–Ti alloys show desirable properties and there is a need to develop a more extensive data base of their mechanical properties and on the effect of the environment on these properties [1]. The mechanical properties of various vanadium alloys have been documented [3] and the effect of hydrogen, which is present in the reactor, has been evaluated in V–Ti alloys [4–6]. It has been shown that hydrogen embrittlement of vanadium is markedly reduced by the addition of titanium. This is a result of an increase in hydrogen solubility and a decrease in hydrogen diffusivity with increasing titanium additions in vanadium [4, 7].

These previous results on the influence of hydrogen on the mechanical properties of V–Ti alloys have shown that in those alloys where hydrogen does induce some embrittlement the ductility returns near 100 K and improves with decreasing temperature to 78 K, the lowest temperature previously studied [5, 6]. This appears to be a general phenomenon in Group VA metals and alloys containing hydrogen [8]. However, information is lacking concerning how hydrogen affects the mechanical behaviour of these metals and alloys at temperatures below 78 K. To study the mechanical behaviour and the ductility return at temperatures below 78 K, a V–5 at % Ti alloy was chosen because earlier work showed that this alloy has a high hydrogen solubility ($\sim$ 2 at %) [9] and that it shows ductile–brittle–ductile behaviour with decreasing temperature [5, 6]. Several hydrogen contents were chosen in order to be able to evaluate the ductility return when hydrogen was in solution or precipitated as hydrides. Two different grain sizes were evaluated because grain size has been shown to have a pronounced influence on the ductility return in hydrogenated Nb–V alloys [8].

2. Experimental procedure

Consumable arc-melted vanadium and 99.96% pure titanium sponge were used to prepare the V–5 at % Ti alloy used in this investigation. Ingots of about 14 mm diameter were prepared by arc melting under purified argon. The ingots were reduced to a final diameter of 2.54 mm by a controlled sequence of swaging at room temperature followed by intermediate vacuum anneals at 1123 K. The finished rod was cut into 50.8 mm length specimens and a 25.4 mm gauge length, 2.03 mm diameter, was centreless ground in each specimen. These as-ground samples were electropolished in a 6 vol % perchloric acid, 94 vol % methanol solution maintained at 203 K in order to remove all grinding marks and provide a clean surface before subsequent thermal treatments. Final annealing of specimens was performed in a vacuum of 10 μPa for 1 h at either 1123 or 1223 K, giving rise to average grain sizes of 8 and 31 μm, respectively. Tensile tests were performed at temperatures between 448 and 15 K using an initial strain rate of $8.3 \times 10^{-5}\,s^{-1}$.

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Chemical analysis by vacuum fusion on several samples showed the average titanium, oxygen, nitrogen and hydrogen contents of the starting alloy to be 4.7, 0.05, 0.01 and < 0.05 at %, respectively. Hydrogen charging of the tensile specimens was done using a charging procedure described previously [9, 10]. For the specimens with the 31 µm grain size the average hydrogen contents obtained were 0.3, 1.8 and 3.8 at %. For the specimens with the 8 µm grain size the average hydrogen contents obtained were 1.9 and 3.9 at %. Hydrides were detected in the V–5 at % Ti alloy with 3.9 at % hydrogen at a temperature of about 230 K, whereas hydrogen remained in solution down to 78 K, the low temperature limit of our equipment, in the alloy containing 1.9 at % hydrogen. Therefore, it was possible to evaluate the effect of hydrogen in solution or as hydride precipitates on the mechanical properties of a V–5 Ti alloy.

Internal friction measurements were performed to detect hydride formation in the hydrogenated alloys [11–13]. The procedure used has been described earlier [11]. Two additional procedures were used to establish the presence of hydride precipitates, metallographic observations and the twisting of wires mounted in a torsion pendulum during cooling below room temperature. The visual procedure involved optical microscope observation of samples containing hydrogen as they were cooled below room temperature and has been previously described [9]. The twisting procedure involves cooling a wire of the sample mounted in an inverted torsion pendulum and observing when rotation of the wire began indicating the initiation of hydride formation [14, 15].

3. Results

Fig. 1 shows the internal friction, Q^{-1}, versus temperature curves for V–5 at % Ti containing 1.9, 3.9 and 9.2 at % hydrogen. Included on the figure are the temperatures where hydride precipitates were observed by metallographic observations and by twisting in an inverted torsion pendulum. At a hydrogen content of 1.9 at % no internal friction peak was observed and the hydrogen remained in solution down to a temperature of 78 K, the minimum temperature analysed. Previous work on a V–5 at % Ti alloy showed that a very small internal friction peak was observed and hydrides were metallographically observed to start forming at 203 K at a hydrogen content of 2.3 at % [11]. This indicates that 1.9 at % hydrogen in V–5 at % Ti is very close to the maximum that can be retained in solution down to 78 K. At a hydrogen content of 3.9 at % the internal friction curve shows a peak and hydride precipitates were observed both metallographically and by twisting in the torsion pendulum at a temperature of about 225 K. At a hydrogen content of 9.2 at % the internal friction peak becomes very pronounced and hydrides are detected at a temperature near 290 K. Because one of the intents of this study was to evaluate any difference in the effect of hydrogen on the mechanical behaviour of V–5 at % Ti when it remains in solution or precipitates as hydrides, a maximum hydrogen content of 3.9 at % in V–5 at % Ti was investigated in order to minimize the difference in hydrogen content.

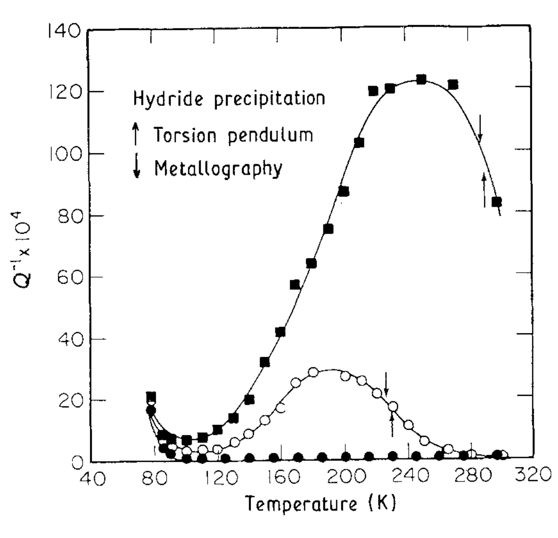


Figure 1 Internal friction, (Q^{-1}) versus temperature for hydrogenated V–5 at % Ti alloys. (●) 1.9 at % H, (○) 3.9 at % H, (■) 9.2 at % H.

Figs 2 and 3 show the effect of hydrogen on the temperature dependence of the yield stress and reduction of area at fracture in the V–5 at % Ti alloy with a grain size of 31 µm. For the pure alloy (< 0.05 at % H)

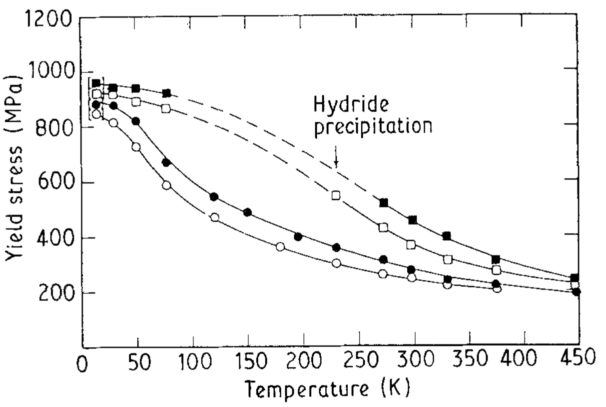


Figure 2 Temperature dependence of the yield stress for non-hydrogenated and hydrogenated V–5 at % Ti alloys with a grain size of 31 µm. (○) < 0.05 at % H, (●) 0.3 at % H, (□) 1.8 at % H, (■) 3.8 at % H, [ ] serrated flow.

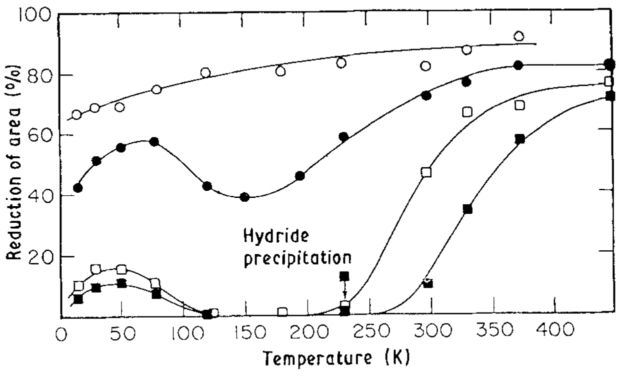


Figure 3 Temperature dependence of reduction of area for non-hydrogenated and hydrogenated V–5 at % Ti alloys with a grain size of 31 µm. For key, see Fig. 2.

and the alloy containing 0.3 at % H the yield stress smoothly increases with decreasing temperature (Fig. 2). As shown in Fig. 3, these alloys remain ductile throughout the temperature range 15–448 K, although the addition of 0.3 at % H to V–5 at % Ti does cause a reduction in ductility at low temperatures. In the alloys containing 1.8 or 3.8 at % H the increase in yield stress with decreasing temperature is more pronounced than in the other alloys, but these alloys become very brittle near 250 K and their curves are shown as dashed lines because valid yield stress values could not be obtained. The brittle nature of the 1.8 and 3.8 at % H alloys is readily apparent in Fig. 3. Comparison of the hydrogen-containing alloys in Fig. 3 shows that their ductility increases at temperatures below about 120 K. This is the ductile–brittle–ductile behaviour that has been observed in various hydrogenated solid solution refractory metal alloys [5, 6, 8, 10, 16–19]. The results in Fig. 3 show that although the ductility does continue to improve below 78 K, the minimum temperature investigated in these earlier studies, it reaches a maximum below 50 K and then decreases again. At temperatures of 78 K and below, yield stress behaviour is again observed and the yield stresses are shown for the 1.8 and 3.8 at % H alloys.

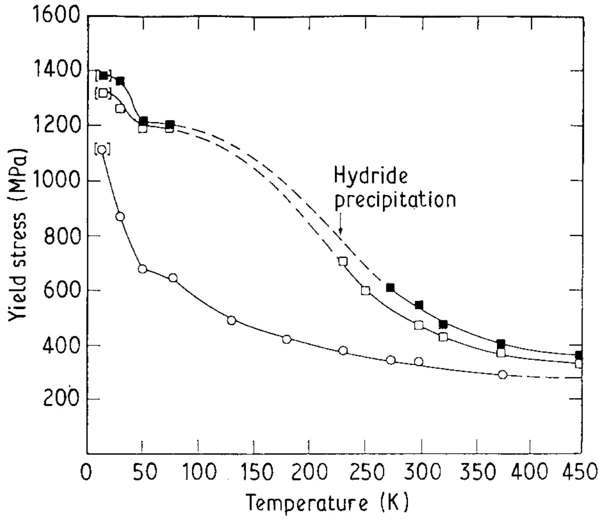


Figure 4 Temperature dependence of the yield stress for non-hydrogenated and hydrogenated V–5 at % Ti alloys with a grain size of 8 μm. (○) < 0.05 at % H, (□) 1.9 at % H, (■) 3.9 at % H, [ ] serrated flow.

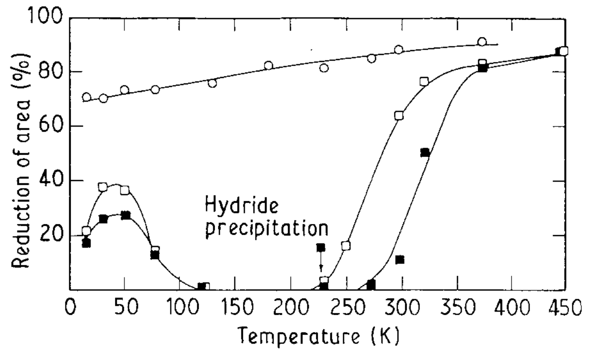


Figure 5 Temperature dependence of reduction of area for non-hydrogenated and hydrogenated V–5 at % Ti alloys with a grain size of 8 μm. For key, see Fig. 4.

Comparison of the 1.8 and 3.8 at % H alloys shows that their mechanical property behaviour is very similar throughout the temperature range studied.

Figs 4 and 5 show the effect of hydrogen on the temperature dependence of the yield stress and reduction of area, respectively, for the V–5 at % Ti alloys with a grain size of 8 μm. Although the pure (< 0.05 at % H) and the hydrogenated V–5 at % Ti alloys with the 8 μm grain size are stronger than the corresponding alloys with the 31 μm grain size, the effect of hydrogen and decreasing temperature on the mechanical behaviour are similar. For both grain sizes the hydrogenated alloys become brittle at about 250 K and show an improvement in ductility at temperatures below about 120 K. The curves in Fig. 4 are shown as dashed lines in this temperature region because valid yield stress values could not be obtained. However, there is an appreciable increase in the yield stress below 50 K in all the 8 μm alloys (Fig. 4) as compared to the corresponding 31 μm grain size alloys (Fig. 2).

A comparison of the 8 and 31 μm grain size alloys shows that all the hydrogenated alloys, except that containing 0.3 at % H, undergo serrated flow and exhibit no yield-point behaviour at 78 K. The non-hydrogenated and 0.3 at % H alloys undergo the typical upper and lower yield point behaviour at both 78 and 50 K that is observed at the higher temperatures. At 50 and 30 K the 1.8 and 3.8 at % H alloys with the 31 μm grain size continue to deform by serrated flow without showing any yield-point behaviour while all the 8 μm grain size alloys, hydrogenated and non-hydrogenated, show upper and lower yield-point behaviour and only some serrated flow in the hydrogenated alloys near maximum load at 50 K. The 0.3 at % H alloy behaves in a similar manner to the higher hydrogen content alloys at 30 K but the 8 μm grain size alloy with < 0.05 at % H still shows typical upper and lower yield-point behaviour at this temperature. At 15 K all of the alloys of both grain sizes, hydrogenated and non-hydrogenated, showed pronounced serrated flow behaviour and maximum values of the load were used for calculating yield stresses.

The brittle nature of the 1.9 and 3.9 at % H alloys with an 8 μm grain size is shown in Fig. 5 and the behaviour is very similar to that observed for the corresponding alloys with a 31 μm grain size. The results in Fig. 5, like those in Fig. 3 for the 31 μm grain size alloys, show the ductility improvement below78 K reaches a maximum below 50 K and then decreases again. However, the improvement in ductility below 78 K is more pronounced for the finer grain sized alloys. This is in agreement with results obtained on Nb–V alloys [8]. Comparison of the 8 μm grain size 1.9 and 3.9 at % H alloys shows that their mechanical property behaviour is very similar throughout the temperature range studied as is observed for the corresponding alloys with a 31 μm grain size. Comparison of the reduction of area curves in Fig. 5 for the 8 μm grain size 1.9 and 3.9 at % H alloys shows that the transition temperatures are about 275 and 320 K, respectively, if the transition temperature is taken as the temperature where the average of the maximum and minimum reduction of area values occurs. For the coarser grained hydrogenated alloys the corresponding temperatures for the 1.8 and 3.8 at % H alloys are 285 and 330 K. It appears that the hydrogenated finer grain size V–5 at % Ti alloys showed improvement in the brittle–ductile transition temperature, the maximum reduction of area values obtained and the degree of ductility return below 78 K.

4. Discussion

The yield stress results for the hydrogenated 31 μm grain size alloys (Fig. 2) are replotted in Fig. 6 to show the increment of strengthening resulting from the hydrogen additions over the temperature range 15–448 K. As previously observed in vanadium and various vanadium alloys [6, 19, 20], strengthening by hydrogen in these materials is a thermally activated process and strengthening is most pronounced in the temperature region where the ductility is minimal. Also shown in Fig. 6 is the temperature where hydride precipitation was observed to occur in the 3.9 at % H alloy in Fig. 1. While hydrides were not detected down to 78 K, the minimum temperature analysed, in the 1.8 at % H alloy the effect of hydrogen on strengthening was much the same as that for the 3.8 at % H alloy. The downward displacement of strengthening in the 1.8 at % H alloy, as compared to the 3.8 at % H alloy, is most likely a result of the higher hydrogen content in the latter alloy. However, as will be discussed later, the strength of the 3.8 at % H alloy near the hydride precipitation temperature and below, where measurements of yield strengths could be made, is less than predicted based on its hydrogen content. This is expected as some of the hydrogen precipitates from solid solution.

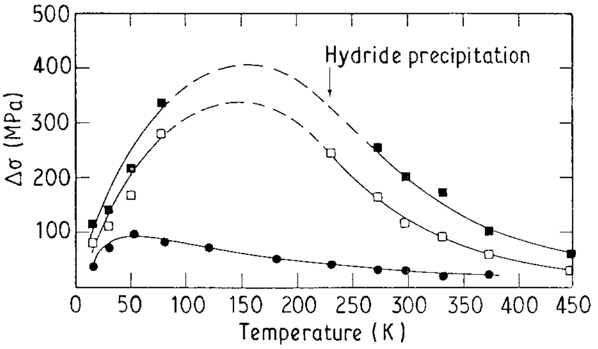


Figure 6 Temperature dependence of the difference in yield stress between hydrogenated and non-hydrogenated V–5 at % Ti alloys (Δσ) with a grain size of 31 μm. (●) 0.3 at % H, (□) 1.8 at % H, (■) 3.8 at % H.

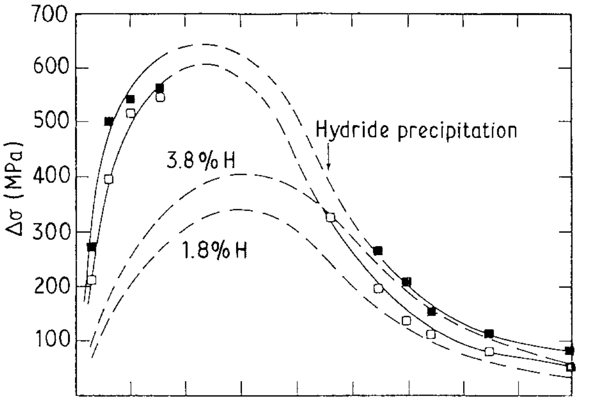


Figure 7 Temperature dependence of the difference in yield stress between hydrogenated and non-hydrogenated V–5 at % Ti alloys (Δσ) with a grain size of 8 μm. Curves for the 31 μm grain size 1.8 and 3.8 at % H alloys are also shown for comparison. (□) 1.9 at % H, (■) 3.9 at % H.

The yield stress results for the hydrogenated 8 μm grain size alloys (Fig. 4) are replotted in Fig. 7 to show the increment of strengthening resulting from the hydrogen additions over the temperature range 15–448 K. The strengthening resulting from hydrogen additions to the 8 μm grain size alloys shows a similar trend to that for the 31 μm grain size alloys, which are also included in Fig. 7 for the corresponding hydrogen contents. However, the maximum strengthening resulting from similar hydrogen additions appears to be appreciably greater in the 8 μm grain size alloys. This difference in behaviour is mainly because of the much greater effect of hydrogen on strengthening in the 8 μm grain size alloys at temperatures of 78 K and below. At temperatures of 230 K and above strengthening from the hydrogen additions was similar in the different grain size alloys. The only apparent difference in stress–strain characteristics of the hydrogenated 8 and 31 μm grain size alloys that could account for the difference in strengthening at temperatures of 78 K and below was that the 31 μm grain size alloys showed no yield-point behaviour and deformed by serrated flow at 78, 50 and 30 K, whereas the 8 μm grain size alloys showed upper and lower yield points at 50 and 30 K. At 78 K the hydrogenated 8 μm grain size alloys underwent serrated flow during yielding, just like the 31 μm grain size alloys.

The serrated flow behaviour observed in the hydrogenated V–5 at % Ti alloys at temperatures of 78 K and below appears to be similar to what has been observed for bcc metals like niobium [21, 22]. The irregularities in the apparent development of serrated flow at these low temperatures is related to its dependence on many of the parameters associated with the deformation conditions, such as temperature, deformation rate, dimensions of specimens, impurities and microstructure. The effect of impurity content on serrated flow is evident in the 31 μm grain size alloys where serrated yielding occurred at 78, 50 and 30 K in the 1.8 and 3.8 at % H alloys but only at 30 K in the 0.3 at % H alloy and not at any of these temperatures in the non-hydrogenated alloy. This is in accord with observations in aluminium showing that the temperature of the onset of discontinuous deformation is lower as the impurity content decreases [21]. In the hydrogenated 8 μm grain size alloys serrated flow was observed at 78 K but not at 50 and 30 K. At 15 K all the alloys showed pronounced serrated flow most likely resulting from twinning. The differences in the strengthening behaviour between the 8 and 31 μm grain size alloys with corresponding hydrogen contents at 50 and 30 K are not easily explained. It could be that these differences are a consequence of more effective hydrogen interactions with dislocations in the 8 μm grain size alloy in this temperature region (compare Figs 2 and 4). However, the fact that serrated flow was observed at 78 K in both the 8 and 31 μm grain size hydrogenated alloys makes this unlikely. In addition, the appreciably better ductility of the 8 μm grain size hydrogenated alloys at 30 and 50 K seems to contrast with this reasoning (compare Figs 3 and 5). The observations that both the strength and ductility of the 8 μm grain size alloys are significantly greater at 30 and 50 K, whereas at 78 K, where the corresponding alloys of both grain sizes showed serrated yielding, only the strength is better, suggests that the difference in strengthening behaviour is related to the improved ductility in the 8 μm grain size alloys.

Figs 8 and 9 show the effects of hydrogen on the yield stresses of the 31 and 8 μm grain size alloys at temperatures between 373 and 230 K. The data show a good correlation with (at % H)$^{2/3}$ except at 230 K where hydride precipitation was observed to occur in the V–5 at % Ti alloy with 3.9 at % H. A two-thirds dependence of strengthening on hydrogen content is in agreement with models of solid solution hardening in bcc metals and alloys [23, 24]. From internal friction results on V–3.9 at % Ti alloys it was shown that a strong peak believed to be due to Ti–H complexes in the matrix was observed near 60 K whether or not hydride precipitates were observed to form [16]. The presence of the peak was taken to indicate that the binding energy of hydrogen atoms to titanium atoms was so strong that hydrogen was retained in the matrix even when hydride precipitates formed. Therefore, the lower than predicted strength at 230 K for the 3.8 and 3.9 at % H alloys (Figs 8 and 9) is expected because some of the hydrogen starts to precipitate as hydrides, as was observed at 230 K (Fig. 1), but the continued strengthening is most likely still a result of the hydrogen in the matrix and not a consequence of the hydride precipitates. Presumably strengthening in these higher hydrogen content alloys can be explained in a similar manner to that proposed previously for V–5 at % Ti containing 0.33 at % H, where stress-induced ordering of hydrogen atoms was shown to predict strengthening in good agreement with the experimental results [6]. Because of the lack of strength data in the peak regions of the curves in Figs 6 and 7, similar calculations cannot be reliably done for these higher hydrogen content alloys. The observation that there was consistent behaviour for the 1.8 and 3.8 at % H alloys (Fig. 8) and the 1.9 and 3.9 at % H alloys (Fig. 9) on the effect of hydrogen on strengthening at temperatures above 230 K, supports the experimental findings that hydride precipitation in the 3.8 and 3.9 at % H alloys was negligible at temperatures above 230 K (Fig. 1).

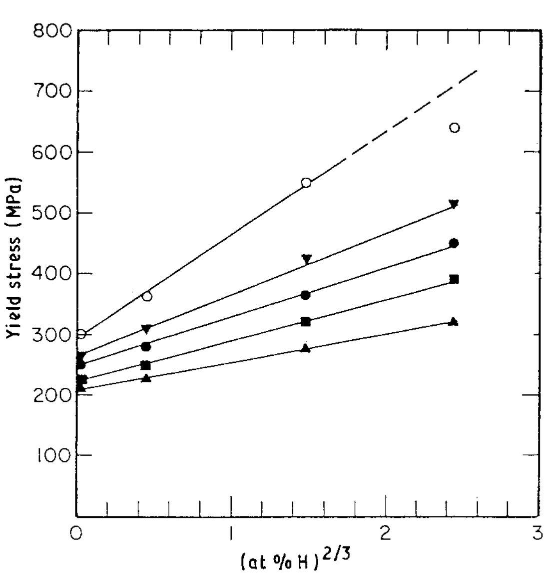


Figure 8 Effect of hydrogen on the yield stress of V–5 at % Ti with a grain size of 31 μm. (○) 230 K, (▼) 273 K, (●) 298 K, (■) 330 K, (▲) 373 K.

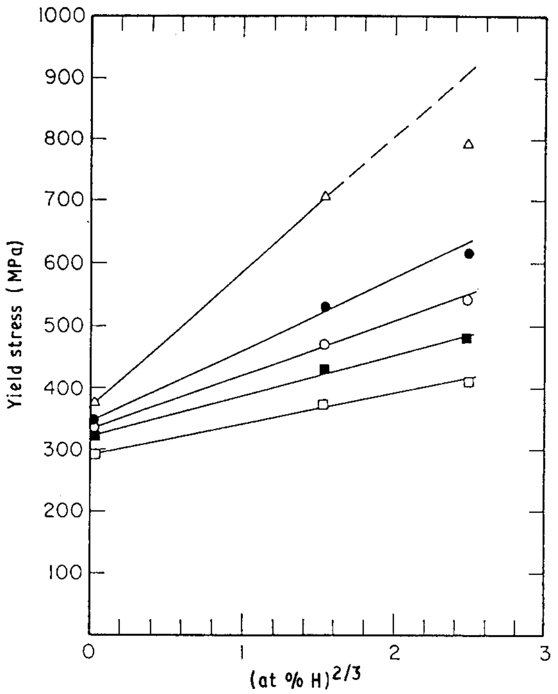


Figure 9 Effect of hydrogen on the yield stress of V–5 at % Ti with a grain size of 8 μm. (△) 230 K, (●) 273 K, (○) 298 K, (■) 320 K, (□) 373 K.

The results for the effect of hydrogen on ductility in the different grain size alloys in Figs 3 and 5 show that the 1.8 and 3.8 at % H alloys and the 1.9 and 3.9 at % H alloys undergo a similar ductile–brittle–ductile behaviour. The effect of the higher hydrogen content is to increase the transition temperature. Therefore, hydride precipitates, which were not detected in the 1.9 at % H alloy down to 78 K, are not necessary for the ductile–brittle behaviour and it is most unlikely that they are responsible for the brittle behaviour even in the 3.8 and 3.9 at % H alloys. In these latter alloys the ductility is reduced to near zero prior to any indication that hydride precipitates have formed. This observation, in conjunction with the previous observation that hydrogen strengthening in the V–5 at % Ti alloys is in accord with a solid solution model at temperatures above 230 K, strongly supports the contention that it is the hydrogen in solution that controls the ductility of these alloys.

The ductility return near 78 K in the hydrogenated V–5 at % Ti alloys is similar to what has been observed previously in Group V–A metals and alloys (5, 6, 8, 9, 19, 25). The beneficial effect of a finer grain size on the degree of the ductility return [8] is substantiated by the present results. However, the ductility decreases again at 15 K. At 15 K all of the alloys, hydrogenated or non-hydrogenated, deformed solely by serrated flow, with the serrations being more pronounced in the 8 μm grain size alloys. In all of the 31 μm grain size alloys and in the non-hydrogenated 8 μm grain size alloy a single neck formed in the gauge length of the tensile specimen. In the non-hydrogenated alloys pronounced necking still occurred even though deformation was solely by serrated flow. In the hydrogenated 8 μm grain size alloys numerous necks formed along the gauge length of the tensile specimen, their number being equal to the number of serrations on the load–elongation curve. However, each neck was not very pronounced, thereby limiting the reduction of area. Similar behaviour has been observed in niobium specimens deformed near liquid helium temperatures [26]. The pronounced serrated flow behaviour at 15 K cannot be the cause of the loss in ductility in the hydrogenated alloys because it is also observed in the non-hydrogenated alloys which show pronounced ductility at this temperature (Figs 3 and 5). In addition, the difference in necking behaviour between the different grain size alloys cannot be attributed to the difference in grain size because single necks formed in both the 8 and 31 μm grain size non-hydrogenated alloys. In addition, the difference in grain size studied here had no apparent effect on ductility in the absence of hydrogen (Figs 3 and 5). Similar observations were made in V–Nb alloys [8]. It appears that a combined hydrogen–grain size effect must be responsible for the difference in deformation behaviour of the hydrogenated 8 and 31 μm grain size alloys. However, it is not apparent from this study what this interaction is or how it would lead to a pronounced change in necking characteristics. Because new necks are evidently formed during each load drop in the hydrogenated 8 μm grain size alloys, rather than a continuation of deformation in the initial neck, it may be that work hardening is more pronounced in the finer grain size hydrogenated alloys or that they are more strain-rate sensitive. However, there is no evidence to support any differences in the work-hardening behaviour or strain-rate sensitivity of the 8 and 31 μm grain size hydrogenated alloys.

It was previously proposed that the ductility return observed near 78 K in hydrogenated V–Nb alloys resulted from hydrogen trapping at grain boundaries [8]. Because the finer grain size alloys have a greater number of trapping sites, a lower hydrogen concentration exists within the grains. These previous results suggest that it is the hydrogen within the grains that is primarily responsible for the mixed transgranular–intergranular crack propagation observed once the intergranularly initiated crack becomes unstable [8]. In general, it was observed that cracks were observed to initiate intergranularly in non-hydride forming alloy systems (hydride precipitates not observed down to 78 K) and transgranularly in hydride forming alloy systems. The cracks then propagated transgranularly across the specimen during fracture in both hydride and non-hydride forming alloy systems [5, 8, 10, 17, 19]. We did not investigate the initiation of cracks in the different hydrogenated alloys, but the fracture surface characteristics of the 8 and 31 μm grain size alloys at temperatures above 78 K were essentially the same as those reported previously in various Group VA alloys [5, 8, 10, 17, 19]. The difference in grain size had some apparent effect on fracture characteristics at these temperatures in addition to the corresponding fracture features being much smaller in the 8 μm grain size alloys. At 448 K all the hydrogenated alloys of both grain sizes fractured in a ductile manner similar to that of the non-hydrogenated alloys. In the transition region where the ductility rapidly decreases for the higher hydrogen content alloys, the fracture surfaces of the 31 μm grain size alloys show both transgranular cleavage and intergranular fracture, with the amount of intergranular fracture increasing with decreasing temperature. Intergranular failure becomes dominant in these alloys in the low ductility region. The corresponding 8 μm grain size alloys mainly exhibit transgranular fracture in both the transition and brittle fracture regions. These observations for the hydrogenated 8 μm grain size alloys are similar to those reported for a V–5 at % Ti alloy of 20 μm grain size containing 0.33 at % H [5]. Apparently the coarser grain size in conjunction with the lower hydrogen content results in similar fracture characteristics as observed here for the hydrogenated 8 μm grain size alloys. While there is no direct comparison with previous work on V–5 at % Ti alloys with hydrogen contents equivalent to those used in this study, previous results for a 20 μm grain size V–10 at % Ti alloy with hydrogen contents up to 4.7 at %, where hydride precipitates were not observed, showed that the fracture surface characteristics changed from ductile rupture to mixed trangranular–intergranular fracture to predominantly intergranular fracture with increasing brittleness [5]. This trend of fracture surface characteristics with increasing brittleness is the same as observed here for the 31 μm grain size alloys.

Representative pictures of the fracture characteristics observed at 78 K and below in the different alloys are shown in Figs 10–12. Fig. 10 shows the fracture surfaces of the four different 31 μm grain size alloys at 15 K. The non-hydrogenated alloy (Fig. 10a) shows typical ductile failure. With a small hydrogen addition (0.3 at %) the fracture surface shows areas of both cleavage and ductile fracture (Fig. 10b). At 1.8 and 3.8 at % H additions, intergranular fracture is prevalent (Fig. 10c and d) as it is in the brittle region of the ductility curves (Fig. 3).

The fracture characteristics for the hydrogenated 8 μm grain size alloys below 78 K were different from those of the 31 μm grain size alloys. This difference is typified in Figs 11 and 12 for specimens tested at 15 and 50 K, respectively. Note that because of the finer scale of the fracture features in the 8 μm grain size alloys, higher magnifications were used for these alloys in Figs 11 and 12 than for the 31 μm grain size alloys. The fracture characteristics of the non-hydrogenated 8 μm grain size alloy at 15 K are similar to

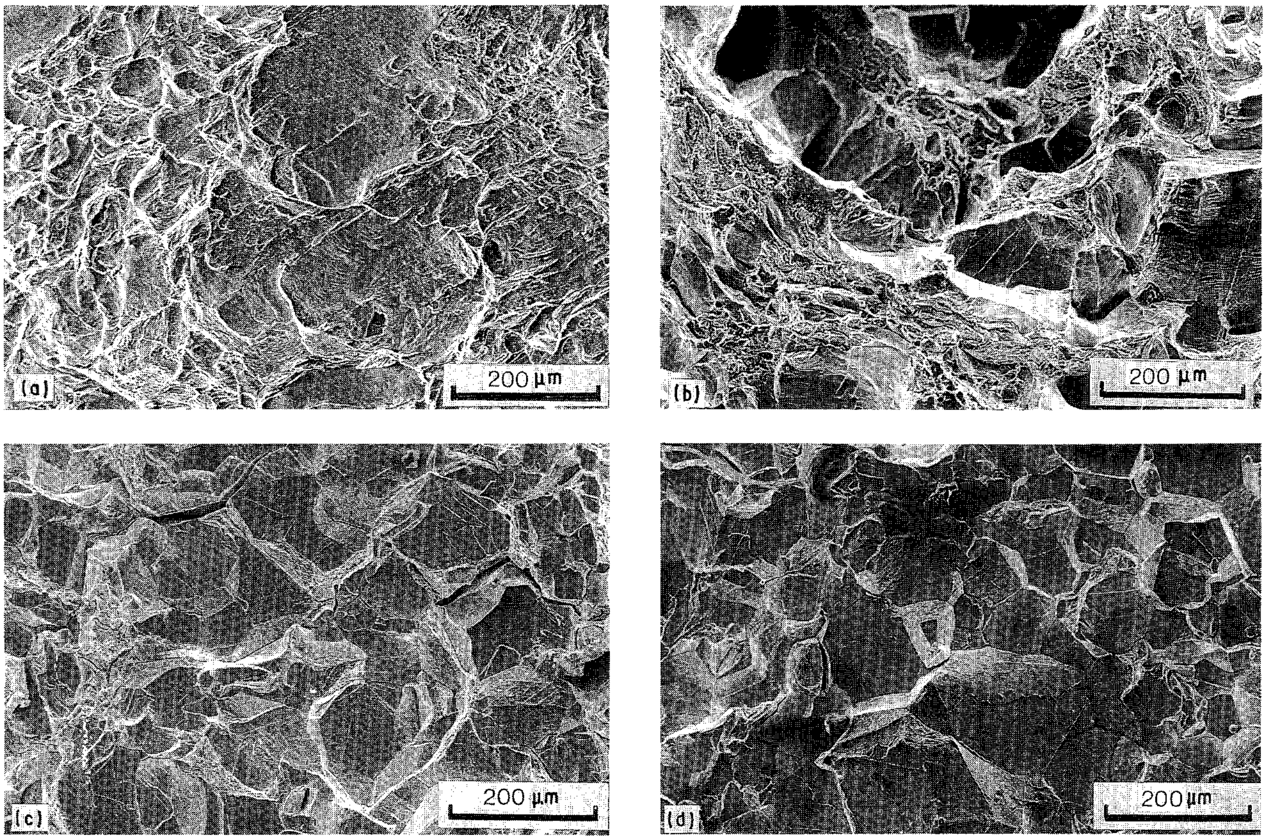
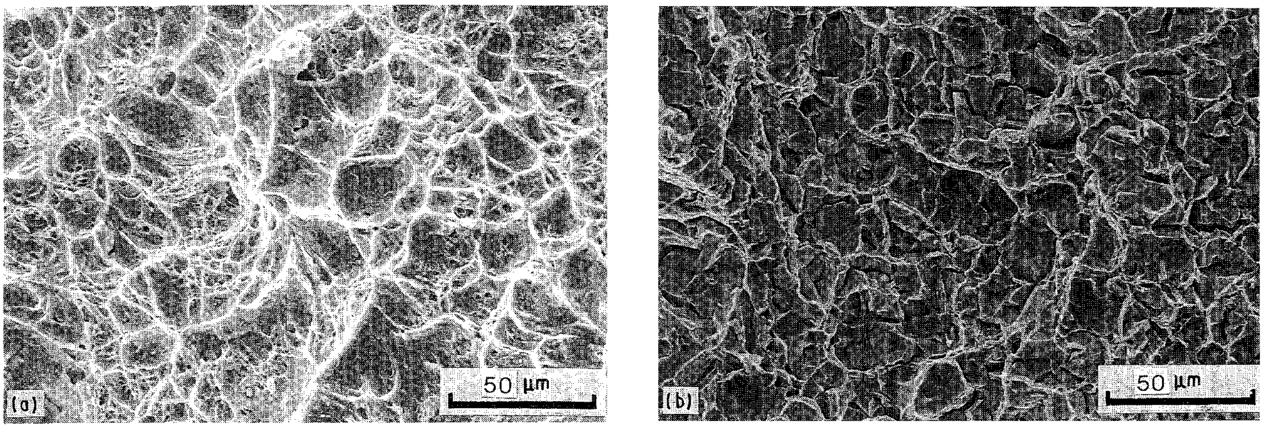


Figure 10 Scanning electron micrographs of fracture surfaces of non-hydrogenated and hydrogenated V–5 at % Ti alloys with a grain size of 31 µm tested at 15 K: (a) < 0.05 at % H; (b) 0.3 at % H; (c) 1.8 at % H; (d) 3.8 at % H.



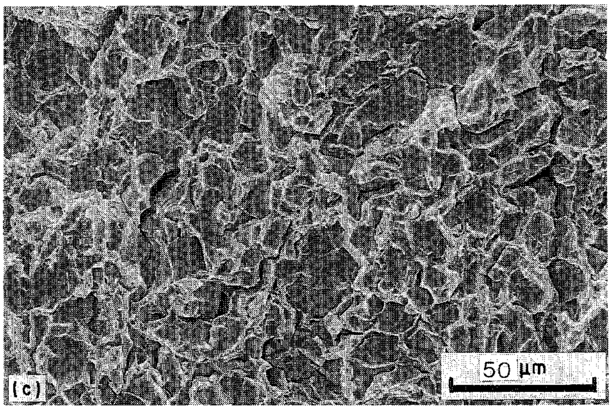


Figure 11 Scanning electron micrographs of fracture surfaces of non-hydrogenated and hydrogenated V–5 at % Ti alloys with a grain size of 8 µm tested at 15 K: (a) < 0.05 at % H; (b) 1.9 at % H; (c) 3.9 at % H.

those of the corresponding coarser grain size alloy as shown by comparing Figs 10a and 11a. Both these alloys remain very ductile and exhibit about the same ductility at 15 K and throughout the temperature range studied (compare Figs 3 and 5). However, as observed in the brittle region of the ductility curves (Fig. 5), the fracture surfaces of the 8 µm grain size hydrogenated alloys do not display the prevalent intergranular fracture characteristics shown by the corresponding coarser grain size alloys. As shown in Fig. 11b and c, the fracture characteristics of the hydrogenated 8 µm grain size alloys are very fine and appear to remain predominantly transgranular in nature. Because of the fine scale of the fracture characteristics in the 8 µm grain size alloys it is difficult to state unequivocally that no intergranular fracture occurs in these alloys. The hydrogenated 8 µm grain size alloys also exhibit greater ductility at 15 K than the maximum value obtained in the ductility return region

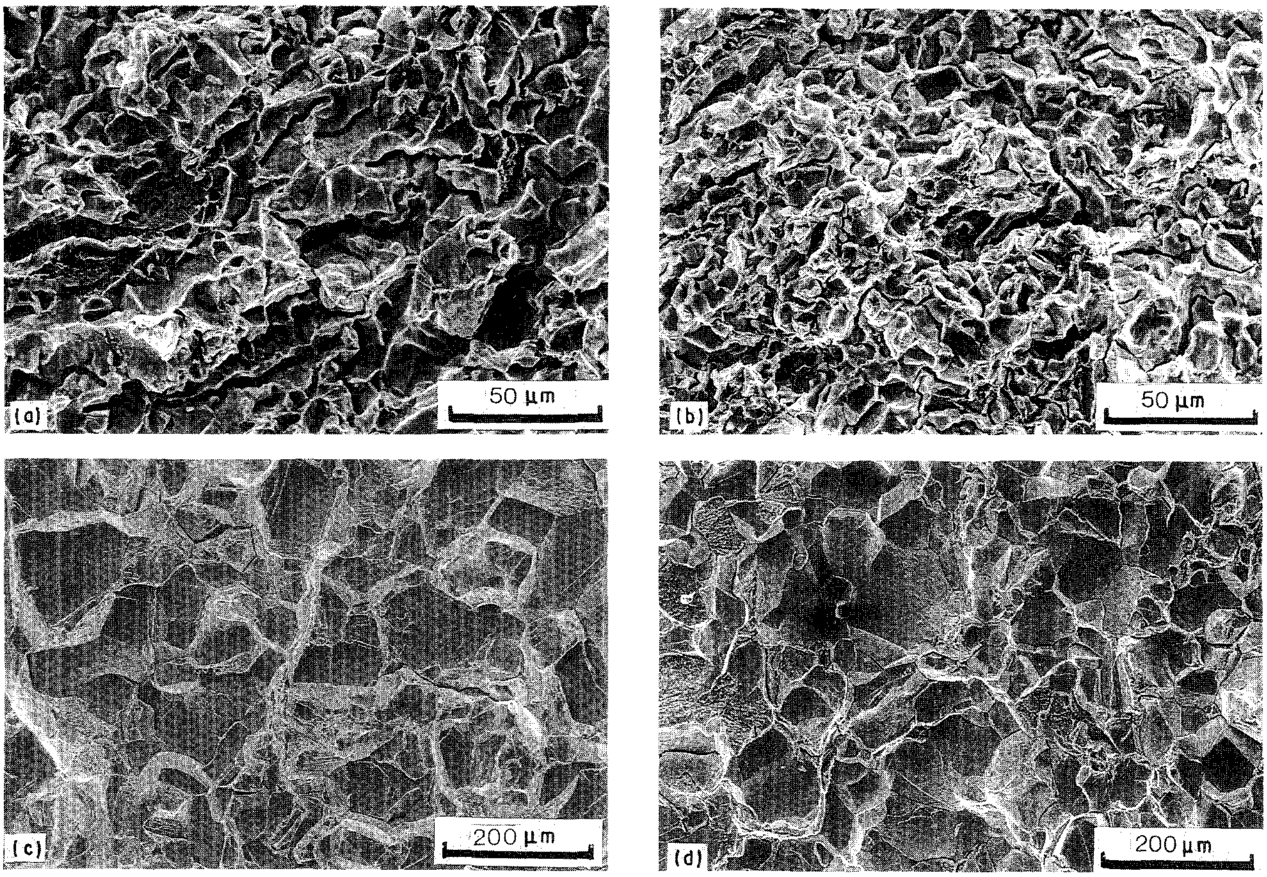


Figure 12 Scanning electron micrographs of fracture surfaces of hydrogenated V–5 at % Ti alloys with a grain size of 8 or 31 μm tested at 50 K. (a, b) 8 μm grain size, 1.9 and 3.9 at % H, respectively; (c, d) 31 μm grain size, 1.8 at % H and 3.8 at % H, respectively.

for the corresponding coarser grain size alloys (compare Figs 3 and 5). As discussed before, at 15 K all the alloys deformed solely by serrated flow, but the hydrogenated 8 μm grain size alloys deformed by multiple neck formation as compared to the 31 mm grain size alloys that showed a single neck. The non-hydrogenated 8 μm grain size alloy also exhibited a single neck. Therefore, the 8 μm grain size produces significant differences in both the deformation behaviour and the ductility in the hydrogenated alloys at temperatures below 78 K. This effect does not appear to be apparent in the absence of hydrogen where the grain size differences had essentially no influence on ductility (compare Figs 3 and 5) or fracture characteristics (compare Fig. 10c and d with Fig. 11b and c).

The fracture surfaces of the corresponding hydrogenated alloys of the two grain sizes at 50 K, where the ductility return reaches a maximum before decreasing again, are compared in Fig. 12. The non-hydrogenated alloys and the 0.3 at % H alloy show similar fracture characteristics as observed at 15 K. The differences in the fracture surface characteristics of the different grain size hydrogenated alloys is still clearly evident in Fig. 12. At this temperature, like at 30 K, the 8 μm grain size hydrogenated alloys did not exhibit serrated yielding as was apparent for the corresponding 31 μm grain size alloys. The fine grain size hydrogenated alloys showed upper–lower yield-point behaviour similar to that of the non-hydrogenated alloys of either grain size. Therefore, the greater ductility improvement in the hydrogenated 8 μm grain size alloys corresponds to a deformation behaviour that is similar to that of the non-hydrogenated alloys. This seems to support the previous proposal [8] that more hydrogen trapping at grain boundaries occurs in the finer grain size alloys, thereby, removing hydrogen from the lattice which gives rise to improved ductility. However, this improved ductility does not appear to manifest itself in any significant qualitative difference in fracture surface characteristics. The finer grain size hydrogenated alloys show similar fracture characteristics below 78 K as they do in the brittle region of the ductility curves. While this is also true for the corresponding 31 μm grain size alloys, the ductility improvement below 78 K is not nearly as pronounced as it is in the 8 μm grain size alloys.

While the present results confirm that the pronounced effect of fine grain size on the ductility return continues at temperatures below 78 K, they do not present much insight into a possible mechanism responsible for this phenomenon. The finer grain size in itself does not have any measurable effect on ductility in these alloys in the absence of hydrogen. Therefore, the effect of the finer grain size must be to reduce the deleterious effect of hydrogen on inducing embrittlement. The previous proposal that decreasing grain size increases the number of hydrogen trapping sites and, as a result, removes hydrogen from the matrix resulting in improved ductility [8], seems to be in accord with the present experimental findings. The present results support the view that there is a partitioning of hydrogen between the grain boundaries and the matrix. It appears that at a given overall hydrogen content the amount of hydrogen in the matrix must be reduced below some minimum concentration in order for deformation to proceed by transgranular cleavage rather than intergranular failure, resulting in enhanced ductility. However, if insufficient grain-boundary area is available, and the hydrogen trapped in the grain boundaries exceeds some critical concentration, fracture occurs by intergranular failure resulting in reduced ductility.

5. Conclusion

The effects of grain size and of hydrogen in solid solution or as hydrides on the strength and ductility of V–5 at % Ti was studied over the temperature range 15–448 K. Comparison of the strength and ductility characteristics of hydrogenated alloys, where hydrides were not observed down to 78 K (1.8 and 1.9 at % H alloys) or where hydrides were observed to form near 230 K (3.8 and 3.9 at % H alloys), indicated that the presence of hydride precipitates had no apparent influence on the strength or ductility characteristics. It appears that the main consequence of hydride precipitation on strengthening is that hydrogen is removed from solid solution making strengthening less effective than expected, based on the total hydrogen content. The hydride precipitates formed in the temperature region where the alloys were already brittle and except for an increase in transition temperature of about 45 K in the higher hydrogen content alloys, the ductility and strength characteristics were similar to those observed in the lower hydrogen content alloys where hydride precipitates were not observed and the hydrogen remained in solid solution.

Decreasing grain size from 31 μm to 8 μm had no apparent effect on ductility in the non-hydrogenated alloys (<0.05 at % H) but it did increase the strength over most of the temperature range and especially at 15 K. Decreasing grain size in the hydrogenated alloys decreased the transition temperature about 10 K in corresponding alloys and it appreciably increased the degree of ductility return at 78 K and below. However, in all the hydrogenated alloys the ductility return exhibited a maximum near 50 K before decreasing below 30 K. The ductility return was greatest in the alloys with the lower hydrogen contents although the difference was not very marked, especially in the 31 μm grain size alloys. As observed previously for V–Nb alloys [8], increasing the hydrogen content from about 1.9 at % to 3.9 at % decreased the ductility return below 78 K but the effect of increasing the grain size from 8 μm to 31 μm was much more pronounced on reducing the ductility return.

The results of this study on V–5 at % Ti alloys are in accord with those previously reported for V–Nb alloys [8] showing that is necessary to have a fine grain size in order to obtain an appreciable ductility return below 78 K in Group VA alloys. In particular the grain size must be finer, the higher the hydrogen content. The results of this investigation support a previous proposal that the finer grain size results in more hydrogen trapping, thereby removing hydrogen from solid solution in the matrix [8]. As a result of a lower matrix hydrogen content in the finer grain size alloys the ductility return below 78 K is increased because the ease with which cracks can propagate through the matrix is reduced. If insufficient grain-boundary area is available for trapping so that the grain boundaries themselves become embrittled, fracture occurs by intergranular failure and the ductility is minimal.

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