Hydrogen-assisted processing of materials

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Abstract

Under certain conditions, hydrogen can degrade the mechanical properties and fracture behavior of most structural alloys; however, it also has some positive effects in metals. Several current and potential applications of hydrogen for enhancing the production and processing of materials are reviewed. These include thermohydrogen processing (THP) and forming of refractory alloys, processing of rare earth-transition metal magnets by hydrogen decrepitation (HD) and hydrogenation–decomposition–desorption–recombination (HDDR), hydrogen-induced amorphization (HIA) and microstructural refinement, extraction of elements from ores and alloys, and the use of hydrogen as a reducing gas for welding and brazing. Hydrogen is found to enhance the formability, microstructure and properties of a large variety of materials, including steels, Ti-based alloys and metal matrix composites (MMCs), refractory metals and alloys, rare earth-transition metal alloys, metalloid-containing metallic glasses, etc. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Hydrogen is often present in metals as a result of production, fabrication, processing and/or service conditions. It may be sometimes regarded as an alloying element. Hydrogen might lead to failure if trapped around structural defects and its local concentration exceeds a critical value. This phenomenon of trapping has already been described in detail [1–14]. Although hydrogen might have a devastating effect on mechanical properties [15–23], it can be used in some cases to enhance the production and processing of materials.

Several beneficial effects of hydrogen on the formability, microstructure and properties of materials are reviewed. An emphasis is given on processes in the metallurgical industry such as thermohydrogen processing and forming of refractory alloys, hydrogen decrepitation, hydrogen-induced amorphization and

microstructural refinement, reduction of metal ores, and welding and brazing. The use of liquid hydrogen and metal hydrides as energy carriers, however, is not discussed here. Comprehensive reviews of such applications are presented elsewhere [24–30]. The use of hydrogen in the chemical [31–34] and electronics [31,34–40] industries is also described elsewhere.

2. Thermohydrogen processing

Thermohydrogen processing (THP), or the use of hydrogen as a temporary alloying element, can strongly enhance the formability and the final microstructure and properties of titanium-based alloys. In this process, hydrogen is added to the titanium alloy by 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 [31,41–48].

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Hydrogen is a unique alloying element in titanium alloys because, unlike other elements, it has a very high diffusivity and can easily be added and removed without melting. Hydrogen alloying destabilizes the low-temperature *hcp* α-phase and stabilizes the high-temperature *bcc* β-phase of titanium alloys. Consequently, the α-phase transforms partly into a hydride phase or into the β-phase, the temperature of the α-to-β phase transformation is decreased, and the temperature interval of the α + β range is increased when hydrogen is added. In addition, the critical rate and the specific temperatures of the martensitic transformation decrease. Furthermore, hydrogen affects the stability of different phases, the diffusivity of alloying elements, and the active slip systems, as described elsewhere [44].

Early studies [49,50] indicate that the hot workability of titanium alloys can be improved by THP. This approach allows the hot working temperature to be decreased while providing the same levels of strength; it also permits the phase composition and microstructure to be modified. The addition of hydrogen also increases the ductility and reduces the flow stress of α, pseudo-α, α + β, and intermetallic-based alloys at the usual temperature of hot working. This allows the application of larger strains at lower temperatures. These generalizations apply to nearly all conventional α and α + β titanium alloys, although the vast majority of the work reported to date has been on the Ti–6Al–4V alloy [44].

Small additions of hydrogen greatly enhance the superplastic-forming (SPF) characteristics of different titanium-based alloys [41]. Forming temperatures can be reduced by 100–150°C, or strain rates increased [51,52]. This improvement has been related to refinement of the originally coarse microstructure, accompanied by an increased volume fraction of the more ductile β-phase in comparison to the α-phase.

THP is particularly amenable to near-shapes such as powder metallurgy (P/M) 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, which offer the largest improvement compared to conventional materials. The use of THP in the compaction of titanium-alloy P/M products generally permits the temperature required for full consolidation to be reduced [51]. The hydrogenated powder can then be consolidated with less energy than when the virgin powder is employed; this translates into a pressure reduction of 34–67 MPa or a temperature decrease of 110–140°C [44].

On the basis of recent advances, it is suggested that consolidation and grain refinement are facilitated by the combined operation of several factors such as an increased amount of the more ductile β-phase (and of the O-phase in Ti–Al intermetallics), the decomposition of the metastable phases during vacuum hot pressing (VHP), the hot isostatic press (HIP) induced microrecrystallization, and the hydrogen-aided chemical activity of the powder surface [44].

Titanium-alloy castings have a coarse lamellar structure and porosity. Consequently, their mechanical properties (especially their fatigue endurance) fall below desired levels. THP transforms the lamellar structure into an equiaxed fine-grained morphology and decreases the porosity, thus leading to a substantial enhancement of the mechanical properties [31,41,44,53]. Table 1 demonstrates the effect of THP on the mechanical properties of Ti–5Al and Ti–6Al–4V castings. THP is found to increase both the yield strength and the ultimate tensile strength of these castings (by 17.4–18.4 and 14.3–15.9%, respectively). In addition, a significant increase in ductility (as reflected by the values of elongation and reduction of area) is evident. For Ti–5Al castings, for example, the values of the elongation and the reduction of area are more than doubled as a result of a THP treatment. It is also evident from Table 1 that THP significantly enhances the fatigue behavior of the casting (e.g. the averaged logarithmic durability is approximately doubled). Because the enhancement in the fatigue properties due to THP is usually more significant than that in the tensile strength values, it may be suggested that the former is not only a consequence of the higher strength levels, but also of the refinement in microstructure per se.

It has been suggested [44] that THP can be an attractive processing technique for improving the mechanical properties (e.g. ductility) of Ti₃Al-based alloys and other intermetallics by microstructural modification. Liao et al. [54,55], for example, studied the changes of the microstructure of the Ti₃Al-based super-

Table 1
The effect of THP on the mechanical properties of titanium–alloy castings [51]

Alloy	Treatment	$\sigma_{y.s.}$ (MPa)[a]	σ_{UTS} (MPa)[a]	Elongation (%)	Reduction of area (%)	K_c (kJ m^{-2})[a]	$\bar{N}_f$ at 500 MPa[a]
Ti–5Al	As-cast	735	796	6.2	15.5	550	5.7×10^4
Ti–5Al	THP, 0.9% H	863	910	13.5	32.3	600	12.0×10^4
Ti–6Al–4V	As-cast	870	940	8.8	18	460	4.9×10^4
Ti–6Al–4V	THP, 0.6% H	1030	1090	12.8	20	450	9.7×10^4

[a] $\sigma_{y.s.}$, yield strength; σ_{UTS}, ultimate tensile strength; K_c, fracture toughness; $\bar{N}_f$, an averaged logarithmic durability.

α_2 alloy (Ti–25Al–10Nb–3V–1Mo) under THP. The hydrogenation treatment was found not only to refine the microstructure and to improve the morphology, but also to promote the formation of the orthorhombic O-phase.

Fiber-reinforced titanium alloy matrix composites are receiving attention because of their high specific mechanical properties and prospective applications at elevated temperatures in comparison with their monolithic counterparts. However, interfacial reactions between the fiber and matrix during fabrication of the composite at elevated temperatures lead to degradation of the composite properties. Consequently, much effort has been devoted to the development of titanium composites in which the interfacial reactions are inhibited.

Yang and Edmonds [56,57] carried out THP to evaluate the effect of hydrogen on the fabrication of titanium alloy matrix composites. It was found that the α (or α_2)-to-β phase transus temperature of three different alloy foils, Ti-1100 (Ti–6Al–3Sn–4Zr), Ti–6Al–4V and super-α_2 (Ti–25Al–10Nb–3V–1Mo), which are to be used as potential composite matrices, could be lowered by the addition of hydrogen. In addition, a better microstructure for hot-deformation could be obtained at a relatively lower temperature for the hydrogenated foils. The latter behavior may lead to the fabrication of composites at a lower temperature so as to improve the fiber/matrix interface properties. Indeed, the subsequent fabrication of Ti-1100 and Ti–6Al–4V matrix composites with SiC fibers, with hydrogen as a temporary alloying element, proved that the fabrication temperature could be lowered by 50°C. This temperature decrease resulted in a significant reduction in thickness of the interfacial reaction layer between the matrix and the reinforcing fibers and in a better fiber/matrix bonding. Additionally, the dual-phase matrix microstructure was found to be refined by this processing method.

3. Hydrogen alloying of refractory alloys

The selection of refractory metals and alloys for complicated shapes depends primarily on their fabricability rather than on their strength and corrosion resistance properties. With the ability to form with minimal hindrance, the properties of these materials offer unique potential applications for high-temperature service [58–60].

Unfortunately, molybdenum and tungsten have rather high ductile-to-brittle transition temperatures (typically 30 and 300°C, respectively), thus posing fabrication problems at normal processing temperatures. Heating above the ductile-to-brittle transition temperature is considered essential for fabrication of these metals. In order to achieve a sufficiently low ductile-to-brittle transition temperature, it is necessary to control the microstructure of Mo- and W-based alloys.

The THP technique may offer more opportunities for the use of refractory alloys. In the refractory metals, which do not have a α-to-β transition such as that in titanium-based alloys, hydrogen still has much potential for promoting superplasticity. Alloying of refractory metals with hydrogen may form small hydride particles that can promote grain refinement. Because the solubilities of interstitial elements in molybdenum and tungsten are very low, their concentrations should be kept extremely low to avoid precipitation at grain boundaries and embrittlement [59,61,62]. This fact limits the potential use of hydrogen as a temporary alloying element in these metals. Niobium and tantalum, on the other hand, behave well during metallurgical processing (especially as pure metals, for which the ductile-to-brittle transition temperatures are −140 and −270°C, respectively). These pure metals are ductile and have a high interstitial solubility of carbon, nitrogen, oxygen, and hydrogen. This high solubility for interstitials allows overcoming the problem of embrittlement during low-temperature fabrication of niobium and tantalum [59]. Therefore, hydrogen can be used as a temporary alloying element in these metals.

When fabricating niobium and tantalum in air at high temperatures, one has to keep the oxygen content in the metal as low as possible. This requirement is due to the devastating effect of high oxygen content, which subsequently leads to a significant reduction in formability at normal temperatures. Hot-forming niobium and its alloys requires hydrogen annealing and processing, resulting in reduction of oxygen pick-up and gaining hydrogen-assisted plasticity. Such hydrogen-assisted plasticity has already been reported for iron [63–67]. For titanium-based alloys it was shown that a critical hydrogen content had to be attained before hydrogen-assisted plasticity could be observed. Similarly, it is necessary to determine the optimum hydrogen content in niobium prior to the forming operation. It is also essential to vacuum-anneal the formed part as a final step in the forming operation.

One mechanism that can contribute to superplasticity in refractory alloys is the grain refinement as a result of hydrogen-induced dynamic recrystallization (e.g. due to strain aging). Wilcox and Huggins [68] investigated strain-aging effects due to hydrogen in niobium. It was found that hydrogen could be responsible for strain-aging in niobium, as shown in Fig. 1. This phenomenon is related to the hydrogen-induced plasticity, which rapidly increases the density of dislocations. During hot-forming, a high dislocation density enhances dynamic recrystallization.

Sagues at al. [69] reported that hydrogen increases the strength of niobium and niobium-based alloys as a result of either solid solution hardening or reorientation of hydrides (or small hydrogen-impurity clusters) in the stress field of moving dislocations. Both of these
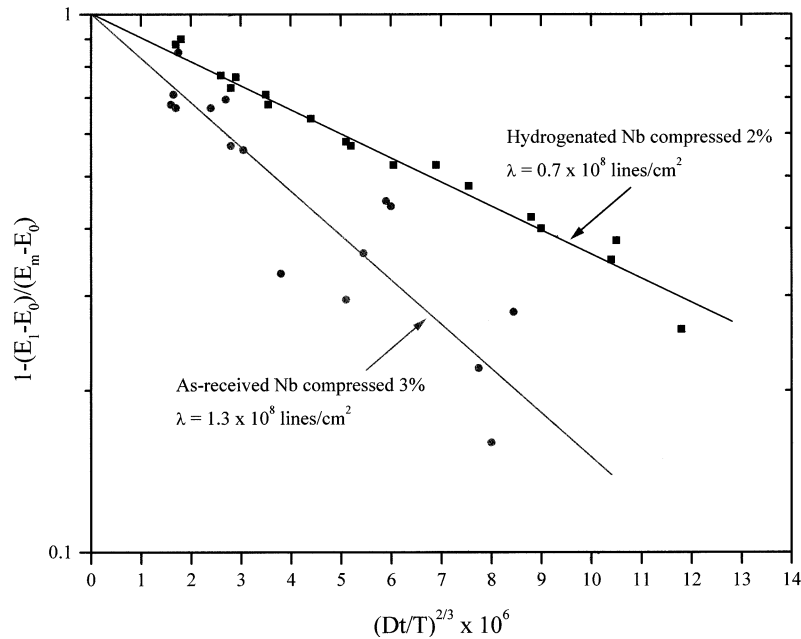
Fig. 1. Plots to determine dislocation densities of as-received commercial Nb and hydrogenated Nb using Harpers modification of the Cottrell–Bilby equation [68].

strengthening mechanisms can be correlated with changes observed in the strain rate sensitivity and ductility as a function of temperature.

4. Hydrogen decrepitation and hydrogenation–decomposition–desorption–recombination

Transition metals such as Ti, Zr, rare earth metals and others become brittle after hydrogen absorption and can be ground into powders. Hydrogen embrittlement and decrepitation are caused by a large volume expansion of the metal lattice when hydrogen-absorbing metallic systems form solid solutions and/or hydrides [70]. The process of hydrogen decrepitation (HD) thus involves absorption of hydrogen with the consequent decrepitation of the bulk material into a friable powder.

Different alloys can be processed into permanent magnets by a number of different routes involving powders, melt-spun ribbons or ingots. Powders can be produced by mechanical crushing, co-reduction, gas atomization, or HD [71]. The manufacture of rare earth-transition metal (Sm_xCo_y-type) magnets by the HD route was first proposed by Harris et al. in 1979 [72]. During the 1980s, after the NdFeB-type magnets were reported, hydrogen absorption by these new materials was studied. It was revealed that a $Nd_{15}Fe_{77}B_8$ alloy absorbs hydrogen very readily at room temperature (provided that it is not oxidized), with the consequent decrepitation of the bulk material into a friable powder. The absorption process was shown to consist

of two stages whereby hydrogen was first absorbed by the Nd-rich grain boundary material and then by the matrix $Nd_2Fe_{14}B$ phase. Additional observations are described in a review of Harris and McGuiness [71] on the use of hydrogen in the processing of NdFeB-type magnets.

The forms of the powder resulting from the HD process depend on the initial state of the alloy, as summarized in Table 2. Therefore, if a NdFeB alloy contains significant quantities of α-Fe, as is often the case in the cast state, a flake-like morphology is obtained. This is typical of a material that exhibits some ductility. The flakes are produced by an onion skin

Table 2
Some possible types of hydrogen decrepitation processes [69]

Type	Appearance
1. Intergranular fracture	Granular form may exhibit equiaxed crystals, columnar or variations thereof. Smooth surface with grain boundary debris sticking to surface.
2. Transgranular fracture	
2.1 Random	Irregular shapes with sharp features. Smooth surfaces if brittle failure.
2.2 Cleavage planes	Regular crystallographic shapes. Smooth surfaces.
2.3 Second-phase interface	Depends on the nature of the interface; could result in needles, platelets, etc.
3. Ductile fracture	'Onion skin' effect — flake-like particles with irregular surface. Poor reflectivity, high surface area.

process by which hydrogen diffuses into the alloy to a certain depth at which a critical strain is set-up owing to the differential volume expansion associated with the hydrogen solubility. If the alloy is homogenized so that the free iron is removed, then the HD material no longer exhibits the flake-like form, but is produced by intergranular and transgranular failure due to the more brittle nature of the alloy [71].

The powder produced by the HD process is extremely friable and is readily milled (using jet or attritor mills) to the 2 μm size required to make sintered magnets. The friability has been related to the presence of microcracks in the particles. After milling, the powder is still in the hydride condition and allows the preparation of fully aligned green compacts with no remanent magnetism. This absence of magnetism facilitates the handling of the green compacts before sintering. The green compacts are then sintered in vacuum so that the absorbed hydrogen is removed during the temperature rise up to the sintering temperature of around 1040°C.

The employment of the HD process has been reported [71] to have many advantages for the production of sintered NdFeB-type magnets. Finer powder and, hence, finer grain sizes are achieved by means of the HD process without undue oxidation. These characteristics are reflected in the greater mechanical strength of the HD magnets, in comparison to the standard (i.e. mechanical crushed) products. The overall advantages of the HD process include:

1. Absence of difficulties encountered with breaking-up the ingot by conventional means due to the presence of free iron.

2. Intergranular failure should ensure the production of single-crystal particles.
3. Significant reduction in the pick-up of oxygen during the process.
4. Almost zero remanent magnetism of aligned green compacts makes them easier to handle.
5. The desorption of hydrogen from the green compacts during heating produces a non-oxidizing environment.
6. The particles are very friable and amenable to further reduction in size by attritor or jet milling.
7. The very clean surfaces are ideal for subsequent sintering.
8. The HD process generally allows control of the particles size, shape and distribution by initial manipulation of the microstructure of the alloy and by control of the HD conditions.

Another related route for the processing of magnets is known as hydrogenation–decomposition–desorption–recombination (HDDR). This process was originally developed for the NdFeB magnet system, and has been reviewed by Takeshita [70]. The HDDR process utilizes a series of four temperature and hydrogen pressure dependent transformations, which hydrogen-absorbing intermetallic compounds undergo in a hydrogen atmosphere. For example, Fig. 2 shows a phase diagram of the hydrogen–$Nd_2Fe_{14}B$ system as well as a hydrogen-sintering path. When the coarse-grained $Nd_2Fe_{14}B$ intermetallic compound is heated to about 300°C under a constant pressure of hydrogen gas (around 1 atm), it first absorbs hydrogen to form $Nd_2Fe_{14}BH_x$ (hydrogenation). Subsequently, when heated under hydrogen to 750–900°C for 2–3 h,
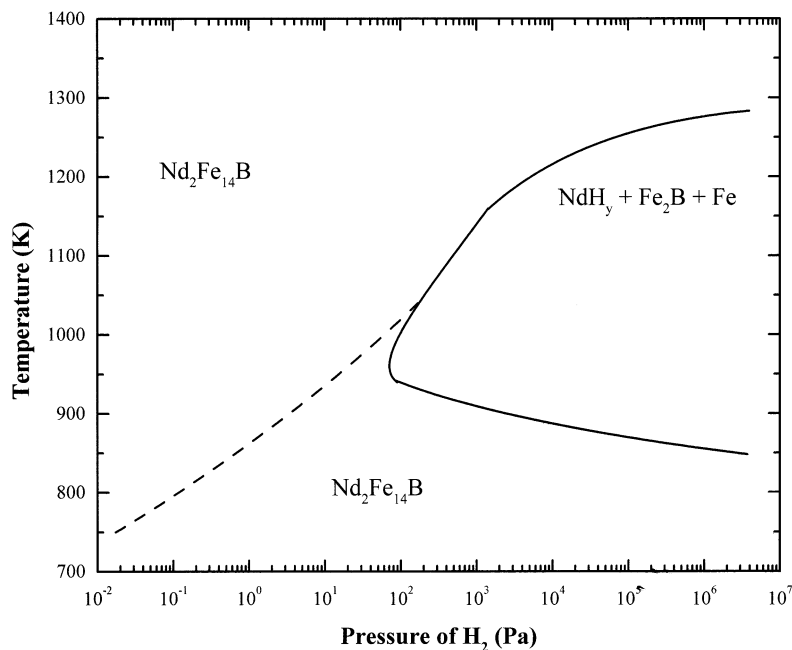

Fig. 2. The phase diagram of the hydrogen–$Nd_2Fe_{14}B$ system with a typical HDDR process [70].

$Nd_2Fe_{14}BH_x$ decomposes into NdH_y hydride, Fe_2B and Fe (decomposition). Next, as the material is held under vacuum at the same temperature for 1 h, the NdH_y hydride desorbs hydrogen (desorption) and recombines with Fe_2B and Fe to form the original $Nd_2Fe_{14}B$ intermetallic compound (recombination). Finally, the material is cooled to room temperature. Typically, the desorption and recombination stages are carried out under vacuum, to produce unique microstructures consisting of very fine crystalline grains [70,71]. It has been found that the HDDR process may also produce metastable phases. These advantages have led to the commercial development of NdFeB anisotropic magnet powders produced by the HDDR process [70].

5. Hydrogen-induced amorphization and microstructural refinement

Hydrogenation of a crystalline or amorphous material may alter its atomic structure; e.g. it can change the lattice symmetry or cause chemical or topological short-range reordering as amorphization in crystalline samples or clusterization [73,74]. It has been reported [75] that in metals which occur in different allotropic forms, the relative stability of these phases is affected by dissolution of hydrogen. The effects of hydrogen on the thermal stability of metallic glasses have been reviewed as part of a more comprehensive review on hydrogen interaction with these materials [30]. Therefore, the following paragraphs will focus on hydrogen effects on the thermal stability of crystalline materials.

Scientists reported [76–78] that the discernable X-ray diffraction (XRD) peaks disappeared after reaction of certain crystalline intermetallics with hydrogen gas. Although the disappearance of the peaks was sometimes [76,77] attributed to amorphous hydride formation, these results could not preclude the existence of microcrystalline phases. If the irreversible decomposition into a binary hydride is the thermodynamically favored reaction, kinetic factors (i.e. inhibited long-range movement of the metal atoms to prevent segregation of the stable product phases) must be responsible for the existence of a ternary hydride whether it is crystalline or amorphous [79]. Since several alloys rapidly absorb hydrogen under high hydrogen pressure at ambient temperature, this exothermic reaction may be sufficient to initiate local decomposition, which would be quenched by spallation effects from the simultaneous large volume expansions of the brittle alloys. The net effect is the generation of extremely fine (but still crystalline) binary or ternary hydride phases that do not exhibit the normal XRD patterns expected from large grain crystalline compounds [80].

An amorphous phase has been reported to form by hydriding crystalline Zr_3Rh intermetallic phases at sufficiently low temperatures ($\sim 200°C$) [81]. XRD patterns, density measurements and superconducting properties confirmed that amorphous alloy hydrides prepared by hydrogenation of crystalline alloys were the same as those hydrides prepared by hydriding rapidly quenched amorphous alloys of the same composition. This phenomenon, known as hydrogen-induced amorphization (HIA), provided a way of amorphization fundamentally different from other existing methods, and opened a possibility for preparing amorphous alloys without restriction to small dimensions. This method has since been studied extensively [82–89], and has led to the amorphization of a large number of intermetallic compounds [89]. Representative systems are RM_2 (where R denotes rare earths and M denotes transition elements) Laves phases and Zr-based compounds [82,83,90,91]. The formation of the amorphous phase in Zr_3Al by hydrogenation starts at lattice defects such as dislocations and grain boundaries [92]. Some researchers have proposed the elastic instability as a cause for amorphization of the Zr_3Al compound during hydrogen absorption [93,94]. The required criteria and physical properties of the resulting amorphous phases have already been comprehensively reviewed [95].

Electrolytic charging has been used [96] as well to form amorphous $Zr_{0.79}Pd_{0.21}H_x$ from the metastable *fcc* $Zr_{0.79}Pd_{0.21}$ alloy. The crystal-to-glass transition was explained to be driven by the large negative heat of mixing of the crystalline reactants that experience strong kinetic constraints (primarily due to low temperature), which prevented development of the crystalline equilibrium phases. A technique of synthesizing amorphous metallic glasses by reaction with hydrogen in solution has been suggested [96]. The technique is claimed to be more powerful than gas-phase hydrogenation. Complete amorphization of metallic ribbons could be achieved in less than 100 s at an equivalent hydrogen fugacity of more than 100 atm. One problem of this technique concerns the mechanical integrity of some electrodes at high hydrogen concentrations. Several alloys break into a fine powder when the concentration of hydrogen reaches a high level, which translates to a loss of electrical contact. Gas-phase hydrogenation does not have this limitation.

HIA in a quasicrystalline ZrCuNiAl alloy following electrochemical charging has also been reported [97–99]. Hydrogenation of the quasicrystalline ZrCuNiAl alloy was found to cause disappearance of the weaker reflections in the XRD patterns as well as electron diffraction patterns (Figs. 3 and 4, respectively). The contrast of the quasicrystals in bright-field images weakened significantly (Fig. 4), but no evidence for the formation of a new crystalline or quasicrystalline phase was revealed after hydrogenation. After degassing, the quasilattice parameter was totally restored. However,

the weak contrast of the quasicrystals as well as the absence of the weak diffraction reflections still remained, thus indicating a high density of defects. A model of the involved structural changes may include the formation of amorphous clusters during hydrogenation [98]. It should be noted that the amorphization reaction in this case is undesirable, as it destroys the thermal stability of the quasicrystalline phase, thus preventing the use of the latter for hydrogen storage applications.

Hydrogen-induced microstructural refinement in both Al–2.3Ti and Al–23.86Ti MMCs following electrochemical charging has also been reported [100]. The XRD patterns of uncharged Al–2.3Ti samples (Fig. 5) showed the presence of *fcc* α-Al, as well as of DO_{22} Al_3Ti phases. The structure of the α-Al in the charged samples was also *fcc*, with lattice parameters identical to the uncharged α-Al. However, the α-Al peaks showed both broadening and intensity reduction following hydrogenation. The reduction in the α-Al peak intensities was not accompanied by new peak formation or growth of the Al_3Ti, as evident from Fig. 5. This result indicated the reduction in crystallinity of the α-Al phase due to hydrogenation. The absence of a change

in lattice parameter after hydrogenation may indicate that the microcrystalline-to-nanocrystalline transition was heterogeneous and that α-Al existed both in the microcrystalline and nanocrystalline states. Similar results were obtained for Al–23.86Ti. In this case, the nanocrystalline material partially recrystallized after aging at room temperature and ambient pressure. A TEM high-magnification view of the α-Al before and after hydrogen charging (Fig. 6a and b, respectively) showed that the uncharged α-Al was composed of small (0.3–1.5 μm) equiaxed grains. After hydrogen charging, a very fine microstructure was observed. This microstructure was composed of nanocrystals (15–30 nm) that formed at the sites of the former equiaxed grains.

Recently, hydrogen has been reported [101,102] to refine the microstructure formed during annealing of quasicrystalline ZrCuNiAl alloy. Uncharged quasicrystals decomposed mainly into hexagonal Zr_6Al_2Ni as well as tetragonal Zr_2Ni and Zr_2Cu; small amounts of the oxygen-stabilized *fcc* 'big-cube' phase were observed as well. As indicated by TEM and XRD, following electrochemical hydrogen charging of the quasicrystals (H/M = 0.05) the same phases formed, but the microstructure was significantly refined (crystals about 10 nm in diameter).
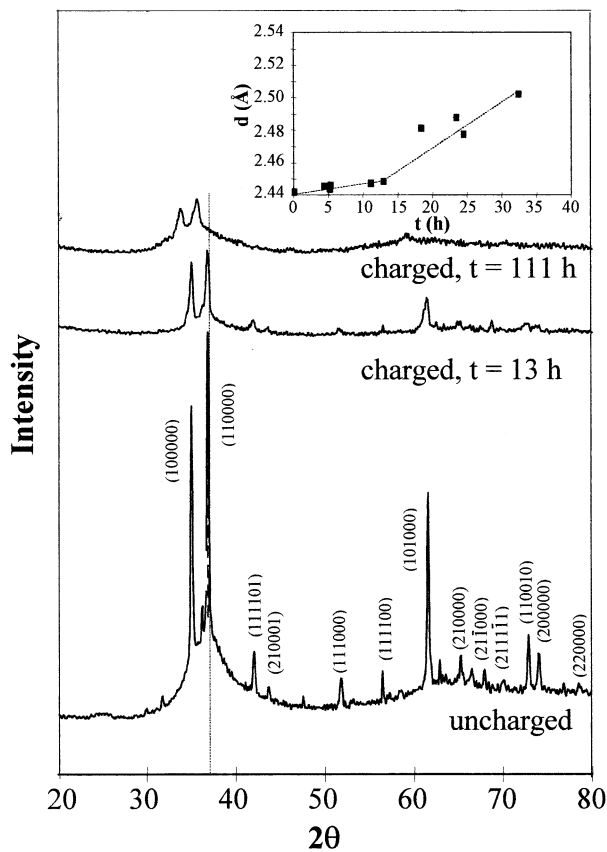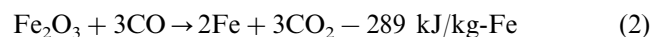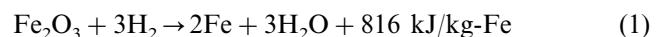
6. Extraction of elements from ores and alloys

A potentially large market for usage of hydrogen is the direct reduction of metal ores (metal oxides) [25,32,34,103]. In such processes, hydrogen or a mixture of hydrogen and carbon monoxide gas (called reducing gas) is reacted with the metallic ore. Usually, the reducing gas flows upward through a falling or fluidized bed of metallic ore. These direct reduction processes offer several advantages such as flexibility of plant location, reduced use of fossil fuels, and reduced pollution problems.

The direct reduction of iron ore to low-carbon sponge iron is achieved with hydrogen gas at 600–900°C or a mixture of hydrogen and carbon monoxide. The raw sponge iron is then further treated in electric furnaces to produce steel. Compared to the conventional blast furnace method, modern direct-reduction plants offer technological advantages in processing iron-rich ores as well as a more efficient energy balance. For applications where the common impurities are especially undesirable, iron produced by direct reduction by hydrogen is preferred [32,34].

The direct reduction of iron ore can be described by the following reaction equations:

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O + 816 \text{ kJ/kg-Fe} \tag{1}$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2 - 289 \text{ kJ/kg-Fe} \tag{2}$$

Fig. 3. X-ray diffraction patterns of quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ alloy before and after hydrogen charging at 10 A m^{-2}. In the inner frame: dependence of the main peak position on hydrogenation time.
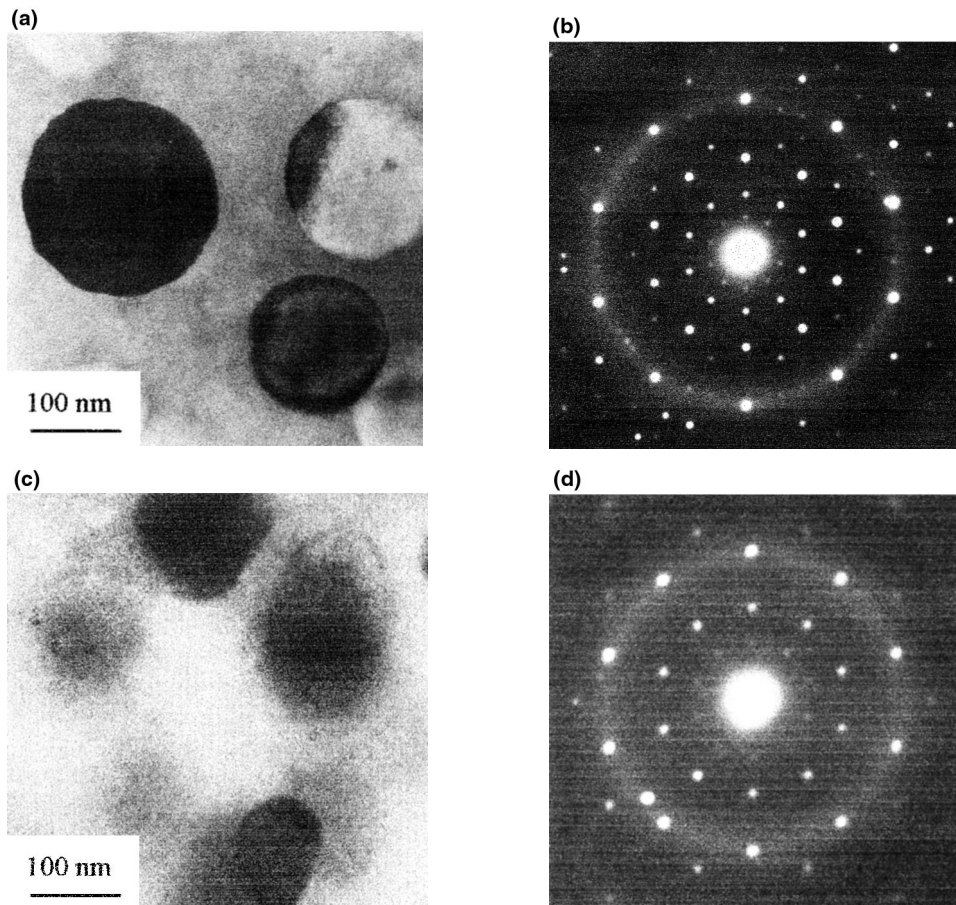
Fig. 4. TEM bright-field and selected area electron diffraction (fivefold symmetry) of a partially quasicrystalline $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ribbon before (a, b) and after (c, d) electrochemical hydrogen charging to a concentration of 1.6 H/M [97].

In these processes, approximately 85–90% of the ore can be metallized.

Hydrogen may also be utilized in the metallurgy of iron and steels to improve properties. The first effects of decarburization of steel under high pressures of hydrogen were experimentally observed at about 200°C [104], and at about 250°C [105]. The ability of hydrogen to react with carbon is greatly increased by the presence of oxygen, water vapor and other oxidizing substances. Moist hydrogen is commonly used for the decarburization and purifying of transformer irons; hysteresis losses may be lowered considerably in this way.

When present in molten steel, hydrogen causes distinct changes in the steel structure after solidification. Within the limits of a certain hydrogen concentration, steel has been suggested [106,107] to have a low surface energy, thus trans-crystallization (formation of coarse dendritic grains) may occur. Hydrogen is also suggested to absorb on the edges of growing crystals and render homogenization more difficult [106]. Enrichment in alloying constituents occurs along the axis of dendrites in alloy steels, followed by strongly developed dendritic segregation. After forging and annealing, such steel may show a normal structure, but overheating some-times causes a secondary segregation and formation of a Widmannstätten structure.

Hydrogen has also been reported [103,108] to possibly increase the hardenability of tool steels. During the casehardening of some types of steel, hydrogen was found to hinder the formation of ferrite and cementite. This phenomenon was attributed to a certain stabilization of cementite by hydrogen, an effect that was also observed in cast irons [103].

There are other cases in which hydrogen may be utilized to extract elements from alloys. Transition metals and their alloys often become processable by rapid solidification methods more easily if certain non-metallic elements such as boron, carbon, or phosphorous are added. Most frequently, transition metal–metalloid metallic glasses contain a certain amount of boron. The boron is very efficient in reducing the melting point and in improving the wetting behavior of such alloys, thus facilitating the chill block casting process. If the final product is to be free of such additive elements, they should be extracted by an annealing procedure, for example. It has been suggested [109] to possibly extract rather large amounts of boron from Fe–Co–B and Fe–B–Si alloys by a proper annealing procedure either in wet or dry hydrogen.

Hydrogen-induced lattice rearrangements are of potential interest as a means for materials preparation. More specifically, hydrogen-induced lattice migration (HILM) may be employed in materials processing. It may, for instance, be possible to interdiffuse certain metals at much lower temperatures than would normally be required in the absence of dissolved hydrogen. In addition, this process may also be employed to prepare materials that cannot be prepared in the absence of dissolved hydrogen.

Flanagan and Noh [110] have shown that dissolved hydrogen may play several different roles in alloy lattice rearrangements. It can shift the equilibrium, e.g. stabilize a particular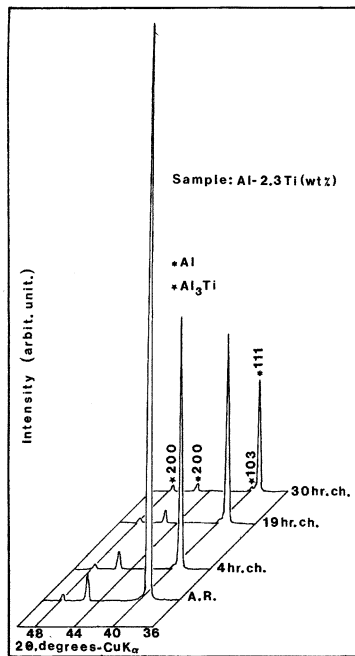 structure or modify a binary to a ternary phase diagram. In addition, it can serve as a catalyst in promoting metal atom diffusion. In some cases, both effects may operate. For example, hydrogen heat treatment (HHT) was found to enhance diffusion and homogenization of an inhomogeneous $Pd_{0.85}Ni_{0.15}$ alloy at an elevated temperature and to lead to segregation at a lower temperature. In the former case the hydrogen concentration was small and it was assumed to play the role of a catalyst. In the latter case the hydrogen concentration was large and it was assumed to play the role of both a catalyst and a part of the equilibrium state. The accelerated metal atom diffusion in the presence of hydrogen is explained by the mechanism of enhanced vacancy concentrations, as suggested by Fukai and Okuma [111].

Hydrogen reduction is feasible in tungsten, molybdenum, nickel, copper, zinc, uranium, and lead. For example, in the manufacture of light bulb filaments, tungsten must be drawn through a series of dies to reduce it to very fine wire. This process is nearly impossible with tungsten containing carbon. Tungsten used for the production of filaments is therefore produced by the direct reduction of tungsten oxide with hydrogen [25].

Fig. 5. X-ray diffraction patterns of Al–2.3Ti before and after electrochemical hydrogenation at 75 mA cm^{-2} and room temperature [100].
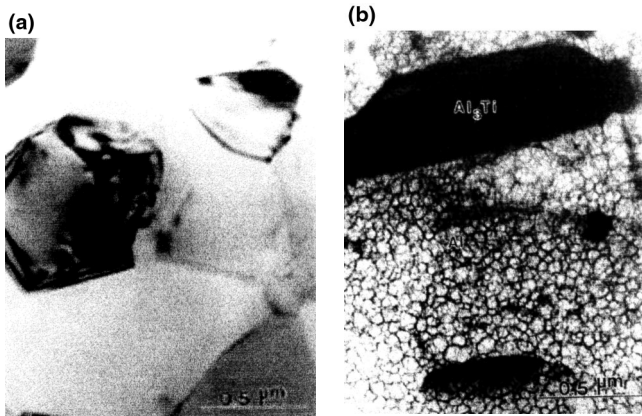

Fig. 6. TEM observations of the α-Al phase in Al–2.3Ti: (a) before; and (b) after hydrogen charging [100].

7. Hydrogen as a reducing gas in welding and brazing

Hydrogen is often used as a heat-treating atmosphere to achieve beneficial properties and superior surface finish. The ingress and egress diffusion of hydrogen into and out of high-strength steel during heat treatment has been investigated [112]. The results showed that with proper heat-treating practice, the advantages of hydrogen anneal and the avoidance of the susceptibility to hydrogen cracking can be economically achieved. Hydrogen is also used by the metallurgical industry for several other purposes, including the use as a reducing blanket gas for high-temperature forming processes. However, due to the low hydrogen content of these protective gases (about 5% in nitrogen or argon) for powder-metallurgical sintering processes or heat treatment of steels, the total demand for hydrogen is relatively small.

In brazing operations involving the joining of high-temperature alloys, the parts to be brazed are coated on the surfaces to be joined with the brazing material and clamped in place. The assembled parts with their holding jigs are then placed in a furnace. The furnace is purged with hydrogen gas to remove the last traces of oxygen and then raised to a temperature somewhat higher than the melting point of the brazing material. During the heating operation, the hydrogen purge is maintained to prevent the leakage of oxygen back into the furnace and to reduce any oxide film on the surface of the metal that might interfere with the formation of

a strong joint. At the high temperature, the brazing material melts and wets the adjoining surfaces of the metal parts being joined. To form a strong bond between brazed parts it is necessary that both surfaces to be joined be completely wet by the molten brazing material. Hydrogen reduces the oxide films and prevents their reformation, thus improving wettability. After sufficient time at a temperature that allows wetting to occur, the parts are cooled to room temperature in the hydrogen atmosphere and then removed for use [25].

Hydrogen-containing shielding and backing gas is sometimes used for welding to improve the wettability and achieve a higher heat input due to higher combined dissociation and ionization energies compared to monatomic shielding gases [113,114]. For example, a proportion of hydrogen in the shielding gas can improve the wettability of the weld pool [115]. A steel welding electrode with a cellulosic covering is often used when welding in a deep edge preparation to generate better protection during the root pass. The next pass with a non-cellulose covered electrode should follow before the weld reaches room temperature to drive out the diffusible hydrogen of the first pass and thus eliminate the concern for hydrogen-assisted cracking. However, one should remember that hydrogen could be responsible for the embrittlement and cold cracking of steels, a serious problem that should be considered when welding *bcc* materials. When welding steels, hydrogen control, preheating, heat input control and, sometimes, post heating are applied as appropriate to avoid embrittlement and cold cracking problems [116,117]. Hydrogen is also in the plasma gas for an industrial plasma cutting torch. The hydrogen increases the plasma temperatures and allows for larger section thickness to be cut.

8. Concluding remarks

Hydrogen is often associated with degradation of mechanical properties and failure. However, this paper has demonstrated that hydrogen may have positive effects on the formability, microstructures and properties of a large variety of materials. For the processes discussed within this paper, the following conclusions can be drawn:

1. Thermohydrogen processing (THP) — the use of hydrogen as a temporary alloying element allows for significant enhancement of the formability, final microstructure and mechanical properties of Ti-based alloys. This processing technique has also been suggested to be attractive for increasing the ductility of Ti$_3$Al-based alloys and other intermetallics by microstructural modification. In addition, THP of fiber-reinforced titanium alloy matrix composites allows their fabrication at lower temperatures, thus improving the fiber/matrix interface properties.

2. Processing of refractory metals — hydrogen may be used as a temporary alloying element to promote grain refinement and superplasticity of niobium and tantalum.

3. Hydrogen decrepitation (HD) and hydrogenation–decomposition–desorption–recombination (HDDR) — rare earth-transition metal magnets have been successfully manufactured by HD. The advantages of the HD process include production of finer powders without undue oxidation, greater mechanical strength of the HD magnets, production of single-crystal particles, almost zero remanent magnetism of aligned green compacts which makes them easier to handle, ease of subsequent processing by sintering and milling, etc. The HDDR process allows production of unique microstructures consisting of very fine crystalline grains. It has been used commercially, for example, to produce NdFeB anisotropic magnet powders.

4. Hydrogen-induced amorphization (HIA) and microstructural refinement — HIA provides a way of amorphization fundamentally different from other existing methods and opens a possibility for preparing amorphous alloys without restriction to small dimensions. In addition, hydrogen has been found to refine the microstructure of a large variety of materials, including Ti-based alloys and composites as well as annealed quasicrystalline ZrCuNiAl alloy.

5. Hydrogen can be used for the direct reduction of metal ores; for decarburizing and purifying of transformer irons; for extraction of metalloids (e.g. boron) from certain metallic glasses; to lower the interdiffusion temperatures of certain metals; etc.

6. Welding and brazing — hydrogen is used as a reducing gas. In brazing, hydrogen reduces the oxide films and prevents their reformation, thus improving wettability. In welding, it is also used to improve the wettability, as well as to achieve higher heat input.

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