Materials Science and Engineering A280 (2000) 220–224

MATERIALS SCIENCE & ENGINEERING A

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Positive effects of hydrogen in metals

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Abstract

Hydrogen is often present in metals as a result of production, fabrication and processing operations or service conditions. Thus, it can be regarded as an alloying element. Although, high hydrogen levels in metals can have a devastating effect on the mechanical properties, many positive effects can also be derived from its high solubility. The objective of this paper is to review some positive effects of hydrogen in metals. An emphasis will be made on enhancements in the processing properties due to hydrogen (thermohydrogen processing (THP)), though other uses of hydrogen, such as an energy storage device and in the electronics industry will also be presented. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen; THP; Metal hydrides

1. Introduction

High hydrogen content levels can degrade the mechanical properties of most engineering materials, as reported extensively [1–10]. Furthermore, even relatively low concentrations of hydrogen can lead to failure if hydrogen is trapped around structural defects and local concentrations exceed a critical value. This phenomenon of trapping has already been described in detail [11–29].

Hydrogen is often present in metals as a result of production, fabrication and processing operations or service conditions. Thus, it can be regarded as an alloying element. Although, hydrogen might have a devastating effect on mechanical properties, it can be utilized in some cases to enhance the production and processing of materials. Some reviews of such applications (mainly hydrogen storage technology) have already been published [30–36]. The aim of this paper is to review our up-to-date knowledge of various applications of hydrogen, focusing on thermohydrogen processing (THP).

2. Thermohydrogen processing

THP, or the use of hydrogen as a temporary alloying element, can strongly enhance processing behavior (fabricability) and final component characteristics of Ti-based alloys [37–41]. In this process, hydrogen is added to the titanium alloy by simply holding the material at a relatively high temperature in a hydrogen environment, heat treatment or thermomechanical processing performed, and the hydrogen removed by a simple vacuum (or inert gas) anneal. The presence of the hydrogen allows the titanium alloy to be: (a) processed at lower stresses and/or lower temperatures, and (b) heat-treated to produce novel microstructures with enhanced mechanical properties.

Froes et al. reviewed [37] the refinement of the microstructure and improvement in mechanical properties, achievable using THP of wrought products, PM materials and castings. The latter product form is reported to offer the largest improvement compared to the conventional material. The mechanisms by which THP enhances processing and final mechanical properties were reviewed as well. In the present work, however, only the basic principles of THP are discussed.

One THP treatment, constitutional solution treatment (CST), is shown superimposed on the pseudo phase diagram (Fig. 1) [42,43] as an example of how the time-hydrogen content excursion relates to position on the phase diagram. The precise microstructural changes

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PII: S0921-5093(99)00670-X

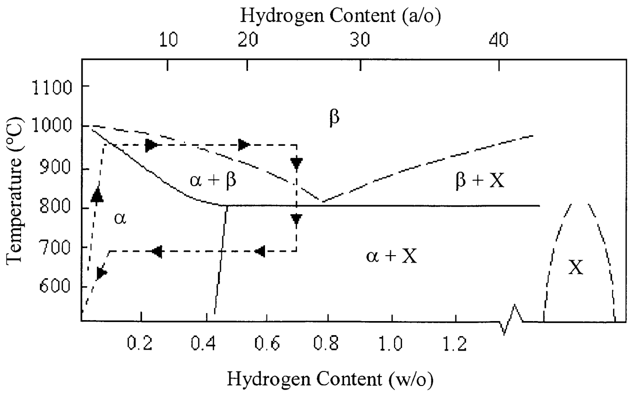

Fig. 1. Pseudo-binary phase diagram for Ti–6Al–4V modified from [42]. The hydride phase is shown as X since the exact composition of this phase has yet to be defined [43]. One THP treatment (constitutional solution treatment) is superimposed.

that occur vary somewhat depending on the details of the specific THP treatment used.

Thermohydrogen processing is particularly amenable to near-shapes such as powder metallurgy products and castings, since the THP treatment does not rely on working of the material to modify the microstructures. However, the technique can also be equally applied to ingot metallurgy products.

The high solubility of hydrogen in a wide range of titanium-based alloys is shown in Fig. 2 [37]. The material for which the chemical activity is lowest will have the highest solubility for hydrogen. Beta titanium alloys have even lower activity values than commercially pure (CP) titanium and a consequent higher hydrogen solubility. In contrast, the equiatomic titanium aluminide (TiAl) has a very high activity, meaning that there is little solubility for hydrogen in this ordered compound [44].

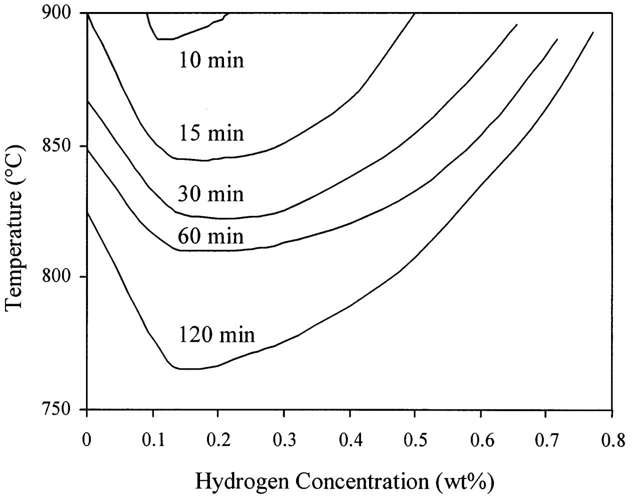

Fig. 3. Enhanced superplastic forming due to presence of hydrogen [47].

Thus, many titanium alloys are amenable to THP although the vast majority of the work reported to date in the Western world has been in the Ti–6Al–4V alloy, the most commonly used titanium alloy for both aerospace and non-aerospace applications. The enhancement in ductility, which can be obtained by room temperature THP, was shown [45,46] for the wrought, β-III alloy (Ti–11.5Mo–6Zr–4.5Sn) charged to various hydrogen levels and upset at room temperature. At normal hydrogen contents (~ 30 ppm) first cracks were observed at a 60% upset. This value was reduced as the hydrogen content increased, but then showed an upward trend at a hydrogen content of 200 ppm to a value approaching 100% in the range 500–2000 ppm hydrogen. Small additions of hydrogen greatly enhance the superplastic forming (SPF) characteristics of different Ti-base alloys [37]. Forming temperatures can be

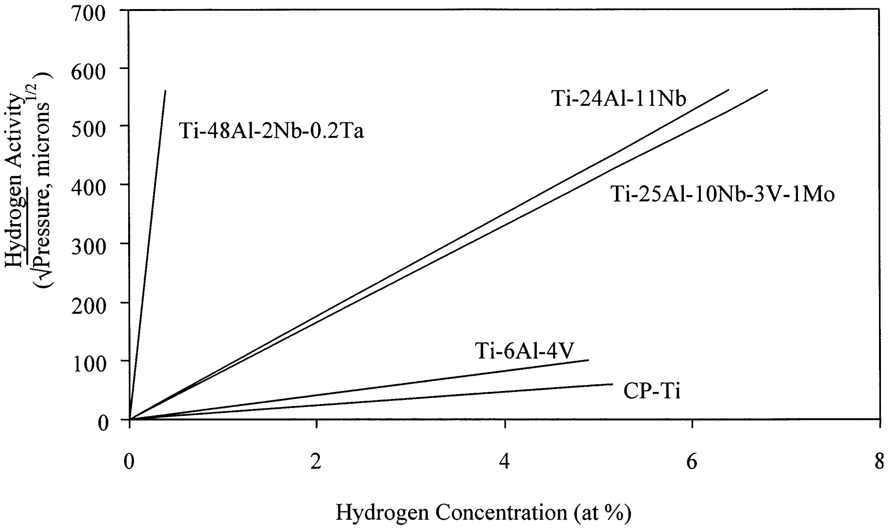

Fig. 2. Hydrogen activity for selected titanium alloys at 800°C [37].

reduced by 100–150°C, or strain rates increased, as shown in Fig. 3 [47]. This improvement can be related to the increase in volume fraction of the more ductile β phase compared to α phase, resulting from a reduction in the β transus temperature when hydrogen content increases. Subsequent dehydrogenation of the alloy can then be done to regain the proper α/β ratio and possible grain refinement for structural applications.

Fang and Wang [48] have shown that the improvements of the superplastic characteristics at lower hot forming temperatures occurred because of the temporary alloying of titanium alloys. This effect changed the microstructure in two distinct ways, depending on hydrogenation temperature. At low hydrogenation temperatures, the microstructure changed in a continuous slow manner, involved with gradual change in the volume fraction of α and β phases. At higher hydrogenation temperatures, however, the microstructure changed abruptly, achieving new ratio of α/β. Temporary formation of a more ductile phase, β, for improved superplasticity of Ti-base alloys was not the only mechanism suggested so far. Gong et al. [49], who also used the THP technique on Ti-base alloys, showed that hydrogen additions refine the originally coarse microstructure of the alloy. This hydrogen-induced grain refinement was shown to have a good relationship with the improvement of the superplastic characteristics of the alloy.

The THP technique can be used to control the microstructure in powder material either by adding the hydrogen to the powder prior to compaction or after compaction; in both cases followed by dehydrogenation in the compacted condition. The former method results in a fine equiaxed α-structure in prealloyed Ti–6Al–4V powder, which has been attributed to formation of 'new' grains between former hydride needles upon dehydrogenation or recrystallization of the β phase.

Currently, the product form for which the THP technique has the most immediate potential for commercialization is castings for which hydrogenation has been conducted at normal and high (up to 5 atm) pressures of hydrogen; the latter to decrease hydrogenation time and temperature. In the Ti–6Al–4V alloy, THP can greatly refine the microstructure of cast product, with a substantial enhancement in fatigue behavior and higher strength levels than as-cast material (Table 1). The improvement in *S* ratio (σ_f/σ_{UTS}) in Table 1 suggests that the enhancement in fatigue behavior is not only a consequence of the higher strength levels but also the refinement in microstructure per se [37]. Other examples of the THP applications can be found in recent reviews [40,41].

Table 1
Ratio between fatigue and tensile strength for Ti–6Al–4V investment castings [37]

Treatment	Mechanical properties		
	σ_{UTS} (MPa)	σ_f (MPa)[a]	S (σ_f/σ_{UTS})
Cast + HIP	958	530	0.55
THP-I	1055	770	0.73
THP-II	1100	745	0.68

[a] At 5 × 10^6 cycles; σ_f is fatigue run-out stress.

3. Other applications of hydrogen

The largest industrial application of hydrogen to date is as a chemical feedstock for production of certain chemicals [50,51]. The bulk of chemical hydrogen consumption is in one of three main industries: ammonia manufacture, petroleum refining and petrochemicals, and methanol production.

Ammonia is produced by the Haber–Bosch process, developed in 1913. In this process, a mixture of nitrogen and hydrogen in a 1:3 ratio is passed over an iron oxide promoted catalyst to produce ammonia. This reaction is exothermic, typical reaction conditions ranging from 400 to 510°C and from 135 to 340 atm. Hydrogen is consumed in the petroleum refining industry in several processing options. These include primarily: (a) removal of sulfur from refinery products (hydrodesulfurization), (b) conversion of heavy oil fractions to lighter more valuable oil fractions (hydrocracking), and (c) chemical conversion (e.g. hydrodealkylation, or the selective hydrogenation of aromatic compounds that leaves the benzyl or other aromatic ring structure unaltered). In this way high-purity benzene, toluene, and naphthalene are produced.

Much chemical synthesis not directly related to petrochemicals requires hydrogen. Hydrogen peroxide, hydrogen chloride gas, uranium hydride, and many organic chemicals all use hydrogen. The pharmaceutical industry uses hydrogen extensively to manufacture certain drugs.

In addition, unsaturated organic oils of soybeans, fish, cottonseed, corn, peanut, and coconuts are hydrogenated. This hydrogen treatment stabilizes these oils and improves odor, color, and consistency characteristics. Inedible oils and greases are hydrogenated for the production of soap and animal feed. Hydrogenation and purification of various greases to rigid specifications produce lubricants for use in food-processing equipment.

Finally, during the production of float glass, the glass melt hardens on the surface of a tin bath, producing a high-quality flat glass (mirror glass, laminated glass). A protective reduction atmosphere is necessary to avoid oxidation of the tin melt and to achieve uniform glass quality and thickness even during high traction speed of the glass sheet. Hydrogen is also consumed in the oxy-hydrogen cutting of glass [50].

Energy storage technology is one of the most significant applications of hydrogen. The use of liquid hydrogen and metal hydrides as energy carriers has been reviewed by Eliaz and Eliezer [10] as well as by other authors (see [30–36]). Actual and potential applications of metal hydrides include hydrogen storage, batteries, fuel cells, purification or separation of hydrogen, isotope separation, hydrogen getters, heat storage, heat pumps and refrigerators, thermohydrogen hydride compressors, sensors and detectors, and catalysts [34,36]. In recent years, interest in hydride technology has been revived by the desire to reduce environmental pollution due to automobile emissions, as well as by the concern over our dwindling natural gas and petroleum reserves [52–54]. One of the most active and interesting uses for metal hydrides has been as a carrier of hydrogen fuel for motor vehicles. Besides using metal hydrides as a storage media of fuel hydrogen, they can be used to store energy as electrochemical energy in solid solution electrodes. Battery applications center around the so-called nickel-hydrogen battery, a highly reliable rechargeable system first developed for satellite applications [55]. These last two applications are described in detail in the review of Eliaz and Eliezer [10].

Hydrogen is being used in the electronics industry as well. Hydrogen plays an important technological and interesting scientific role in semiconductors. First, the electronics industry requires high-purity hydrogen for the production and processing of silicon. To avoid the formation of oxide layers during the production of integrated semiconductor structures, the oxygen content of the protective gas must be reduced to a very low level via catalytic reaction with hydrogen [51].

Furthermore, a number of metallic impurities (e.g. Au, Pt, Pd, Mo) are intentionally used as lifetime controllers in silicon, and many can act as generation-recombination centers because of their high capture cross-sections for both electrons and holes. Precipitates of these impurities, particularly Fe, might bridge across the emitter-collector region of transistors, creating a short circuit. Many of these metal-related deep levels in silicon can be neutralized by reaction with atomic hydrogen [56]. Hydrogen passivation of defects at interfaces on silicon surfaces was already observed in 1968 by Brown and Gray [57]. Typically, this passivation is achieved by placing the sample containing the electrical level in hydrogen plasma. It is also clear that hydrogen can bond to a dangling bond that is created chemically by the hydrogen. Electrical activity of the shallow acceptors (B, Al, Ga, In, Tl) can be neutralized by the association with atomic hydrogen, while the shallow donors (P, As, Sb) are unaffected by hydrogenation [56].

Hydrogen is also used as an alloying element in various amorphous materials (e.g. a-Si:H, a-Ge:H, a-C:H and a-SiC:H). Due to the absence of long-range order an amorphous material has a large number of dangling bonds, which are not attached to the nearest neighbors. These dangling bonds trap the conduction band electrons. In pure amorphous silicon, the number of the localized states is so high that the material is unsuitable for most device applications. On the other hand, amorphous silicon films prepared by glow-discharge decomposition of silane (SiH_4) gas have a relatively low density of defect states in the energy gap. The amorphous silicon obtained by this process has a very large concentration of hydrogen. The hydrogen atoms tie up these dangling bonds and decrease the density of localized states in the energy gap. Electron and hole mobilities in a-Si:H films are orders of magnitude smaller than in crystalline Si. However, very large area high-quality a-Si:H films may be inexpensively deposited in a continuous process (e.g. by plasma-enhanced chemical vapor deposition from silane at substrate temperatures lower than 300°C) on a large variety of different substrates, making this material very attractive for applications requiring large-area devices and circuits. These technological advantages over crystalline silicon technology have resulted in the development of advanced amorphous semiconductor devices such as a-Si:H thin-film transistors (TFTs) addressed flat panel color television displays, p-i-n photocells, electrophotography, field-effect transistors (FETs) and image sensors. Growing successive layer of different hydrogenated amorphous films, one can produce heterostructure devices, which are especially important for solar cell applications [58–60].

Additional uses of hydrogen, such as in extraction of elements from ores and alloys, preparation of amorphous alloys via hydrogen-induced amorphization (HIA), brazing and welding, and fabrication of refractory metals and alloys, will be presented elsewhere (N. Eliaz, D.L. Olson, D. Eliezer, unpublished research).

4. Conclusions

1. The use of thermohydrogen processing of titanium alloys can assist both in enhancing the processing (fabrication) and in improving the mechanical-property combinations in the final product. The majority of the work performed to date has been on the Ti–6Al–4V alloy, but it has also been applied to other terminal and intermetallic base alloys.
2. Hydrogen is being widely used for production of certain chemicals, energy storage (hydride) technology, and in the electronics industry.

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