Abstract: Processes and apparatus for batch annealing work pieces in a hydrogen atmosphere use pressure swing sorption to recover hydrogen from the annealing exhaust. In preferred embodiments, hydrogen for the batch annealing is generated by reforming and the recovery of hydrogen is integrated with the reforming operation.
INTEGRATED REFORMER AND BATCH ANNEALING PROCESSES
AND APPARATUS THEREFOR

FIELD OF THE INVENTION

[0001] This invention pertains to integrated apparatus and processes for operating apparatus for generating hydrogen for batch annealing and the recovery and use of hydrogen from the annealing.

BACKGROUND TO THE INVENTION

[0002] Annealing metal, especially steel strip, rods, wire or coils, is a long used technique for improving metal properties. Annealing furnaces have been of both batch and continuous design. Continuous annealing apparatus and processes have generally been considered to provide more consistent mechanical properties and surface finish than do batch apparatus and processes. Batch annealing facilities are, however, commercially attractive, especially for smaller metal product fabricating operations. Usually a batch annealing facility will have a plurality of vessels, or furnaces. U.S. Patent Nos. 5,388,809 and 5,730,930 disclose bell-type furnaces for annealing.

[0003] With the advent of using hydrogen, either in a mixture with nitrogen or essentially pure hydrogen, in the atmosphere for batch annealing, any product quality gap that existed with respect to continuous annealing had narrowed, if not been eliminated. The batch processes could take advantage of the high thermal conductivity and low density of hydrogen to provide annealed products of desirable quality. Advantages include more consistent mechanical properties and surface finish as well as increased throughput. Stanescu, et al., in Troubleshooting Hydrogen Annealing of Steel Strip, Parts 1 and 2, appearing at Industrial Heating web site (www.industrialheating.com), postings of February 7, 2003, and March 10, 2003, disclose the operation, including operating cycles, for batch annealing furnaces to provide high quality products. One significant problem noted by the authors is the potential for carbonaceous deposits on the metal that adversely affect the product. The authors suggest that optimizing the hydrogen flow rate, the hydrogen flow rate pattern and the timing and frequency of turning on and off hydrogen flow during the annealing cycle can eliminate or reduce the problem of carbonaceous deposition on the work piece being annealed.

[0004] In a batch annealing process based on hydrogen, the process proceeds through a number of stages. First, the ambient atmosphere must be purged, usually with nitrogen. Stanescu, et al., propose that during the nitrogen purge, the vessel be at an elevated
temperature to assist in the removal of oils and other sources of carbon. Then hydrogen is introduced and the temperature increased to annealing temperatures. The hydrogen would be cycled on and off to maintain the desired hydrogen purity in the vessel. The next stage is cooling, still in a hydrogen atmosphere followed by purging with nitrogen. The cycle is usually operated at close to atmospheric pressure. The specific cycle, or recipe, for the annealing will vary depending upon the nature of the work piece and the properties sought to be exhibited by the annealed work piece.

[0005] During the cycle, hydrogen-containing streams will be exhausted from the vessel. The compositions of these exhaust streams will vary considerably depending upon the stage of the cycle. During the purging steps, the exhaust will contain hydrogen and nitrogen of varying proportions. As the vessel is brought to the annealing temperature, usually about 500 to 600°C, and during the annealing, the exhaust may contain carbon monoxide and methane. The exhaust streams, especially at the beginning of the cycle, may contain oils and other hydrocarbons from the previous processing and handling of the metal undergoing the annealing process. The exhaust streams are typically vented.

[0006] Typically, facilities practicing batch annealing are remote from hydrogen production facilities and thus hydrogen must be shipped to the site. Hydrogen production is usually accomplished by steam reforming. Economies of scale are a significant determinant of the cost of generating hydrogen as are the cost of the feed and energy required in the reforming process. Commercial-scale facilities generally are designed to operate at a relatively constant production rate. Numerous proposals have been made for steam reforming and partial oxidation reforming (including autothermal reforming) on a smaller scale and with some turn-up and turn down capabilities. Not only are the economies of scale lost, but also, turndown capabilities tend to increase the complexities of operation of the reformer and thus would further adversely affect the economic viability of the use of such a reformer for a batch annealing process.

[0007] U.S. Patent No. 6,881,242 proposes the use of hydrogen metal membranes such as palladium for the recovery of hydrogen from certain exhaust streams from, inter alia, an annealing furnace. The patent provides no disclosure on the operation of a batch annealing apparatus, let alone how to handle the widely varying, in volume and composition, exhaust streams to enhance the operation and economics of a batch annealing process. Moreover, membranes of the type disclosed in the patent require large pressure differentials at high temperatures to achieve economically viable hydrogen flux.
[0009] A need exists for such batch annealing apparatus and processes that recover and use hydrogen contained in the exhaust to enhance the economics associated with batch annealing, and especially to make commercially viable hydrogen production capabilities dedicated to the annealing facility. The challenges in providing such an apparatus are even more substantial where the apparatus must handle different recipes requiring different amounts of hydrogen at different points of time in the cycle. Moreover, where a facility has a number of batch annealing vessels, the simultaneous use of different recipes increases the complexities in recovering and reusing the hydrogen and in generating hydrogen.

SUMMARY OF THE INVENTION

[0010] In accordance with this invention, processes are provided for batch annealing which efficiently use hydrogen while providing desirable annealed metal products. During the annealing, hydrogen is provided to the batch annealing zone and pressure swing sorption is used to treat at least a portion of the off gases emitted from the batch annealing zone. The pressure swing sorption can provide a high purity hydrogen product that can, if desired, be recycled for annealing. Advantageously, the processes comprise reforming a hydrocarbon-containing feedstock to provide at least a portion of the hydrogen for annealing. The pressure swing sorption can be integrated with the reforming step, thus further enhancing the attractiveness of the processes of this invention. One method for integration is by combusting the reject stream from the pressure swing sorption to provide heat for reforming. By the use of pressure swing sorption, desirable hydrogen product purity can be obtained over a wide range of off gas compositions, thereby providing flexibility for handling off gases at various points of time during the annealing cycle as well as enabling the annealing to operate over a wide range of annealing cycles, or recipes.

[0011] In its broadest aspects, the batch annealing processes of this invention comprise

a. providing in an annealing zone a metal work piece having carbon-containing substance associated therewith which under annealing conditions can cause coke formation;
b. purging free oxygen from the annealing zone containing the metal work piece with an inert gas and withdrawing a pre-annealing purge effluent containing said inert gas and free oxygen;
c. thereafter providing to said annealing zone a hydrogen-containing gas, said gas comprising at least about 50, often at least about 80 and sometimes at least about 90, volume percent hydrogen, said supply being (i) in an amount sufficient to achieve and maintain a hydrogen concentration in said annealing zone, preferably a hydrogen concentration of at least about 50, often at least about 75 and sometimes at least about 90, volume percent during annealing, and (ii) at a rate, continuous or intermittent, to enhance annealing and provide an off gas containing hydrogen and carbon-containing substance, wherein for at least a portion of the time while the hydrogen-containing gas is supplied, said annealing zone is heated to a temperature for a time sufficient to anneal said metal work piece;
d. ceasing providing said hydrogen-containing gas;
e. cooling said annealing zone commencing before or after the cessation of providing said hydrogen-containing gas;
f. purging hydrogen from said annealing zone with an inert gas and withdrawing a post-annealing purge effluent containing said inert gas and hydrogen; and
g. removing said metal work piece from the annealing zone,
wherein at least a portion of the off gas containing hydrogen of step (c) is subjected to pressure swing sorption on a solid sorbent to provide a hydrogen product containing at least about 70, preferably at least about 90, and sometimes at least about 95, volume percent hydrogen and is substantially devoid of carbon-containing substance and a reject stream having a lower concentration of hydrogen than the off gas and containing carbon-containing substance. Preferably, sufficient hydrogen is provided continuously or intermittently during the annealing of step (c) that the concentration of carbon-containing substances in the off gas is less than about 5 volume percent. Preferably, at least a portion of the hydrogen product is used as hydrogen-containing gas for annealing.

[0012] In a preferred embodiment of the processes of this invention, at least a portion of the hydrogen-containing gas for step (c) is provided by reforming a hydrocarbon-containing feedstock under reforming conditions, which typically include elevated temperature, and at least a portion of the reject stream is combusted to provide at least a
portion of heat to achieve reforming conditions. Generally, the reformate contains hydrogen and at least one of carbon monoxide and carbon dioxide. In a preferred embodiment, the reformate is subjected to pressure swing sorption on a solid sorbent to provide a reformate hydrogen product containing at least about 90 volume percent hydrogen which is substantially devoid of carbon monoxide and carbon dioxide and a reject stream containing hydrogen and at least one of carbon monoxide and carbon dioxide.

[0013] In the embodiments where a reformate is generated and is purified by pressure swing sorption, the purifications of the off gas from the annealing and the reformate may be integrated in various manners. For instance, the off gas to be subjected to pressure swing sorption can be admixed with the reformate and the admixture is subjected to pressure swing sorption. Thus, the reformate hydrogen product comprises hydrogen derived from the off gas. Alternatively, at least a portion of the hydrogen product from the pressure swing sorption of off gas is admixed with the reformate hydrogen product and at least a portion of the reformate hydrogen product is used for annealing. In another alternative, at least a portion of the reject stream from the pressure swing sorption of the off gas is admixed with the reformate and is subjected to pressure swing sorption with the reformate. In yet a further alternative, at least a portion of the reject stream from the pressure swing sorption of the reformate is admixed with the off gas and is subjected to pressure swing sorption with the off gas.

[0014] The processes of this invention permit the annealing of metal work pieces that have the presence of oils. In one preferred embodiment, the oils are removed so as not to provide carbon deposits or other undesirable effects on the work pieces by vaporizing the oils as the work piece is being heated to annealing temperatures. Thus, the off gas from the annealing will contain oils at least initially during the annealing cycle. In one preferred process of this invention, at least a portion of the oils are removed from the off gas prior to the off gas being subjected to pressure swing sorption. Any suitable process can be used to remove the oils from the off gas. For instance, the oils may be adsorbed or absorbed or the oils may be condensed and the liquid removed by detrainment. Alternatively, or in addition, the initial off gas from the annealing can be diverted. Thus the load on the oil removal operation may be reduced or even eliminated to provide an off gas of sufficiently low oil content to be acceptable for pressure swing sorption.

[0015] The processes of this invention are particularly useful for facilities having a plurality of batch annealing zones. Preferably, the sequencing of steps (a) to (e) for at least
one annealing zone is time shifted from the sequencing of steps (a) to (e) for at least one other annealing zone.

[0016] In one aspect, the batch annealing apparatus of this invention comprises:

a. at least one annealing vessel adapted for annealing a work piece at elevated temperature in the presence of hydrogen, said annealing apparatus having at least one gas inlet and at least one gas outlet;
b. an oil removal system adapted to remove oil from hydrogen-containing gas, said vessel having at least one gas inlet and at least one gas outlet, said inlet being in fluid communication with at least one gas outlet of said annealing vessel; and
c. a pressure swing sorption unit containing sorbent suitable for removing carbon oxides and methane from hydrogen, said unit having at least one gas inlet and at least one gas outlet adapted to provide a reject stream and at least one gas outlet adapted to provide a product stream, said at least one gas inlet being in fluid communication with said at least one gas outlet of the oil removal system.

[0017] The oil removal system may comprise one or more components including an adsorber containing adsorbent selective for the removal of oil, an absorber containing absorbent suitable for the selective removal of oil, or a detrainment vessel adapted for removal of liquid from gases, especially where the oil removal system comprises a cooler adapted to condense at least a portion of the oil contained in the effluent from the annealing vessel.

[0018] In another broad aspect, the batch annealing apparatus of this invention comprises:

a. at least one annealing vessel adapted for annealing a work piece at elevated temperature in the presence of hydrogen, said annealing apparatus having at least one gas inlet and at least one gas outlet;
b. a reforming unit adapted to reform a hydrocarbon-containing feedstock to produce hydrogen, said unit having at least one outlet;
c. a pressure swing adsorber in fluid communication with at least one outlet of said reforming unit, said pressure swing adsorber containing sorbent suitable for removing carbon oxides and methane from hydrogen, said unit having at least one gas outlet adapted to provide a reject stream and at least one gas outlet adapted to provide a product stream, said at least one gas outlet adapted to provide a product
stream being in fluid communication with at lest one gas inlet of said annealing
vessel; and

d. a pressure swing adsorber in fluid communication with at least one gas
outlet of said annealing vessel, said pressure swing adsorber containing sorbent
suitable for removing carbon oxides and methane from hydrogen, said unit having
at least one gas outlet adapted to provide a reject stream and at least one gas outlet
adapted to provide a product stream, said at least one gas outlet adapted to provide a
product stream.

[0019] In a preferred embodiment, the pressure swing adsorber in fluid communication
with at least one outlet of said reforming unit is also the pressure swing adsorber in fluid
communication with at last one gas outlet of said annealing vessel. In an alternative
preferred embodiment, the pressure swing adsorber in fluid communication with at least
one outlet of said reforming unit and the pressure swing adsorber in fluid communication
with at last one gas outlet of said anneal vessel are separate. In a more preferred
embodiment; the reforming unit comprises a burner adapted to provide heat for reforming
and at least one gas outlet adapted to provide a reject stream of said pressure swing
adsorber in fluid communication with at least one gas outlet of said anneal vessel is in
fluid communication with the burner.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Figure 1 is a schematic depiction of an apparatus useful in practicing the
processes of this invention.

[0021] Figure 2 is graphic depiction of a batch annealing cycle.

[0022] Figure 3 is a cycle diagram for a plurality of batch annealing zones.

[0023] Figure 4 is a schematic depiction of a section of an annealing apparatus showing
the integration of two pressure swing sorption units.

[0024] Figure 5 is a schematic depiction of a section of an annealing apparatus showing
an alternative integration of two pressure swing sorption units.

DETAILED DESCRIPTION

[0025] An integrated reformer and annealing apparatus is depicted in Figure 1 and is
generally designated by the numeral 100. Raw materials for reforming hydrocarbon-
containing feedstock are individually or in combination supplied by feed lines 102 to
reformer 104. While only one line is shown, it is often the case that one or more lines are
used to carry one or more of the raw materials to reformer 104.
Reformer 104 may be any suitable type of reformer for converting hydrocarbon-containing feedstock to hydrogen and carbon oxides. The most common types of reformers are steam reformers and partial oxidation reformers, including autothermal reformers, where at least a part of the heat required for the endothermic conversion is generated by combustion of a portion of the hydrocarbon-containing feedstock in the reforming zone. In steam reforming, the feed comprises steam and the hydrocarbon-containing feedstock. An external supply of heat is required for steam reforming and partial oxidation reforming other than autothermal reforming. Typically this heat is provided by combustion of a combustible material such as a hydrocarbon-containing feedstock or a hydrogen-containing waste gas. Where partial oxidation reforming is used, the raw materials supplied by lines 102 will include an oxygen-containing gas such as air, oxygen-enriched air or even pure oxygen.

Reformer 104 may contain other reaction unit operations in addition to a reforming operation such as a water gas shift reaction or a selective oxidation reaction to reduce the presence of carbon monoxide. One of the advantages of the annealing processes of this invention is that pressure swing sorption can effectively remove carbon oxides from a reformate to levels suitable for annealing, and even for use in carbon monoxide-sensitive fuel cells to generate electricity. See, for instance, PCT Published Patent Application WO 2005/009892.

Reformer 104 provides reformate containing hydrogen and carbon oxides, and especially with a partial oxidation reformer using air or oxygen-enriched air in the feed, nitrogen. The reformate is passed via line 106 to header 108 which is in fluid communication with pressure swing adsorber (PSA) 110. Desirably the pressure swing adsorption provides a hydrogen product stream of at least about 98, preferably at least 99, volume percent and contains less than about 100, preferably less than about 10, ppmv of carbon monoxide (dry basis). Usually the pressure swing adsorption recovers at least about 65, preferably at least about 80, percent of the hydrogen contained in the stream fed to the pressure swing adsorption.

Any suitable adsorbent or combination of adsorbents may be used for the pressure swing adsorption. The particular adsorbents and combinations of adsorbents used will, in part, depend upon the components of the feed to the pressure swing adsorber, the sought compositions in the purified hydrogen product and the geometry and type of pressure swing adsorber used. Adsorbents include molecular sieves including zeolites,
metal oxide or metal salt, and activated carbon. Particularly advantageous sorbents include a combination of sorbents with the first portion of the bed being composed of activated carbon which is particularly effective for water and carbon dioxide removal followed by one or more molecular sieves such as NaY, 5A, lithium or barium exchanged X, and 13X.

The pressure swing adsorber may be of any suitable design including rotary and multiple bed. The purging of the bed may be by vacuum, but most conveniently for simplicity, the purge is above ambient atmospheric pressure. A preferred pressure swing adsorption system for low maintenance operation uses at least four fixed beds. By sequencing the beds through adsorption and regeneration steps, a continuous flow of purified hydrogen stream can be achieved without undue loss of hydrogen. With at least four beds, one bed at a given time will be adsorbing, another will be providing purge, another will be undergoing purging and another will be undergoing repressurization.

The operation of the pressure swing adsorber will also be influenced by the cycle time and the ratio of the pressures for the swing. As stated above, the sorption may be at 500 to 1500 KPa, the purge usually occurs within about 100, preferably within about 50, say, 10 to 50, KPa above ambient atmospheric pressure. The cycle times are selected to provide the hydrogen product of a desired purity. For a given pressure swing adsorber system, as the cycle times become shorter, the purity achievable increases, but also, less hydrogen is recovered. Thus, the cycle times and adsorber sizing can be selected for a given unit based upon the hydrogen specification and sought recovery as well as the range of compositions to be fed to the pressure swing adsorber. Hence, the pressure swing adsorber enables operation of the apparatus over annealing cycles and with different annealing cycles.

In one mode of operation, the cycle times may change when the hydrogen rate changes. Thus, when an increase in hydrogen production occurs, the cycle times may shorten, for instance, to maintain substantially constant hydrogen product purity. In another mode, the cycle times may remain substantially constant over a range of hydrogen production rates. Hence, the cycle times may vary in a step manner with constant cycle times over ranges of hydrogen production rates, or may be constant over the entire range of hydrogen production rates. In this mode of operation of the pressure swing adsorber where the cycle times are maintained constant at least over a range of hydrogen production rates, the cycle time is preferably set to provide acceptable hydrogen purity at the highest expected feed rate to the adsorber and the highest expected carbon monoxide
concentrations at steady state operation (excluding momentary peaks of carbon monoxide content due to instability in the operation of the hydrogen generator). The cycle time would remain the same even at operations within lower production rate ranges. Although some efficiency loss will occur, complexities and costs in the control of the pressure swing adsorber can be avoided.

[0033] PSA 110 provides a reject stream that will be discussed later and a hydrogen product stream which is withdrawn via line 112 and passed to storage vessel 114. Storage vessel 114 can serve one or more functions. Clearly, it provides a supply of hydrogen to meet peak demands and to enable start-up. It also acts as a buffer during periods where demand for hydrogen is less than the total hydrogen make in the reformer and in the recycle. This reduces the need to change operating conditions for reformer 104. Typically reformers require time to establish a new steady state operating condition. Hence, system stability can be enhanced. In yet a further advantage, storage vessel can also serve to blend hydrogen product of varying purity to provide a more constant hydrogen product. Thus, the PSA may be operated without change of the cycle times during periods of peak flow rates or lower hydrogen contents in header 108, especially caused by the cycling of each batch annealing unit in the facility.

[0034] Storage vessel 114 supplies hydrogen via line 116 to hydrogen header 118. Apparatus 100 is also provided with nitrogen header 120.

[0035] As shown, the apparatus has 3 annealing vessels, 126a, 126b and 126c. Some batch annealing operations employ many more annealing vessels, say between 20 to 100 or more. Nevertheless, the principles set forth for three annealing vessels can be extended to these larger facilities. Similarly, the principles set forth herein can readily be extended by the artisan to multivessel annealing facilities where different annealing recipes are employed at the same time.

[0036] Each of annealing vessels 126a, 126b and 126c have valve assemblies 122a, 122b and 122c in fluid communication via lines 124a, 124b and 124c, respectively. The valve assemblies are, in turn, in communication with each of hydrogen header 118 and nitrogen header 120. The valve assemblies regulate the supply of each of nitrogen and hydrogen to the respective annealing vessel.

[0037] The exhaust from each of the annealing vessels passes via line 128a, 128b and 128c to valve assembly 130a, 130b and 140c, respectively. Each valve assembly directs the exhaust to either exhaust header 132 or recycle hydrogen header 134. Exhaust header
132 typically passes the gases to the atmosphere. These gases are typically those rich in nitrogen. The exhaust containing greater amounts of hydrogen is preferred for recovery of hydrogen therefrom. Often, these exhaust gases will contain at least about 30, preferably at least about 40, volume percent of the exhaust.

[0038] Generally the work pieces to be annealed have oils thereon. The oils may be lubricants used in the shaping of the work piece or may be from a quench or may be a protective coating. The compositions of the oils may vary widely from various hydrocarbons to oxygenated hydrocarbons such as esters, ethers, glycols, and polyalkylene glycols. Usually the oils have a normal boiling point greater than about 120°C. The exhaust may contain not only these oils but also degradation products. For purposes herein, the term oils, when referring to components in the exhaust, also comprises degradation products having a normal boiling point greater than 50°C. These oils can adversely affect adsorbents used to selectively separate hydrogen from carbon oxides (carbon monoxide and carbon dioxide), nitrogen and other gaseous components.

[0039] In the preferred processes of the invention, the concentration of any oil in the exhaust to the pressure swing sorption is below that which significantly adversely affects the sorbent. The processes of the invention provide for achieving this low oil content exhaust by several means which may be used exclusively or in combination with one or more others. For instance, as the oils will be volatilized from the work piece as it is being heated to annealing temperatures, the exhaust from a first portion of the annealing cycle, even though rich in hydrogen, can be sent to exhaust header 132 until the oil content of the exhaust is suitable for processing for hydrogen recovery.

[0040] Another technique for removal of oils from the exhaust is by cooling the off gases from the annealing vessel to condense oils and then removing the liquid from the gases. One embodiment of this technique is described in further detail below. Oil separation may be effected by adsorption or absorption. The adsorbent or absorbent may be a single use sorbent or may be capable of being regenerated, e.g., by heating (thermal swing), combustion of the oil, or pressure (pressure swing), especially using a sweep gas such as nitrogen or a hydrogen-containing purge gas from a pressure swing sorption. Any suitable adsorbent or absorbent may be used. Preferred adsorbents include silica gel and activated carbon due to their abilities to be regenerated and effectiveness in sorbing oils. As state above, these techniques may be used in combination. A preferred combination is the use of the by-pass of the off gases from the annealing vessel until the concentration of
the oils has achieved a suitably low level, usually less than about 0.01 weight percent, and sometimes less than about 500 parts per million by weight, and then using an adsorption. Preferably, the treated off gases from the annealing vessel contain less than about 5 parts per million by weight of oils to prevent undue fouling of the sorbent.

The gases in the recycle hydrogen header are compressed in compressor 136 and passed to detrainment vessel 138 where liquid is removed. While the drawing is described with reference to a detrainment vessel, vessel 138 could be an adsorber or absorber, or could also contain an adsorber or absorber as described above. Alternatively, the detrainment vessel or adsorber or absorber can be upstream of compressor 136. Detrainment vessel may contain structure designed to facilitate removal of entrained liquids which may be of any suitable design. Often the structure comprises mesh packing or chevron flow diverters. The detrainment vessel preferably provides a gas stream in which residual liquid is in an amount insufficient to unduly adversely affect the sorbent used for pressure swing sorption. Line 140 is adapted to remove liquid from detrainment vessel 138.

Often, the pressure of the gases in the hydrogen header is less than 200, more frequently between about 105 to 150, kPa absolute and the compression in compressor 136 brings the gases to a pressure of at least about 500, say, about 700 to 1500, kPa absolute. This gas stream is then passed via line 142 to storage tank 144 and from there into header 108. Storage tank 144 can provide similar functions to storage tank 114. For instance, it can assure a constant supply of recycle hydrogen stream to the PSA, and it can blend the recycle hydrogen from various points in the annealing cycles of the annealing units to provide a stream of relatively uniform composition.

Returning to PSA 110, a reject stream is withdrawn via line 146 and is passed to valve assembly 148. Valve assembly 148, for purposes of this illustration, is a proportionating valve assembly to provide sufficient reject gas via line 150 to reformer 104 for combustion to provide heat for reforming. As the reject stream contains hydrogen, significant heating value remains in the stream. Usually the combustion is catalytically enhanced. Any portion of the reject stream not required for combustion for heating reformer 104 is passed to valve 154 via line 152. This stream may be used to periodically purge liquid build-up in detrainment vessel 138. As shown, the reject stream passes via line 156 to detrainment vessel 138 and the liquid-containing purge is exhausted via line
140. Alternatively, or in addition, valve assembly 148 directs reject stream to exhaust header 132.
[0044] Reference is made to Figures 2 and 3 for purposes of describing one of the many potential recipes for annealing to illustrate operation of the apparatus. Additionally, neither Figure 2 nor 3 is intended to be presented in an accurate time scale but rather are presented to facilitate understanding of the invention. Some recipes call for a relatively long period of the annealing soak and cooling steps, which is often from about 12 to 40 hours or more, with the other steps of the processes being much briefer.
[0045] In Figure 3, a block diagram is presented for the steps of the processes for each of annealing vessels 126 a, 126b and 126c. As stated before, many batch annealing operations will contain many more annealing vessels and an artisan will be able to expand the simplified discussion herein to operations that use many more vessels. With reference to the block diagram designated as "a" (referring to annealing vessel 126a and its accompanying valve assemblies), time block S is the period in which the annealed work piece is removed and a work piece to be annealed is positioned in annealing vessel 126a. Upon sealing annealing vessel 126a, nitrogen from nitrogen header 120 is used to purge the vessel and hence remove oxygen that could combust with hydrogen used in the annealing. This is step Pl. As shown in Figure 2, nitrogen, represented by the dotted line designated as N₂ is passed into annealing vessel 126a and exhausted is a stream containing nitrogen and air. Once the residual oxygen content is below a level that could combust with hydrogen, often less than about 0.1, preferably less than 0.01, volume percent, the nitrogen flow can be terminated and hydrogen flow commenced. Hence valve assembly 122a switches to enable hydrogen from hydrogen header 118 to be passed to annealing reactor 126a. During step Pl, valve assembly 130a directs the exhaust from the annealing vessel to header 132.
[0046] The heating of annealing vessel 126a may commence during step Pl or after the flow of hydrogen has commenced. Where the heating is initiated during step Pl, liquids on the work piece may be evaporated and exhausted. Typically where heating is commenced during step P1, the temperature of the ambient atmosphere in annealing vessel 126a, is at least about 80°C, preferably at least about 150°C, say, between 150° to 400° or even 600°C. Upon commencing the flow of hydrogen to annealing vessel 126a, the operator has several options. The initial exhaust gases will contain nitrogen which will be in an ever decreasing amount as the hydrogen concentration in the annealing vessel increases. This
initial stage is designated as step A1 on Figure 3 and commences at point A on Figure 2. One option is that the exhaust gases be directed to exhaust header 132 during at least a portion of step A1. Figure 2 contemplates such an operation and at point B, valve assembly 130a directs exhaust from annealing vessel 126a from exhaust header 132 to recycle header 134. One advantage of this mode of operation is that any liquid removed from the work piece is exhausted from the system. Alternatively, the exhaust during step A1 can be directed to recycle header 134 and combined with the exhausts from other annealing vessels and the contained nitrogen removed by PSA 110. This mode of operation conserves hydrogen values. The use of detrainment vessel 138 attenuates the presence of any liquid being removed from the work piece during step A1.

[0047] Usually the temperature of the annealing zone is increased during step A1. It is not necessary that the volume of hydrogen flowing through annealing vessel 126a be substantial during the heating. As shown in Figure 2, the flow rate of hydrogen is gradually increased during step A1. Desirably, the flow rate of hydrogen where the temperature in annealing vessel is above about 450°C is such that the concentration of hydrogen is at least about 75, preferably at least about 85, volume percent. Preferably, the concentration of carbon oxides and hydrocarbons at temperatures above 450°C is less than about 5 volume percent.

[0048] In step A2, the annealing continues. Typically annealing temperatures are at least about 500°, preferably about 550° to 700°C. The flow rate of hydrogen is such that the hydrogen concentration is at least about 50 volume percent. The flow rate of hydrogen may vary during step A2 or may remain relatively constant. Most preferably, during step A2, the concentration of carbon oxides and hydrocarbons in the ambient atmosphere within the annealing vessel is less than about 3 volume percent.

[0049] Typically, at the conclusion of step A2, the heating of annealing vessel 126a is ceased and cooling occurs, at least partially while supplying hydrogen. Alternatively or in addition, cooling can occur during the next step, a purge to remove hydrogen, herein designated as step P2. As shown in Figure 2, the flow rate of hydrogen to annealing vessel 126a tails off at the end of step A2 which is during cooling. Point C demarks entry into step P2. At this time, valve assembly 122a directs nitrogen from nitrogen header 120 to annealing vessel 126a. At the beginning of step P2, the operator has a choice either to continue directing exhaust from annealing vessel 126a to recycle header 134 until the hydrogen concentration of the exhaust falls below a level attractive for recovery or to direct
immediately the exhaust to exhaust header 132. Cooling usually continues during step P2. Thereafter, annealing vessel 126a can restart the process at step S.

[0050] As shown on the cycle diagram of Figure 3, the cycles for annealing vessels 126b and 126c are substantially the same but staggered. Staggering the cycles enables a relatively constant flow of recycle hydrogen to PSA 110 and can enable reformer 104 to operate at a relatively constant rate. If, however, significant variations in flow rates and compositions to PSA 110 occur, the processes and apparatus of this invention can accommodate such variations by changing the cycle times of the PSA and by providing storage to buffer the changes in supply rate.

[0051] For purposes of illustrating the extent of the differences that can exist for annealing recipes, another recipe involves first purging the vessel with nitrogen while heating, then, while continuing the heating, introducing hydrogen until the desired hydrogen concentration is obtained. The heating is continued and the vessel is held at about the maximum cycle temperature for a soak cycle involving little, if any, introduction of hydrogen. The soak step is then followed by a cooling cycle as the temperature is allowed to drop slowly until the desired annealing is achieved. The cooling rate, in the presence of hydrogen, accelerates and then a nitrogen purge completes the cycle. The apparatus of this invention, by changing the PSA cycle times, can accommodate the changes in hydrogen concentration in the off gases from the annealing and flow rate of the off gases.

[0052] While Figure 1 depicts all hydrogen being directed to the annealing vessels, it is within the scope of this invention that a portion of the hydrogen product be used for other purposes such as a feed to a fuel cell or for a chemical process such as a hydrogenation. As the PSA enables relatively pure hydrogen, often at least about 95, preferably at least about 99, and sometimes at least about 99.9, volume percent hydrogen with less than about 100 parts per million by volume (PPMV) of carbon monoxide, to be produced, a wide range of alternative uses for hydrogen are feasible.

[0053] Figures 4 and 5 depict alternative portions of the apparatus of Figure 1 that use two pressure swing sorption units. The principles and sorbents suitable for the additional PSA units are the same as that describe for PSA 110. In each figure, the same numbers are used to reference common elements with Figure 1.

[0054] With reference to Figure 4, header 108 passes recycle hydrogen to pressure swing adsorber (PSA) 402 which provides a reject stream withdrawn via line 404 and
passed to line 106 to PSA 110. The hydrogen product of PSA 402 is combined with the hydrogen product from PSA 110 that is contained in line 112. In this embodiment, PSA 402 can be operated with the objective of providing pure hydrogen product without concern for the amount of hydrogen contained in the reject stream since the reject stream is fed to PSA 110. Thus not only can the size of PSA 402 be reduced, but the control systems can be simplified which is particularly attractive with feed streams that vary in volume and hydrogen concentration.

[0055] The portion of the apparatus depicted in Figure 5 is particularly attractive in operations where a constant amount of reformate is generated. As shown, header 108 passes recycle hydrogen to pressure swing adsorber 502. The hydrogen product from PSA 502 is passed via line 506 to line 112 and the reject stream is passed via line 504 to line 150. Valve assembly 148 is adapted to provide in aggregate with the reject stream from line 504, sufficient fuel values with the reject stream (line 146) from PSA 110 to provide the sought heat for reforming. The remaining reject stream is passed via line 152 to the inlet to PSA 502. If needed a purge may be removed from line 152.

[0056] The portion of the apparatus of Figure 5 provides several advantages. First, PSA 110 can be operated at relatively constant cycle times as its feed is solely from reformer 104. Hence, only PSA 502 need have its cycle times changed in light of changes in hydrogen flow rate and composition from the annealing vessels. Second, additional hydrogen values are obtained from the reject stream from PSA 110.

[0057] As a significant portion of the hydrogen passed to the annealing vessels can be recovered in accordance with this invention, the volume of hydrogen needed to be generated for make-up is frequently a minor portion of the total hydrogen flow to the annealing vessels. Often, the hydrogen from the reformate provides less than about 40, preferably less than about 25, volume percent of the total hydrogen flow.

[0058] While the principles of the invention have been described with respect to the drawings, the broad scope of the invention does not require the use of all elements depicted. For instance, storage tanks 114 and 144 are optional. Detrainment vessel 138 is optional, especially where the initial exhaust withdrawn from annealing vessels during step A1, and perhaps also A2, are sent to exhaust header 132.
IT IS CLAIMED:

1. A batch annealing process comprising:
   a. providing in an annealing zone a metal work piece having carbon-containing substance associated therewith which under annealing conditions can cause coke formation;
   b. purging free oxygen from the annealing zone containing the metal work piece with an inert gas and withdrawing a pre-annealing purge effluent containing said inert gas and free oxygen;
   c. thereafter providing to said annealing zone a hydrogen-containing gas, said gas comprising at least about 50 volume percent hydrogen, said supply being (i) in an amount sufficient to achieve and maintain a hydrogen concentration in said annealing zone and (ii) at a rate, continuous or intermittent, to enhance annealing and provide an off gas containing hydrogen and carbon-containing substance, wherein for at least a portion of time while the hydrogen-containing gas is supplied, said annealing zone is heated to a temperature for a time sufficient to anneal said metal work piece;
   d. ceasing providing said hydrogen-containing gas;
   e. cooling said annealing zone commencing before or after the cessation of providing said hydrogen-containing gas;
   f. purging hydrogen from said annealing zone with an inert gas and withdrawing a post-annealing purge effluent containing said inert gas and hydrogen; and
   g. removing said metal work piece from the annealing zone,
   wherein at least a portion of the off gas containing hydrogen of step (c) is subjected to pressure swing sorption on a solid sorbent to provide a hydrogen product containing at least about 50 volume percent hydrogen and is substantially devoid of carbon-containing substance and a reject stream having a lower concentration of hydrogen than the off gas and containing carbon-containing substance.

2. The process of claim 1 wherein at least a portion of the hydrogen product is used as hydrogen-containing gas for annealing.

3. The process of claim 1 wherein at least a portion of the carbon-containing substance associated with the metal work piece is, under the conditions of step (c) converted to methane and the carbon-containing substance in the off gas of step (c) comprises methane.
4. The process of claim 1 wherein at least a portion of the hydrogen-containing gas for step (c) is provided by reforming a hydrocarbon-containing feedstock under reforming conditions.

5. The process of claim 4 wherein the reforming conditions comprise elevated temperature and at least a portion of the reject stream is combusted to provide at least a portion of heat to achieve reforming conditions.

6. The process of claim 4 wherein the reforming provides a reformate containing hydrogen and at least one of carbon monoxide and carbon dioxide, and the reformate is subjected to pressure swing sorption on a solid sorbent to provide a reformate hydrogen product containing at least about 90 volume percent hydrogen which is substantially devoid of carbon monoxide and carbon dioxide and a reject stream containing hydrogen and at least one of carbon monoxide and carbon dioxide.

7. The process of claim 6 wherein the off gas to be subjected to pressure swing sorption is admixed with the reformate and the reformate hydrogen product comprises hydrogen derived from the off gas.

8. The process of claim 6 wherein at least a portion of the hydrogen product from the pressure swing sorption of off gas is admixed with the reformate hydrogen product and at least a portion of the reformate hydrogen product is used for annealing.

9. The process of claim 8 wherein at least a portion of the reject stream from the pressure swing sorption of the off gas is admixed with the reformate and is subjected to pressure swing sorption with the reformate.

10. The process of claim 8 wherein at least a portion of the reject stream from the pressure swing sorption of the reformate is admixed with the off gas and is subjected to pressure swing sorption with the off gas.

11. The process of claim 1 wherein the hydrogen-containing gas contains at least about 90 volume percent hydrogen and the annealing zone achieves a hydrogen concentration of at least about 90 volume percent during annealing.

12. The process of claim 11 wherein sufficient hydrogen is provided continuously or intermittently during the annealing that the concentration of carbon-containing substances in the off gas is less than about 5 volume percent.

13. The process of claim 1 wherein the metal work piece contains oils and at least a portion of the oils are removed from the off gas prior to the off gas being subjected to pressure swing sorption.
14. The process of claim 13 wherein the separation of oils is effected by adsorption.

15. The process of claim 1 wherein the metal work piece contains oils and at least a portion of the oils are contained in the off gas as the temperature of the annealing zone is increased to annealing temperatures, and the off gas is subjected to pressure swing sorption when the oil content of the off gas is acceptable for pressure swing sorption.

16. The process of claim 1 wherein at least a portion of the off gas produced during the annealing is accumulated to provide a constantly available source of off gas for pressure swing sorption that has a more uniform hydrogen concentration.

17. The process of claim 1 wherein at least a portion of the hydrogen product is used as hydrogen-containing gas for annealing and at least a portion of the hydrogen product is accumulated to provide a constantly available source of hydrogen product for annealing.

18. The process of claim 17 wherein said hydrogen product is accumulated with externally provided hydrogen.

19. The process of claim 18 wherein said externally provided hydrogen is from a reformer and at least a portion of the reject stream is used to provide at least a portion of heat to achieve reforming conditions.

20. The process of claim 1 wherein at least a portion of the hydrogen product is used as hydrogen-containing gas feed to a fuel cell.

21. The process of claim 1 wherein a plurality of annealing zones exist and the off gases from the annealing zones are combined and subjected to pressure swing sorption.

22. The process of claim 21 wherein the sequencing of steps (a) to (e) for at least one annealing zone is time shifted from the sequencing of steps (a) to (e) for at least one other annealing zone.

23. An apparatus for batch annealing comprising:
   a. at least one annealing vessel adapted for annealing a work piece at elevated temperature in the presence of hydrogen, said annealing apparatus having at least one gas inlet and at least one gas outlet;
   b. an oil removal system adapted to remove liquid from gas, said system having at least one gas inlet and at least one gas outlet, said inlet being in fluid communication with at least one gas outlet of said annealing vessel; and
c. a pressure swing sorption unit containing sorbent suitable for removing carbon oxides and methane from hydrogen, said unit having at least one gas inlet and at least one gas outlet adapted to provide a reject stream and at least one gas outlet adapted to provide a product stream, said at least one gas inlet being in fluid communication with said at least one gas outlet of the oil removal system.

24. An apparatus for batch annealing comprising:
   a. at least one annealing vessel adapted for annealing a work piece at elevated temperature in the presence of hydrogen, said annealing apparatus having at least one gas inlet and at least one gas outlet;
   b. a reforming unit adapted to reform a hydrocarbon-containing feedstock to produce hydrogen, said unit having at least one outlet;
   c. a pressure swing adsorber in fluid communication with at least one outlet of said reforming unit, said pressure swing adsorber containing sorbent suitable for removing carbon oxides and methane from hydrogen, said unit having at least one gas outlet adapted to provide a reject stream and at least one gas outlet adapted to provide a product stream, said at least one gas outlet adapted to provide a product stream being in fluid communication with at least one gas inlet of said annealing vessel; and
   d. a pressure swing adsorber in fluid communication with at least one gas outlet of said annealing vessel, said pressure swing adsorber containing sorbent suitable for removing carbon oxides and methane from hydrogen, said unit having at least one gas outlet adapted to provide a reject stream and at least one gas outlet adapted to provide a product stream, said at least one gas outlet adapted to provide a product stream.

24. The apparatus of claim 23 wherein the pressure swing adsorber in fluid communication with at least one outlet of said reforming unit is also the pressure swing adsorber in fluid communication with at least one gas outlet of said annealing vessel.

25. The apparatus of claim 23 wherein the pressure swing adsorber in fluid communication with at least one outlet of said reforming unit and the pressure swing adsorber in fluid communication with at least one gas outlet of said anneal vessel are separate; the reforming unit comprises a burner adapted to provide heat for reforming and at least one gas outlet adapted to provide a reject stream of said pressure swing adsorber in fluid communication with at least one gas outlet of said annealing vessel is in fluid communication with the burner.
FIGURE 2
3/4

FIGURE 3