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Effect of vacuum-treatment on mechanical properties of W–Ni–Fe heavy alloy

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The effect of heat-treatment in vacuum and hydrogen on the ductility and UTS of the sintered 96W–2.8Ni–1.2Fe (by wt%) heavy alloy has been studied. The elongation of the as-sintered alloy is about 8%, but after a few minutes of heat treatment in vacuum at 800° C it increases markedly to about 19%. When the sintered specimen is heat-treated in vacuum at 600° C, the elongation increases rapidly with time, reaching 20% after about 10 min. The values of UTS also increase after vacuum treatment. Heat treatment in hydrogen, however, shows no change in mechanical properties from the as-sintered state. The effect of vacuum treatment is thus attributed to the removal of hydrogen embrittlement. Based on the hydrogen diffusion model, a practical guide line is suggested for determining the optimum vacuum treatment conditions. The scanning electron micrographs of the fracture surfaces show that hydrogen weakens mainly the interface between tungsten grains and matrix.

1. Introduction

Several recent studies [1–8] have shown that the mechanical properties of sintered W–Ni–Fe heavy alloys could be improved by heat treatment at about 1000° C. This effect has been attributed either to the removal of hydrogen embrittlement in vacuum [1–3] or to the phase changes occurring in the alloy system [7, 8]. The heat treatments were mostly performed at 1000° C for fixed times (about 1 h), and the results were insufficient for determining the practical optimum condition for the heat treatment.

The purpose of this investigation is to show that hydrogen retained in the alloy after sintering causes the embrittlement and it can be removed by heat treatment in vacuum. The effect of hydrogen is demonstrated by observing the temperature and time dependence of the heat treatment, and by comparing the results obtained in vacuum and hydrogen. Some specimens, heat treated in vacuum, were heat treated again in hydrogen to determine if the embrittlement effect could be restored.

The scanning electron micrographs of the fractured surfaces were also compared between the sintered and the vacuum-treated specimens in order to examine the effect of hydrogen on fracture mode.

2. Experimental procedure

The tensile specimens of 96W–2.8Ni–1.2Fe (by wt%) alloy were prepared by the normal powder metallurgy techniques which were similar to those described earlier [9]. Commercial grade tungsten, nickel, and iron powders of 1.2, 6, and 5 μm, respectively, by Fisher subsieve sizer were used. After ball-milling the powder mixtures for 24 h, 0.75 wt% of paraffin dissolved in benzene was added. The tensile specimen die was the "Sweden type" [10] with a total length of 55 mm and a rectangular cross-section of 5 mm x 3 mm over a length of about 25 mm. The powder was compacted at 98 MPa pressure in a floating die system. The compacts were presintered at 950° C for 1 h and sintered at 1460° C for 1 h in a tube furnace with a flowing hydrogen atmosphere. The heating and cooling rates during sintering were about 40° C min^{-1}.

The sintered specimens were heat treated in a quartz tube furnace under a vacuum of about

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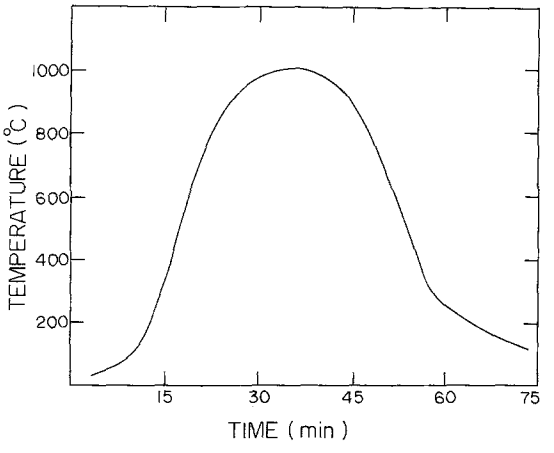


Figure 1 The heat-treatment cycle for "0" time at 1000° C.

10^{-2} torr at temperatures between 400 and 1000° C for various times. The heat-treating time was measured from the moment that the specimens was placed in the zone of the desired temperature in a preheated furnace. The heating and cooling rates were similar to those of the sintering treatment. A typical heating and cooling curve for the vacuum treatment at 1000° C is shown in Fig. 1. Tensile tests were performed with a crosshead speed of 0.1 mm min^{-1}. (The strain rate was about 5×10^{-5} sec^{-1}.) The elongation was determined on a gauge length of 20 mm.

3. Experimental results

The typical microstructure of the sintered 96W–2.8Ni–1.2Fe specimen, shown in Fig. 2, is similar to those observed previously [9, 11]. The density of the sintered specimens was 99.7 ± 0.2% of the theoretical density and no pores were found on polished surfaces.

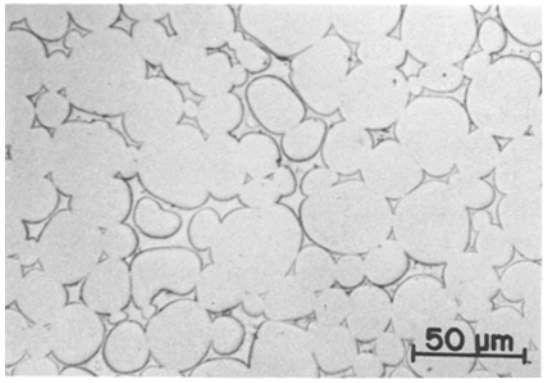


Figure 2 The microstructure of the sintered 96W–2.8Ni–1.2Fe alloy.

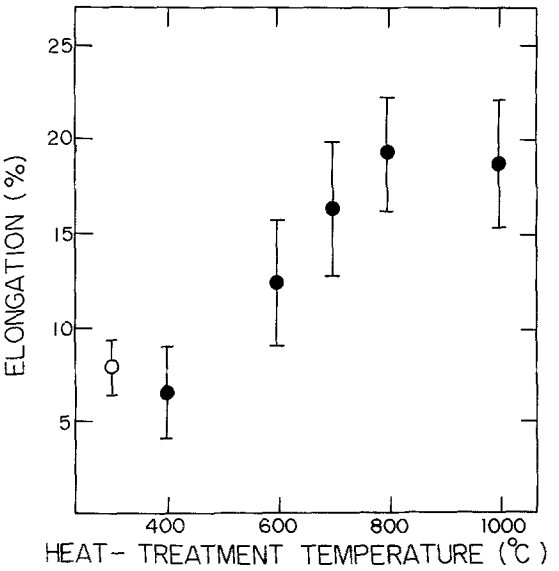


Figure 3 The observed variation of elongation with the temperature of heat treatment in vacuum for "0" time. (The open circle is for the as-sintered specimens.)

The average values of elongation and UTS were obtained from about five specimens prepared and heat treated under the same conditions. The results showed considerable scatter and the standard deviations are shown as the error bars in the figures.

The observed variations of elongation and UTS with the temperature of heat treatment in vacuum are shown in Figs. 3 and 4, respectively. These

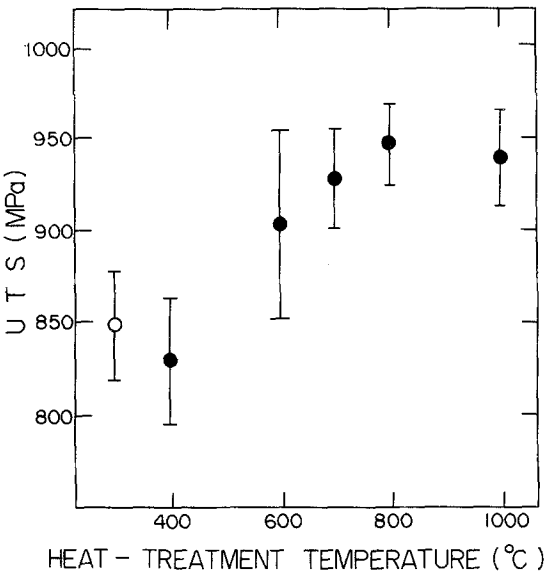


Figure 4 The observed variation of UTS with the temperature of heat treatment in vacuum for "0" time. (The open circle is for the as-sintered specimens.)

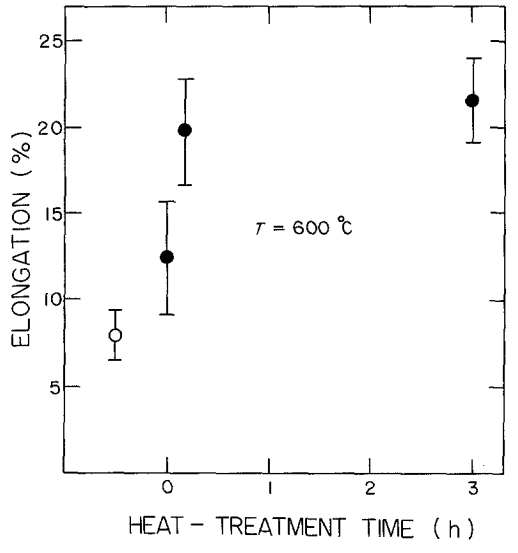


Figure 5 The variation of elongation with the time of heat treatment in vacuum at 600° C. (The open circle is for the as-sintered specimens.)

results show that the elongation and the UTS after the vacuum treatment increased significantly over the temperature range between 400 and 800° C. Fig. 5 shows the effect of heat-treating time at 600° C in vacuum. The elongation increased sharply during the first few minutes of vacuum treatment; the UTS showed a similar change. Fig. 6 shows the values of elongation obtained after heat treatment in vacuum and in flowing hydrogen

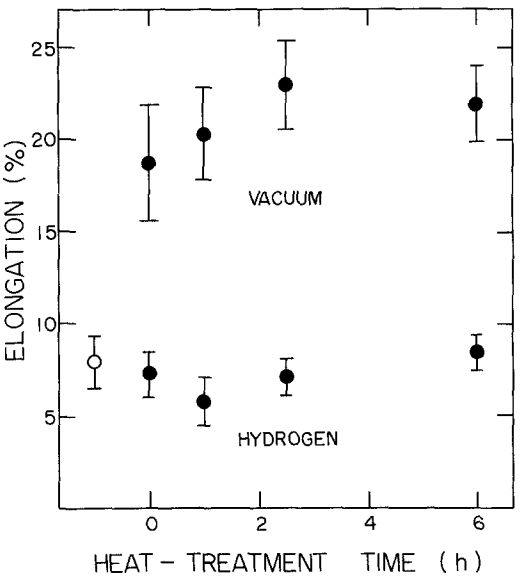


Figure 6 The variation of elongation with the time of heat treatment in vacuum and in hydrogen at 1000° C. (The open circle is for the as-sintered specimens.)

at 1000° C for various times. Heat treatment in hydrogen has no effect on elongation in constrast to the pronounced increase after heat treatment in vacuum. The UTS data showed a similar behaviour.

In order to confirm the pronounced embrittling effect of hydrogen shown in these results, some sintered specimens were first heat treated in vacuum and then in hydrogen at 1000° C. Final heat treatment in hydrogen reduced the elongation and UTS to those of the as-sintered specimens. Furthermore, when the furnace atmosphere was changed from hydrogen to nitrogen at about 1000° C during cooling after the sintering treatment, the elongation and the UTS increased close to those obtained after the vacuum treatments.

Fig. 7 shows the scanning electron micrographs of the fracture surfaces of the as-sintered and the vacuum-treated specimens. The specimens heat treated in hydrogen showed fracture micrographs similar to those of the as-sintered specimens.

4. Discussion

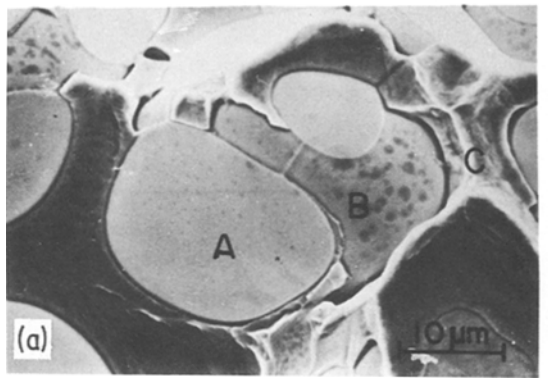
The increase of elongation and UTS by vacuum treatment observed in this alloy is in accord with the results obtained for the alloys of similar composition in the previous investigations [1, 3]. These results demonstrate a strong embrittling effect of hydrogen in this alloy and its removal by heat treatment in vacuum.

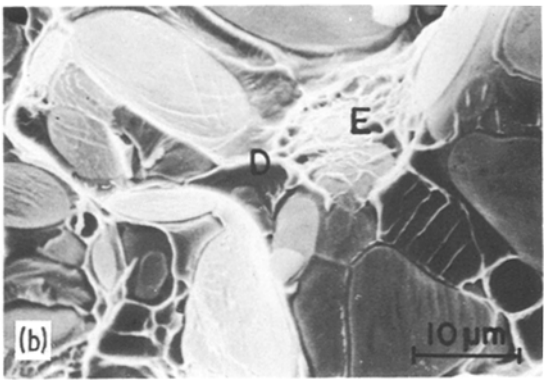
The process of hydrogen removal by vacuum treatment in these specimens may be described as diffusion in a cylinder of infinite length. If the initial hydrogen content is uniform at C_i and the surface concentration is maintained at C_s, and t is the time required to reduce the average hydrogen concentration to $\bar{C}$, $(C_i - \bar{C})$ is the quantity of hydrogen which has left the specimen after time t, and $(C_i - C_s)$ is the corresponding quantity after infinite time. These two quantities are related by [12]

$$\frac{C_i - \bar{C}}{C_i - C_s} = 1 - \sum_{n=1}^{\infty} \frac{4}{r^2 \alpha_n^2} \exp(-D\alpha_n^2 t) \quad (1)$$

where r is the radius approximately equal to 2 mm for these specimens, D is the hydrogen diffusivity, and $r\alpha_n$'s are the roots of the Bessel function of the first kind of order zero. Since $r\alpha_n$ increases rapidly with n, only the first term in the series may be retained to give,

$$t = -\frac{r^2}{(2.4)^2} \ln \left[\frac{(2.4)^2}{4} \left(\frac{\bar{C} - C_s}{C_i - C_s} \right) \right]. \quad (2)$$





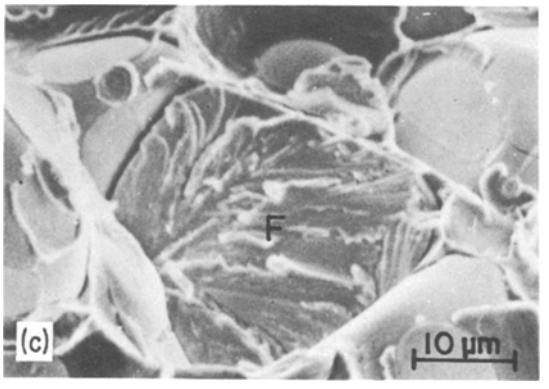


Figure 7 Scanning electron micrographs of the fracture surfaces of (a) the as-sintered and (b), (c) the vacuum-treated alloy.

From this equation the time required to remove the hydrogen embrittlement effect can be estimated. Although most of the hydrogen in this alloy will be contained in the matrix as shown in earlier works [2, 13], the heat-treatment time t can be estimated by using the apparent diffusivities measured by Powell [13] in an alloy of similar composition. From the rate of hydrogen evolution in vacuum, Powell [13] determined that the apparent D of hydrogen in a 95W–3.5Ni–1.5Fe alloy can be expressed as $D\ (\mathrm{cm^2\,sec^{-1}}) = 0.057 \times \exp(-10\,800/1.987T)$ over the temperature range between 500 and 1000° C.

Since C_s in vacuum is close to 0, t in Equation 2 will be determined by $\bar{C}/C_i$. The hydrogen retained in the alloy (the value of C_i) after sintering or heat treatment in hydrogen has not been accurately determined yet. As the specimen is cooled from the sintering temperature the hydrogen content is expected to decrease following the saturation values when the diffusion rate is high. But at temperatures around 800 to about 1000° C, the diffusion time estimated from the $l = (DT)^{1/2}$ relationship becomes long enough (about 1 and 2 min, respectively) to retain hydrogen at its saturation value at these temperatures. Powell [13] determined the hydrogen solubility in a 95W–3.5Ni–1.5Fe alloy at 1000° C to be 390 ± 30 wt ppb ($3.9 \pm 0.3 \times 10^{-5}$ wt %). Since the 96W–2.9Ni–1.2Fe specimens used in this study have a lower matrix content – and hydrogen is contained mainly in the matrix – the estimated hydrogen content in this alloy is about 310 ± 25 wt ppb after sintering or heat treatment in hydrogen. Ekbom [2] also determined the hydrogen content in a relatively brittle 90W–5Ni–5Fe specimen to be 950 wt ppb, which is equivalent to 380 wt ppb for the 96W–2.8Ni–1.2Fe alloy when reduced by the matrix volume ratio. It appears, therefore, that the 96W–2.8Ni–1.2Fe alloy contains about 300 to 400 wt ppb of hydrogen after sintering or heat treatment at 1000° C in hydrogen.

The hydrogen content $\bar{C}$ at which the embrittling effect is eliminated is not known accurately either. But Ekbom [2] showed, without specifying the sintering and heat-treating procedures, that ductility was increased if the hydrogen content was reduced by 50% in an alloy of 90W–5Ni–5Fe composition. The $\bar{C}/C_i$ ratio required to remove the embrittling effect can be also estimated from the present results. From Fig. 5 the time required to remove the hydrogen embrittlement effect at 600° C is estimated to be about 15 min, including about 5 min near 600° C during heating and cooling. The $\bar{C}/C_i$ ratio estimated from Equation 2 and Powell's value of D is 0.16. It appears, therefore, that the hydrogen embrittlement effect is removed when the $\bar{C}/C_i$ ratio reaches the range between 0.5 and 0.1.

With these values of $\bar{C}/C_i$, the vacuum-treatment time required to remove the hydrogen embrittle-

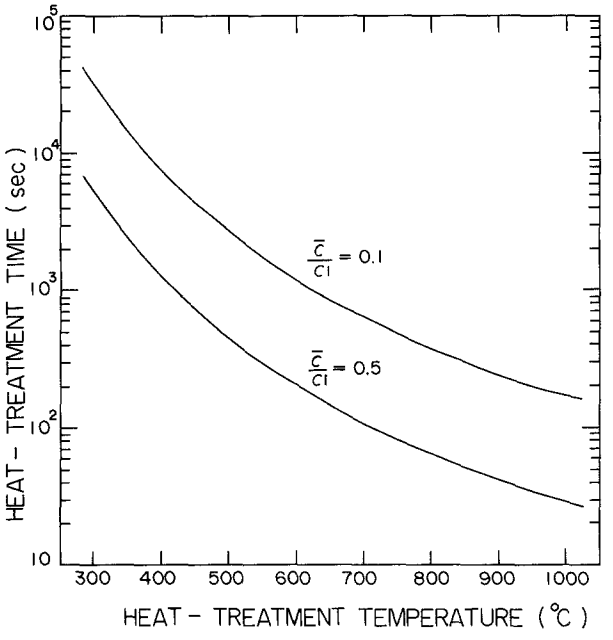


Figure 8 The calculated heat-treatment time required to remove the hydrogen embrittlement in a specimen of 2 mm radius at various heat-treatment temperatures.

ment effect was calculated at various temperatures using Equation 2 and Powell's [13] value for D. The results are shown in Fig. 8. The temperature dependence behaviour shown here appears to be consistent with the experimental results in Fig. 3. The annealing cycle for "0" time shown in Fig. 1 indicates that the specimens remain at temperatures near the peak for about 5 to 10 min. Then from the curve for $\bar{C}/C_i = 0.1$ in Fig. 7 the effect of heat treatment for "0" time at temperatures below 400° C is expected to be little, while it should increase rapidly with temperature above 600° C. Further increase of the temperature above 800° C will not increase the elongation because the hydrogen diffusion is very rapid. Since Fig. 8 was obtained from the temperature dependence of the effective hydrogen diffusion rate in this alloy, its consistency with the experimental observation of Fig. 3 is an indirect evidence that the hydrogen removal during heat treatment is the cause for the ductility increase.

For relatively small specimens of 2 mm in radius the embrittlement effect can be removed in short times at temperatures above about 600° C. For larger specimens, the required heat treatment time will increase in proportion to the square of their linear dimension. Therefore, a more practical heat treatment temperature might be in the range between 800 and 1000° C. In any case, Fig. 8 can be a useful guide for determining the heat treatment conditions, and its reliability will be greatly enhanced if $\bar{C}$ and C_i are more accurately known from direct measurements.

Another important observation to be made from the results in Fig. 6 is that the heat treatment at 1000° C in hydrogen does not markedly affect the mechanical properties. This result is in contrast with some previous reports [5–8] that ductility and toughness were increased by a heat treatment process at this temperature, which was attributed to the phase transformations in this alloy system. Although such a possibility cannot be entirely ruled out, the results shown here demonstrate that a pronounced increase of ductility can occur by removal of the hydrogen embrittlement and any direct heat treatment effect appears to be comparatively negligible.

The typical fracture surfaces of the as-sintered and the vacuum-treated specimens are shown in the scanning electron micrographs of Fig. 7. The as-sintered specimen showed many areas of W–W grain boundary failure (indicated by A in the figure) and extensive decohesion of the matrix from the W grains (B). The matrix itself fractured to shear lips (C) by ductile shear type failure. In contrast, the fracture surface of the vacuum-treated specimens was characterized by the tendency of the matrix to adhere to the grains and limited occurrence of its decohesion from the grains. The matrix failure occurred by the formation of shear lips (D) and tensile dimples (E). In addition, the vacuum-treated specimens showed

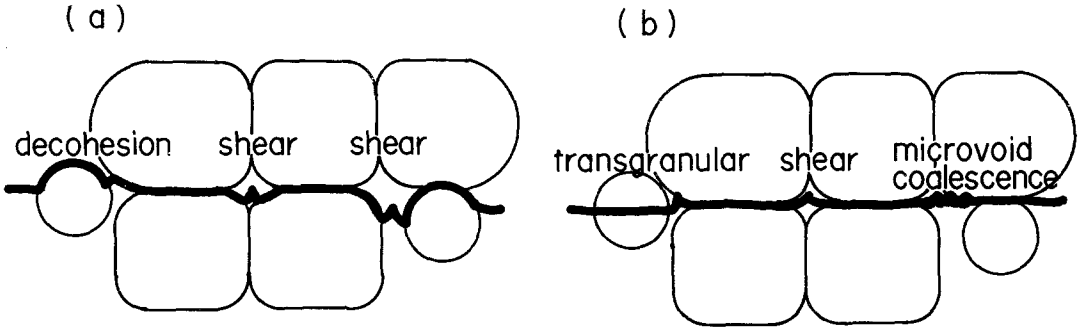


Figure 9 Illustration of the fracture modes in (a) the as-sintered and (b) the vacuum-treated alloy.

some transgranular failures of the tungsten grains as indicated by F in Fig. 7c.

The fracture behaviour of the specimens which were first heat treated in vacuum and then in hydrogen at 1000° C was similar to that of the as-sintered specimens. This observation demonstrates that the hydrogen, which can be retained in the alloy after sintering or final heat treatment in hydrogen atmosphere, has a strong embrittling effect on the fracture behaviour of these alloys.

The observed fracture modes are illustrated in Fig. 9 for the as-sintered and the vacuum-treated specimens. During the tensile test of the as-sintered specimens, the cracks must have first formed at the W–W grain boundaries as had been demonstrated in the previous studies [2, 9]. The cracks initiated at the W–W boundaries appeared to propagate preferentially along the W–matrix interfaces, causing the decohesion of the tungsten grains from the matrix. The hydrogen, therefore, appears to have a strong embrittling effect on the W–matrix interface as had been previously suggested by Ekbom [2], and Sczerzenie and Rogers [3] for these alloys.

In as-sintered specimens, the cracks appear to propagate sometimes through the matrix. Such behaviour can occur probably under certain stress conditions when, for instance, the direction of the crack propagating along the W–matrix interface becomes almost parallel to the applied stress. The grain size of the matrix itself was observed to be so large that a crack could rarely encounter the grain boundaries within the matrix. The matrix, therefore, appears to fracture by transcrystalline failure due to plastic shearing. Such a ductile behaviour of the matrix is consistent with the earlier observations [14] that the hydrogen had no embrittling effect in nickel single crystals in contrast to the pronounced effect in polycrystalline nickel and Ni–Fe alloys.

In the specimens which were heat treated in vacuum, the hydrogen removal appears to have increased the cohesive strength of the W–matrix interface. The fracture surfaces showed a strong tendency of the matrix to adhere to the grains and only a little decohesion was observed. In these alloys, the cracks produced initially at the W–W boundaries can be thus effectively stopped by the matrix while they undergo a substantial elongation. When the cross-section of the matrix subjected to the tensile stress is relatively large, microvoids can probably appear during plastic deformation of the matrix, producing the dimples at fracture. On the other hand, when the matrix cross-section is small, failure can probably occur by plastic shearing, producing the shear lips similar to those found in the as-sintered or the hydrogen-treated specimens. While these alloy specimens undergo deformation, the tungsten grains, which will be under the hydrostatic pressure of the surrounding matrix, also elongate substantially as shown previously [2, 9, 11]. At a certain critical stress level, the tungsten grains can fail by transcrystalline fracture as is often found on these fracture surfaces.

Conclusion

The most important contribution of this work is the definitive experimental demonstration that the tungsten base heavy alloy is subject to hydrogen embrittlement and it can be removed by heat treatment in vacuum. The observed temperature dependence of the vacuum-treatment effect is consistent with the diffusional removal of hydrogen. The ductility does not increase if heat treatment is done in hydrogen atmosphere after sintering and the embrittlement effect is restored in a ductile specimen (obtained by heat treatment in vacuum) by heat treatment in hydrogen.

The conditions (temperature and time) for heat

treatment in vacuum were also more clearly defined than those presented in previous results. For small tensile specimens, vacuum treatment for about 10 min at 600° C is sufficient to increase the tensile properties to the maximum. For large pieces, temperatures from 800 to 1000° C appear to be more practical.

These results also indicate that the tensile properties of this alloy can be sensitive to the atmosphere and the cooling rates during sintering. Since the hydrogen diffusion is rapid, the hydrogen content will be reduced to the saturation values even in a hydrogen atmosphere if the cooling rate is slow. When rapidly cooled, large amounts of hydrogen corresponding to the saturation value at high temperatures will be retained.

The observation of the fracture surfaces shows that the hydrogen embrittlement occurs mainly by weakening of the W–matrix interface. But further study will be required to determine definitely if the matrix itself is unaffected by hydrogen.

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