

PROCESS FOR CRACKING AMMONIA

Field

The present invention relates to a process for catalytically cracking ammonia. The present
5 invention further relates to a reaction vessel, optionally a tubular reaction vessel, for use in the
catalytic cracking of ammonia.

Background

There is renewed interest in using hydrogen as a green, carbon free, fuel in a variety of
10 industrial settings. Hydrogen may be combusted to produce heat energy or electricity.
Alternatively, hydrogen may be used to produce electrochemical energy in, for example, a fuel
cell.

Ammonia has received interest as a possible compound to enable the storage and transport
15 of hydrogen. Liquid ammonia has a higher hydrogen density than liquid hydrogen and may be
transported using existing infrastructure which is already in use for this purpose, such as that
used for the transportation of ammonia in the agrochemical fertiliser industry.

Once the liquid ammonia has been transported it may be combusted directly or converted to
20 hydrogen by the process of cracking.

The catalytic cracking of ammonia into hydrogen and nitrogen has been known for many
years. The reaction may be depicted as follows:



The ammonia cracking reaction is endothermic and may usefully be achieved by passing
ammonia over a suitable catalyst in heated catalyst-containing reaction vessels such as
externally heated catalyst-containing reaction tubes disposed in a furnace. Such furnaces are
30 known, for example, for the steam reforming of natural gas or naphtha feedstocks.

However, the heated catalyst-containing reaction tubes disposed in the furnace may react with
the ammonia containing gas or the cracked gas forming unwanted metal nitrides within the
tube material. This unwanted material damage mechanism, known as nitriding, may cause the
35 accelerated failure of the reaction tubes, in particular, at a location within the reaction tubes
where nitriding potential is highest (e.g., location of highest partial pressure of ammonia/

nitrogen, location of highest temperature, and/or location where a combination of ammonia/nitrogen partial pressure and temperature results in the highest nitriding potential).

5 Reaction tube failures require a complete shutdown of the ammonia cracking reactor, and result in significant plant down time. Moreover, nitriding, and failure, of the reaction tubes presents a serious safety hazard.

10 It is an aim of the present specification to address the aforementioned problem of nitriding and provide a process for the catalytic cracking of ammonia with improved operability and increased safety.

Summary

15 One option for addressing the problem of nitriding in a process for catalytically cracking ammonia is to change the operating conditions of the process to reduce nitriding potential within the reaction tubes. For example, reducing the operating temperature and/or partial pressure of ammonia within the reaction tubes. However, this may lead to a reduction in the efficiency of the ammonia cracking process.

20 Another option for addressing the problem of nitriding in a process for catalytically cracking ammonia is to change the material used to form the reaction vessels/tubes. That is, construct the reaction vessels/tubes from a material which is more resistant to nitriding. However, while alloys which are resistant to nitriding are known, many of these are either very expensive and/or do not have the thermal and/or mechanical characteristics required to maintain mechanical integrity when exposed for extended time periods to the harsh environment of an ammonia cracking process. For example, due to the high temperatures and pressures which are required for the ammonia cracking reaction to occur, heat-resisting materials are required for containment. Deformation of the catalyst-containing reaction tubes can occur which may result in the eventual failure of the reaction tubes. Heat-resisting materials have resistance to attack by the hot gases, but also possess suitable mechanical properties at high temperatures under long-term loading. This property is known as creep strength. However, while alloys which have a high creep strength are known, many of these are susceptible to nitriding and/or are prohibitively expensive.

35 It has been noted that the nitriding potential of a process environment is directly linked to the partial pressure of the nitrogen bearing species in the gas as well as the temperature of the gas. As ammonia cracking is performed at pressures and temperatures that are known to be highly nitriding, the most resistant alloys will be required for containment. These alloys have

high nickel/ cobalt content and are costly, but also by minimising nitride forming alloying elements in the containment alloy that are valuable as strengthening elements, the most resistant alloys to nitriding are not necessarily also suitable to resist creep deformation. Thus far, most ammonia cracking reactions have been conducted at low pressure and at a moderate scale where high temperature mechanical properties and economics of use of nitride resisting alloys has been more acceptable. Ammonia cracking at the scale required for hydrogen production for the energy sector will require high pressures, therefore higher required creep strength, but also will be highly influenced by the most economic metallurgy/ design.

As it is difficult to find a single alloy which meets all the requirements for ammonia cracking at the scale now required for hydrogen production (nitriding resistance, thermal/mechanical resistance, cost) the present specification provides a process for ammonia cracking which utilizes reaction vessels/tubes constructed of at least two different alloys, one of which is more resistant to nitriding and the other of which provides mechanical support under high pressure and high temperature loading.

In light of the above, the present specification provides a process for the catalytic cracking of ammonia, the process comprising supplying an ammonia feed gas to one or more heated catalyst containing reaction vessels disposed within an ammonia cracking reactor and cracking the ammonia in the ammonia feed gas in the one or more catalyst containing reaction vessels to produce a hydrogen containing stream, the or each of the reaction vessels having a wall which is composed of at least a first alloy and a second alloy, wherein the first alloy is more resistant to nitriding than the second alloy and the second alloy provides mechanical support to the first alloy, and wherein at least a portion of the wall adjacent the catalyst is composed of the first alloy.

In the aforementioned process, at least a portion of the reactor vessel wall which is adjacent the catalyst is formed of more nitriding resistant alloy to reduce nitriding while the remainder of the reactor vessel wall provides mechanical support to meet thermal and mechanical requirements for containment over long periods of being exposed to high pressures and temperatures in use.

Optionally, the second alloy has a higher creep strength and/or mechanical stability than the first alloy. However, it is also envisaged that the first alloy could be selected to have a higher creep strength than the second alloy in addition to higher nitriding resistance. In that case, the two-alloy system may still be preferred as a first alloy which has both high nitriding resistance and high creep strength is likely to be very expensive and thus limiting the amount of such a

first alloy will be advantageous. The second alloy will still provide mechanical support to the first alloy, especially if a small quantity of the first alloy is used relative to the second alloy.

- 5 The, or each, reaction vessel may be in the form of a reaction tube in which catalyst is disposed. In this case, the second alloy may be in the form of a tube and the first alloy may form a coating or layer over at least a portion of the interior surface of the tube. The first alloy may be provided in a region of the reaction vessel where nitriding potential is highest, i.e., where ammonia/nitrogen partial pressure and/or temperature is highest. This may be in a region closer to an inlet of the reaction vessel than an outlet of the reaction vessel with respect to gas flow. Alternatively, or additionally, at least 50%, 60%, 70%, 80%, 90% or substantially all of the surface of the reactor vessel adjacent the catalyst may be formed of the first alloy. The, or each, reaction vessel may comprise a lower wt% of the first alloy compared to the second alloy.
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- 15 The first and second alloys may be provided as layers of the reactor vessel wall with the first alloy layer having a thickness which is less than the second alloy layer. Such configurations can reduce nitriding of the reactor vessel while limiting the amount of nitriding resistant alloy which is required.
- 20 It may also be noted that additional materials/alloys may be provided to form the walls of the reaction vessels, e.g., as additional layers. For example, a layer of another material/alloy may be provided between the first and second alloys to improve adhesion and/or thermal expansion coefficient matching between the first and second alloys, e.g., an alloy with a thermal expansion coefficient intermediate between that of the first and second alloys.
- 25 Additionally, or alternatively, an intermediate layer (e.g., pure Ni or Co) can be employed that has a low nitrogen solubility to delay transport of nitrogen through to the mechanical alloy, or that has a high proportion of nitride forming elements to consume and tie up nitrogen to also delay nitrogen transport to the mechanical support layer.
- 30 Furthermore, an additional layer of oxide or oxide forming material may be provided on at least a portion of the surface adjacent the catalyst material to further enhance nitriding resistance. Such an oxide layer may be an aluminium oxide layer formed from aluminium in the first alloy. The ammonia feed gas comprises oxidizing species, such as oxygen and/or water, to ensure oxidizing conditions in the reaction vessels and aid in maintaining the oxide layer. These oxidizing species may be naturally present in the ammonia feed gas or deliberately added. Maintaining water in the process flow gas is preferred in the context of high pressure, high
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temperature nitriding in ammonia as it shows a large advantage over the other means of oxide formation and ensures good healing of the oxide through the operating period if damaged.

Optionally the first alloy comprises nickel and/or cobalt, e.g., in an amount greater than 11 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, or 75 wt%, of the first alloy. While in principle up to 100 wt% nickel / cobalt could be used as the first alloy, optionally the first alloy also comprises one or more of Cr, Si or Al (e.g., a small proportion of these elements in addition to Ni and/or Co). Optionally the amount of nickel and/or cobalt in the first alloy is greater than the amount of nickel and/or cobalt in the second alloy. Optionally, the second alloy comprises iron, nickel, and/or chromium. Optionally, the second alloy comprises at least 10 wt%, 15 wt%, 20 wt%, or 30 wt% Cr. For example, the second alloy may be a Ni or Fe based alloy containing a proportion of Cr.

The process as described above provides a process for the cracking of ammonia to produce hydrogen with improved operability, reduced downtime, and increased safety and also does so in a cost-effective manner in terms of materials of constructions for the reaction vessels/tubes. The one or more reaction tubes/vessels used in the process are resistant to nitriding and to creep and/or embrittlement damage under the high temperatures and pressures of ammonia used in the catalytic cracking of ammonia and can also be made more cost competitive than tubes manufactured wholly from an alloy resistant to nitriding.

The present specification also provides a reaction vessel for use in the above-described process. The reaction vessel contains an ammonia cracking catalyst and has a wall which is composed of at least a first alloy and a second alloy, wherein the first alloy is more resistant to nitriding than the second alloy and the second alloy provides mechanical support to the first alloy, and wherein at least a portion of the wall adjacent the catalyst is composed of the first alloy. In other respects, the reaction vessel is as described in relation to the process for cracking ammonia. Also provided is an ammonia cracking reactor comprising one or more catalyst containing reaction vessels (e.g., reaction tubes) as described herein.

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Brief Description of the Drawings

For a better understanding of the present invention and to show how the same may be carried into effect, certain embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:

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Figure 1 shows a schematic of a reaction tube along its axial length x and in the plane x,y - a circular cross-section of the reaction tube may be seen in the y,z plane;

Figure 2 shows a schematic of the cross-section of a reaction tube in the plane y,z with “a” representing the thickness of the inner region of the tube, whilst “b” represents the thickness of the outer region; and

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Figure 3 shows an illustration of an ammonia cracking reactor comprising catalyst filled reaction tubes and burners for providing heat energy to the reaction tubes.

Detailed Description

10 Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise.

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A process of the present specification comprises the step of supplying an ammonia feed gas to one or more heated catalyst containing reaction tubes disposed within an ammonia cracking reactor. The ammonia feed gas may be derived from any source. The ammonia feed gas can be produced by the catalytic combination of hydrogen and nitrogen, for example the ammonia
20 feed gas may be produced from a Haber-Bosch ammonia synthesis process. The ammonia feed gas may be produced in an ammonia production facility located upstream of the ammonia cracking reactor. Alternatively, the ammonia feed gas may be provided from an ammonia gas storage facility, an ammonia storage unit, an ammonia storage tank, or an ammonia gas pipeline.

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The ammonia feed gas may be pre-heated prior to being supplied to the one or more catalyst containing reaction tubes. Accordingly, the process may comprise the step of pre-heating the ammonia feed gas. The ammonia feed gas may be pre-heated to a temperature of greater than 350°C, greater than 400°C, greater than 450°C, greater than 500°C, or greater than
30 550°C. The ammonia feed gas may be pre-heated to a temperature of less than 1000°C, less than 950°C, less than 850°C, less than 750°C, or less than 700°C. The ammonia feed gas may be pre-heated to a temperature of from 350°C to 1000°C, from 400°C to 950°C, from 450°C to 850°C, or from 500°C to 750°C, such as from 550°C to 700°C.

35 Suitable ammonia cracking reactors are known and may comprise a fuel combustion zone having a radiant section comprising one or more burners to which one or more fuel streams and an oxygen feed gas, such as air, oxygen enriched air, or oxygen, are fed. The radiant

section may comprise the one or more catalyst containing reaction tubes through which the ammonia feed gas is passed. Combustion of one or more fuel streams in the one or more burners of the fuel combustion zone, creates heat energy (e.g., radiant heat) for heating the one or more catalyst containing reaction tubes. There may be tens or hundreds of catalyst
5 containing reaction tubes in the radiant section. If desired, downstream of the radiant section, a flue gas from the combustion of the one or more fuel streams may be used to pre-heat one or more feed streams in a convection section. Reactors comprising a radiant section containing catalyst containing reaction tubes and a convection section for preheating feeds are known in steam methane reforming and may be applied to the present process for
10 ammonia cracking.

Alternative ammonia cracking reactors may be used. For example, where the combustion of the one or more fuel streams in a fuel combustion zone is separate to the reactor comprising the catalyst containing reaction tubes. Such a reactor may be a compact reformer available
15 from Johnson Matthey Davy Technologies Limited. Other alternative forms of reactor include a plate exchanger heated by molten salts, a rotary heater such as by Coolbrook, or a printed circuit heat exchanger. In certain configurations the tubes may be fired and the region outside of the tubes contains the ammonia. Alternatively still, the tubes may be electrically heated, induction heated, or concentrated solar heated.

20 The catalyst may be any ammonia cracking catalyst. For instance, nickel catalysts and/or ruthenium catalysts may be used. The catalyst may comprise 3 to 30% by weight nickel, preferably 8 to 20% by weight nickel, expressed as NiO, on a suitable refractory support, such as alumina or a metal aluminate. The catalyst may be in the form of pelleted shaped units,
25 which may comprise one or more through holes, or may be provided as a wash coat on a structured metal or ceramic catalyst. A particularly preferred catalyst is KATALCO[™] 27-2 available from Johnson Matthey PLC, which comprises 12% nickel, expressed as NiO, on a cylindrical pellet formed from a high surface area calcium aluminate support.

30 The process of the invention comprises the step of cracking the ammonia in the ammonia feed gas in the one or more heated catalyst containing reaction tubes to produce a hydrogen containing stream.

35 In a fired reactor, flames will typically be greater than 1000°C. These may impinge on the reaction tubes during operation but typically the reaction tubes will be heated to a temperature in a range 500 to 1000°C. Furthermore, typically one end of the reactor tubes will be hotter

than the other. This can be due to variations in process gas temperature (e.g., cooler inlet gas) and/or heat distribution variations in the radiant section.

5 The temperature of the ammonia feed gas at the inlet to the one or more catalyst containing reaction tubes may be in the range of 350 °C to 1000 °C, from 400 °C to 950 °C, from 450 °C to 850 °C, or from 500 °C to 750 °C, such as from 550 °C to 700 °C. The temperature of the hydrogen containing stream exiting the one or more catalyst containing reaction tubes will influence the equilibrium position of the cracking reaction, and may be in the range of 500 to 950°C. Where nickel catalysts are used in the one or more catalyst containing reaction tubes,
10 the temperature of the hydrogen containing stream exiting the one or more catalyst containing reaction tubes may preferably be greater than about 700°C.

The pressure inlet to the one or more catalyst containing reaction tubes will be set by the flowsheet design and may be: at least 1, 10, 30, 50 or 100 bar; no more than 1000, 500, 100,
15 75, or 50 bar; or within a range defined by any combination of the aforementioned lower and upper values. Example ranges include 1 to 100 bar absolute, 10 to 100 bar absolute, or 30 to 75 bar absolute.

20 The ammonia cracking reaction produces a hydrogen containing stream. The hydrogen containing stream contains H₂. The hydrogen containing stream also contains nitrogen, and may further contain residual ammonia (e.g., unreacted ammonia).

The hydrogen containing stream may comprise 40 mol% or more H₂, 50 mol% or more H₂, or 60 mol% or more H₂. The hydrogen containing stream may comprise 75 mol% or less H₂, 70
25 mol% or less H₂, or 65 mol% or less H₂. For example, the hydrogen containing stream may comprise from 40 mol% to 75 mol% H₂, from 50 mol% to 70 mol% H₂, or from 60 mol% to 65 mol% H₂.

30 As described in the summary section, the process of the present specification uses catalyst containing reaction vessels composed of at least a first alloy and a second alloy, wherein the first alloy is more resistant to nitriding than the second alloy and the second alloy provides mechanical support to the first alloy, and wherein at least a portion of the wall of the reaction vessels adjacent the catalyst is composed of the first nitriding resistant alloy. In the configuration in which the reactions vessels are in the form of catalyst containing tubes then
35 the first nitriding resistant alloy is provided on an interior surface of the tubes. Alternatively, if the heating is provided by tubes and the catalyst is disposed in a reactor region outside the

tubes, then the first nitriding resistant alloy is provided on an exterior surface of the tubes, i.e., the side of the tubes adjacent the catalyst.

5 Nitriding may cause the accelerated failure of the reaction tubes, in particular, at a location within the reaction tubes where nitriding potential is highest or where temperatures driving nitriding are highest. This may typically be at a location towards the inlet end of the reaction tubes (e.g., closer to the inlet than the outlet, optionally at the inlet) where ammonia partial pressure is highest. However, as temperature may not be highest at the inlet location, depending on the reactor design, the location with highest nitriding potential may be somewhat
10 down the reaction tubes from the inlet. By providing a nitriding resistant alloy at least where nitriding potential is highest then this damage mechanism can be reduced while at the same time using another alloy material to provide mechanical support.

15 In the following description, the configuration in which catalyst is provided within the reaction tubes is described wherein one or more reaction tubes have an outer region comprising a mechanical support composition, and an inner region comprising a nitriding resistant composition. In this configuration the outer region of the reaction tube is exposed to the heat source used to provide heat energy to the one or more catalyst containing reaction tubes and which heat is used to support the endothermic ammonia cracking reaction in the ammonia
20 cracking reactor. The inner region of the reaction tube refers to the interior of the reaction tube which contains the catalysts used to catalytically crack the ammonia in the ammonia feed gas.

The reaction tube has an inlet side and an outlet side defining an axial length, x , of the reaction tube. It will be understood that catalyst for the ammonia cracking reaction is disposed inside
25 of the reaction tube along the axial length, x . It will further be understood that the ammonia feed gas is passed from the inlet side of the reaction tube, over the ammonia cracking catalyst disposed therein, and that the hydrogen stream exits the reaction tube via the outlet side of the reaction tube. Figure 1 shows the axial length, x , of a reaction tube in the x,y plane.

30 The reaction tube has a cross-section in the plane perpendicular to the axial length in the y,z plane. The cross-section may take on any shape and is not particularly limited. For instance, the cross-section may be circular, elliptical, quadrilateral (e.g., square or rectangular), or triangular in shape. Typically, the cross-section is circular. Where the cross-section is circular, the reaction tube will be understood to be a cylindrical tube.

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The outer region and the inner region have a thickness as measured in the plane of the cross-section of the reaction tube. An example of a cross-section, in the y,z plane, of a reaction tube

is shown in Figure 2 where the cross-section is circular in shape, and where “b” and “a” represent the thickness of the outer region and the inner region, respectively. Preferably the outer region has a thickness greater than the inner region (i.e., $b > a$).

- 5 The outer region (the second “mechanical support” alloy) may have a thickness of: at least 1 mm, 3 mm, 5 mm, 8 mm, or 10 mm; no more than 100 mm, 50 mm, 20 mm, 15 mm, or 14 mm; or within a range defined by any combination of the aforementioned lower and upper limits. An example thickness range is 8 to 14 mm, optionally 10 to 14 mm. However, it is noted that these ranges are for standard fired reactor designs and thicknesses may vary for other
10 types of reactor configuration. For example, printed circuit heat exchangers and plate exchanges may use a lower thickness, e.g., 0.1 – 2 mm, optionally 0.25 - 1 mm.

- The inner region may have a thickness of: at least 0.05 mm, 0.1 mm, 0.5 mm, or 1 mm; no more than 10 mm, 8 mm, or 5 mm; or within a range defined by any combination of the
15 aforementioned lower and upper limits. An example thickness range is 1 to 5 mm.

- The outer composition is a heat resistant alloy which may comprise iron, nickel, and/or chromium. For example, the outer composition may be a heat-resistant and corrosion-resistant alloy comprising at least 10 wt%, 15 wt%, 20 wt%, or 30 wt% chromium (e.g., a nickel
20 or iron based alloy containing this proportion of chromium). For the avoidance of doubt the amount of any component of the outer composition or inner composition is expressed as the weight percentage of that composition.

- Optionally, the amount of nickel and/or cobalt in the outer composition is lower than the
25 amount of nickel and/or cobalt in the inner composition. Suitable alloys for the outer composition are commercially available and the most preferred alloy will depend on specific operating conditions for the ammonia cracking process which may vary according to reactor design. For example, the outer composition may be an alloy selected from alloy 625, alloy 800/H/HT, alloy 20/32, alloy 20/32Nb/ CT15C, HK 40, HP Nb, HP Microalloy, Microalloy,
30 25/35Nb, Sanicro 25, Super304H, 314, 347, or P91.

- Heat resisting materials for use above 550°C tend to be based on the iron-nickel-chromium alloy system for petrochemical applications where economics strongly influence material selection over other factors. These alloys tend to have chromium contents between 8-30 wt%,
35 or aluminium or silicon to form protective oxide layers. Chromium can be used most universally as it is very soluble in nickel, iron and cobalt with a low tendency to form detrimental intermetallic phases. Chromium content between 20-30 wt% provide the best protection from

oxidation up to roughly 1000°C. Aluminium oxide is generally more protective above 1000°C but is alloyed to a much lower proportion than chromium.

5 Suitable creep strength and metallurgical stability/ predictability allows for a longer service life of the metal alloy components before becoming prone to distortion, cracking, and eventual loss of containment or replacement. Metal alloy components may lose strength or strength may actually go up, but the material forms voids and cracks where the material moves overtime leading to loss of containment.

10 Heat resisting alloys of the iron-nickel-chromium system suitable for use at ammonia cracking temperatures include austenitic stainless steels such as those of the 300 series alloys, such as but not limited to 304, 309, 310, 314, 316, 321, 330, 347, and variants thereof. Or similarly of the 200 series of austenitic stainless steels, or the 400 series of ferritic and martensitic stainless steels. At the lower temperature range even alloy steels such as P91 could be
15 considered.

At higher temperatures alloys with increasing quantities of nickel and/or cobalt can be considered, e.g., alloy 800 and its variants, alloy 825, 253MA, 353MA, UNS S31035, alloys of the 600 series, such as 600, 601, 602 CA, 625, 690, etc. as well as alloys manufactured in
20 centrifugally casting processes for reforming and ethylene cracking applications and the like.

Alloys of the nickel, chromium, iron, molybdenum system, such as C-276, C22, C2000, alloy 59, etc., may also be considered, however the economics for simple high temperature strength and oxidation resistance applications would tend to discourage the use of these more costly
25 alloys.

Precipitation hardening alloys may also be considered, such as alloy 718 and other nickel and chromium containing alloys optionally containing significant cobalt and/or tungsten, e.g. alloys 188, 230, C-276, 617, etc...
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Nitrogen and nitrogen-containing gases are widely utilised in the process industries, including ammonia (NH₃), either as feedstocks, intermediates, products or as fuels. In the presence of these gases the nitrogen can react with the alloying elements of the process containment vessels to form nitrides. Different elements have differing affinity to nitrogen and so form nitride
35 more or less readily than others. Nickel and cobalt are known to be weak nitride formers, whereas aluminium and titanium are strong nitride formers, chromium being intermediate. The formation of these nitrides in the alloy components can cause severe materials issues as they

can cause embrittlement but also reduce the effective wall thickness. Common nitrides in commercial heat-resisting alloys at high temperatures are $\text{Fe}_4\text{N}/\text{Fe}_2\text{N}$, $\text{CrN}/\text{Cr}_2\text{N}$, AlN , and $\text{TiN}/\text{Ti}_2\text{N}$.

- 5 Additionally, it has been shown that nickel and cobalt based alloys have significantly higher nitrogen solubility than iron-based alloys such as stainless steels. Higher nickel/ cobalt content has been shown to increase an alloy's ability to resist nitriding and the associated detrimental mechanical issues. However, nickel and cobalt are significantly more costly than iron, and the cost ratio is likely to continue to rise as these elements are required for the expanding battery
10 material market.

New scaled ammonia cracking applications are pushing the boundaries of what is currently required in terms of reactor vessel alloys, particularly in relation to the concurrent issue of the need for economically viable creep strength plus high nitriding resistance. There are some
15 alloys that have been shown to be both of high creep strength and highly nitride resistant, but these contain cobalt and high levels of nickel, and so can be prohibitively costly. Increasing iron content lowers the cost of the tubes, but iron should be avoided in contact with the nitriding environment as it is a strong nitride former. At the scale these reactor tubes will need to be produced for ammonia cracking for the energy industry, the economics of a bimetallic tube
20 may be preferable to simply moving to higher levels of cobalt and nickel in a single metal alloy solution. The present solution of using more than one alloy type is thus considered advantageous over simply using more nitriding resistant alloy and not operating at high pressures/temperatures, using more costly alloys, or making the containment vessel thicker.

- 25 The inner composition can be an alloy comprising nickel and/or cobalt, e.g., in an amount greater than 11 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, or 75 wt% (either singly or in total combined amount). While in principle up to 100 wt% nickel / cobalt could be used, optionally the inner composition also comprises one or more of Cr, Si or Al. Optionally the amount of nickel and/or cobalt in the inner composition is greater than the amount of nickel and/or cobalt
30 in the outer composition. The inner layer is for nitriding resistance while at the same time thrifting on the costly Ni and Co by not requiring the entirety of the reaction tubes to be formed of costly Ni/Co rich alloy material. The two-alloy approach for the reaction tubes also allow more optimum compositions to be used for the separate functions of nitriding resistance on the interior of the tube and mechanical support/thermal stability on the outside of the tubes.
35 The exact composition of nickel/cobalt for the inner composition will depend on the nitriding potential, which is dependent on temperature, plus partial pressure and type of nitriding

species. Some examples of suitable alloys for different operating temperatures, pressures, and nitriding potentials are given in the tables below.

Outer alloy material selection:

	Low pressure (0-10 bar)	Moderate pressure (10-40 bar)	High pressure (>40 bar)
0-500°C	Carbon steel up to 425°C, CrMo Alloy Steels		
500-700°C	P91 (up to 600°C), 304, 321, 347, 316	304H, 316H, 321H, 347H, 310H,	Sanicro 25, 310MoNbN, 674 Super 304, 347HFG, Essete 1250, 706, 718, 725, X750/1, Nimonic 901
700-1000°C	Alloy 800, 600, 690, 309, 310	Alloy 800, 625, 253MA	617, 253MA, 353MA, 740H (up to 815°C), 230, Nimonic 80A, 90, 105, UDIMET 520
>1000°C	601, 699, 693, 310	253MA, 353MA	602CA, 617, HX, 890, Nimonic 86, 115, Incotherm TD, UDIMET L-605

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Inner alloy material selection:

Low nitriding potential	Moderate nitriding potential	High nitriding potential
304, 316, 321, 347, 410, 446,	309, 310, alloy 800, 253MA, X, 333, 330, 825, 686, 890	Alloy 625, 600, 602CA, 617, 230, 601, 699, 693, 200, 201, 270, 803, 804, S, 160, 214, 188, C-276, 25, MA47P, Incotherm TD

Additional components may include any welding consumables and metal powders of the same or similar compositions to the above for overlay/ thermal spray/ powder metallurgy route, e.g.,

10 low / medium / high Ni/Co and presence or not of Al.

The inner surface of the inner alloy may comprise an oxide layer which sits on the inner alloy on the surface exposed to the process fluid. It forms from reaction of the alloy with oxygen in the air when being fabricated. The oxide layer will also grow and heal in the process environment provided oxygen is available. Less oxygen partial pressure is required to form alumina in aluminium containing alloys. Controlling oxidizing species content (e.g., water and/or oxygen) in the process flow gas within the reaction tubes during operation can ensure oxidizing conditions and aid in maintaining a protective oxide layer. Alternatively, naturally present oxidizing species in the process flow gas may fulfil this function. That said, maintaining water in the process flow gas is preferred in the context of high pressure, high temperature nitriding in ammonia as it shows a large advantage over the other means of oxide formation and ensures good healing of the oxide through the operating period if damaged. The oxide

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layer can provide a layer which protects the reaction tube from the nitriding effect of the ammonia feed gas.

5 The inner composition may comprise an alloy that includes of Cr, Si and/or Al to give a greater advantage in terms of oxide formation, with Al oxides being preferred. It is to be noted that the present specification anticipates that the nitriding resistant alloy may be selected to take advantage of oxide scales for nitriding resistance, or optimised Ni/Co content for nitriding resistance, or both. The preferred option will be dependent on nitriding potential and economics. For example, the inner composition may be an alloy selected from alloy 600, alloy 601, alloy 200, alloy 214, or MA47P.

10 The outer region and inner region of the reaction tube may be bonded together by a metallic bond. The outer region and inner region of the reaction tube may be bonded together, for example by a metallic bond. The bonding may be homogenous across the entire axial length of the reaction tube to form a single interface between the inner composition and the outer composition. In other words, the inner region and the outer region may be bonded together such that the reaction tube has one inner surface and one outer surface. Metallurgically bonding processes may include, for example, extrusion bonding, explosion bonding, hot isostatic pressing, and centrifugal casting.

20 Optionally, the reaction tube may comprise a further bonding layer in between the inner and outer layers. This may be advantageous for various reasons, e.g., better metallurgical bonding between two dissimilar alloys, better match of thermal expansion coefficients, etc. Optionally, the inter-layer can be of an alloy that is not so good an oxide former, but is an excellent nitrogen barrier, e.g., pure Ni/Co.

30 The reaction tube may be manufactured using processes known in the art. For instance, the outer region comprising the outer composition may first be formed into a base tube using centrifugal casting or seamless tube rolling processes, also known as pilgering. To the base tube, the inner region comprising the inner composition may be disposed by processes such as weld overlay or thermal spray. Alternatively, the outer region and the inner region may be formed into the reaction tube simultaneously using a process of co-extrusion or co-rolling during pilgering or through hot isostatic pressing (HIP) of powders.

35 In addition to the ammonia cracking process as described above, the present specification also provides a reaction vessel such as a reaction tube, for use in the catalytic cracking of ammonia, the reaction tube containing an ammonia cracking catalyst. The ammonia cracking

catalyst is contained inside of the reaction tube. That is, the ammonia cracking catalyst is contained inside the reaction tube along its axial length. The ammonia cracking catalyst may be any catalyst known as suitable for catalysing the cracking of ammonia to hydrogen and nitrogen. It may be preferred that the catalyst is a nickel-based catalyst, such as nickel on an
5 inert support (e.g. an alumina, silica, or another refractory oxide). For example, the catalyst may be KATALCO 27-2^{RTM}, available from Johnson Matthey PLC. Alternatively, it may be preferred that the catalyst is a noble metal catalyst, such a ruthenium-based catalyst.

Also provided is an ammonia cracking reactor comprising one or more catalyst containing
10 reaction vessels (e.g., reaction tubes) as described above. Figure 3 shows an illustration of an ammonia cracking reactor comprising catalyst filled reaction tubes and burners for providing heat energy to the reaction tubes.

While this invention has been particularly shown and described with reference to certain
15 examples, it will be understood to those skilled in the art that various changes in form and detail may be made without departing from the scope of the invention as defined by the appended claims.

Claims

1. A process for the catalytic cracking of ammonia, the process comprising:
supplying an ammonia feed gas to one or more heated catalyst containing reaction
5 vessels disposed within an ammonia cracking reactor; and
cracking the ammonia in the ammonia feed gas in the one or more catalyst containing
reaction vessels to produce a hydrogen containing stream,
wherein the or each of the reaction vessels has a wall which is composed of at least a
first alloy and a second alloy, wherein the first alloy is more resistant to nitriding than the
10 second alloy and the second alloy provides mechanical support to the first alloy, and wherein
at least a portion of the wall adjacent the catalyst is composed of the first alloy.
2. A process according to claim 1, wherein the second alloy has a higher creep strength
and/or mechanical stability than the first alloy.
- 15 3. A process according to claim 1 or 2, wherein the or each reaction vessel is in the form
of a reaction tube in which catalyst is disposed.
4. A process according to claim 3, wherein the second alloy is in the form of a tube and
20 the first alloy forms a coating or layer over at least a portion of the interior surface of the tube.
5. A process according to any preceding claim, wherein the first alloy is provided in at
least a region of the or each reaction vessel where nitriding potential is highest.
- 25 6. A process according to any preceding claim, wherein the first alloy is provided in at
least a region of the or each reaction vessel closer to an inlet of the reaction vessel than an
outlet of the reaction vessel with respect to gas flow.
7. A process according to any preceding claim, wherein at least 50%, 60%, 70%, 80%,
30 90% or all of the surface of the or each reactor vessel adjacent the catalyst is formed of the
first alloy.
8. A process according to any preceding claim, wherein the or each reaction vessel
comprises a lower wt% of the first alloy compared to the wt% of the second alloy.

35

9. A process according to any preceding claim, wherein the first and second alloys are provided as layers of the or each reactor vessel wall with the first alloy layer having a thickness which is less than the second alloy layer.
- 5 10. A process according to any preceding claim, wherein the first alloy has an oxide layer disposed on the surface thereof.
11. A process according to any preceding claim, wherein an intermediate adhesion layer is provided between the first and second alloys.
- 10 12. A process according to any preceding claim, wherein the first alloy comprises nickel and/or cobalt in an amount greater than 11 wt%, 15 wt%, 20 wt%, 30 wt%, 50 wt%, or 75 wt%, of the first alloy.
- 15 13. A process according to any preceding claim, wherein the first alloy comprises nickel and/or cobalt in a wt% amount which is greater than in the second alloy.
14. A process according to any preceding claim, wherein the first alloy comprises one or more of Cr, Si or Al.
- 20 15. A process according to any preceding claim, wherein the second alloy comprises iron, nickel, and/or chromium.
16. A process according to any preceding claim, wherein the second alloy comprises at least 10 wt%, 15 wt%, 20%, or 30% chromium.
- 25 17. A reaction vessel for use in the process according to any preceding claim, wherein the reaction vessel comprises an ammonia cracking catalyst and has a wall which is composed of at least a first alloy and a second alloy, wherein the first alloy is more resistant to nitriding than the second alloy and the second alloy provides mechanical support to the first alloy, and wherein at least a portion of the wall adjacent the catalyst is composed of the first alloy.
- 30 18. An ammonia cracking reactor comprising one or more reaction vessels according to claim 17.
- 35