



(51) International Patent Classification:

B23K 35/38 (2006.01) *B23K 9/04* (2006.01)
C22C 14/00 (2006.01) *C23C 8/24* (2006.01)
B23K 103/14 (2006.01)

(21) International Application Number:

PCT/AU2012/000163

(22) International Filing Date:

20 February 2012 (20.02.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2011900638 24 February 2011 (24.02.2011) AU

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD OF FORMING DURABLE WORKING SURFACES

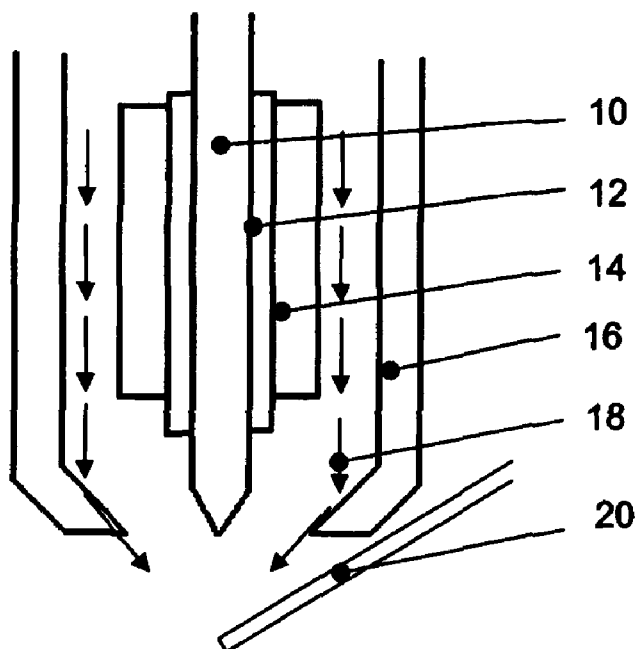


Figure 2

(57) Abstract: Disclosed are methods describing the formation of hard weld deposits using a number of different welding techniques. The weld deposits produced contain an amount of metal nitride which has the effect of increasing hardness. The welding consumables and substrate metals for which these methods are appropriate include, but are not limited to, titanium, tantalum, zirconium, hafnium, molybdenum, vanadium, niobium, tungsten, iron, nickel and their alloys.

METHOD OF FORMING DURABLE WORKING SURFACES

5 FIELD OF THE INVENTION

The present invention relates to forming durable working surfaces. In particular, the invention relates to forming hardfacing surfaces by welding at the surface of metal components. The invention finds its primary application in mining operations where operating conditions may be corrosive, abrasive, and erosive or a combination of these.

BACKGROUND

Traditionally, iron-based alloys have been used for components in high wear applications because, although alternative materials (such as titanium) have a longer service life, the increased service life was not sufficiently longer to make them economically viable.

Over the last 50 years, the commercial production of titanium and titanium alloys has increased steadily. Because of their relatively high strength to weight ratio, they initially found use in aircraft where their inherently high corrosion resistance properties were advantageous in many applications. High cost in the manufacture of titanium raw material saw its use limited principally to military applications. In recent years, however, the cost of producing alternative materials (such as high quality titanium and titanium alloy) has decreased significantly. As a consequence, these materials are finding increased use in the mining and mineral processing industries, where equipment manufacturers and designers are specifying their use because of their chemical and mechanical properties.

30

The types of products that are being manufactured from Titanium & Titanium alloys for use in the said industries include pipes, pipe fittings, valve components, agitation components and pressure vessels to name some. In the presence of abrasive particles and flowing conditions, these components can sustain life limiting

damage in the form of accelerated material loss. Common failure or degradation mechanisms encountered include high angle and low angle abrasion, adhesive wear, erosion, erosion – corrosion and cavitation. This is primarily because of the relatively low hardness and poor tribological properties of titanium and titanium alloys.

As a means of improving the performance of titanium & titanium alloys, for example, operating in conditions conducive to accelerated material loss, a number of surface engineering techniques have been, and continue to be, applied. Broadly speaking, the methods used can be divided into three main categories, namely –

- 1) Heat Treatment,
- 2) Coatings, and
- 3) Thermochemical Treatment

Heat Treatment

A number of different surface heat treatment technologies are used on Titanium & Titanium alloys to improve wear and tribological properties. Included in this group are the use of lasers and plasma to alter the microstructure of the surface layers (without altering the chemistry) by rapid melting and solidification.

Coatings

Many types of coatings can be applied to Titanium & Titanium alloys to alter the surface properties. Included here are processes such as plating (eg copper, hard chrome and electroless nickel), physical vapour deposition (eg sputtering of TiN onto drill bits) and thermally sprayed coatings (eg plasma spraying and high velocity oxyfuel).

Thermochemical Treatment

These processes involve altering both the microstructure and chemistry of the substrate to achieve the desired surface properties. Titanium & Titanium alloys are very chemically active and react readily with interstitial elements. As such, these materials can be hardened by the diffusion of oxygen, carbon, nitrogen and boron at

elevated temperatures (almost always in the solid state), where they form hard phases within the surface layers.

5 In all of the processes mentioned above, the treated substrate will possess an effective or transformed layer that is very thin. In many cases, this will be <200µm and in almost all cases, it will be <1000µm. In practical terms, components employed in the mineral processing and mining industries, that are treated using any of these techniques, would not return any significant benefit in service life.

10 The object of the invention is to provide alternative methods for preparing durable working surfaces on metal components.

SUMMARY OF THE DISCLOSURE

15 The applicant recognises that substantial influence on service life of metal components can be achieved by providing a thick layer (>1mm) of hardened material that possesses the integrity to sustain prolonged exposure to the operating environment. The applicant also recognises the positive influence of nitrogen and nitrides on the mechanical and corrosion properties of metal alloys. The applicant
20 seeks to combine those influences in a metal component by providing a process which produces a durable working surface that takes advantage of both.

In accordance with the present invention, existing welding technologies and processes are modified to create weld deposits possessing properties that are
25 desirable for the intended applications. This invention, therefore, enables the production of hard weld deposits at the surface of metals to provide a durable surface that is corrosion resistant, erosion resistant and/or wear resistant.

The term "metal component" as used throughout this specification is taken to
30 mean a product formed of a transition metal or a transition metal alloy.

The term "weld deposit" as used throughout this specification is taken to mean that volume of molten metal that has solidified on the surface of a component, or previous deposit, as a result of a welding process.

Particularly, in accordance with a first aspect of the invention, there is provided a method for producing a durable working surface on a metal component by forming a weld deposit comprising metal nitrides.

5

The method involves controlling the content of nitrogen in a shielding gas to cause nitrogen gas to react with metal in a weld pool so that, upon solidification, the weld deposit comprises an amount of metal nitrides. Preferably the metal nitrides comprise 20 to 90 vol% of the weld deposit. This is considered to be a useful range of metal nitride for providing the principal purpose of increased wear resistance under various aggressive operating conditions. It is believed that below 20 vol% metal nitrides, the increase in bulk hardness achieved may not in some cases be sufficient to provide adequate wear resistance.

15 Welding metals that have a high affinity for oxygen, as is the case with many of the transition metals, traditionally involves using a shielding gas. Typically, the shielding gas comprises predominantly, or wholly, of argon. The purpose of the shielding gas is to prevent contamination of the weld deposit caused by reaction with the general atmosphere. The formation of unwanted phases or constituents in the weld deposit, such as metal oxides, are deleterious to the weld integrity. Accordingly, the shielding gas used is protective in nature and does not react with the weld metal. By displacing atmospheric air from the weld pool during melting and solidification, reaction with the general atmosphere is prevented and as a result, contamination of the weld is avoided.

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In this first aspect of the invention, the welding operation is conducted not with the typical shielding gas, but with a shielding gas containing nitrogen. As the welding consumable and component substrate become molten, nitrogen is absorbed into the weld pool. When the weld pool cools and solidifies to become the weld deposit, metal nitride is formed. The volume and composition of the metal nitride produced is dependent largely upon the amount of nitrogen absorbed during the welding operation. By altering welding parameters, it is possible to control, within limits, the quantity of nitrogen absorbed and the composition and hardness of the weld deposit.

30

In relation to this first aspect of the invention, it is known that the welding operation can be influenced by a number of operating variables. These include voltage, current, wire consumable diameter, welding travel speed, shielding gas composition, shielding gas flow rate and the consumable grade. In order to produce the desired weld deposit properties, suitable weld procedure specifications must be established for the materials being welded.

The shielding gas substantially will comprise nitrogen. Specifically, the shielding gas may comprise at least 50 vol% nitrogen, preferably at least 70 vol%, more preferably at least 80 vol% and even more preferably at least 90 vol%. However, the shielding gas may comprise nitrogen and argon or nitrogen and helium or nitrogen, argon and helium. The relative make up of the balance of the shielding gas is not critical however, where additional arc energy is beneficial to the welding operation, helium may be used in preference to argon. Alternatively, the shielding gas may totally comprise nitrogen.

In a second aspect of the invention, there is provided a hard facing weld deposit comprising a transition metal or a transition metal alloy produced by a welding method according to the first aspect wherein the weld deposit comprises metal nitride in the range of 20 to 90 vol%.

The weld deposit may have a thickness on a work piece in the range of 0.1 to 30mm. The weld deposit may comprise multiple layers of weld. The thickness may be 0.1 to 5mm for a single layer, and greater than 5mm and more preferably greater than 10mm, for multiple layers.

The weld deposit may possess a bulk hardness in the range of 400 to 1000 HV. This range may be higher or lower depending on the transition metal consumable used and welding parameters adopted.

In one form, the method uses the gas metal arc welding (GMAW) process incorporating transition metal or transition metal alloy wire consumable. It is preferable, though not necessary, to conduct the process using a constant voltage, direct current power supply.

It should be noted that the invention as described can also be applied to other forms of fusion welding. In particular, the commonly used process of gas tungsten arc welding (GTAW) is an appropriate welding technique for producing weld deposits using transition metal and transition metal alloy consumables. As is the case with
5 GMAW, the shielding gas used must contain an appropriate quantity of nitrogen such that the formation of metal nitride occurs.

The welding parameters must be appropriately developed for the consumable such that the transition metal nitride forms in sufficient quantities and with a
10 distribution and morphology that imparts desirable metallurgical qualities. Acicular and dendritic morphologies are considered to be acceptable, whereas metal nitride that is present as a grain boundary film would be considered to be a deleterious morphology. A uniform distribution of the acicular and dendritic nitrides is preferred. The method according to the first aspect can be applied to both manual and
15 automatic GTAW.

Another suitable welding process that can be adapted to this invention is plasma transferred arc welding (PTAW). Unlike GMAW & GTAW where solid wire consumable is melted at the torch, this process uses metal powder to form a deposit.
20 In order to produce a hard deposit containing transition metal nitride, the same principle applies. The shielding gas must include appropriate levels of nitrogen and suitable welding parameters adopted.

While three examples of different welding processes suitable for producing
25 durable working surfaces have been described, this should not be taken to limit the application of the invention to these processes. Any welding operation that utilises a heat source to melt a metallic consumable and fuse it to a metallic substrate is suitable for using this invention. By way of example and in addition to the welding processes already mentioned, other suitable processes include solid state laser
30 welding, gaseous laser welding, fibre optic laser welding and hybrid-laser welding.

It is known that the propensity for cracking to occur within the weld deposit during hard facing may increase with the volume of metal nitride formed. A means of minimising the impact of this solidification cracking is to deposit multiple layers of

weld metal. This has the effect of increasing the weld integrity in two ways – firstly by providing greater bulk strength and, secondly, by covering over the pre-existing surface cracks. This reduces their size and changes crack type from continuous to dis-continuous.

5

BRIEF DESCRIPTION OF THE DRAWINGS

It will be convenient to further describe the invention with reference to preferred embodiments of the welding processes.

10

Figure 1 is a schematic cross-section of a typical GMAW head assembly in operation.

Figure 2 is a schematic cross-section of a typical GTAW head assembly in operation.

15

Figure 3 is a schematic cross-sectional sketch of a typical PTAW head assembly in operation.

Figure 4 is a photograph showing the microstructure of weld deposit produced according to the first aspect of the invention with a GTAW method containing ~30 vol% titanium nitride.

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Figure 5 is a photograph showing the microstructure of weld deposit produced according to the first aspect of the invention with a GTAW method containing ~60 vol% titanium nitride.

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Figure 6 is a photograph showing the microstructure of weld deposit produced according to the first aspect of the invention with a GTAW method containing ~80 vol% titanium nitride.

30

DESCRIPTION OF PREFERRED EMBODIMENTS

It will be appreciated from the preceding disclosure that the method of forming a durable work surface can be applied to metal components of transition metal and transition metal alloys. The following description of an embodiment of the invention is limited to titanium or titanium alloy metal components. However, this should not be taken as limiting the overall application of the invention to titanium or titanium alloy metal components.

Referring to Figure 1, there is shown a schematic drawing of a cross-section of a typical GMAW head in operation, comprising of a wire consumable 10, contact tube 12, gas diffuser 14, and nozzle 16. Shielding gas 18 is supplied to the head and passes through the diffuser 14. Not shown is the wire feed unit, power supply unit and the gas supply.

When the control switch or trigger is pressed on the torch handle by the operator, a number of things occur simultaneously. Feeding of the wire consumable, electric power and supply of gas are all initiated, causing an electric arc to form. The arc melts the consumable 10 and a portion of the substrate causing them to mix together. While in the molten state, nitrogen from the shielding gas 18 is absorbed into the weld pool. As the torch moves along the work piece, the weld pool cools and solidifies behind it, forming a deposit containing crystalline titanium nitride. The welding variables are regulated to produce a weld deposit possessing the desired properties.

Figure 2 shows a schematic cross-section of a typical GTAW head. Not shown is the power source, gas supply and commonly used cooling system. Found within the head is a non-consumable tungsten electrode 10, a supporting collet 12, a collet body 14, and a gas diffuser 16. A high frequency generator (or similar device) is used to initiate an arc between the work piece and tungsten electrode 10. As the filler consumable 20 is manually or automatically fed into the path of the arc, it melts forming a weld pool. Nitrogen-containing shielding gas 18 is supplied to blanket the molten weld pool and heat affected zones, until such time as the weld solidifies. Prior

to solidifying, the weld pool absorbs a quantity of the introduced nitrogen which reacts with the metal to produce a deposit containing an amount of titanium nitride.

Figure 3 is a schematic cross-section of a typical PTAW head. It shows a central tungsten electrode 10 located within a copper plasma nozzle 14, which contains the primary ionising or plasma gas 12. Powdered consumable 16 is introduced to the tip of the electrode 10 via a second nozzle 18. The consumable is usually delivered with a carrier gas to improve the flow and increase the feed rate. Located at the tip of the nozzle is a small, constricting orifice. A pilot arc is initiated between the tungsten electrode 10 and copper plasma gas nozzle 14, and this arc is then transferred to the work piece. Consumable powder 16 is introduced into the arc stream in the presence of the plasma gas 12. By forcing the powder 16 and plasma gas 12 through the constricting orifice, the energy delivered to the work piece surface is very concentrated, producing high quality weld deposits. In addition to the plasma gas 12, a secondary gas is used for shielding of the molten weld pool. In operation, the shielding gas 20 contains a substantial amount of nitrogen so that titanium nitride can form in the weld deposit upon solidification. To assist in the nitrogen absorption by the molten weld pool, nitrogen can also be added to the plasma gas 12. The whole assembly is contained within an outer housing 22.

Test work carried out by the applicant involved using the GTAW process to apply Grade 12 titanium alloy wire consumable to 20mm commercially pure titanium alloy plate. The hardness of the titanium alloy plate prior to welding was ~190 HV. The test work involved producing three different weld beads on the same titanium alloy as separate examples. The test welds were produced under identical welding parameters except for the amount of nitrogen delivered to the weld zone. The

Parameter	Test 1	Test 2	Test 3
Position	1G	1G	1G
Consumable	Ti Gr 12	Ti Gr 12	Ti Gr 12
Voltage, V	14	14	14
Current, A	130	130	130
Travel Speed, mm/min	125	125	125
Shielding Gas, Vol %	30 N / 70 Ar	60 N / 40 Ar	80 N / 20 Ar
Shielding Gas Flow Rate, L/min	15	15	15
TiN Content, Vol %	~30	~60	~80
TiN Morphology	Acicular	Dendritic	Dendritic *
Deposit Hardness, HV5	~430	~700	~950

* Contained within the dendrites was a second (nitride) constituent or phase displaying linear markings along preferred crystallographic planes.

5 Test 1 (Figure 4) produced a weld deposit having a TiN content of ~30 vol%. The TiN content is attributed with raising the hardness of the weld deposit to ~430 HV5. This is 240 HV greater than the parent titanium substrate. The high hardness and depth of the weld deposit make the titanium alloy more suited to applications in which higher wear resistance is important.

10

Test 2 (Figure 5) produced a weld deposit having a TiN content of ~60 vol% and a hardness around 700 HV5. This was more than 500 HV higher than the underlying plate hardness and 270 HV harder than Test 1.

15 Test 3 (Figure 6) produced a weld deposit having a TiN content around 80 vol % with a bulk hardness of ~950 HV5. The increase in hardness achieved over Tests 1 & 2 was 520 & 250 HV respectively.

20 Accordingly, it can be seen that by adjusting the nitrogen content in the shielding gas, a direct, causal influence on the vol% of nitride formed in the weld deposit, and therefore hardness, is produced. It follows, therefore, that the hardness of a weld deposit can be controlled by the relative nitrogen content of the shielding gas. It is also recognised that making changes to other parameters, such as

consumable feed rate, travel speed and welding current can also result in changes to the mechanical and metallurgical properties of the weld deposit.

5 These results further suggest that a hardness exceeding 1000 HV may be obtained in titanium and its alloys by manipulating the welding parameters in a knowledgeable way.

10 The examples provided above are for just one grade of titanium alloy consumable. Hard, nitride containing weld deposits can also be produced using other transition metals and their alloys using similar principles. These include, but are not limited to, tantalum, zirconium, tungsten, niobium, chromium, molybdenum, vanadium and their alloys.

15 In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

20

In the claims which follow, the term 'shielding gas' is used to describe shielding gas, and / or carrier gas, and / or plasma gas as appropriate for the welding process being described or discussed.

25 Statements regarding welding practices being "known" or "common" or to similar effect are not an admission that the practices form part of the common general knowledge of a skilled person in Australia or in any other jurisdiction.

30 Modifications and variations, as would be apparent to a skilled addressee, are deemed to be within the scope of the present invention.

CLAIMS

1. A method of producing a durable working surface on a metal component by forming a weld deposit comprising metal nitride.
2. The method defined in claim 1, wherein the weld deposit contains metal
5 nitride in the range 20 to 90 vol%.
3. The method defined in claim 1 or claim 2, wherein the method involves controlling the content of nitrogen in a shielding gas to cause nitrogen gas to react with metal in a weld pool so that the solidified weld deposit comprises metal nitride.
4. A gas metal arc welding process as defined in claim 3, wherein the shielding
10 gas is composed substantially of nitrogen.
5. A gas metal arc welding process as defined in claim 3, wherein the shielding gas is composed totally of nitrogen.
6. A gas metal arc welding process as defined in claim 3, wherein the shielding gas contains nitrogen and argon.
- 15 7. A gas metal arc welding process as defined in claim 3, wherein the shielding gas contains nitrogen and helium.
8. A gas metal arc welding process as defined in claim 3, wherein the shielding gas contains nitrogen, helium and argon.
9. The method defined in any one of the preceding claims, wherein the method
20 is a gas metal arc welding process, a gas tungsten arc welding process, a plasma transferred arc welding process, a laser beam welding process or a hybrid laser welding process.
10. A hard facing weld deposit comprising titanium or titanium alloy produced by a welding method according to the first aspect wherein the weld deposit comprises
25 metal nitride in the range of 20 to 90 vol%.

11. The hardfacing weld deposit defined in claim 10, wherein the weld deposit has a thickness on a work piece in the range of 0.1 to 20mm or greater than 20mm.

12. The hardfacing weld deposit defined in claim 10 or claim 11, wherein the weld deposit possesses a bulk hardness greater than 300 HV.

- 5 13. A method described in any of the preceding claims whereby the welding consumable and substrate are manufactured from transition metals including, but not limited to, tantalum, zirconium, tungsten, niobium, chromium, molybdenum, vanadium, iron and their alloys.

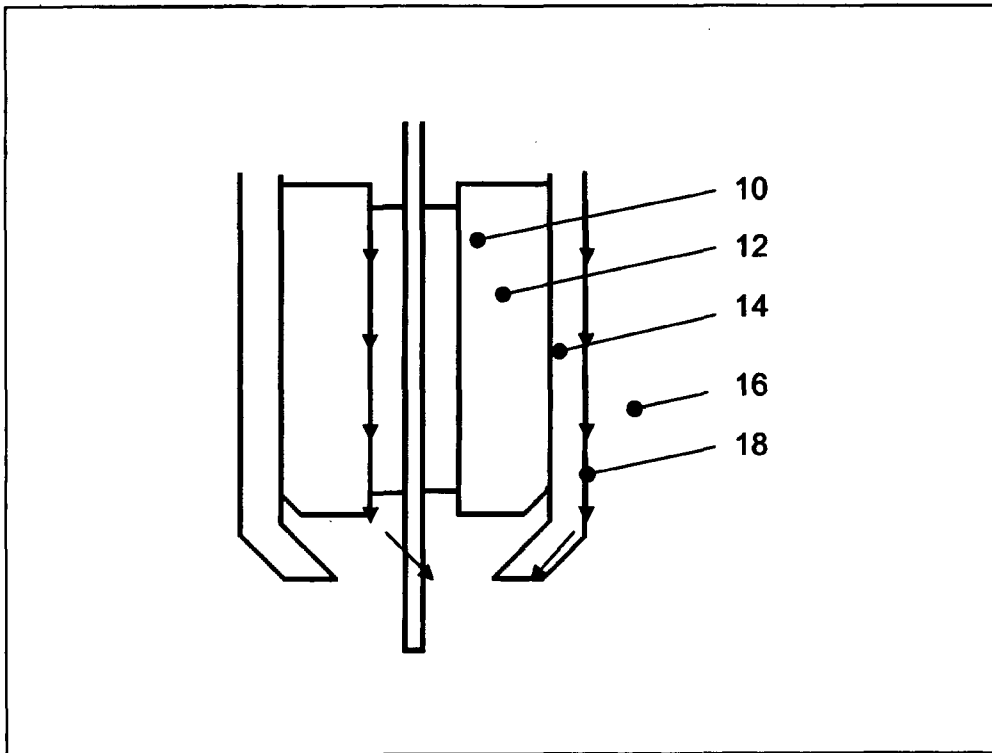


Figure 1

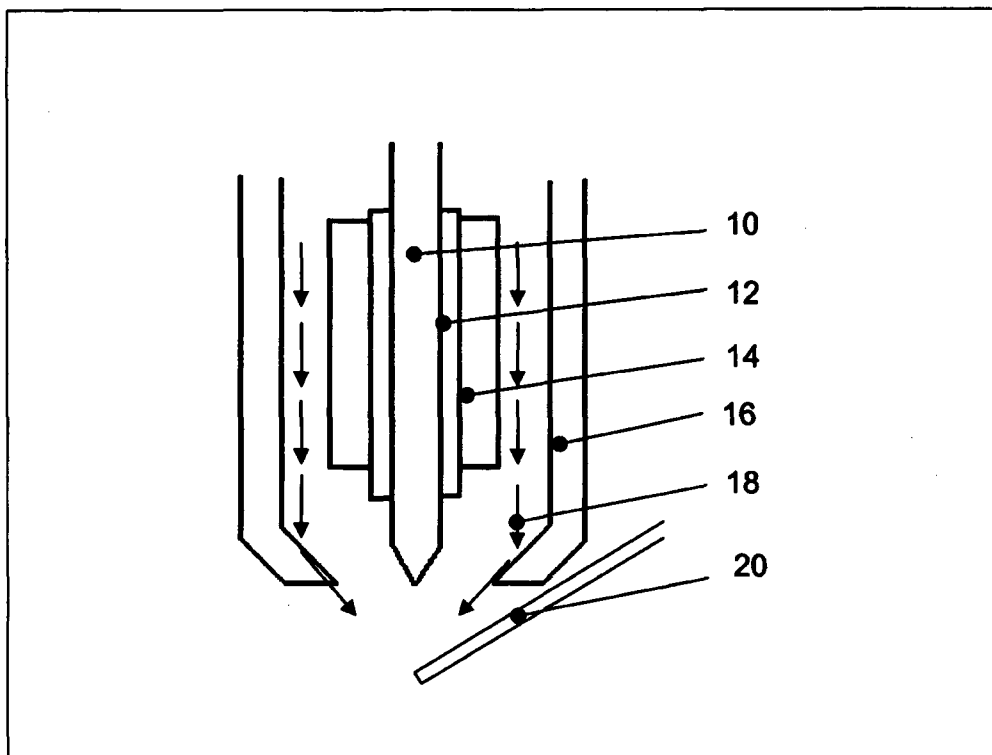


Figure 2

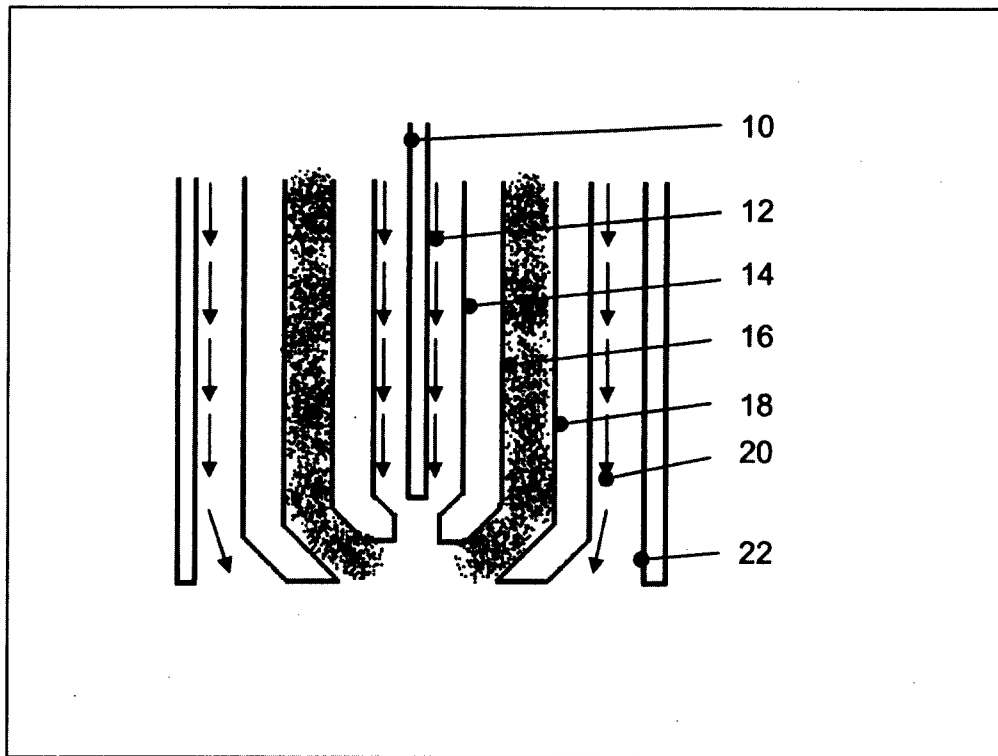


Figure 3



Figure 4

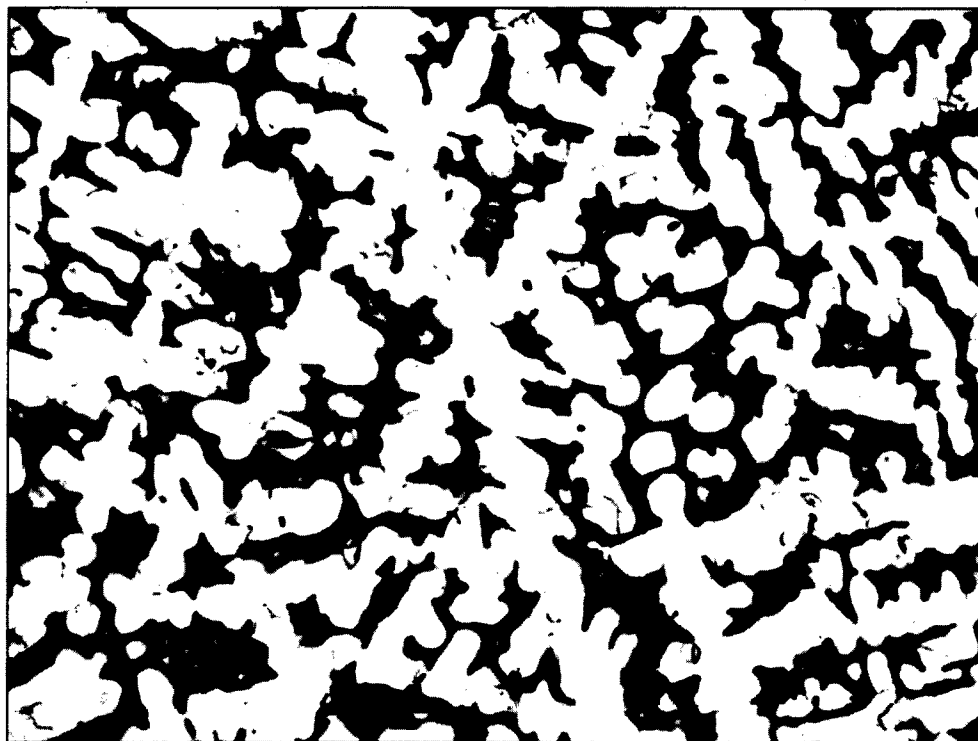


Figure 5



Figure 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2012/000163

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B23K 35/38 (2006.01)

C22C 14/00 (2006.01)

B23K 103/14 (2006.01)

B23K 9/04 (2006.01)

C23C 8/24 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, TOTALPATENTS: (TITANIUM OR TI); (NITROGEN OR NITRIDE?); OR SURFAC+, OVERLAY+, HARD+, TOUGH, DURAB+, WEAR, EROS+); (SHIELD+ 2D GAS+); (OR CLAD+, PLATE+, PLATING, COAT+, DEPOSIT+); (WELD+ OR B23K/IC/EC/ECNO) and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2328221 A (BRUNEL UNIVERSITY) 17 February 1999 Refer to whole document and in particular to pg 7, lines 1-3; pg 3 Experimental Procedure;	1, 3-6, 9, 13
X	WO 2007/124310 A2 (MATERIALS & ELECTROCHEMICAL RESEARCH CORP.) 1 November 2007 Refer to whole document and in particular to pg 1, line 31-33; Example 3 on pg 6 lines 3-4; Examples 11 & 12 on pg 7; Example 13 on pg 8; claims 2, 34 to 36; Fig. 5	1-5, 7, 9-13



Further documents are listed in the continuation of Box C



See patent family annex

* Special categories of cited documents:

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"&" document member of the same patent family

"P" document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search

24 April 2012

Date of mailing of the international search report

27 April 2012

Name and mailing address of the ISA/AU

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2012/000163

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3111434 A (ZENICHIRO TAKAO <i>et. al.</i>) 19 November 1963 Refer to whole document and in particular to Example 4	1, 3, 6-9, 13
X	Derwent Abstract Accession No 2006-259523, JP 2006-095589 A (TEIGU KK) 13 April 2006 Refer to Derwent abstract and machine translation para [0031]	1, 9, 13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2012/000163

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
GB	2328221	NONE					
WO	2007124310	AU	2007240431	CA	2612534	CN	101444149
		EP	2007543	JP	2009534535	KR	20080110960
		US	2008000881				
US	3111434	CA	713159	CH	414302	FR	1271837
		GB	906895				
JP	2006095589	NONE					
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							