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Effect of hydrogen on the mechanical properties of a deformation processed Cu–20% Nb composite

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The influence of H on the mechanical properties of a deformation processed Cu–20% Nb composite was analysed and compared with the results on similarly processed pure Cu and pure Nb. In this composite the matrix phase (Cu) is relatively resistant to H while the filamentary phase (Nb) is highly susceptible to H embrittlement. The results show that H, in an amount equivalent to that which causes embrittlement of pure Nb, causes no significant deleterious influence on the mechanical properties of Cu–20% Nb. Apparently the ductile Cu matrix creates a favourable stress state for the hydrogenated Nb filaments so that they are constrained from fracturing and continue to deform in a ductile manner.

1. Introduction

Deformation processing of Cu–Nb alloys results in composite materials where very thin and highly aligned Nb filaments of large aspect ratio are formed in a Cu matrix [1–3]. These composite materials have very high strengths [4–6], good electrical and thermal conductivities [7–9] and good thermal stabilities [10]. Because of this combination of properties these composites are potential replacements for Cu alloys which are fairly resistant to H embrittlement and used in H environments such as rocket liners or combustion chambers [11]. The presence of Nb in the composites, which is highly susceptible to H embrittlement [12], makes the potential use of these composites in H environments questionable. Previous work has shown that deformation processed Cu–20% Nb behaves more like b c c Nb than f c c Cu which suggests it might be readily embrittled by H [13]. The purpose of this study is to clarify the roll of H on the mechanical behaviour of deformation processed Cu–20% Nb. It appears that little research has been done on H effects in materials composed of phases with contrasting affinities for H embrittlement as is the case for Cu and Nb.

2. Experimental procedure

A Cu–20 vol % Nb billet was prepared by consumable arc melting an electrode containing Nb strips in a Cu cylinder as previously described [5, 14]. The billet was about 7.6 cm in diameter and was machined to 7.4 cm and then diametrically opposite flats were machined in the billet to give a nearly rectangular cross section of 6.1 cm × 7.4 cm. The billet was rolled at room temperature from 6.1 cm to 0.16 mm using reductions of about 10% per pass. The total rolling strain was 6.0. Pure Cu and pure Nb were processed in the same manner as the Cu–20% Nb but the total rolling strain was 5.5 for sheet with a thickness of 0.16 mm.

Hydrogen charging of the 0.16 mm sheets of Cu, Nb and Cu–20% Nb was done at 300 °C to minimize recovery and filament coarsening and the subsequent loss in strength in Cu–20% Nb [10]. Prediction of the rate of transport and the internal distribution of H in a two phase material such as the Cu–20% Nb alloy is much less certain than in a single phase alloy. Copper is the continuous phase with small isolated strands of Nb. Hydrogen is much more soluble in Nb than in Cu. At 300 °C the molar concentration in Nb would be 600 000 times the concentration in Cu under the same pressure of H. Diffusion in both metals is relatively fast but in Nb it is about twenty times as fast as in Cu. Hydrogen diffusion in Cu at 300 °C is 3.3×10^{-6} cm$^{2/5}$ which means that a 0.16 mm slab or sheet of Cu would be 93% saturated in 8.8 s.

The high solubility of H in Nb requires a larger flux to saturate the Cu–20% Nb alloy than for pure Cu and this will greatly increase the time required to charge a given thickness. A satisfactory model for calculating this time has not been established at this time. The H charged into Cu–20% Nb was absorbed over a period of 72 h at 300 °C. A similar treatment was used for pure Cu, which did not absorb a measurable amount of H, and for pure Nb, which absorbed H very rapidly. The H in Cu–20% Nb would be located almost exclusively in the Nb filaments because of the solubility relationships. Hydrogen compositions were verified by a hot vacuum extraction method on the ends of failed tensile specimens.

Tensile specimens were machined from the rolled sheets and had a gauge cross section of 0.5 cm by 0.16 mm with a 12.5 cm gauge length. All tests were done using a nominal strain rate of 1.7×10^{-4} s^{-1}. At least two specimens were tested for each condition for

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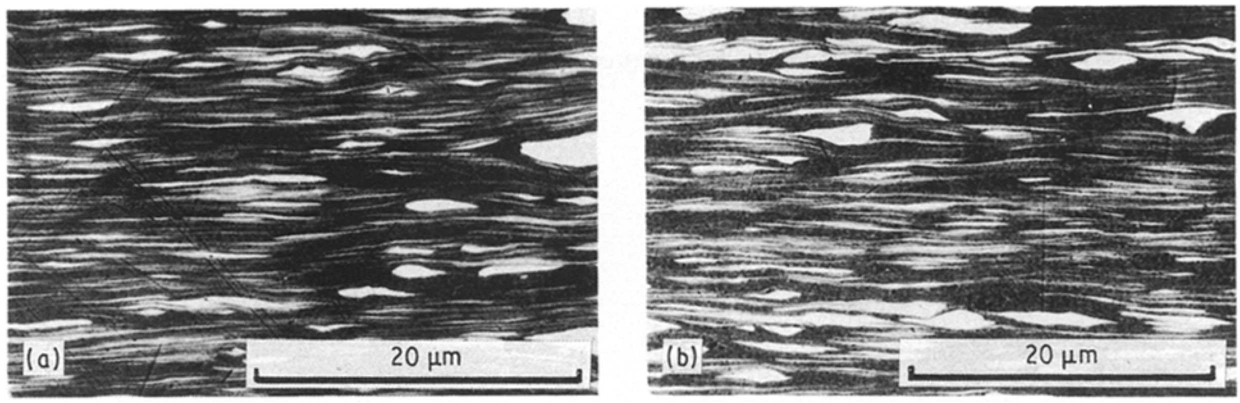

Figure 1 SEM images of transverse sections of (a) annealed and (b) hydrogenated Cu–20% Nb sheet.

TABLE I Hydrogen concentrations in Cu, Nb and Cu–20% Nb after annealing and hydrogenation treatments at 300 °C for 72 h.

Material	Annealed (at %)	Hydrogenated (at %)
Cu–20% Nb	0.42[a]	1.95[a]
Nb	0.12	1.64
Cu	0.13	0.15

[a] all H assumed to be in Nb

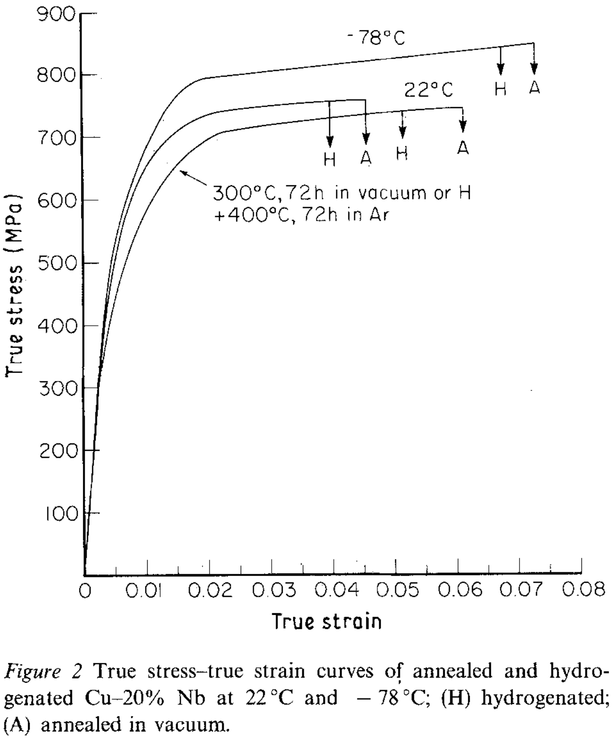

Figure 2 True stress–true strain curves of annealed and hydrogenated Cu–20% Nb at 22 °C and − 78 °C; (H) hydrogenated; (A) annealed in vacuum.

Cu, Nb and Cu–20% Nb. The fracture strain was calculated from the change in thickness of the specimen. The thickness in the necked region was measured by examining the fractures in a scanning electron microscope (SEM). An average thickness near the centre of the specimen was used because the edges of the fracture region were generally wavy. Filament thicknesses and spacings were determined using standard stereographic intercept procedures as previously reported [5].

TABLE II Ultimate tensile stress (σ_{UTS}), uniform strain (ε_u), fracture strain (ε_f), Nb filament spacing ($\bar{\lambda}$) and thickness ($\bar{t}$) for Cu–20% Nb before and after annealing and hydrogenization treatments

Condition	σ_{UTS}(MPa)	ε_u	ε_f	$\bar{\lambda}$(μm)	$\bar{t}$(μm)
22 °C					
As-rolled	778	0.032	0.62	0.34	0.085
300 °C for 72 h					
vacuum	730	0.039	0.65	0.52	0.13
H	729	0.033	0.68	0.53	0.13
300 °C for 72h + 400 °C for 72 h in Ar					
vacuum	697	0.054	0.68	0.61	0.15
H	695	0.045	0.69	0.59	0.15
− 78 °C					
300 °C for 72 h					
vacuum	789	0.066	0.61	0.52	0.13
H	792	0.060	0.59	0.53	0.13

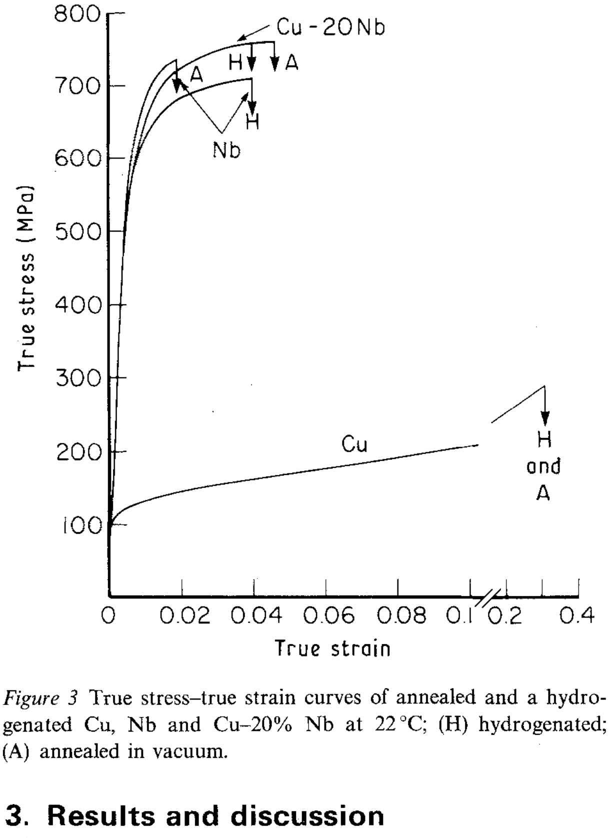

Figure 3 True stress–true strain curves of annealed and a hydrogenated Cu, Nb and Cu–20% Nb at 22 °C; (H) hydrogenated; (A) annealed in vacuum.

3. Results and discussion

The amount of H desired in the Cu–20% Nb composite was 1.5 at % or greater because previous work showed that this level of H should embrittle Nb at

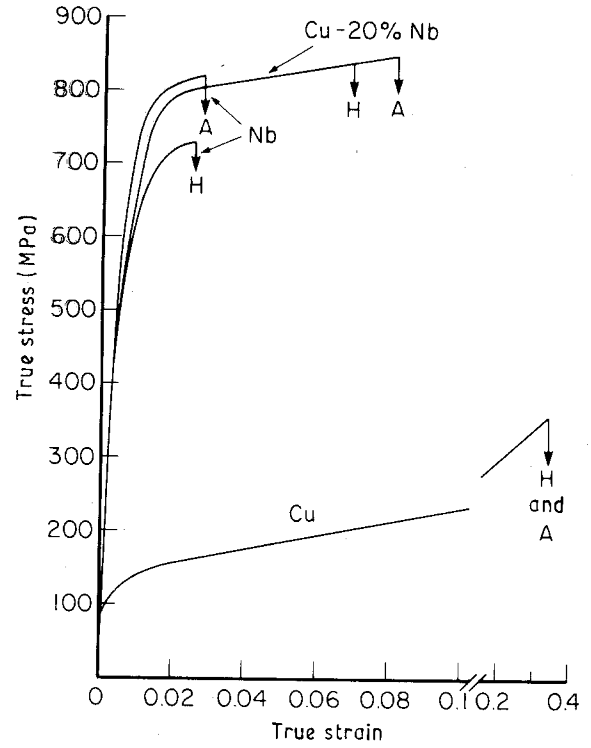

Figure 4 True stress–true strain curves of annealed and hydrogenated Cu, Nb and Cu–20% Nb at − 78 °C; (H) hydrogenated; (A) annealed in vacuum.

TABLE III Ultimate tensile stress (σ_{UTS}), uniform strain (ε_u) and fracture strain (ε_f) for Cu and Nb before and after annealing and hydrogenization treatments

Condition	Temperature (°C)	σ_{UTS} (MPa)	ε_u	ε_f
Cu				
As-rolled	22	465	0.018	[a]
300 °C for 72 h				
vacuum	22	211	0.30	[a]
H	22	213	0.28	[a]
vacuum	− 78	266	0.30	[a]
H	− 78	262	0.32	[a]
Nb				
As-rolled	22	745	0.022	[a]
300 °C for 72 h				
vacuum	22	702	0.012	[a]
H	22	687	0.032	1.1
vacuum	− 78	802	0.018	[a]
H	− 78	715	0.019	0.15

[a] chisel edge fracture

room temperature [12]. The actual amount of H in the hydrogenated Cu–20% Nb specimens was 1.95 ± 0.07 at % while the H content in the non-hydrogenated specimens was 0.42 at %, assuming that all of the H in the samples was in the Nb. Table I

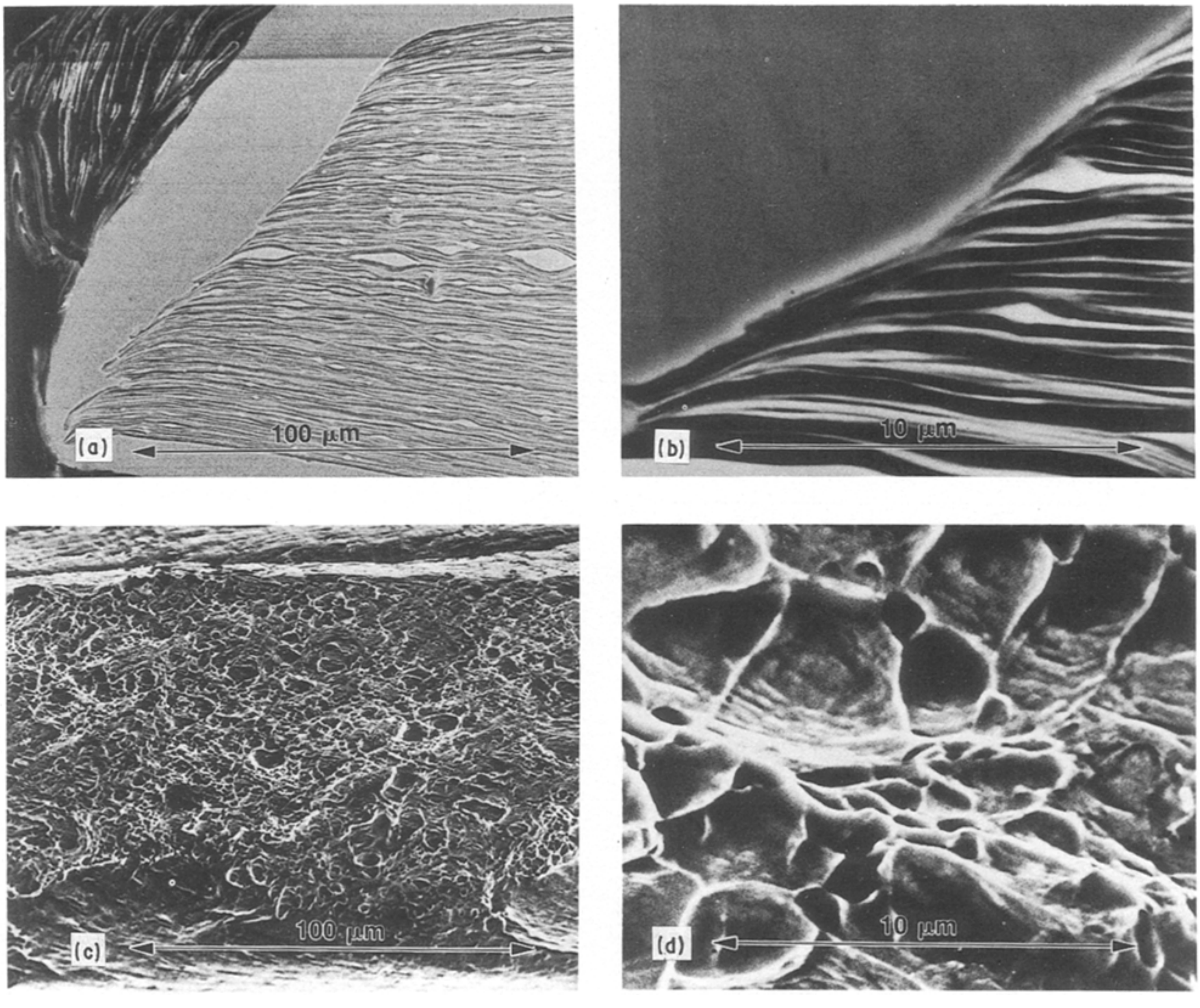

Figure 5 SEM images of fracture profile (a and b) and fracture surface (c and d) of annealed Cu–20% Nb tested at 22 °C.

shows the average H contents in the Cu, Nb and Cu–20% Nb specimens after annealing or hydrogenization at 300 °C for 72 h. The values shown in Table I were determined from analyses on the grip ends of deformed specimens.

Fig. 1 shows transverse sections of Cu–20% Nb sheet that was annealed at 300 °C for 72 h in vacuum or under a partial pressure of H. There is no evidence of any voids or differences in the microstructure as a result of the hydrogenization treatment. Fig. 2 shows stress–strain curves of the sheet specimens tested at 22 °C and −78 °C. The effect of the annealing or hydrogenization treatments was to increase the Nb filament spacing ($\bar{\lambda}$) and thickness ($\bar{t}$) and this was the primary cause of the reduced strengths after these treatments as compared to the as-rolled condition, as shown in Table II. In one series of tests the annealed and hydrogenated specimens were given an additional annealing treatment at 400 °C for 72 h to try to insure that the H was uniformly distributed throughout the hydrogenated specimens. This additional treatment coarsened the Nb filaments further and reduced the strength but did not cause embrittlement indicating that the H was uniformly distributed in the sample after the 300 °C treatment. The results in Table II show that H had no affect on the strength and fracture strain of Cu–20% Nb. The only apparent effect of H on Cu–20% Nb was to slightly reduce the uniform elongation.

The tensile tests at −78 °C shown in Fig. 2 were done to further examine the effect of H on Cu–20% Nb because at this temperature Nb containing only 0.23 at % H has only limited ductility having a fracture strain of about $\varepsilon_f = 0.15$ [12]. The results in Fig. 2 and Table II show that the hydrogenated Cu–20% Nb retained its ductility even at −78 °C further supporting the room temperature observations that H has no appreciable affect on the ductility of this material. The consistent observation that H slightly reduced the uniform strain of Cu–20% Nb suggests that void nucleation or void growth may be somewhat enhanced by H. However, the apparent absence of any similar influence of H on fracture strain contrasts with this suggestion. Perhaps the difficulty in accurately measuring the final thickness of the fractured specimens was the reason for the apparent lack of a reduction of fracture strain in the presence of H.

Figs 3 and 4 compare the stress–strain behaviour of annealed and hydrogenated Cu, Nb and Cu–20% Nb at 22 °C and −78 °C, respectively. Fig. 3 shows that H has a much greater influence on the mechanical behaviour of Nb as compared to Cu–20% Nb and

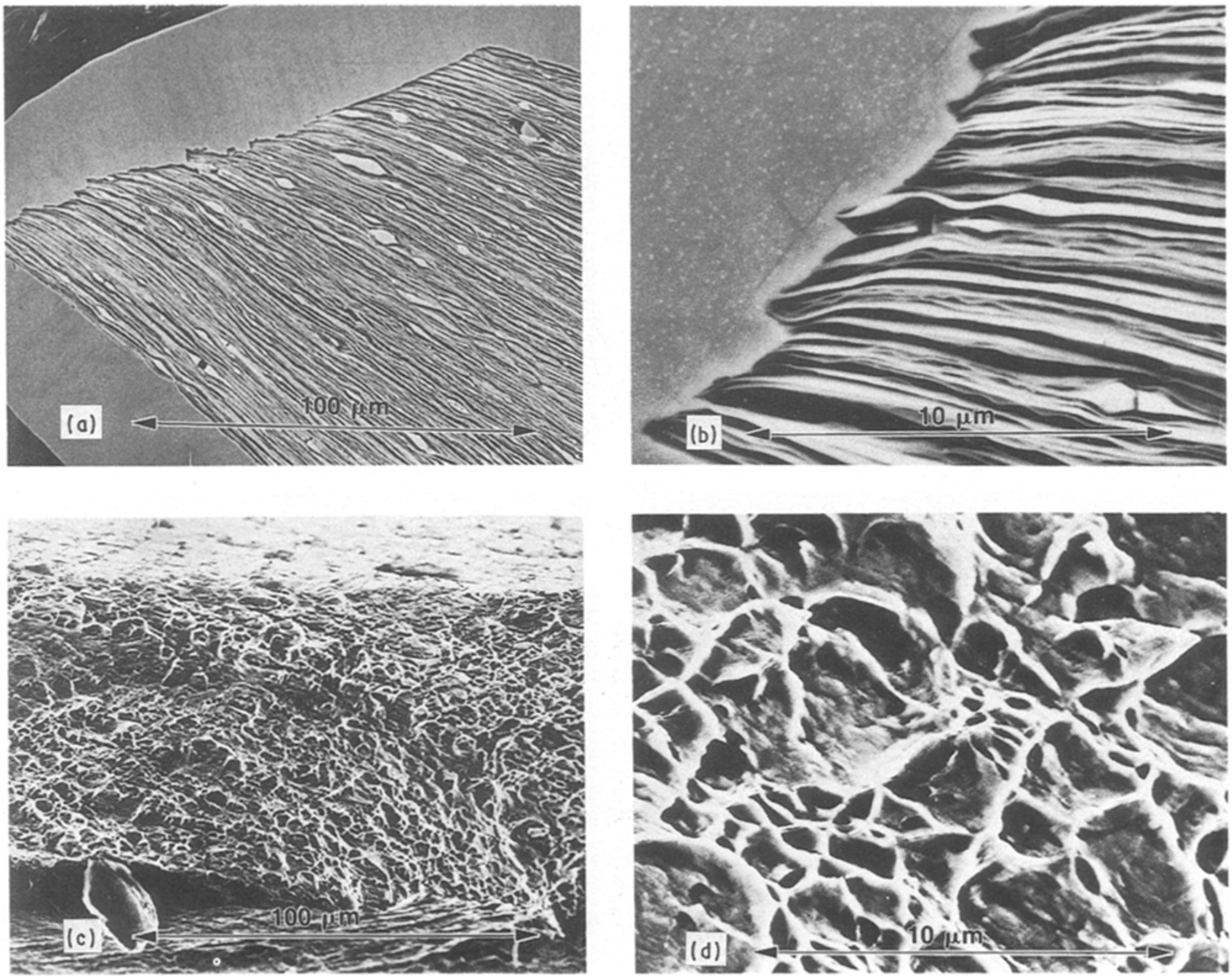

Figure 6 SEM images of fracture profile (a and b) and fracture surface (c and d) of hydrogenated Cu–20% Nb tested at 22 °C.

that H has no apparent affect on the stress–strain behaviour of Cu. However, as shown in Table I the hydrogenization treatment used introduced little if any H into Cu. In Nb, H produced softening and slightly decreased the fracture strain although Nb remained ductile, as shown in Table III.

At −78 °C the ductility of hydrogenated Nb appreciably reduced to a fracture strain value of only 0.15, which is similar to that observed previously for hydrogenated Nb at temperatures below the ductile–brittle transition temperature [12]. However, a similar amount of H in Cu–20% Nb did not reduce the fracture strain (Table II).

Figs 5 and 6 compare the fracture profiles and fracture surfaces of annealed and hydrogenated, respectively, Cu–20% Nb specimens tested at 22 °C. Comparison of these figures shows no apparent differences in fracture behaviour. The fracture profiles (a and b in Figs 5 and 6) show the filaments appear to fail in a ductile fashion with or without H present. The fracture surfaces (c and d in Figs 5 and 6) show that both annealed and hydrogenated Cu–20% Nb failed in a ductile manner. These fracture observations reflect the lack of changes of mechanical properties when H was present in Cu–20% Nb (Table II).

The fracture behaviour of annealed and hydrogenated Cu–20% Nb specimens tested at −78 °C are shown in Figs 7 and 8, respectively. There is no obvious difference in the fracture behaviour of the annealed and hydrogenated specimens. The fracture profiles (a and b in Figs 7 and 8) show that the filaments remain ductile whether H is present or absent. The fracture surfaces (c and d in Figs 7 and 8) show that both annealed and hydrogenated Cu–20% Nb failed by ductile rupture. The similarity in fracture behaviour in annealed and hydrogenated Cu–20% Nb at −78 °C is in accord with the mechanical property results (Table II).

Fig. 9 shows the fracture surfaces of annealed (Fig. 9a) and hydrogenated (Fig. 9a–d) Nb tested at −78 °C. Fig. 9a and b contrast the fractures of annealed and hydrogenated Nb. The annealed Nb shows a chisel edge fracture which is also typical to that observed for all the Cu specimens. The hydrogenated Nb specimen shows brittle fracture behaviour along with the presence of numerous cracks which appear to be parallel to the sheet surface. These cracks are probably associated with the deformation bands that develop during heavy deformation in bcc metals [15, 16]. Perhaps H segregates within or along these deformation bands thereby leading to cracking during subsequent tensile deformation. These cracks are most likely the cause of the apparent softening and the low ductility of the hydrogenated Nb specimens (Table III).

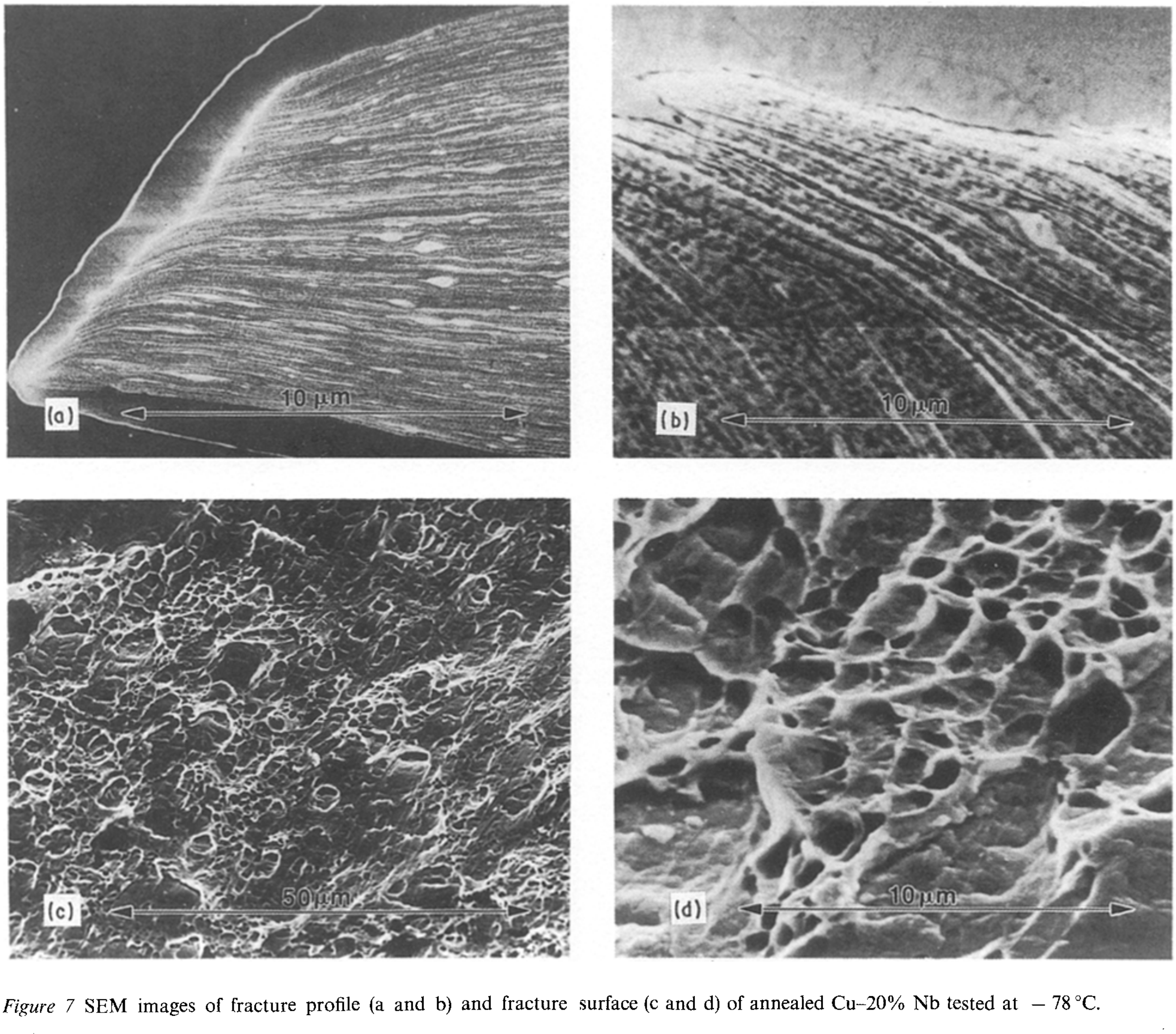

Figure 7 SEM images of fracture profile (a and b) and fracture surface (c and d) of annealed Cu–20% Nb tested at −78 °C.

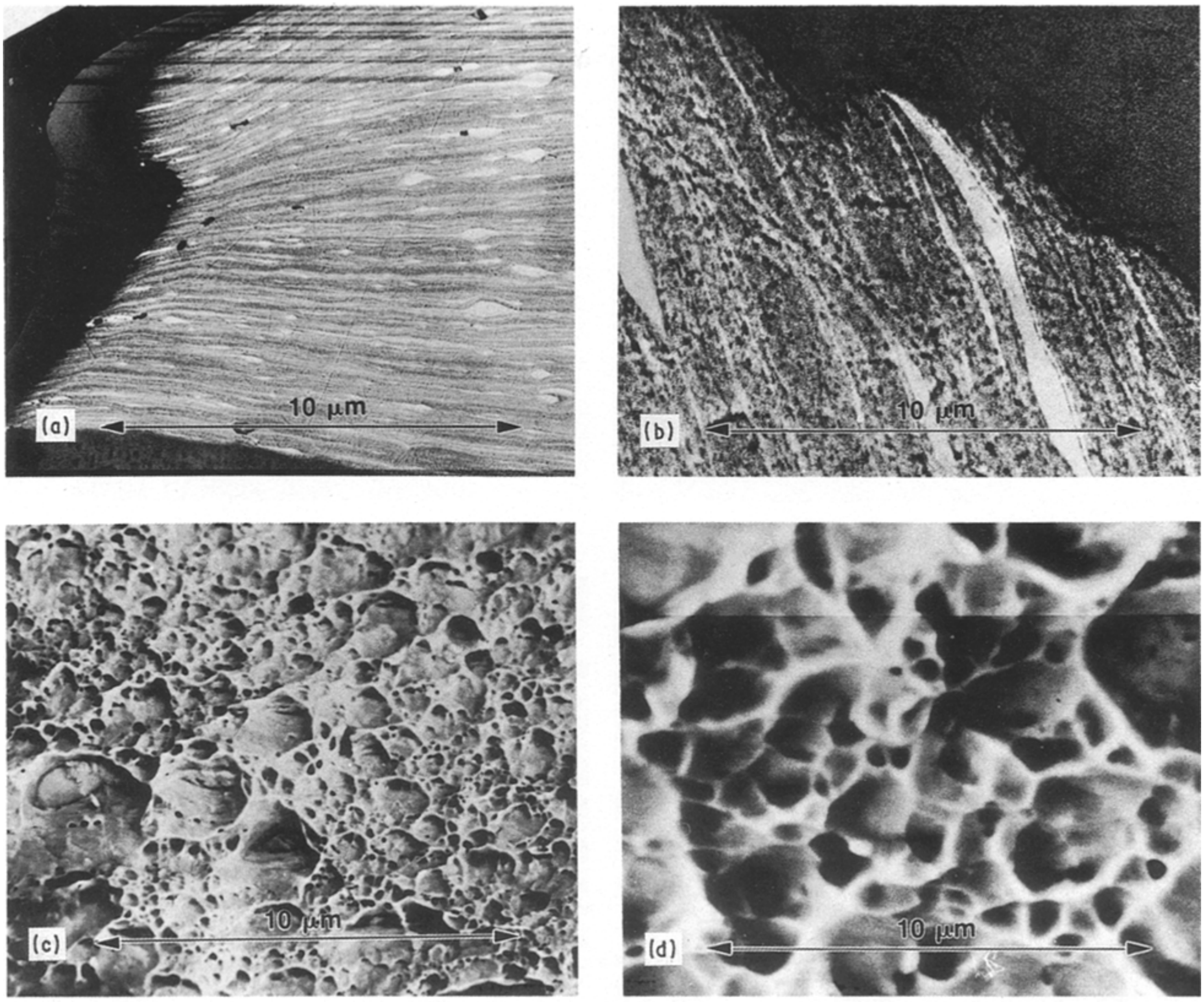

Figure 8 SEM images of fracture profile (a and b) and fracture surface (c and d) of hydrogenated Cu–20% Nb tested at −78 °C.

Because they are parallel to the tensile direction the cracks do not lead to catastrophic fracture. The hydrogenated Nb specimens tested at 22 °C also showed some small cracks parallel to the sheet surface but the specimens were still quite ductile although they did show reduced strengths (Table III).

4. Conclusions

The main goal of this study was to investigate the effect of H on the mechanical properties of a Cu–20% Nb deformation processed composite where the matrix phase (Cu) is relatively resistant to H while the filamentary phase (Nb) is highly susceptible to H embrittlement. The results show that H, in an amount equivalent to that which causes pure Nb to become brittle, has no significant deleterious influence on the mechanical properties of a Cu–20% Nb composite. Results showing that H does slightly reduce the uniform elongation suggest that void nucleation or void growth may be somewhat enhanced by H but there is no evidence that H affects the fracture strain. The ability of the hydrogenated Nb encapsulated in the Cu matrix to continue to display ductile behaviour does not appear to be unusual. Similar behaviour has been observed in a Cu–17% Cr deformation processed composite [17]. In this case the Cr is inherently brittle but when encapsulated in Cu the Cr can be extensively drawn to produce a filamentary composite. Apparently the ductile Cu matrix creates a favourable stress state for the hydrogenated Nb filaments so that they are constrained from fracturing and continue to deform in a ductile manner. This is somewhat analogous to deformation under a superimposed hydrostatic pressure where ductility increases as the hydrostatic pressure increases [18]. It is generally believed that the hydrostatic pressure retards the development of the defects causing fracture.

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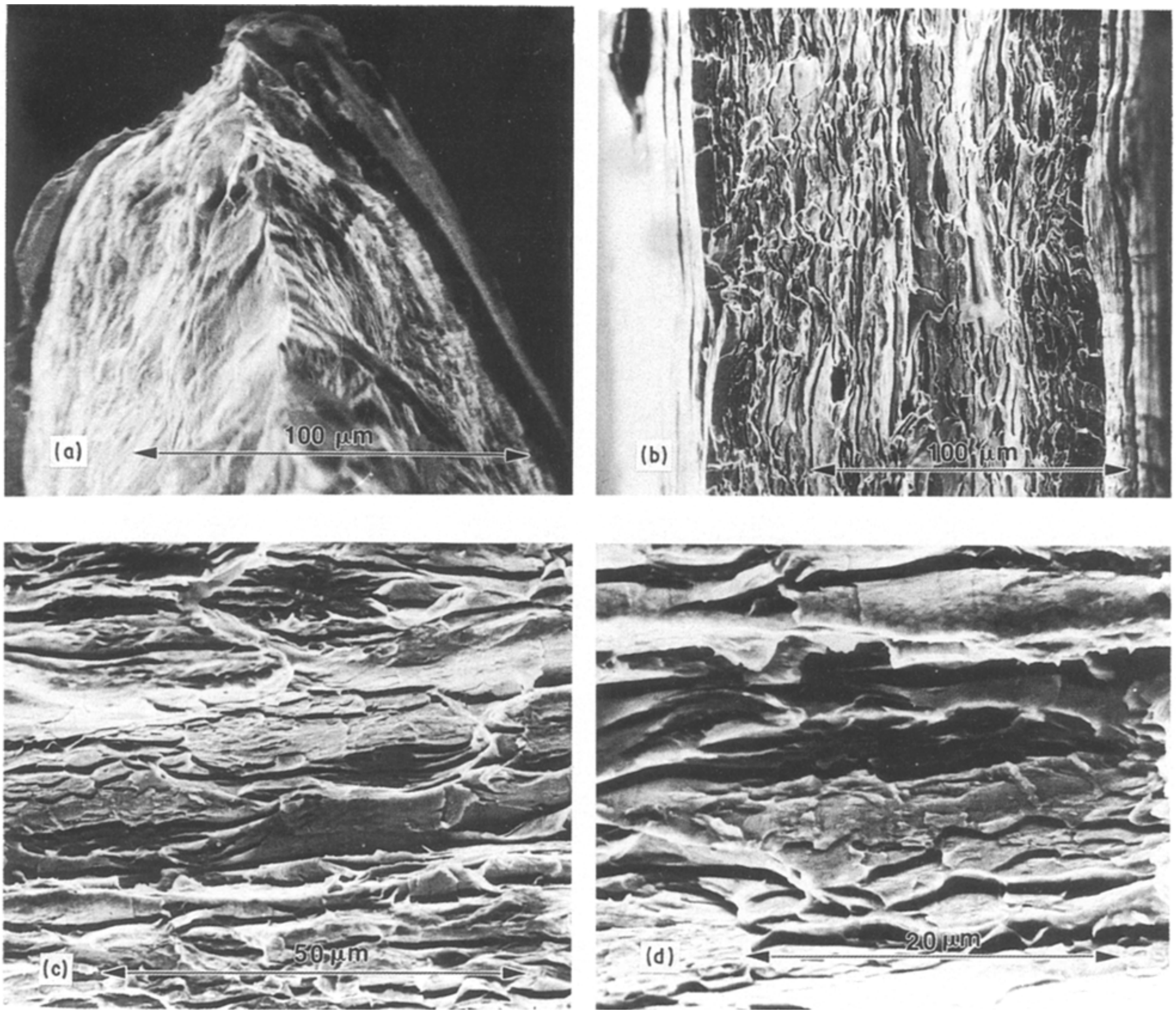

Figure 9 SEM images of fracture profile (a and b) and fracture surface (c and d) of annealed (a) and hydrogenated (b–d) Nb tested at − 78 °C.

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