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Generating Hydrogen for Thermal Processing and Coatings

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Atmosphere thermal processing improves the properties of fabricated metals. Operations include annealing, brazing, sintering (for powdered metals, metal injection molding and additive manufacturing) and glass or ceramic-to-metal sealing.

Oxygen, in the thermal-processing atmosphere or bound in surface contamination on the parts, must be reduced to ensure quality results. Chemically reducing atmospheres actively scrub oxygen to enhance results and protect metal surfaces.

Hydrogen is a widely used reducing agent in thermal-processing atmospheres. Reducing atmospheres generally contain hydrogen (H_2) and may contain carbon monoxide (CO) to scrub oxygen. CO may affect metal properties and is poisonous, requiring special care in use. Where hydrogen is the sole reducing agent, it may come from hydrogen delivery, pure hydrogen generation or ammonia dissociation.

Hydrogen/nitrogen thermal-processing atmospheres may range from dilute 95% N_2, 5% H_2 “forming gas” to pure hydrogen. Pure nitrogen is required by NFPA 86 Furnace Standard for purge. Certain atmospheres have specific processing capabilities and materials compatibility (e.g., brazing and carbon-steel parts are processed in forming gas), while certain grades of stainless steels require pure H_2.

Because pure H_2 costs up to 10 times more than N_2, the less hydrogen you need, the less your atmosphere will cost. Drier (lower dew point) atmospheres may enable you to use a lower hydrogen-percentage atmosphere. Availability of pure hydrogen enables more atmosphere blend flexibility than dissociated ammonia of fixed composition (75% H_2, 25% N_2). Furnace atmosphere blend flexibility and drier gas may enable improved results at lower costs.

Applications for Hydrogen Atmospheres

Atmospheres containing hydrogen are used in continuous and batch atmosphere furnaces, and hydrogen may be used in vacuum furnaces as a partial-pressure backfill. In addition to its chemical reducing activity, hydrogen’s high thermal conductivity provides superior heat transfer to speed full-depth materials processing. Hydrogen may enable cycling parts more quickly – running the furnace faster – because of higher heating and cooling heat-transfer speed.

Both hydrogen and ammonia are classified by EPA and OSHA as highly hazardous chemicals (HHCs) and are subject to many storage regulations. Whether by EPA, OSHA, local fire marshal or your facility SH&E staff, prepare for scrutiny if you store ammonia or hydrogen. Storage of more than 10,000 pounds requires emergency-response planning, record-keeping, training and equipment subject to OSHA Process Safety Management (PSM) and EPA Responsible Management Planning (RMP).

Fig. 1. PEM water-electrolysis hydrogen generators are available in a range of capacities to match any thermal-processing application.

Sourcing Gases

Various approaches exist to receive and store (or generate) gases for your furnace atmospheres. Anhydrous ammonia, hydrogen and nitrogen may be delivered as liquid via tanker truck or as compressed gases delivered and stored in cylinders or tubes. Liquid hydrogen and nitrogen are stored in cryogenic tanks as pressurized liquid ammonia.

Alternatively, you may generate your furnace atmosphere gases. Ammonia dissociators thermally/catalytically crack stored ammonia to generate dissociated ammonia (DA) of 75% hydrogen and 25% nitrogen. Proton exchange membrane (PEM) water-electrolysis hydrogen generators crack pure water into pure, dry, pressurized product hydrogen and by-product oxygen. Nitrogen generation is reliable, economical and well-suited for atmospheres. Nitrogen generators filter pure nitrogen from air, removing oxygen, water and CO_2. They can economically reach 99.999% nitrogen purity (10 ppm residual oxygen).

Major users of stored hydrogen may use liquid hydrogen, typically limiting the amount stored to <16,000 gallons (<9,999 pounds, ~1.9MM scf), whether by tank size or so-called administrative controls, in order to stay below the HHC trigger level of 10,000 pounds stored. Users of ammonia to make DA are limited to <1,467 gallons (<9,999 pounds, ~450,000 scf of DA gas) to avoid triggering the HHC regulations. In contrast, the largest PEM hydrogen generator typically serving thermal-processing contains only 14 grams (0.03 pounds) of H_2.

Hydrogen from Ammonia

DA requires ammonia storage, has limited turndown and is energy-intensive because the dissociator must remain heated 24/7 to at least 1,700°F (927°C). Dissociators offer no atmosphere flexibility with only 75% hydrogen and 25% nitrogen. Leaner atmospheres can be blended down with nitrogen, but purer hydrogen is unavailable.

DA-generated atmosphere is often wetter than optimum, and many installed systems are old and maintenance-intensive. Repair expertise for dissociators is becoming rare. Fewer producers of metallurgical-grade ammonia means that ammonia prices are unpredictable and generally rising.

Ammonia leaks are frequent and disruptive. Accidental ammonia releases occur daily from agricultural tanks, ice rinks and food-processing/storage facilities. These leaks are widely reported, resulting in evacuations, publicity and expensive fines. Anhydrous ammonia is toxic and corrosive to mucus membranes and tissue. If released, it disperses slowly and has a unique and powerful odor.

Many existing installations are grandfathered and do not meet current standards for distance and security. A serious new cause of leaks is sabotage and theft of ammonia for illicit drug production. Thermal-processor ammonia users are often better stewards than refrigeration and agricultural users, but all users suffer bad publicity when releases occur.

Using delivered and stored hydrogen to replace stored ammonia may not be attractive because the rules for storing hydrogen make it as challenging as ammonia. Like ammonia, hydrogen is an HHC, and storage must comply with OSHA, EPA and NFPA (National Fire Protection Association) regulations and any requirements mandated by your local authorities having jurisdiction (AHJ) – usually your fire marshal.

Fig. 2. An atmosphere furnace heat treating parts to adjust their hardness and improve appearance.

- One pound of hydrogen has the energy potential of over 30 pounds of TNT.
- Hydrogen has a very wide flammability range and low activation energy – compressed-hydrogen leaks generally ignite.
- NFPA rules for hydrogen storage may require expensive, leak-prone underground piping to achieve required spacing.
- With stored hydrogen, damaged piping may permit the entire hydrogen contents of your storage to leak almost instantly into your facility, creating an emergency.

Generating Hydrogen

To avoid the hassles of PSM and RMP compliance, you might shrink your stored quantity of HHCs. If you choose to shrink your storage capacity, you will have to increase the frequency of deliveries – when most mishaps occur. Telling a driver to fill a tank only partly full (called "administrative controls" in the regulations) is rarely successful long-term.

PEM water-electrolysis hydrogen generation is preferred to storing hazardous delivered hydrogen or ammonia. PEM hydrogen generation makes pure, dry, pressurized hydrogen from water using water electrolysis. Water (H_2O) is broken into hydrogen and oxygen. The pure, dry, pressurized hydrogen is captured for your process, and the oxygen is vented. No hydrogen storage is required for PEM water electrolysis because hydrogen is made at the same rate that it is being used by your furnace.

On-site generation offers a safer hydrogen-containing atmosphere supply. Hydrogen is leak-prone and highly flammable. While all hydrogen sources require piping that can suffer leaks, generated hydrogen mitigates the severity of possible leaks because the maximum leak rate is limited to the maximum generation rate. Also, supply piping can be shorter since the hydrogen generator is placed indoors, closer to the furnace.

While hydrogen suppliers charge more for high-purity delivered hydrogen, PEM equipment generates extremely pure (99.9995+%) hydrogen at no premium. On-site PEM water-electrolysis hydrogen-generation systems are integrated, compact and available in a range of capacities. They are easily permitted, delivered quickly, straightforward to install and operate, and provide hydrogen at process pressure for blending and subsequent use in your furnace. They load-follow, and you can turn them off and on as your work schedule permits to save electricity.

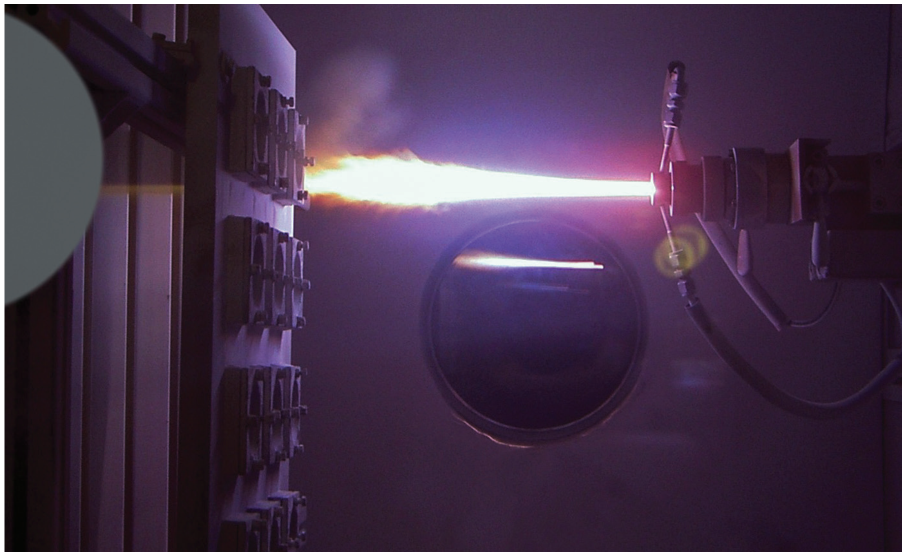

Fig. 3. Thermal spray applying a coating to improve part performance in service.

From an NFPA standpoint, you essentially create hydrogen and use it instantly – no storage. The systems are zero clearance and install in a non-classified environment, even nearby your furnace. Indoor siting negates underground piping that can corrode and cause leaks.

Considerations

Consider custom blending generated-hydrogen and nitrogen atmospheres to meet the precise furnace atmosphere requirements for each product you thermally process. You might need a gas blender or might have blend panels on your furnace(s). You will need high-purity (low-oxygen) nitrogen – liquid or generated. You may choose to distribute pure hydrogen and pure nitrogen gases in individual piping and blend at each furnace.

Alternatively, you may choose to blend centrally and distribute a gas blend analogous to your previous DA. The goal is that your new plant atmosphere will operate like your old DA atmosphere from the furnace operator's standpoint for consistent operator procedures.

Relative to the required gas purity, PEM-generated hydrogen is very pure at 99.9995% or better, and nitrogen can be generated in a range of purity levels. The cost of generated nitrogen partially depends on the purity level. Thermal processing generally requires nitrogen of minimum 99.995% purity, which is easily generated using modern PSA nitrogen generators.

Consider several factors to achieve a successful change from a DA system. Document your current costs – electric, gas, dissociator maintenance, ammonia tank rental and all ammonia charges. Remember that DA atmospheres are 25% nitrogen, and size your nitrogen and hydrogen equipment accordingly. If you use liquid nitrogen, a higher potential usage volume is an opportunity to negotiate pricing.

Study your furnace(s) and determine how much gas flow is needed. Indicators and instruments on your furnaces must be calibrated for the gas you are using, or you must convert readings. It is unfortunately common to see flow meters calibrated for air or nitrogen being used for DA.

Your furnace will require a certain minimum atmosphere flow to keep air out. Determine what gas flow and composition is needed in each furnace zone. When you blend gases, you can vary the composition by furnace zone and take advantage of supplying hydrogen only where it is required. If using a dilute atmosphere blend, make sure it is sufficiently flammable so that your safety systems (e.g., pilot lights and flame curtains) operate. Comply with NFPA 86.

When you change from DA to generated/blended hydrogen/nitrogen atmospheres, atmosphere-system changes will include the removal of your ammonia tank and ammonia dissociator. You may also remove your ammonia and DA piping or repurpose the piping. Consult a knowledgeable consultant and the Fuel Gas Code to determine piping reusability. Nitrogen is probably permitted, and hydrogen is dependent on materials and fittings.

Conclusions

If you make the changeover to PEM on-site-generated hydrogen, you will realize superior atmosphere quality and flexibility at stable, competitive atmosphere cost. You will eliminate the need for hazardous material deliveries, handling and inventories – complying with all local hazmat storage requirements and eliminating the need to connect and disconnect fittings that are often responsible for mishaps. Finally, these on-site hydrogen generators can be expanded in the field if your thermal-processing requirements increase.

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