ROLE OF STRAIN-ASSISTED TRANSPORT OF HYDROGEN ON THE INTERGRANULAR FRACTURE OF NICKEL BASE ALLOYS

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ABSTRACT

Tensile tests were performed on small samples of alloy 600 containing a controlled concentration of hydrogen (H) : 1850 at.ppm, in order to investigate the role of a possible built up of a transient H concentration in the vicinity of grain boundaries associated with dislocation transport during straining. A particular attention has been paid to the dependence of H-induced intergranular rupture on the carrying capacity of moving dislocation. For a given initial H concentration (closed system) the later depends on the ability of H to interact both with moving traps (dislocation) and static defects (forest dislocation,...) which is a function of strain rate, temperature, and the concentration of diffusible hydrogen. The role of these parameters on the tensile behavior of hydrogenated alloy 600 shows a good correlation beetween the extent of intergranular rupture and two antagonistic mechanisms : the ability of H to be transported toward GB and the dissipation of the resulting local H supersaturation. The present results are in favor of a determinant role of dislocation transport on H-induced intergranular fracture of alloy 600.

1 INTRODUCTION

The hydrogen embrittlement sensitivity (H.E.) of nickel base alloys and the related intergranular fracture have been evidenced and discussed for a long time (Jones[1]). More recently the determinant role of H-plasticity interactions in the environmental degradation mechanisms have been emphasized (Moody[2], Birnbaum[3]). Whereas hydrogen affects the deformation mechanisms (enhancement of the dislocation motion and stress relaxation, effect on the stacking fault energy and the planar slip,Sofronis[4], Delafosse[5]), the deformation plays a role on H absorption and redistribution in the material (strain-induced damage in film barrier, stress and strain assisted trapping and transport of H,…) (Brass[6]). H-induced intergranular rupture must be considered as a consequence of a local enhancement of H concentration.

This concentration enhancement may result from these interactions and in particular from the transport of hydrogen by moving dislocations. In Ni base alloys this transport mechanism has been clearly evidenced (Chêne[7]) and recent experimental results strongly suggest that this mechanism controls H-induced intergranular rupture of alloy 600 in a wide temperature range (Chêne[8]).

However due to the dynamic character of these interactions and the strong interdependence of the parameters which control H-dislocation interactions in a given alloy (H activity, density and occupancy fraction of trapping sites, temperature, strain rate,), more detailed experimental work is required for a predictive analysis of H-induced intergranular fracture.

2 EXPERIMENTAL

This study is focused on the role of internal H on the mechanical behaviour of small flat tensile specimens (8x2x0.5 mm) of alloy 600 in the mill-annealed (MA 820°C) conditions.

The samples were hydrogenated by cathodic charging for 4h at 423K in molten salts (Chêne[8]) in order to ensure a concentration of about 1850 at. ppm homogeneously distributed in the bulk. The precise H concentration in each specimen and its possible evolution change with the testing conditions was measured with a melt extraction method. Tensile tests were conducted at various temperatures and strain rates ranging from 77 to 550K and from 10^{-5} to 10^{-1} s^{-1}. Specific tensile straining procedures were carried out in order to evidence the strain-assisted transport of H and to test the possible influence of strain-induced local transient concentration of H on the ductility loss :

- some tensile tests were performed at 293K on tritiated samples in order to characterize by liquid scintillation counting (Chêne[7]) the strain-assisted desorption of tritium.
-« interrupted tensile tests » performed at 293K with a 2% increase of the plastic deformation were conducted step by step after aging for 2 hours at 293K between each successive step,
- some tests were performed at 77K in order to ensure a plastic deformation of the hydrogenated samples while the H atoms are « freezed » in the microstructure in order to avoid any H redistribution during deformation. Different combinations of tests involving either a prestraining at 77K or the fracture at 77K of samples prestrained at higher temperatures were used to characterize the respective influence of the strain-induced redistribution of H and of the strain-induced increase of the trapping sites density.

A particular attention has been paid to the influence of the testing conditions on the H-induced uniform elongation loss (embrittlement index : I_f) and on H-induced changes in the fracture mode.

3 RESULTS AND DISCUSSION

3 .1 Strain-assisted transport of hydrogen in alloy 600

The liquid scintillation counting technique developed to study the dislocation transport of tritium in Ni base single crystals (Chêne [7]) was successfully used to evidence a significant strain-assisted desorption of tritium from alloy 600. However in this polycristalline material the extent of the dislocation transport is strongly dependent on the grain size of the tritiated alloy and on the strain level. Increasing the grain size favors the strain-assisted desorption indicating that grain boundaries act as a barrier to long range dislocation transport. The decrease in the strain-assisted desorption observed in prestrained samples is presumably due to the combined effect of a decrease of the mean free path of dislocation with increasing the density of the forest dislocation and of a decrease in the concentration of diffusible H with increasing the density of dislocation acting as trap for hydrogen.

3.2 Effect of temperature and strain rate on HE

A comparison of the tensile behaviour of hydrogenated and H free specimens shows two major effects of H on alloy 600 : a large elongation loss associated with a significant drop of the ultimate tensile strength and a change of the fracture mode from fully ductile (H free samples) to fully intergranular. The dependence of these effects as a function of the testing temperature and the strain rate are illustrated in figure 1. The ductility loss occurs in a wide temperature range (200-500K) and the embrittlement domain shifts slightly toward higher temperatures with increasing the strain rate.

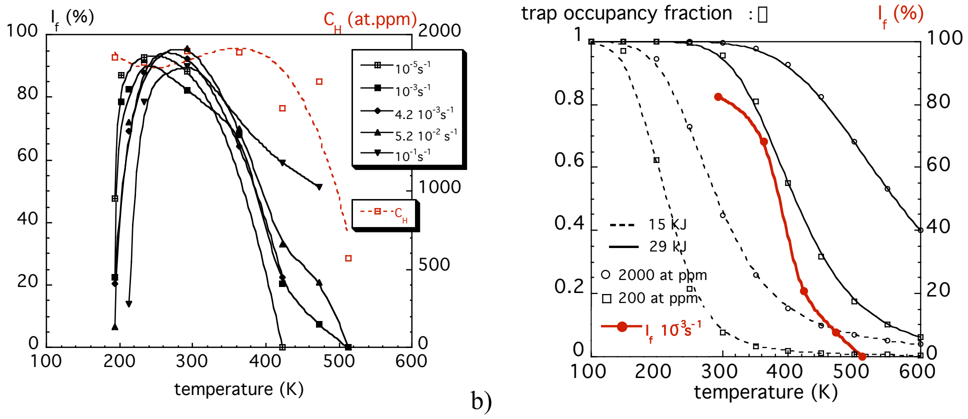
3.21 Effect of temperature

A major observation is the absence of any ductility loss of the hydrogenated samples strained at low temperature (below 180K). This observation indicates that H-induced intergranular fracture requires some strain-induced redistribution of H which cannot occur at low temperature when the H diffusivity is extremely small. It also demonstrates that a possible H trapping at grain boundaries and/or on the intergranular chromium carbides of the mill-annealed microstructure cannot account for the intergranular cracking without a strain–induced segregation of H. Moreover, whereas the ductility loss is very large at room temperature, the absence of any embrittlement when the hydrogenated sample is annealed for 3h at 563K in order to desorb the diffusible hydrogen, reflects the absence of irreversible damages associated with the introduction of H in the specimen and confirms the detrimental role of diffusible H.

The gradual drop of the ductility loss with increasing the testing temperature could be associated with H desorption from the specimen during the test. However the H concentration values measured in the strained samples (fig. 1a) show that no significant H desorption occurs during the tensile tests up to 473K whereas the embrittlement starts to decrease at 360K. Therefore the HE drop which occurs when the temperature is increased needs an alternative explanation based on the built up of a transient concentration in the G.B. vicinity associated with H transport by dislocations (§ 3.5).

3.22 Effect of strain rate

The results reported in figure 1a show that H-induced intergranular cracking is favored by lowering the strain rate at low temperature and by increasing it at high temperature. The shift at low temperature of the critical HE temperature has been explained in detail by a predominant role of H transport by moving dislocations on the intergranular rupture (Chêne[8]). Indeed, for the diffusible H to interact with a moving dislocation at low temperature, the segregation velocity of H to the dislocation has to be equal or larger than the dislocation mean velocity. At high temperature the significant increase of H.E . with increasing strain rate can be rationalized by taking into account the possible dissipation by thermal diffusion of the local H supersaturation raised by dislocation transport in the GB vicinity . Due to the large diffusivity of H at high temperature this effect is expected to be minimized with increasing the strain rate to reduce the time allowed for the dissipation of the local concentration. « Interrupted tensile tests » have been performed to check the validity of this hypothesis at room temperature when H-induced intergranular fracture is optimal.



a) b)

Figure 1. Effect of temperature and strain rate on H-induced intergranular rupture of alloy 600

a) role of the testing temperature and the strain rate on the ductility loss of H-precharged (1850 at.ppm) samples,

b) role of temperature and H concentration on H trapping on an edge dislocation for two values of the binding energy ; correlation with the ductility loss.

3.3 Interrupted tensile test at 293K

The results of interrupted tensile tests performed with the procedure reported in § 2 are illustrated by figure 2a. When the specimen is given successive 2% deformations at 293K, with a 2 hour aging at 293K of the unloaded sample between each deformation, the H-induced ductility loss is reduced by a factor of 2. This effect is not related with any desorption of H from the specimen during aging as H diffusivity at room temperature has been shown to be low (Chêne[9]). This is confirmed by concentration measurements performed on the strained samples showing no significant H desorption during the tensile tests. On the opposite, the aging time is expected to reduce, by diffusion, the concentration transient in the GB vicinity and/or to favor a drop in the concentration of diffusible H associated with H trapping on strain-induced defects (§ 3.5).

3.4 Role of the temperature of predeformation on HE

Another way to test the influence of the strain-induced H redistribution and its dependence on the strain level (antagonistic effects of H transport by moving defects and H trapping on the forest dislocations) is to compare the extent of H-induced ductility loss recorded on specimens prestrained at a temperature different from the temperature used to to fracture the samples. These tests are performed in such a way that the strain-assisted transport of H is only allowed to occur during the prestraining step (prestraining at 293K followed by fracture at 77K) or when the specimen is pulled to fracture (prestraining at 77K followed by fracture at 293K).

The results of such tests are illustrated in figure 2b. In this set of experiments, the hydrogenated samples were given à 4% prestrain at 77 or at 293 K .The comparison of the tensile behavior of the prestrained alloy with the tensile curves obtained without prestraining clearly shows that prestraining at low temperature reduces the intergranular fracture at 293K whereas prestraining at 293K reduces the ductility at 77K. This show that, in spite of the limited prestrain level, when the prestrain temperature allows the transport and redistribution of H in the specimen (293K) a significant ductility loss results from H deformation interactions. On the opposite, when the prestrain temperature allows the density of strain-induced defects to be increased without H redistribution (77K), a reduced ductility loss is measured at 293K.

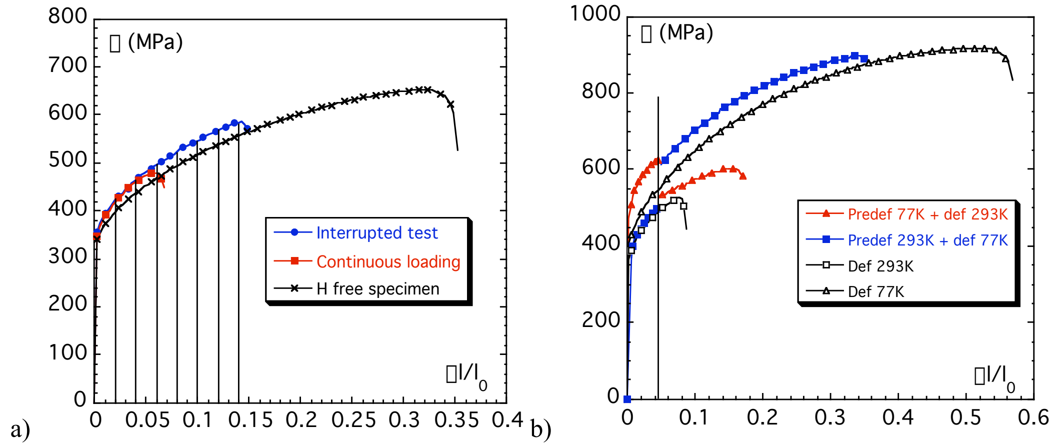


Figure 2. Role of the tensile testing procedure on H-induced ductility loss and intergranular fracture

a) Comparison of the extent of the ductility loss obtained with conventional tests and with « interrupted tests » (10^{-3} s^{-1}, 20°C).

b) Role of a 4% predeformation at 77 or 293K on the ductility loss (10^{-3} s^{-1}).

3.5 Discussion

A mechanism involving H transport by moving dislocation which leads to H local supersaturation in the vicinity of GB's acting as a barriers to the dislocation motion can account for the observed tensile behavior of alloy 600.

3.51 Correlation between the carrying capacity of moving dislocations and the intergranular fracture

For a given value of the binding energy (□H_b) associated with H trapping to dislocations, the carrying capacity of a moving dislocation is considered to depend on its occupancy fraction (□) a function of temperature, H activity in the lattice (C_0) and of the respective velocity of H segregation to dislocations versus the dislocation motion. Assuming the absence of hydrogen loss during tensile tests, the precharged tensile specimen can be considered as a closed system and with the assumption of a local equilibrium the occupancy fraction (□) can be obtained with the following relationship (Hirth[10]) : □/(1-□) = C_0exp[□H_b/RT] (1).

The temperature dependence of □ in alloy 600 computed with (1) is reported in figure 1b for two values of the binding energy and of the concentration of diffusible hydrogen.

A comparison of the segregation velocity of H to dislocations and of the dislocation mean velocity during the tensile tests (Chêne[8]) shows that H atmospheres can keep up with the moving dislocations above 320K. As a consequence, above this temperature, the dislocation occupancy fraction controls H transport and local supersaturation and presumably the resulting H embrittlement (I_f). The temperature dependence of I_f and □ is compared in figure 1b. While the H desorption is small below 500K (figure 1a), the simultaneous decrease of □ and I_f with increasing the testing temperature strongly supports the existence of a mechanism of H transport by moving dislocations leading to the observed intergranular fracture. However the efficiency of this mechanism is expected to decrease with increasing the time or the temperature or with decreasing the concentration of diffusible H, as a consequence of a H supersaturation drop in the GB vicinity.

3.52 Effect of H redistribution during or after straining

When compared to conventionnal tensile tests, the significant HE drop measured at the same strain rate during interrupted tensile tests (figure 2a), confirms the transient character of the H concentration in the GB vicinity which favors the intergranular embrittlement. A levelling of the strain enhanced H concentration near the GBs may result from the diffusion of H during the 2 hour aging at 20°C given to the samples between each deformation step . However the efficiency of the strain assisted transport mechanism can also decrease because the strain-induced rise in the density of defects (dislocations and vacancies) favors H trapping. In this case the concentration of diffusible H would decrasse in a closed system and thus the trap occupancy fraction (□).

Figure 3 illustrates the combined evolution, as a function of temperature, of H occupancy fraction of dislocations and of the H lattice concentration, in a closed system when the H concentration available for the interaction with traps is small and when the dislocation density is large. Assuming a local equilibrium, this picture shows that an increase of the forest dislocation (occuring during the tensile deformation) would favor the lattice concentration of H to drop to zero at low or moderate temperatures in such a way that further H transport by dislocation is not expected to occur since the carrying capacity of newly created dislocations is reduced to almost zero.

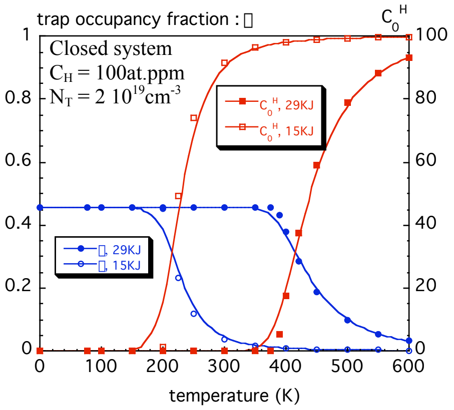


Figure 3. Evolution, as a function of temperature and for two values of the binding energy, of the trap occupancy fraction and of the lattice concentration in a closed system with a low H concentration and a high density of trapping sites.

4 SUMMARY

H induced intergranular rupture of mill annealed alloy 600 is shown to be strongly correlated with a strain-assisted transport and redistribution of H. The role of strain rate, temperature and H concentration on the extent of the related ductility loss indicates that the intergranular fracture depends on two antagonistic mechanisms : the ability of H to be transported toward GBs by moving dislocations and the dissipation of the resulting local H supersaturation.

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