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(54) Title: METHOD FOR THE MANUFACTURE OF METAL FOAMS BY ELECTROLYTIC REDUCTION OF POROUS OXIDIC PREFORMS

(57) **Abstract:** A method for the manufacture of a foamed metal or alloy article including the steps of: A) selecting a particulate feedstock having suitable proportions of a metal element or combination of metal elements M_1 contaminated by one or more contaminants X to form an alloy suitable for the foamed article; B) mixing the feedstock with a binder to form a slurry; C) preforming the slurry into a near net shape of the desired article and drying the preform to remove the binder; D) sintering the dried preform to provide a bonded foamed article; E) introducing the sintered article into an electrochemical cell, the cell containing a liquid electrolyte comprising a fused salt or mixture of salts generally designated as M_2Y in which contaminant(s) X is soluble, and a relatively inert anode; F) conducting electrolysis under conditions favourable to the selective dissolution of the contaminant(s) X in preference to the M_2 cation; and G) following electrolysis reclaiming the purified foam article from the cathode.

METHOD FOR THE MANUFACTURE OF METAL FOAMS BY ELECTROLYTIC REDUCTION OF POROUS OXIDIC PREFORMS

This invention relates to methods for the manufacture of metal foams and to novel applications for these technologies. The invention is more particularly directed to, but not limited to manufacture of titanium and titanium alloy foams.

WO99/64638 and the applicant's co-pending applications British Patent applications nos. GB 0003971.9 and GB 0010873.8 (the disclosures of which are incorporated herein by reference) describe methods for the electrolytic reduction of metal compounds.

Certain embodiments of these methods involve the electrolysis of metal oxides or other compounds (M_1X) in a cell containing a liquid (fused salt M_2Y) electrolyte and an anode, the metal oxide or other compound forming the cathode. Conditions are controlled so as to bring about the selective dissolution of the oxygen or other contaminant of the cathode in preference to deposition of the metal cation. Improved efficiency of this process can be achieved by various methods as described in GB 0003971.9 and GB 0010873.8 some of which are summarised below.

Feedstock production by addition of binder to rutile and amorphous titania

The manufacture of titanium dioxide from the raw ore (sand mined illemite) comprises a large number of steps in the production of titanium.

During one of these stages titanium dioxide in the form of an amorphous slurry undergoes calcining. The titanium dioxide slurry can be used as the principle feedstock in the above described electrolytic method. A small percentage of calcined material is mixed with amorphous material and a binder to obtain the most satisfactory results after sintering. The calcined material should constitute at least about 5% by weight of the mixture.

Production of metal foams

Metal foams, more typically titanium foams, are attractive for a number of applications such as filters, medical implants and structural fillers. The fabrication of a sponge-like sintered oxide pre-form from the starting material M_1X can be converted into a solid metal/alloy foam via the electrolytic method previously described. Various established methods may be used to make the foam like material from the mixture of oxide powders. The foam preform desirably has open porosity that is, porosity which is interconnected and open to the exterior.

In a preferred embodiment of this method, a natural or synthetic polymeric foam is infiltrated with a metal (eg titanium) oxide slip, then dried and fired to remove the polymeric foam, leaving an open "foam" which is an inversion of the original polymeric foam. The sintered preform is then electrolytically reduced in accordance with the previously described method to convert it into a titanium/titanium alloy foam. The foam is then washed or vacuum distilled to remove the salt.

Alternatively, the metal oxide powder may be mixed with organic foaming agents. These materials are typically two liquids which when mixed, react to evolve a foaming gas, and then cure to give a solidified foam with either an open or closed structure. The metal powder is mixed with one or both of the precursor liquids prior to production of the foam. The foam is then fired to remove the organic material, leaving the ceramic foam which is then electrolytically reduced in accordance with the previously described method.

Production of metal or metal alloy components

A near net shape component may be made using the previously described electrolytic method by reducing a ceramic facsimile of the component made from a mixture of a metal oxide or mixture of metal oxide and the oxides of other alloying elements. Again this method is particularly suited to the manufacture of titanium metal and alloy components. The ceramic facsimile may be produced using any of a variety of well known production methods for ceramic articles which include; pressing, injection moulding, extrusion and slip casting, followed by firing (sintering). Full density of the metallic component can be achieved by sintering with or without the application of pressure, either in the electrochemical cell, or in a subsequent operation. Shrinkage of the component during the conversion to metal or alloy should be allowed for by making the ceramic facsimile proportionally larger than the desired component.

Electrolysis of a preformed sintered mass

The electrolysis is performed on a preformed sintered mass comprising a mixture of metal oxide made up of a proportion of particles of size generally greater than 20 microns and a proportion of finer particles of less than 7 microns. Preferably the finer particles make up between 10 and 55% by weight of the sintered block.

High density granules of approximately the size required for the powder are manufactured and then are mixed with very fine unsintered metal oxide (e.g., titanium dioxide), binder and water in the appropriate ratios and formed into the required shape of feedstock. This feedstock is then sintered to achieve the required strength for the reduction process. The resulting feedstock, after sintering but before reduction, consists of high density granules in a lower density (porous) matrix.

The feedstock can be reduced in block form using the previously described electrolytic method and the result is a friable block which can easily be broken up into powder.

The calcine discharge used can be replaced by cheaper amorphous TiO_2. The key requirement for this "matrix" material is that it sinters easily with significant shrinkage during the sintering process. Any oxide or mixture of oxides which fulfil these criteria would be usable. In the case of TiO_2 this means the particle size must be less than about 1 μm. It is estimated that at least 5% of the matrix material should be present in order to give any significant strength to the sintered product.

The starting granules for this method need not be rutile sand but could be manufactured by a sintering and crushing process, and in principle there is no reason to suppose that alloy powders could not be made by this route.

In any of the aforementioned methods X may be a metalloid such as oxygen, sulphur, carbon or nitrogen, preferably, X is oxygen. M_1 may be a Group IVA element such as Ti, Si, Ge, Zr, Hf, Sm, Nd, Mo, Cr, Nb or an alloy of any of the preceding metals, preferably, M_1 comprises titanium. A preferred electrolyte, M_2Y, is calcium chloride ($CaCl_2$). Other suitable electrolytes include but are not limited to the molten chlorides of all common alkali and alkaline earth metals. Other preferred metals for M_2 are barium, caesium, lithium, strontium and yttrium. The anode of the cell is preferably of a relatively inert material. One suitable anode material is graphite.

Processing conditions suitable for the favourable dissolution of the contaminant X require that the potential of the cell preferably be maintained at a potential which is less that the decomposition potential of the molten electrolyte M_2Y during the process. Allowing for polarisation and resistive losses in the cell, it will be understood that the cell potential may be maintained at a level equal to, or marginally higher than, the decomposition potential of M_2Y and still achieve the desired result. Potentiostatic methods may be used to control the potential.

It is also preferred that the temperature of the cell is maintained at an elevated temperature which is significantly above the melting point of M_2Y but below the boiling point of M_2Y. Where M_2Y is $CaCl_2$ suitable processing parameters include a potential of up to about 3.3V and a processing temperature of between about 825 and 1050 °C.

A method for the manufacture of a foamed metal or alloy article may include the steps of:

A. selecting a particulate feedstock having suitable proportions of a metal element or combination of metal elements M_1 contaminated by one or more contaminants X to form an alloy suitable for the foamed article;

B. mixing the feedstock with a binder to form a slurry;

C. preforming the slurring into a near net shape of the desired article and drying the preform to remove the binder;

D. sintering the dried preform to provide a bonded foamed article;

E. introducing the sintered article into an electrochemical cell, the cell containing a liquid electrolyte comprising a fused salt or mixture of salts generally designated as M_2Y in which contaminant(s) X is soluble, and a relatively inert anode;

F. conducting electrolysis under conditions favourable to the selective dissolution of the contaminant(s) X in preference to the M_2 cation; and

G. following electrolysis reclaiming the purified foam article from the cathode.

Conveniently, the binder is water. Preferably, prior to drying, the preform in step C is subjected to foaming by the blowing of a gas through the slurry. As well as removing some of the water from the preform and assisting in the drying process, this step results in the formation of bubbles in the preform which are retained as cells in the foam. Alternatively, foaming agents may be introduced into the slurry to form gas bubbles within the body of the preform. Optionally, the preform in step C may be provided by packing the slurry into the open cells of a foam article which is provided in the desired net shape of the preform. This foam template should comprise a material with a vaporisation point significantly lower than the melting point of the contaminated metal or alloy to be foamed. The foam template can then subsequently be burnt off leaving a network of open cells within the resulting metal article.

The present invention provides a method for the manufacture of a metal or alloy mass from a metal oxide or mixed metal oxide feedstock, by electrolysis in a fused salt M_2Y, wherein M_2 is a metal cation and Y is a suitable anion, or a mixture of such salts in which oxygen is soluble under conditions favourable to the dissolution of oxygen rather than deposition of metal cations from the fused salt, wherein the feedstock consists of a foamed, dried and sintered metal oxide preform and produces a foamed metal or alloy mass.

In one embodiment of the method, a quantity of crushed titanium oxide feedstock is mixed with around 300 ml of water per kilo of the feedstock and placed in a mould of the desired foamed article. The article has dimensions of the order of a few centimetres. Air is blown through the mould to assist in foaming the preform. The preform is then left to dry at room temperature and pressure for about 5 days. Once dried, the article is sintered in an oven at between about 1100°C to 1300°C for around 2 hours.

The sintered article is then introduced to an electrochemical cell comprising a molten calcium chloride bath and carbon graphite anode and electrolysis performed in accordance with methods previously described to remove the contaminant oxygen. Once the desired quantity of oxygen has been removed by this method, the purified foamed titanium article is reclaimed from the cell.

Various applications for metal foams produced by the method of this invention may occur to the skilled addressee.

One application may include the manufacture of armour. A foamed titanium alloy such as Ti-6Al-4V alloy may be preformed into the net shape of the armour in accordance with the invention. The foamed alloy is considerably lighter than full density armour for similar high strength, high stiffness and high temperature properties. The foaming provides the additional advantage that the foamed structure begins to collapse on impact thereby absorbing energy from the projectile penetrating the armour and considerably reducing the risk or extent of injury to the protected persons.

Another application may be in the manufacture of orthopaedic and other medical implants. Titanium alloys are widely recognised as good bio-materials as they are relatively inert in the environment provided by a human body. Recent developments on orthopaedic research suggest that the life of an implant and the health of tissue surrounding the implant can be greatly improved where the implant is provided with a knurled or otherwise pitted surface. Tissues, in particular bone tissue surrounding the pitted surface of the implant, grow into the pits providing anchorage for the implant and resulting in more even distribution of load from the implant to the bone. It is widely accepted that bone strength and health is compromised by prolonged periods of under loading, hence bone health may be improved by the provision of pits or channels within an orthopaedic implant.

By using the present invention, foamed titanium alloy implants may be provided by forming the preform in the near net shape of the implant. Since the foam structure provides channels passing in varying directions through the implant, exceptional anchorage and load transfer to the bone can be predicted. Where the impact loads of the implant are particularly high, it may be desirable to retain a fully dense alloy core to the implant with an outer foamed layer. This can easily be accommodated by planting a fully dense core at the centre of the preform and coating with the slurry to be foamed. Previous attempts to obtain articles of this sort have involved drilling of holes in the fully dense implant or other complex or cumbersome machining operation, all of which add significantly to the cost of the implant, risk damage to the structural integrity of the implant and provide a far less random and extensive network of channels through which the bone may grow. Thus the present method may be used to provide a more cost effective product with significantly improved clinical performance.

Other applications for metal foams made in accordance with the invention include, the manufacture of filters, sound proofing applications, particularly in high temperature or highly corrosive environments and any structural applications requiring high strength and stiffness and with low weight. Such structural applications might include aircraft components, windmill propellers and the like.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for the manufacture of a metal or alloy mass from a metal oxide or mixed metal oxide feedstock, by electrolysis in a fused salt M_2Y, wherein M_2 is a metal cation and Y is a suitable anion, or a mixture of such salts in which oxygen is soluble under conditions favourable to the dissolution of oxygen rather than deposition of metal cations from the fused salt, wherein the feedstock consists of a foamed, dried and sintered metal oxide preform and produces a foamed metal or alloy mass.

2. A method according to claim 1 wherein the preform is foamed by passing a gas through a slurry comprising a metal oxide particulate binder and water.

3. A method according to claim 1 wherein the preform is foamed by gas evolved from a chemical reaction of organic foaming agents and the foam is then fired to remove the organic material.

4. A method according to claim 1 wherein the preform is made by infiltrating a natural or synthetic polymeric foam with a slurry comprising a metal oxide particulate, binder and water and subsequently burning off the polymeric foam.

5. A method according to claim 4 wherein the vaporisation point of the foam template is lower than the melting point of the metal oxide or mixed metal oxide to be foamed.

6. A method according to any preceding claim wherein the preform is in the near net shape of the intended metal or alloy article.

7. A method as claimed in any preceding claim wherein the metal oxide comprises TiO_2.

8. A method as claimed in any preceding claim wherein Y is chloride.

9. A method as claimed in any preceding claim wherein M_2 is calcium.

10. A method as claimed in any preceding claim wherein the alloy is a beta titanium alloy.

11. A method as claimed in any preceding claim further comprising applying a metal working process to the metal or alloy mass after it has been reclaimed.

12. A method as claimed in claim 1 and substantially as herein described.

13. Armour manufactured according to the method of any one of claims 1 to 12.

14. Armour as claimed in claim 13 wherein the alloy is Ti-6-Al-4V alloy.

15. An orthopaedic implant for a human or animal body manufactured according to the method of any one of claims 1 to 12.

16. An orthopaedic implant according to claim 15 wherein said implant comprises a fully dense core and an outer foam layer.

Dated this 27th day of June, 2003-06-27
QinetiQ Limited
By Its Patent Attorneys
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