Utilization of Vacuum Technology in the Processing of Refractory Metal, Titanium and Their Alloys for Powder Applications

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Increased usage of refractory metals, titanium and their alloys in the aerospace and electronics industries has led to the use of the hydride/dehydride (HDH) heat-treating process for recovery of spent materials. The HDH process has been known for many years in the manufacturing of transition-metal powders.[1]

Gaseous hydrogenation of spent parts containing tantalum, niobium, vanadium or titanium provides a process in which unwanted end-use material can be converted to a crushed aggregate – including fine powder – and later degassed to provide clean material for new applications.

Hydrogenation of Metals

Transition metals such as tantulum, niobium, vanadium and titanium have a high affinity for hydrogen. However, the reaction between the metal and the gas is reversible (Equation 1). Through careful manipulation of the reaction process, the equilibrium reaction can be pushed toward the right to favor hydride formation. In the case of these transition metals, the hydride reaction is exothermic – heat is released to the environment. The extent of the exothermic reaction is dependent on the metal and the strength of the metal-hydrogen bond. Although the overall heat of reaction between the metal and the metal hydride is negative, there is an initial energy barrier (activation energy) that must be achieved before the reaction is self-sustaining (Fig. 1).

$$M + (X/2)\ H_2 \rightleftarrows MH_x + \text{Heat}$$

Equation 1: The reversible metal-hydride reaction, where M is the metal and MH_x is the metal hydride. Heat is the enthalpy of the reaction, which depends on the strength of the metal-hydrogen bond.

Solar Atmospheres' research and development program was based on three well-known facts of hydrogen solubility in transition metals.[2] First, the diffusion coefficient for hydrogen in the various metals is relatively high. Second, the maximum solubility within the virgin metal requires heating to high temperatures in high vacuum for purification and activation. Third, once degassed, the metal readily absorbs hydrogen at moderate temperatures.

The solubility of hydrogen in a metal occurs in three stages (Fig. 2). Initially, the hydrogen molecules adsorb as a layer

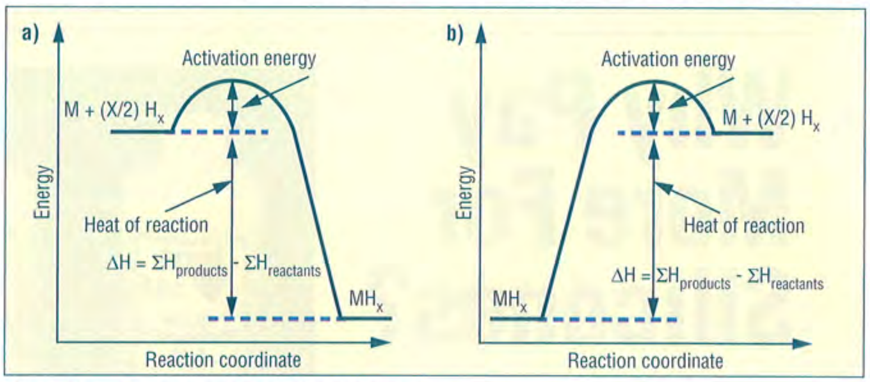

Fig. 1. Reaction energy vs. reaction pathway
1a. Exothermic reaction pathway, ΔH<0, heat is released to the environment as the reaction proceeds. 1b. Endothermic reaction pathway, ΔH > 0, heat must be supplied to the reaction.

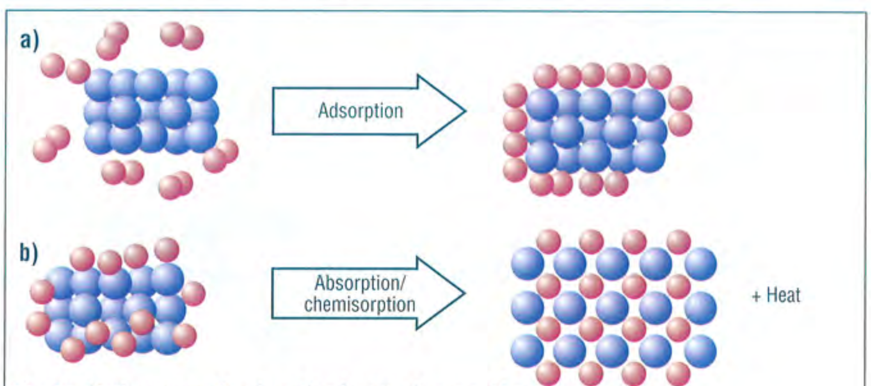

Fig. 2a. Hydrogen molecules adsorb onto the metal lattice.
Fig. 2b. Absorption and chemisorption lead to an expanded metal lattice.

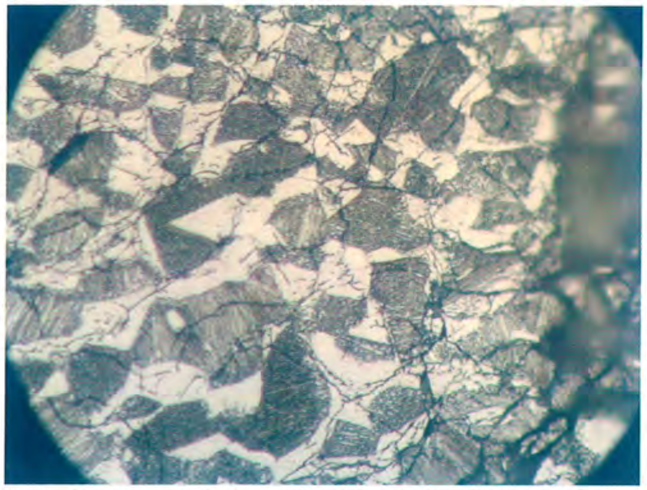

Fig. 3. Metallograph (1000x) of hydrided Ti alloy shows cracking that accomodates hydrogen at the interstitial sites

onto the surface of the metal. The molecules then dissociate on the surface to hydrogen atoms, which diffuse into the metal lattice through two processes called absorption and chemisorption to form an interstitial hydride. Interstitial hydrides are a subset of metallic hydrides – a two-phase system consisting of a solid solution (α phase) with hydrogen located on the interstitial sites and the hydride (β phase, MH_x).[3] A simple model looks like an expanded metal lattice with hydrogen in the interstitial sites (Fig. 2b). The resulting increased volume leads to cracking[4] and embrittlement (Fig. 3).

Parts arriving in various forms – from sponge to waste clippings to ingots – require different reaction parameters in the vacuum furnace. A program that began in a small R&D furnace (4- to 6-pound loads) has developed into an economical and reproducible production process.

Furnace and Process Modifications for Hydrogen Safety

Safety modifications were made to the production furnaces before working with large volumes of hydrogen in those vacuum furnaces. Oxygen probes were added to detect potential air leaks in the vacuum system. If a leak were to occur, an alarm would alert the operator. At the same time, the hydrogen supply would shut off and a purge would be initiated with an inert gas.

Even during normal operation, the furnace is programmed to shut off the hydrogen flow when it has reached a set pressure. Processing procedures require performing a leak check on the vacuum chamber prior to each run – leak-up rate should be less than 15 microns per hour. As an added precaution at the end of each cycle, evacuation of excess hydrogen to 0.1 torr is performed prior to quenching with helium or argon.

Hydriding Cycle Development

Two different cycles for hydriding were developed based on maximum load sizes of 2,500 and 10,000 pounds (Fig. 4). Each cycle begins with a high-temperature and high-vacuum purification step. During the initial stage of hydrogenation, work temperature is monitored and hydrogen flow rate is adjusted to prevent overheating. A eutectic reaction between the process material and the fixturing is thereby avoided. The exothermic hydrogenation reaction provides enough heat energy to keep the reaction self-sustaining. The furnace power can therefore be shut off or substantially reduced for the remainder of the cycle.

The first cycle, for 2,500-pound loads, starts in vacuum and gradually rises in pressure to slightly above atmosphere (Fig. 5), during which there is an approximate eight-hour period where the hydrogen pressure is between 150 and 900 torr. Working with hydrogen gas in the 150–900 torr range introduces certain safety

Fig. 4a. Standard production furnace for 2,500-pound loads

Fig. 4b. Car-bottom furnace for 10,000-pound loads

concerns.[5] An increase in load size up to 10,000 pounds would increase the time spent in this pressure range. Therefore, the development of a low-torr hydriding process was investigated.

The amount of hydrogen required depends on the metal or alloy in process and the percent hydrogen necessary for powder formation. A simple estimate based on the stoichiometric hydride, the weight percent of hydrogen and the density of hydrogen provides a maximum hydrogen requirement for a typical cycle. Hydrogen uptake is measured via installation of an in-situ hydrogen totalizing meter (Fig. 6).

Initial low-torr runs at 2,500 pounds in a standard production furnace were discouraging. The time to complete the low-pressure process was 60% longer to meet the customer's needs. The use of the larger furnace, however, allows four times the amount of material to be processed in a single cycle. Running a 10,000-pound furnace load at 125–150 torr and comparing the cycle time to what would be four runs in a smaller production furnace was warranted (Fig. 7). As can be seen from the data in Table 1, the use of the low-torr process in the larger furnace is just as economical as four smaller production loads performed at positive pressure, and overall completion time is decreased.

Dehydrogenation of Metal Powders

The endothermic dehydrogenation step of the HDH process is run on the powdered-metal hydride to provide low-oxygen, low-nitrogen, non-sintered metal powder. The dehydrogenation mechanism occurs in a two-stage process.[6] In the first stage, the adsorbed hydrogen is readily released upon heating to give a sub-hydride. The second step in the process – the rate-determining step – requires the breaking of the M-H. Utilizing vacuum technology during the heating process helps push the process towards the free metal (Equation 2) and requires a balance between heat rate and final process vacuum levels to provide a non-sintered product.

$$\text{Heat} + MH_X \rightarrow MHy \rightarrow M + (X/2)\,H_2$$

Equation 2: Dehydrogenation Reaction – two-stage dehydrogenation is an endothermic process and is dependent on the strength of the M-H bond (y<x).

Cycle Development

Studies of powders with various particle distributions were performed to determine how heating rate and temperature affect the final product. Heating and vacuum levels were determined for each metal hydride. Temperature profiles used depended on the amount of agglomeration acceptable in the end product.

The finer the particle size, the lower the initial dehydrogenation temperature

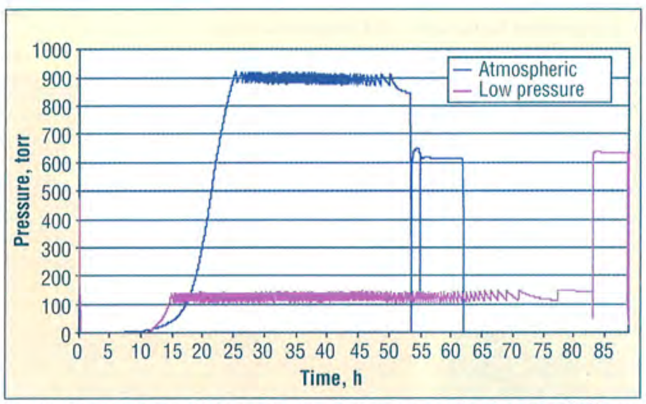

Fig. 5. Comparison of the cycle time for an atmospheric cycle and low-torr cycle for a 2,500-pound load in a standard production furnace.

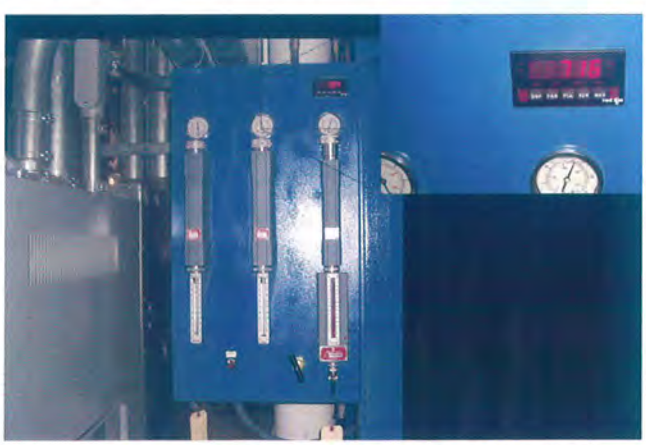

Fig. 6. Digital hydrogen totalizer provides accurate measure of hydrogen input during the hydriding process.

Table 1. Economic Comparisons One 10,000-pound vs. four 2,500-pound loads
HT-73 – Car Bottom Furnace
Load size: 10,000 lbs.
Max. H_2 flow rate: 1900 ft^3/hr.
Max. pressure per run: 150 Torr
Total process time (hydride + quench): 6 days
HT-14
Load size: 2,500 lbs.
No. of loads/10,000 lbs.: 4
Max. H_2 flow rate: 800 ft^3/hr.
Max. pressure per run: 900 Torr
Total process time (hydride + quench) per load: 2.5 days
Days to process 10,000 lbs.: 10 days

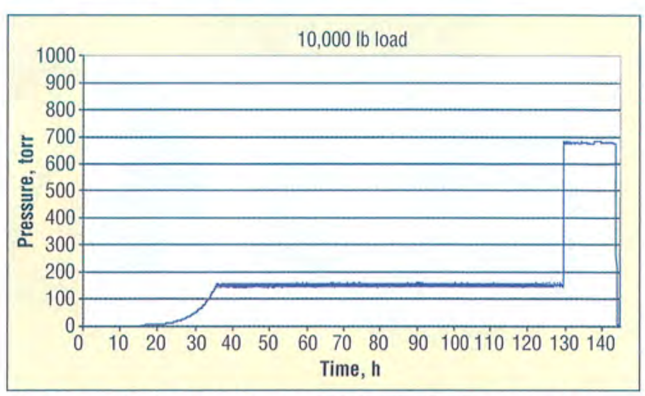

Fig. 7. Overall time for a single 10,000-pound low-torr run in a large car-bottom furnace

required. However, the finer the particle size, the greater the tendency towards sintering. Studies have shown that as the particle size decreased, an increase in movement of adjacent particle clusters occurred in vacuum, leading to an increased tendency to sinter.[5] Carefully programmed heating rates based on particle size allowed more efficient degassing with less agglomeration. In addition, limiting time spent in high vacuum at the highest process temperature further minimized sintering. Utilizing our standard vacuum-furnace system, we found that load mass and bed depths are limited to a maximum of 1,500 pounds and 2 inches, respectively, to provide an acceptable end product.

Summary

Solar Atmospheres' current development of the HDH process has resulted in two hydriding cycles. The first is a positive-pressure hydriding process, which is economical but limited in load size. The second is a low-torr hydriding process developed for 10,000-pound loads, which is just as economical as the smaller production load performed at positive pressure. The processed metal-hydride powder is readily dehydrided with a minimum of sintering to provide a low-oxygen, low-nitrogen product. All furnaces have been outfitted with safety switches and alarms for working with large volumes of hydrogen. **IH**

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Additional related information may be found by searching for these (and other) key words/terms via BNP Media SEARCH at www.industrialheating.com: hydrogenation, exothermic, sinter, hydriding, endothermic

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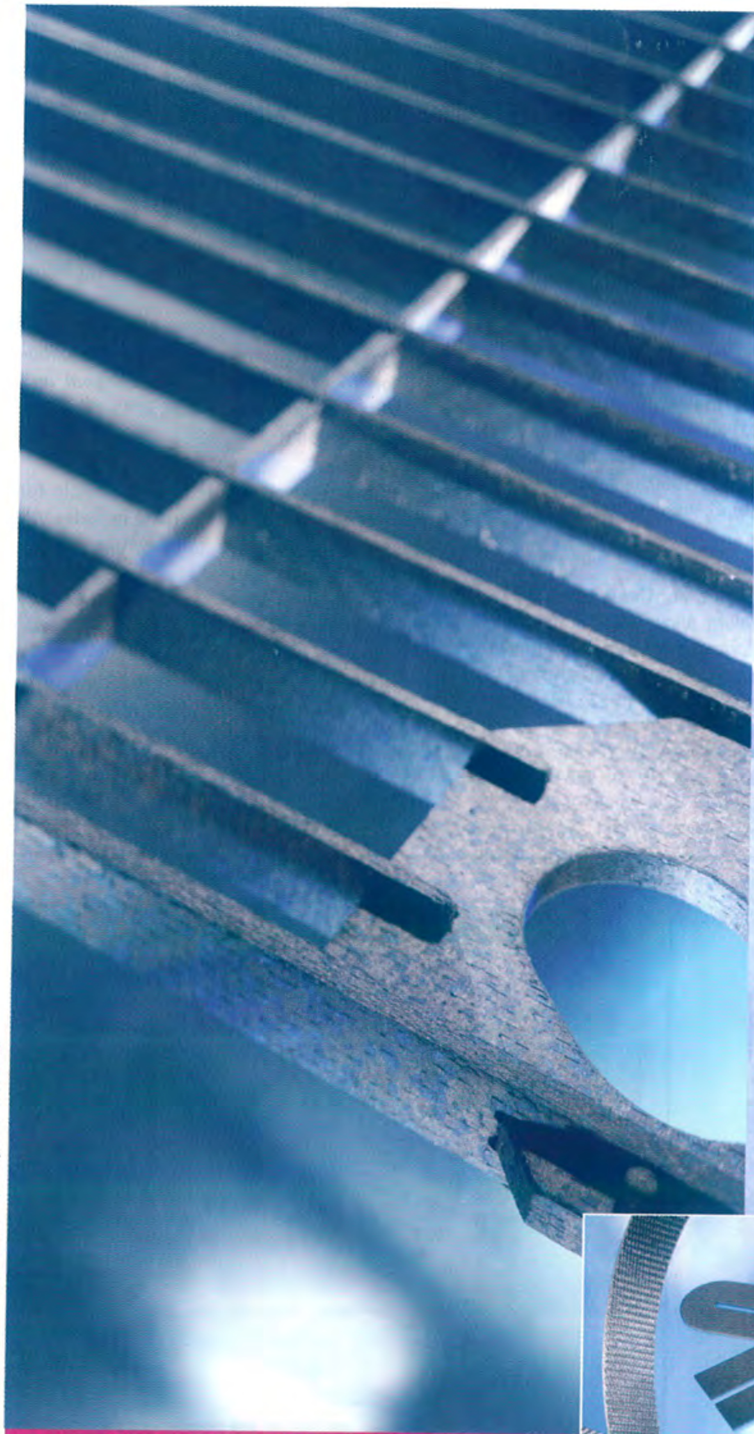

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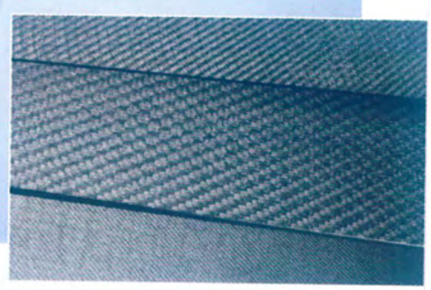

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