Microstructure evolution in Ti-6Al-4V alloy during hydrogen dosing at elevated temperature

by L.A. Matthews* and R.D. Knutsen*

Synopsis

The embrittlement of the Ti-6Al-4V alloy by hydrogen dosing at elevated temperature has been investigated. Metal coupons were subjected to isothermal treatments in a partial hydrogen atmosphere in the temperature range from 650°C–950°C and the degree of embrittlement after treatment was determined by drop-weight impact testing. Embrittlement was found to be inversely related to reaction temperature as a result of the combined effects of greater hydrogen absorption and titanium hydride precipitation at the lower isothermal temperatures.

Keywords

Titanium, hydrogen embrittlement, impact energy

Background

The interaction between titanium and hydrogen, especially at high temperature, is known to cause hydrogen embrittlement[1] which is detrimental in applications where loss of ductility results in component failure. On the other hand, embrittlement by hydrogenation is advantageous for the production of fine titanium particles through crushing or grinding during milling to produce metal powder. The shape and size of powder particles produced during milling, as well as the energy efficiency of the milling process, is determined by the level of embrittlement that is achieved during the hydrogenation treatment. The present work focuses on defining the hydrogenation conditions that optimize the embrittlement of the Ti-6Al-4V alloy for conversion of metal scrap to powder.

The reversible hydride-dehydride process is used very effectively to convert sponge metal to metal powder at the end of the primary process chain. Hydrogenation of the sponge metal produces titanium hydride (TiH or TiH_2) which after milling is converted back to titanium metal by expunging the hydrogen at elevated temperature in a vacuum environment. In the case of the Ti-6Al-4V alloy, hydride formation can occur but it can be assumed that aluminium and vanadium will also influence the level of embrittlement that can be obtained[2]. The motivation to convert Ti-6Al-4V scrap to metal powder lies in the ability to produce feedstock for sintered metal components at much lower cost than the conventional metal atomization route. Consequently, it is important to understand (i) what microstructural constituents are necessary to cause embrittlement, and (ii) what is the sensitivity of hydrogenation parameters to the development of embritlement. Although there are several options for introducing hydrogen into the alloy, our study is restricted to elevated temperature hydrogenation at ambient pressure where the principal variables are soak time and temperature. The degree of embrittlement is evaluated through impact testing and fractography whereas the microstructures are assessed using scanning electron microscopy (SEM).

Experimental procedure

In order to conduct a basic parametric study to determine the influence of thermo-hydrogen process (THP) conditions on embrittlement, test coupons were cut from 1 mm thick rolled Ti-6Al-4V sheet. The coupons measured 34 mm x 34 mm in order to accommodate the furnace and impact tester requirements. The THP conditions are presented in Table I. Essentially three parameters were varied, namely gas composition (hydrogen + argon balance), soak temperature and isothermal soak time. Sample mass was recorded before and after THP treatment to establish the level of hydrogen absorption during the THP cycle. Control samples were vacuum annealed at each of the THP temperatures in order to assess the influence of grain growth and phase morphology on the impact properties.

* *Centre for Materials Engineering, Mech Eng, University of Cape Town.*

This paper was first presented at the, Light Metals Conference, 27–29 October 2010, Misty Hills, Muldersdrift.

Table I

Thermo-hydrogen process (THP) parameters

Sample	% H_2 gas		Treatment temperature (°Celsius)				Treatment time (hours)						
	5	15	950	850	750	650	0.5	1	1.5	2	3	5	7.5
3h/950/5H	x		x								x		
5h/950/5H	x		x									x	
7.5h/950/5H	x		x										x
3h/850/5H	x			x							x		
5h/850/5H	x			x								x	
7.5h/850/5H	x			x									x
1h/850/15H		x		x				x					
2h/850/15H		x		x						x			
3h/850/15H		x		x							x		
0.5h/750/15H		x			x		x						
1h/750/15H		x			x			x					
1.5h/750/15H		x			x				x				
2h/750/15H		x			x					x			
3h/750/15H		x			x						x		
0.5h/650/15H		x				x	x						
1h/650/15H		x				x		x					
2h/650/15H		x				x				x			
3h/650/15H		x				x					x		
3h/950/VacAn			x								x		
3h/850/VacAn				x							x		
3h/750/VacAn					x						x		
3h/650/VacAn						x					x		

The degree of embrittlement was determined by performing drop-weight impact tests using an instrumented Instron Dynatup 9210 impact tester. At least two specimens were tested for each THP condition and the impact energy value corresponding to the maximum load was recorded in each case. The microstructural condition and fractography was assessed using SEM.

Results

Hydrogen absorption

The degree of hydrogen absorption over the THP treatment range is presented in Figure 1. As would normally be expected, hydrogen absorption increases with soak time and gas concentration. However, it is interesting to note that greater hydrogen absorption occurs at lower THP temperatures.

Impact energy

The impact energy as function of THP treatment is plotted in Figure 2. In addition to recording the impact energy at peak load, several observations regarding the impact condition were noted. The 850/5H_2 condition exhibited surface cracking without gross failure. The 950/5H_2 condition showed slightly more cracking but the condition did not alter significantly with increasing soak time. For the specimens treated in the 15% hydrogen mix, all the impact tests resulted in gross brittle fracture. Furthermore, there is a general trend towards lower impact energy with increasing soak time, but a more significant effect is demonstrated by decreasing soak temperature.

Fractography

Examination of the fracture morphology for the various treatment conditions revealed good correlation between the measured impact energy and the fracture mode. As a

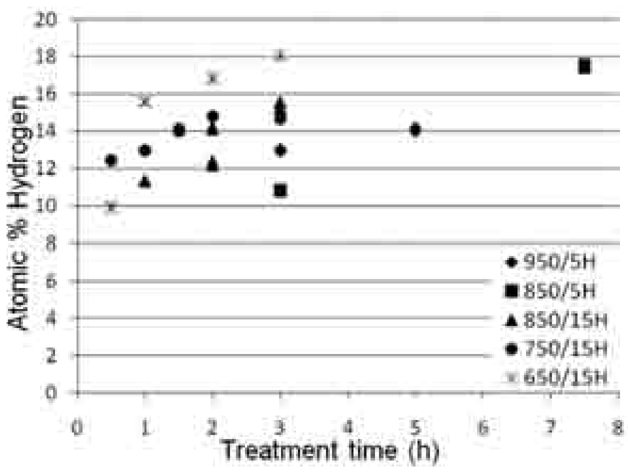

Figure 1—Hydrogen absorption as function of THP treatment condition

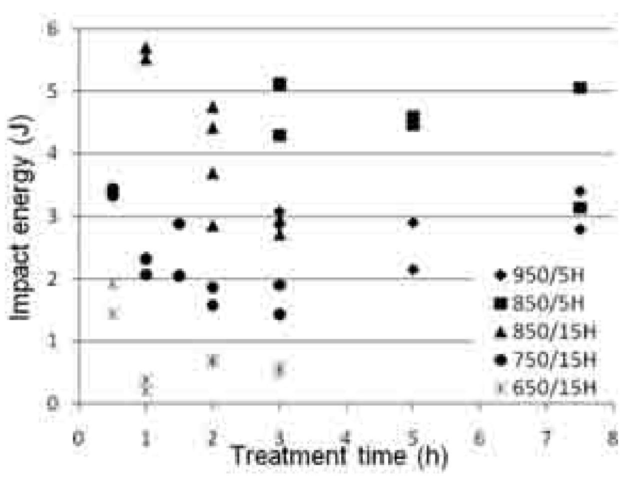

Figure 2—Impact energy as function of THP treatment

benchmark, the vacuum annealed condition (Figure 3(a)) demonstrates classic ductile dimple fracture that one would expect from the Ti-6Al-4V alloy, whereas the THP treatment 3h/850/15H_2 displays facetted brittle cleavage (Figure 3(b)).

The fracture surface that resulted from the 950/5H_2 treatment (Figure 4(a)) reveals quasi-cleavage which is a combination of brittle fracture and ductile tearing. Furthermore, significant directionality in the fracture morphology can be identified, which will be later shown to be related to the microstructural features. The highly brittle 650/15H_2 treatment produces a flat, granulated fracture surface with no signs of plastic deformation (Figure 4(b)).

Microstructure analysis

The 950/5H_2 treatment gives rise to a plate-like Widmanstätten structure after cooling to room temperature. The Widmanstätten morphology has formed as a result of the partial decomposition of the β-phase to α-phase during cooling, and since the transformation is incomplete, the alternating plates of α and β dominate the microstructure (Figure 5(a)).

Closer observation of this microstructure (Figure 5(b)) reveals dense distribution of very fine precipitates in some of the lamellar plates. Comparison of Figure 4(a) and

Figure 5 suggest that the directionality observed on the fracture surface may be related to the plate-like Widmanstätten morphology in the microstructure.

The microstructures formed after the treatments at 850°C and 750°C exhibit martensitic structures, although the acicular nature of the martensitic transformation is much finer for the microstructure evolved from the 750°C treatment. Figure 6(a) exhibits the microstructure after the THP cycle 850/5H_2. Apart from the patterned martensite morphology, the occurrence of small spherical precipitates (light phase) is clearly visible and accentuates the crystallographic form of the martensite structure. The treatment at 650°C, on the other hand, gives rise to a dense, homogeneous distribution of fine needle-like precipitates as shown in Figure 6(b).

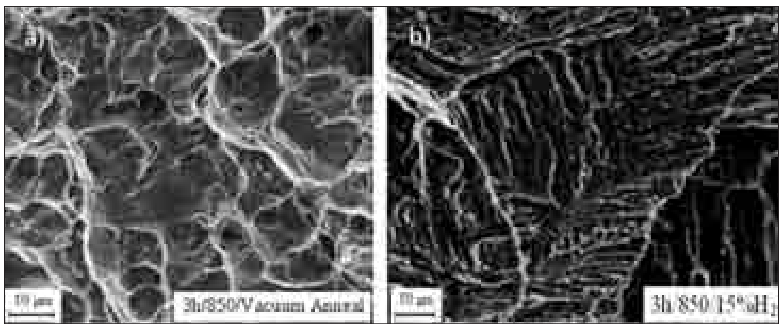

Figure 3—(a) Ductile-dimple fracture surface of vacuum annealed (850°C) specimen, (b) facetted brittle cleavage after 3h/850/15H_2 treatment

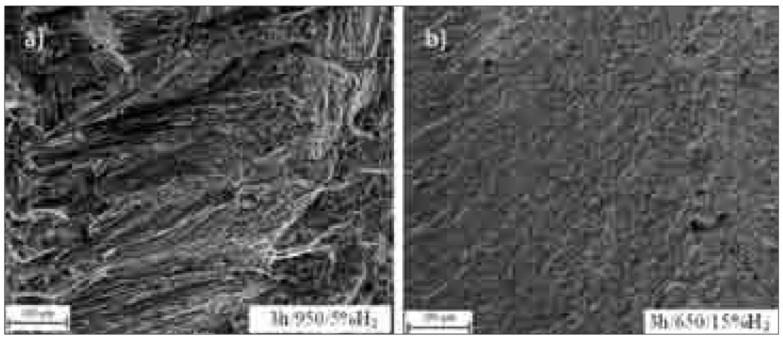

Figure 4—(a) Facetted quasi-cleavage after 3h/950/5H_2, (b) fine granulated fracture surface appearance after 3h/650/15H_2

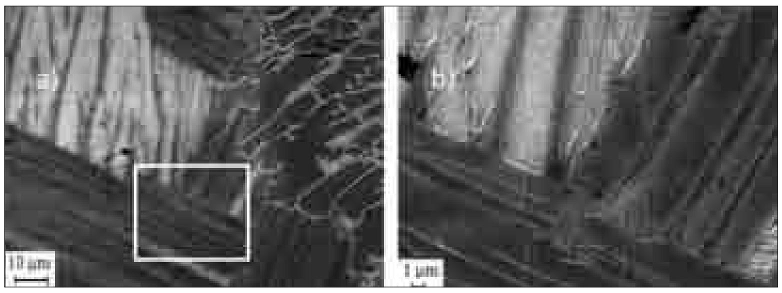

Figure 5—(a) Widmanstätten (α+β) plate morphology evolved from the 950/5H_2 treatment, (b) higher magnification (see window in (a)) indicates fine precipitate (light phase) within some plates

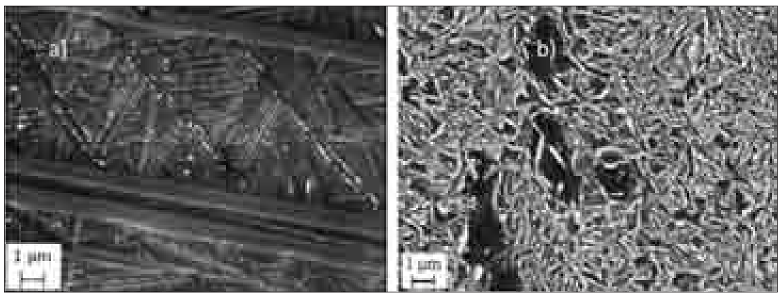

Figure 6—(a) Small spherical precipitates (light phase) visible within some martensite plates (3h/850/5H_2), (b) Dense distribution of needle-like precipitates formed at 2h/650/15H_2

Discussion

The anticipated hydrogen absorption during the THP cycles relies on the premise that hydrogen gas will dissociate and diffuse atomically into the metal during the isothermal treatments. In so doing, it is reasonable to assume that diffusivity will be influenced by temperature and time in that greater hydrogen absorption will occur at higher temperatures and longer reaction intervals. This is indeed the case with respect to reaction time, but not so in relation to THP temperature. Greater hydrogen absorption occurs at lower temperatures and manifests in abundant precipitation of titanium hydrides. Although the β-transus temperature for Ti-6Al-4V occurs at 890ºC[3], the β-transus is lowered in the presence of hydrogen[4,5] and the THP treatments at 750ºC and above demonstrate that the microstructure is fully β-phase at the reaction temperature. This deduction is supported by the Widmanstätten morphology that occurs after the 950ºC treatment and the martensitic conditions that prevail after the 750ºC and 850ºC treatments. Hydrogen is soluble in the β-phase and consequently it is surprising that lower hydrogen absorption occurs at the higher temperatures. However, an explanation of this behaviour possibly lies in the fact that minor oxygen absorption also occurs during the THP cycles. Although the THP treatments were preceded by establishing good vacuum in the furnace chamber, it is possible that minor contamination of the H_2-Ar mix caused significant oxygen to be absorbed into the near surface of the test coupons and consequently retard the uptake of hydrogen. Since the oxygen activity increases with temperature, the retardation becomes more marked at the higher reaction temperatures.

It is possible that the higher hydrogen content alone could explain the greater degree of embrittlement (lower impact energy) experienced by the specimens treated at 650ºC. However, the morphology of the microstructures and the ratio between dissolved hydrogen and titanium hydride population is important in explaining the embrittlement process. Since hydrogen is highly soluble in the β-phase[1], significant hydrogen is expected to remain in solid solution in the retained β-phase or martensite phase at room temperature. Hydrogen in solid solution contributes significantly less to the embrittlement process. On the other hand, the low solubility of hydrogen in the α-phase leads to profuse precipitation of brittle titanium hydrides that in turn promote crack initiation and propagation during the fracture event[3]. As a result, it is not only the hydrogen content, but also the microstructure morphology and phase constitution that gives rise to the highest level of embrittlement after the THP cycle at 650ºC.

Conclusions

Certain hydrogenation treatments that were performed within the chosen parameter set produced significant embrittlement of the Ti-6Al-4V alloy. More specifically, the following conclusions are emphasiszed:

- The degree of embrittlement is sensitive to soak temperature with a general inverse relationship between soak temperature and degree of embrittlement.
- Fracture morphology is related to the microstructure morphology that evolves from the different THP treatments.
- The microstructure morphology and phase constitution controls the degree of embrittlement that evolves during the THP treatments. Hydrogen remains in solid solution at soak temperatures of 750°C although heterogeneous precipitation of hydrides does occur. A significantly higher volume fraction of titanium hydrides occurs in the case of the 650°C treatment as a result of the low solubility of hydrogen in the α-phase with a consequent high degree of embrittlement.
- The inverse relationship between embrittlement and THP temperature is fortunate in that it provides opportunities to lower the cost of the embrittlement process.

Acknowledgements

The authors gratefully acknowledge the financial contributions of the Advanced Manufacturing Technology Strategy (AMTS) and the National Research Foundation (NRF).

References

1. Tal-Gultelmacher, E. and Eliezer, D. High fugacity hydrogen effects at room temperature in titanium based alloys. *Journal of Alloys and Compounds*, vol. 613, 2005, pp. 404–406.
2. Mitkov, M. and Božić, D. (1996) Hydride-Dehydride conversion of Solid Ti6Al4v to Powder Form. *Materials Characterisation*, vol. 37, 1996, pp. 53–60.
3. Tal-Gultelmacher, E. and Eliezer, D. The Hydrogen Embrittlement of Titanium-Based Alloys. *Journal of the Minerals, Metals and Materials Society*, vol. 57, 2005, pp. 46–49.
4. Senkov, O.N. and Froes, H.F. (1999) Thermohydrogen processing of titanium alloys. *International Journal of Hydrogen Energy*, vol. 24, 1999, pp. 565–576.
5. Qazi, J.I., Senkov, O.N., Rahim, J., Genc, A., and Froes, F.H. Phase Transformations in Ti-6Al-4V-xH Alloys. *Metallurgical and Materials Transactions*, vol. 32A, 2001, pp. 2453–2463. ◆