

The effect of hydrogen on the bainite transformation

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The effect of hydrogen on the upper bainite transformation in two silicon containing steels has been investigated. For comparison, isothermal transformation at the same temperature has also been performed in a helium atmosphere. In both Fe-0.2C-3Mn-2Si and Fe-0.4C-4Ni-2Si (nominal wt %) alloys it was discovered that the bainite reaction proceeds further towards completion when the transformation is carried out in a hydrogen atmosphere. This can result in the reduction or elimination of the martensite phase which forms from residual austenite upon quenching to room temperature. The resultant microstructure of specimens heat treated in hydrogen was a fine aggregate of upper bainitic ferrite and interlath retained austenite. This effect is discussed in terms of hydrogen interactions in the lattice undergoing bainite transformation via a displacive mechanism. Additionally, it is found that the stability of the retained austenite in the final bainitic microstructure is not markedly influenced by hydrogen. © 1999 Kluwer Academic Publishers

1. Introduction

The influence of hydrogen in metals has been a topic worthy of examination for many years, principally because its many effects have been detrimental; for example, hydrogen embrittlement or hydrogen cracking [1–4]. However, in a few instances, hydrogen has been proven to have a beneficial effect. One such example, found relatively recently, is its potential use as a *temporary* alloying element in titanium alloys, allowing a reduction in mechanical working or processing temperature, and resulting in an improved microstructure [e.g. 5, 6]. (The hydrogen is described as temporary because it is removed from the solid alloy after the desired processing steps are complete.) This procedure has been referred to as *thermochemical processing*. The present paper identifies similar behaviour in steels through the effect of hydrogen on the progress of the bainite transformation during heat treatment, and an explanation for this can be developed from the premise that the bainite reaction is displacive in character. In steels where austenite is retained following the bainite transformation, the effect of hydrogen on the stability of this retained austenite is also of interest.

For the purpose of this study two experimental Si-containing steels were used for which the bainitic microstructures and mechanical properties have been previously documented [7–11]. In the upper bainite transformation region the presence of Si suppresses the formation of cementite and leads to the retention of an austenite phase which depending upon its carbon content and morphology can transform to martensite on

cooling to room temperature. The presence of martensite packets in the microstructure leads to low tensile ductility [10] and fracture toughness [11]. Greater susceptibility to hydrogen-induced cracking [1–4] would also follow. Elimination or restriction of martensite should improve the toughness of the microstructure and if effected by the presence of hydrogen could arguably make such microstructures less susceptible to the embrittling effect of hydrogen. Additionally, the stability, either thermal or mechanical, of the retained austenite, if influenced by hydrogen, could have an effect on whether these regions of retained austenite can subsequently form a brittle martensite.

2. Experimental procedure

The chemical compositions of the steels used are given in Table I. The steels were supplied in the form of 12 mm diameter rod.

Alloying of the steels with hydrogen was achieved by placing samples in a sealed stainless steel chamber with a vacuum and gas-inlet facility, located on a trolley. Prior to treatment the chamber was evacuated and purged three times with helium at 50 atm. pressure. After reevacuation the chamber was inserted into a furnace at 920 °C for 30 min to austenitize the samples, whilst simultaneously introducing 2 atm. of “0 grade” hydrogen into the chamber to bring about their hydrogenation. Specimen temperature inside the chamber was measured accurately via chromel-alumel thermocouples spot-welded to the samples. The chamber

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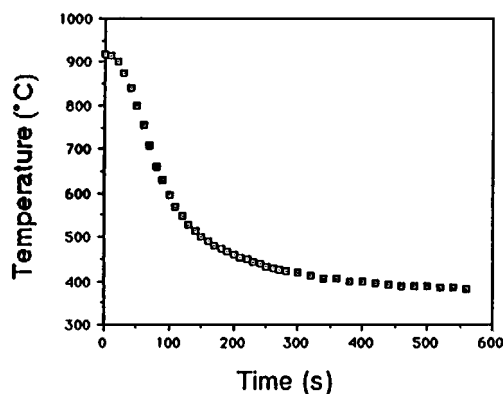
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TABLE I Chemical compositions of the experimental steels

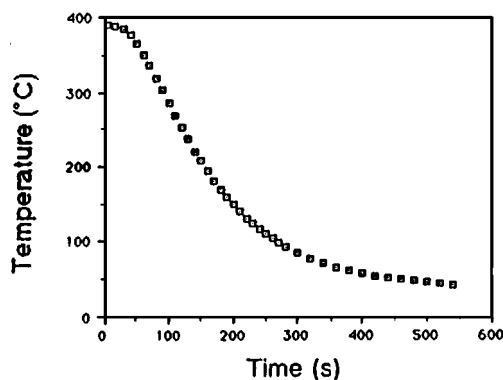
| Material | C | Ni | Mn | Si | S | P | Fe |
|---------------------|------|------|------|------|-------|--------|---------|
| Mn-containing alloy | 0.20 | — | 3.00 | 2.10 | 0.002 | 0.0016 | Balance |
| Ni-containing alloy | 0.40 | 4.09 | — | 1.99 | 0.002 | 0.0015 | Balance |

was then removed from the furnace and cooled in a water spray for 60 s before re-inserting it into a second furnace at 390 °C to allow isothermal transformation for 60 min. Following this heat treatment the chamber was removed and cooled by water spray for 100 s. Typical cooling curves of the specimens from the austenitization temperature, and from the isothermal transformation temperature, are given in Fig. 1.

In order to identify the effect of hydrogen on the isothermal transformation the same heat treatment was also carried out under 2 atm. pressure of helium for comparison. Helium was chosen as a comparative atmosphere because of its inert nature and also to eliminate any effect due to differences in thermal conductivities of the gases on cooling and transformation behaviour. The thermal conductivities of hydrogen and helium are very similar to each other, $1684 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-1}$ for hydrogen and $1415 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-1}$ for helium.



(a)



(b)

Figure 1 Cooling curves of specimens isothermally transformed in hydrogen or helium atmospheres: (a) cooling from the austenitization temperature, and (b) cooling from the isothermal transformation temperature.

The influence of hydrogen on the stability of retained austenite was evaluated by cathodically charging with hydrogen. This was carried out electrolytically in 0.1 M H_2SO_4 solution poisoned with 250 mg As_2O_3 in order to prevent recombination to the molecular form of adsorbed hydrogen atoms on the surface. The electrolyte was purged with nitrogen gas for 120 min before hydrogen charging in order to reduce the oxygen content. A platinum counter electrode was used as a cathode. The hydrogen charging current was typically 10 mAcm^{-2} applied for 300 s and the solution was held at 80 °C. Specimens were previously degreased in trichloroethane and chemically cleaned in 1 M H_2SO_4 .

The effect of hydrogen on mechanical stability was also evaluated by measuring the change in austenite volume fraction after 2% nominal plastic strain. In order to prevent hydrogen escape from specimens during tensile testing, hydrogen-charged specimens were cadmium coated for 20 min in an ammonium fluoborate solution consisting of 60 gl^{-1} ammonium tetrafluoborate in distilled water to which 0.5 gl^{-1} sugar was added to act as a brightener, held at 40 °C. Room-temperature tensile tests were carried out on Hounsfield-type specimens in an Instron tensile machine at a nominal strain rate of $8.33 \cdot 10^{-5} \text{ s}^{-1}$. Quantitative X-ray analysis techniques were used to determine the retained austenite content. A Philips PW1710 diffractometer was used at 40 kV and 30 mA, with Fe-filtered Co-K_{α} radiation and a graphite monochromator. The retained austenite content was calculated from the integrated intensities of a minimum of three austenite and three ferrite peaks with separation techniques where necessary, and the effect of texture was taken into account in accordance with the work of Dickson [12].

Specimens for light microscopy were prepared by mechanical polishing to 1/4 μm diamond paste followed by etching in 2.5% nital solution. Thin foil specimens for transmission electron microscopy were prepared from 0.3 mm thick discs slit from 3 mm diameter rod by first mechanically polishing to approximately 75 μm and then electropolishing in a Fischione twinjet unit using a standard chromium trioxide—acetic acid solution of 75 g CrO_3 , 400 ml CH_3COOH and 21 ml distilled water. The voltage employed was in the range 35–45 V and the temperature 8–10 °C. Foils were stored under vacuum and examined in a Philips CM20 electron microscope operated at 200 kV.

3. Results

The microstructures observed in the light microscope for both alloys isothermally transformed in hydrogen or helium atmospheres are shown in Fig. 2. Transmission electron microscopy revealed a structure consisting of sheaves of ferrite laths, with interlath films of retained austenite, but devoid of carbides owing to the effect of the silicon addition. This structure is shown in Fig. 3 for both alloys after conventional heat treatment and is typical of the upper bainite formed in these alloys [7–11, 13–18]. The thin interlath films of austenite are more wavy in the Ni-containing alloys, whilst the bainite in the Mn-containing alloy is more similar to

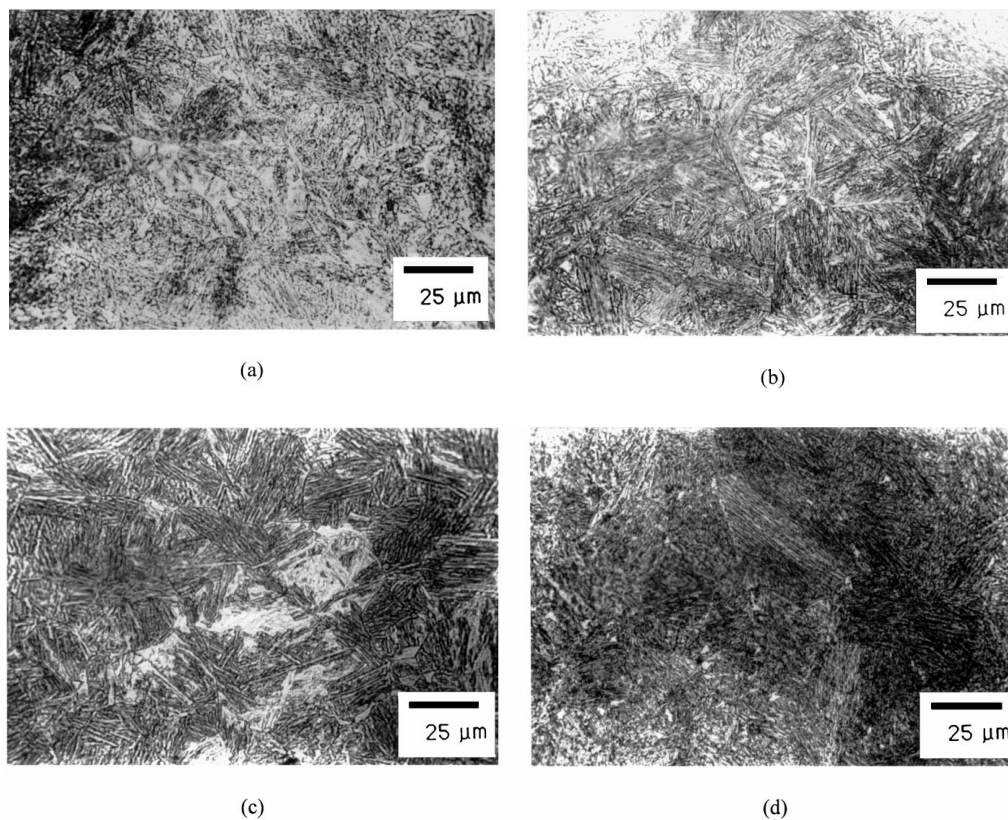


Figure 2 Light micrographs after isothermal transformation at 390 °C for 60 min in (a) He and (b) H₂ [Mn-containing alloy], and (c) He and (d) H₂ [Ni-containing alloy].

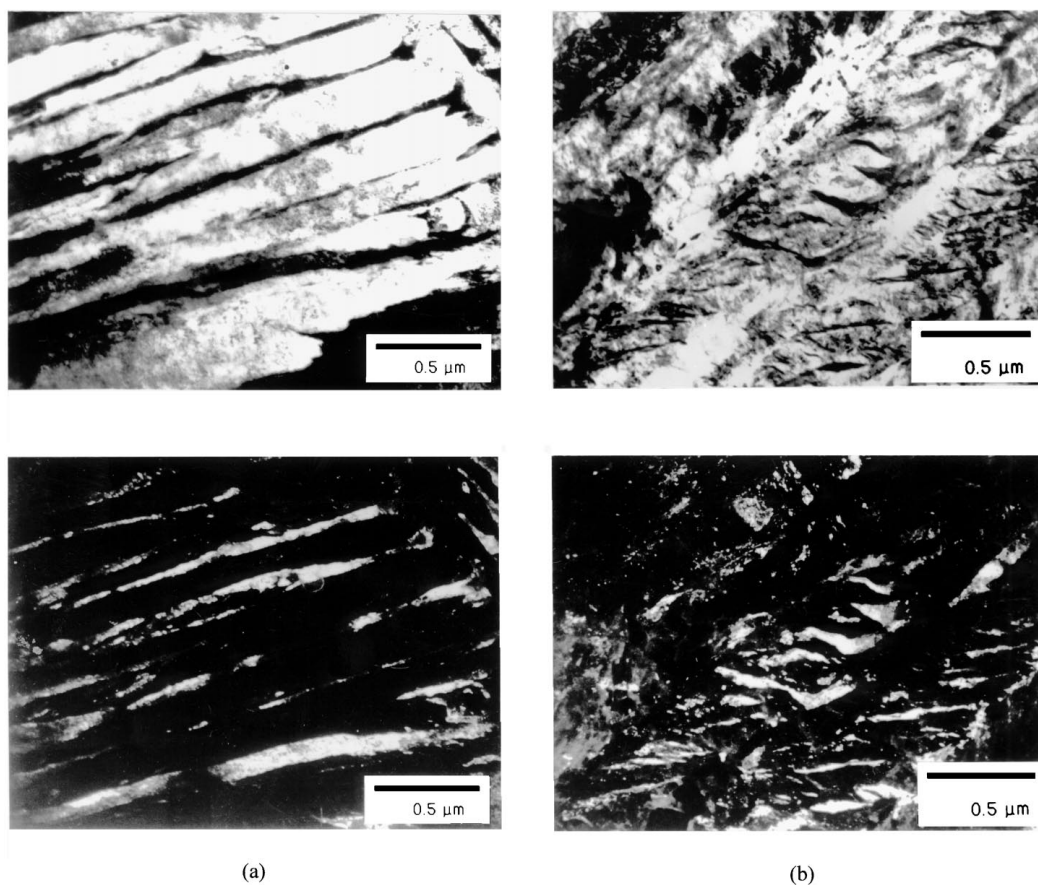


Figure 3 Bright- and dark-field transmission electron micrographs of the bainitic microstructure after isothermal transformation at 325 °C for 60 min: (a) Mn-containing alloy, and (b) Ni-containing alloy.

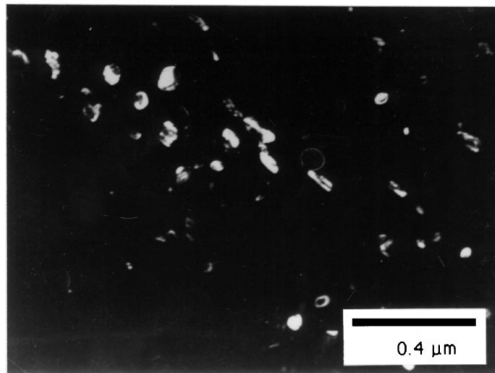
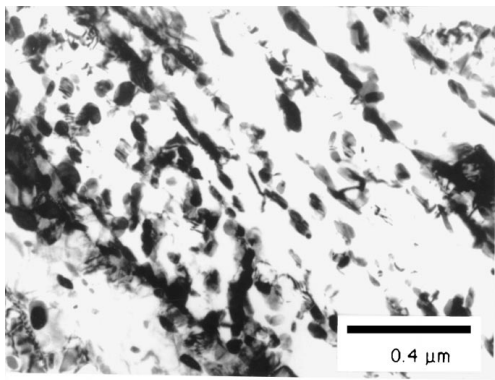


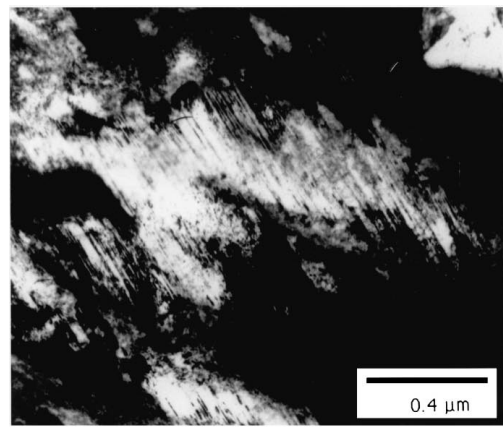
Figure 4 Bright- and dark-field transmission electron micrographs of the bainitic microstructure after isothermal transformation at 325 °C for 60 min and tempering at 500 °C for 60 min [Ni-containing alloy].

lath martensite. These thin austenite films have previously been shown to be both thermally and mechanically stable [7–11], but they can decompose into ferrite and carbide after prolonged high-temperature annealing treatments (Fig. 4).

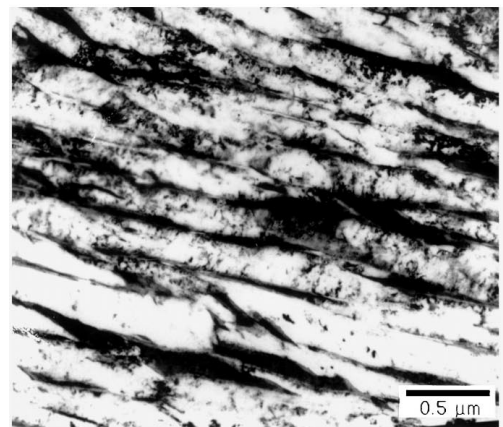
The bainite reaction appeared to be less complete in both alloys after transformation in the helium atmosphere; large blocky regions of residual austenite were observed, and in many cases these had subsequently decomposed to a high-carbon twinned martensite on cooling to room temperature (Fig. 5a). These coarse unstable regions of austenite were absent after transformation in the hydrogen atmosphere under equivalent conditions (Fig. 5b). Additionally, the bainitic ferrite lath structure appeared much finer than after transformation in helium. In the hydrogenated Mn-containing alloy the bainitic ferrite lath width was reduced from $0.31 \pm 0.06 \mu\text{m}$ in helium to $0.21 \pm 0.09 \mu\text{m}$ in hydrogen. Both the effect on further reaction and the effect on refinement were more obvious in the Ni-containing alloy. Hardness measurements (Table II) indicated that the alloys possessed higher hardness values after trans-

TABLE II Hardness values of the experimental alloys isothermally transformed at 390 °C in different environments

| Alloy | Mn-containing alloy | | Ni-containing alloy | |
|------------------|---------------------|----------|---------------------|----------|
| | Helium | Hydrogen | Helium | Hydrogen |
| Environment | | | | |
| HV ₃₀ | 367 | 409 | 364 | 383 |



(a)



(b)

Figure 5 Transmission electron micrographs of the Mn-containing alloy isothermally transformed at 390 °C in (a) He, and (b) H₂.

formation in the hydrogen atmosphere, consistent with the refined microstructure.

Data indicating the influence of hydrogen on the thermal and mechanical stability of retained austenite are given in Tables III and IV, for the Mn- and Ni-containing alloys, respectively. These show the percentage volume fraction of retained austenite before and after hydrogenation of heat treated specimens, and after 2% nominal tensile straining of specimens before and after hydrogenation. This level of strain does appear to reduce the amount of retained austenite significantly; percentage reductions up to 75% are determined from Tables III

TABLE III Effect of hydrogen on the thermal and mechanical stability of retained austenite in the Mn-containing alloy

| Transformation temperature (°C) | Retained austenite content (%) | | | |
|---------------------------------|--------------------------------|------------------------|-----------|----------------------------|
| | Uncharged | H ₂ charged | 2% strain | H ₂ + 2% strain |
| 250 | 10.73 | 10.43 | 6.95 | 6.68 |
| 275 | 10.95 | 10.86 | 7.85 | 7.15 |
| 300 | 13.25 | 13.95 | 8.36 | 9.24 |
| 325 | 11.70 | 10.65 | 11.76 | 9.81 |
| 350 | 12.96 | 13.91 | 5.39 | 5.88 |
| 375 | 15.51 | 16.70 | 3.99 | 9.46(*) |
| 400 | 17.24 | 16.89 | 4.20 | 9.69(*) |

(*) : Fracture occurred before 2% strain.

TABLE IV Effect of hydrogen on the thermal and mechanical stability of retained austenite in the Ni-containing alloy

| Transformation temperature (°C) | Retained austenite content (%) | | | |
|---------------------------------|--------------------------------|------------------------|-----------|----------------------------|
| | Uncharged | H ₂ charged | 2% strain | H ₂ + 2% strain |
| 250 | 10.49 | 9.87 | 4.23 | 4.86 |
| 275 | 9.66 | 9.75 | 5.83 | 5.76 |
| 300 | 10.51 | 10.45 | 6.35 | 6.15 |
| 325 | 11.28 | 10.95 | 9.10 | 8.26 |
| 350 | 14.66 | 14.45 | 8.39 | 8.88 |
| 375 | 20.51 | 22.16 | 11.41 | 10.81 |
| 400 | 20.64 | 21.35 | 12.65 | 12.05 |

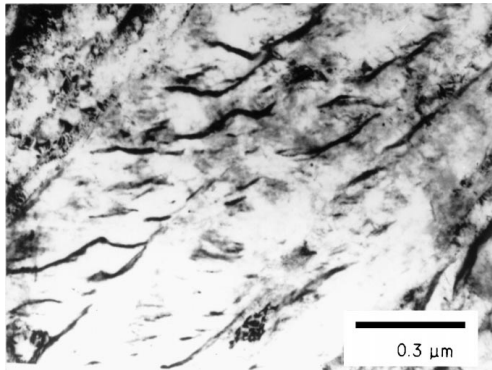
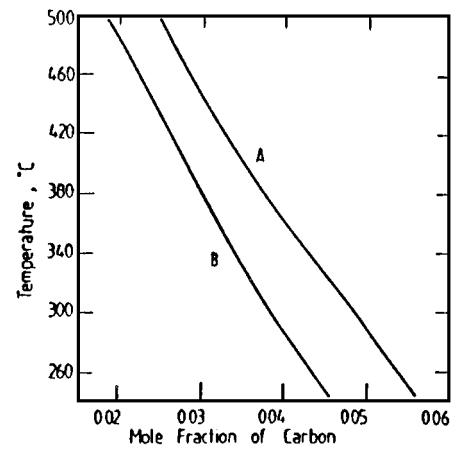


Figure 6 Transmission electron micrograph of the bainitic structure formed by isothermal transformation at 325 °C for 60 min in the Ni-containing alloy after 2% tensile strain.

and IV. Fig. 6 shows the bainitic microstructure after strain, and distortion of the thin films of retained austenite is apparent. However, hydrogen appears to have no significant effect on the amount of retained austenite, either before or after strain.

4. Discussion

The metallographic results show that the bainite reaction goes further towards completion and the microstructure becomes finer when the isothermal transformation is carried out under hydrogen. This apparent effect of hydrogen can be considered as an influence on the displacive mechanism of bainite formation. It is argued that by this mechanism bainitic ferrite forms by a shear-type transformation, and the supersaturation of carbon is relieved either by carbide precipitation or rejection into residual austenite [13–18]. In Si-containing steels, such as those used in the present work, carbide precipitation is suppressed by the Si and the excessive carbon concentration in the residual austenite stabilizes it against further transformation. Consequently, the bainite in the experimental steels consists of bainitic ferrite laths and retained austenite, as the results demonstrate. The retained austenite can exist as large volumes (blocky austenite) or thin interlath regions, mainly dependent on the extent of transformation. The fraction of blocky austenite, reflecting more untransformed regions between packets of bainitic ferrite laths, is an inverse function of the percentage transformation, and decreases as the transformation proceeds further towards completion. The carbon content of these larger



A: Fe-4.08Ni-2.05Si; B: Fe-3.00Mn-2.02Si

Figure 7 T_0 curves for compositions close to the two experimental steels (after [8]).

regions is lower and consequently they are stabilized less and often transform to martensite upon cooling to room temperature. In contrast, the thin interlath films of austenite are likely to be more effectively stabilized by a higher carbon content and their refined size.

The calculated T_0 temperatures of Fe-3Mn-2Si-C and Fe-4Ni-2Si-C alloys are shown in Fig. 7, taken from [8]. The T_0 temperature defined here is the temperature at which the free energies of austenite and ‘supersaturated’ bainitic ferrite phases are equal for a given carbon content. The T_0 curves of Fig. 7 vary only as a function of the substitutional alloying element content and are unaffected by the carbon content of the alloy. However, they indicate the amount of carbon which residual austenite can tolerate at a particular isothermal transformation temperature before the bainite reaction, via a displacive mechanism, becomes impossible. Thus it can immediately be seen that the austenite in the Ni-containing alloy can tolerate more carbon before bainitic ferrite formation must cease, thus increasing the extent of the bainite reaction at any isothermal transformation temperature, and this is consistent with the experimental observations of the present work and confirmatory of former studies.

It follows that an increase in the extent of the bainite reaction could also be achieved by reducing the carbon content, so that the critical concentration in the austenite at which displacive transformation becomes impossible is reached at a later stage in the reaction. One of the roles that hydrogen might play can initially be discussed in this context. It is proposed that hydrogen may have a retarding effect on carbon diffusion which delays the carbon enrichment of the residual austenite, leading to an increase in the amount of bainite formation allowed according to the above T_0 criterion. The effect of hydrogen on carbon diffusivity does not appear to have attracted significant attention, but the reverse situation, the effect of carbon on hydrogen diffusivity, has been studied [19–21], and shows that as the carbon content increases the diffusivity of hydrogen sharply decreases. Assuming that hydrogen diffuses interstitially, and that the number of available sites is large, especially for the low concentrations of carbon and hydrogen involved,

the most plausible explanation for this behaviour is that carbon and hydrogen undergo temporary bonding with each other in the interstitial lattice. Thus it seems likely that hydrogen could retard the carbon diffusivity and thus increase the extent of bainite transformation. This argument need not imply a higher final residual supersaturation in the bainitic ferrite because this could rapidly be relieved after bainitic ferrite formation ceases, by carbide precipitation or diffusion to residual austenite.

A displacive transformation can be regarded as a deformation and change of crystal structure of the parent phase. Movement of the glissile interface is thus a combination of transformation and deformation, and the role of hydrogen may additionally be discussed as an effect on this deformation. As an example of this behaviour for the present situation, it is known from early work [22] that application of tensile stress during transformation leads to an increase in the extent of the bainite reaction. More recent studies have demonstrated preferential selection of bainitic plate variants caused by externally applied stresses [23]. These observations may be explained as the mechanical work of the applied stress assisting with the progress of the transformation by adding to the chemical free energy change, or in other words, boosting the driving force. Lowering of the flow stress by hydrogen has been repeatedly reported for iron and iron alloys [24–27], although not at the temperatures of interest here. However, it might be argued that a reduction of the flow stress by hydrogen at the bainite formation temperature would have an equivalent effect to the application of external stress by lowering the transformation energy barrier, reducing the energy required to accomplish the transformation deformation. Thus the extent of transformation might be enhanced.

It has recently been suggested that plastic strain in the parent phase can dictate the course of the bainite transformation [28]. The argument relies on the premise that transformation strain is relieved in the parent austenite by plastic deformation (for which there is experimental evidence) and that this eventually restricts the glissile movement of the displacive transformation interface. This can be illustrated as being consistent with the accepted effect of transformation temperature on the displacively transformed microstructures: at lower temperatures where recovery mechanisms are relatively difficult, thin lower bainite plates result; as the transformation temperature increases, recovery reduces the austenite dislocation content and allows larger laths of upper bainite to form; Widmanstätten ferrite then represents continual development at a temperature high enough to give full recovery of the dislocation structure and hence little resistance to growth. Without being too speculative, it is not inconceivable that hydrogen could interfere with these mechanisms, either through an influence on the flow stress of the parent phase or by interaction, possibly involving carbon, with recovery processes, to extend the amount of transformation.

The present results also indicate that although hydrogen has a clear effect on the extent of transformation, it has little or no influence on the thermal or mechanical

stability of the retained austenite phase. Previous work has similarly failed to reveal any effect of hydrogen on the thermal stability of retained austenite phase in a high chromium ferritic steel [29], nor on the mechanical stability of austenite phase in stainless steels [30]. This result is important in the context of hydrogen embrittlement mechanisms operative in carbon and low alloy steels containing either bainitic microstructure or regions of retained austenite. The results indicate that the retained austenite phase is not de-stabilized by hydrogen which would increase the possibility of forming hard brittle high-carbon martensite, itself also less resistant to hydrogen embrittlement.

The greater stability of the interlath thin-film form of retained austenite is consistent with a probable higher carbon content coupled with size stabilization. The latter reflects the small size of the austenite region which must be decomposed by plate martensite formation requiring suitable conditions for nucleation, migration of the martensitic interfaces and accommodation of the transformation strains.

5. Conclusions

The effect of hydrogen on the extent of the bainite transformation and the stability of retained austenite has been studied. It was found that hydrogen causes the bainite reaction to proceed further towards completion. This has been discussed in terms of possible influences that hydrogen may have upon carbon diffusivity, flow stress and mechanisms of accommodation of transformation strains, all of importance in the displacive mechanism of bainite formation. The possible effects of hydrogen are not inconsistent with this concept. It was additionally shown that hydrogen has little or no effect on the thermal or mechanical stability of retained austenite phase in the alloys studied.

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