



- (51) **International Patent Classification:**  
C04B 37/00 (2006.01) C04B 37/02 (2006.01)
- (21) **International Application Number:**  
PCT/EP2017/051692
- (22) **International Filing Date:**  
26 January 2017 (26.01.2017)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
62/287,517 27 January 2016 (27.01.2016) US
- (71) **Applicant: MORGAN ADVANCED CERAMICS, INC.**  
[US/—]; 2425 Whipple Road, Hayward, CA 94544 (US).
- (71) **Applicant (for DZ only): BOFF, James** [GB/GB]; 5 Pemberton Row, London EC4A 3BA (GB).
- (72) **Inventor: SANDIN, Thomas**; 807 Bain Place, Redwood City, California 94062 (US).
- (74) **Agent: PHILLIPS & LEIGH**; 5 Pemberton Row, London EC4A 3BA (GB).
- (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, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, KM, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

- as to the identity of the inventor (Rule 4.17(i))
- of inventorship (Rule 4.17(iv))

**Published:**

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

(54) **Title:** BRAZEABLE ZIRCONIA CERAMICS, METHODS OF BRAZING ZIRCONIA CERAMICS, AND BRAZED ZIRCONIA CERAMICS

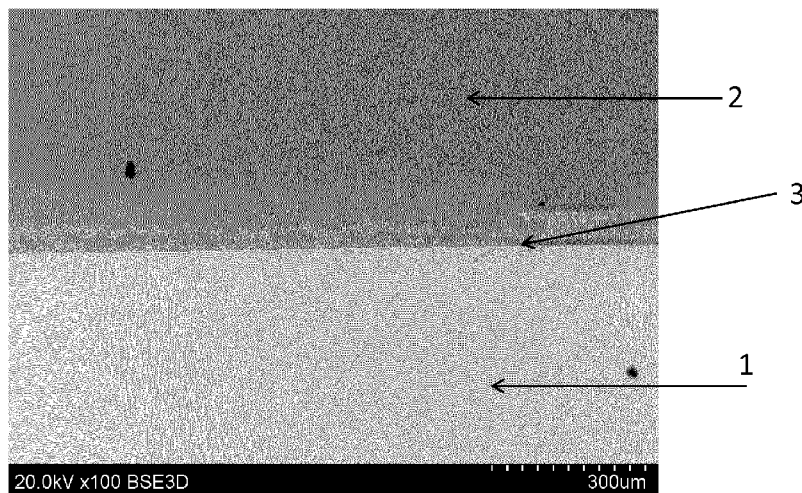


Fig. 1

(57) **Abstract:** A method of brazing a sintered zirconia ceramic body, comprises: •providing a sintered zirconia ceramic body having a surface; •chemically reducing the sintered zirconia ceramic body in whole or in part to form a reduced surface to the sintered zirconia ceramic body; •applying a brazing material to at least part of the reduced surface to form an assembly comprising said brazing material and sintered zirconia ceramic body; •heating said assembly to a temperature sufficient to at least partially melt the brazing material such that the brazing material wets the reduced surface; and •cooling the assembly to solidify the brazing material.



## **Brazeable zirconia ceramics, methods of brazing zirconia ceramics, and brazed zirconia ceramics**

This invention relates to brazeable zirconia ceramics, methods of brazing zirconia  
5 ceramics, and brazed zirconia ceramics.

### Zirconia ceramics

By “zirconia ceramics” is meant ceramic materials comprising at least 5wt% ZrO<sub>2</sub> and optionally at least 50wt% ZrO<sub>2</sub>, or at least 70wt% ZrO<sub>2</sub>, or at least 80wt% ZrO<sub>2</sub>, or at least 90wt% ZrO<sub>2</sub>.

10 Zirconia is an oxide (ZrO<sub>2</sub>) that is used in ceramics but which, in its pure form, suffers from a tetragonal/monoclinic phase change that makes manufacture of sintered bodies of pure zirconia ceramics difficult. For this reason zirconia ceramics for use as sintered bodies generally comprise other components that lock the material wholly or partially into a high temperature cubic phase or stabilise the tetragonal phase. Typical  
15 components to achieve this effect include, for example, CaO, MgO and Y<sub>2</sub>O<sub>3</sub>. Zirconia ceramics may also contain other components (e.g. hafnia, HfO<sub>2</sub>).

Typical zirconia containing ceramics include (among other types):

- Precipitation hardened/transformation toughened ceramics such as partially stabilised zirconia (PSZ) which comprises tetragonal t-ZrO<sub>2</sub> particles and  
20 stabilised cubic c-ZrO<sub>2</sub> grains [e.g. yttria stabilized zirconia (Y-PSZ), magnesia stabilized zirconia (MSZ) and ceria stabilized zirconia (CSZ)].
- Tetragonal zirconia polycrystal ceramics (TZP) which comprise fine grained tetragonal t-ZrO<sub>2</sub> particles (e.g Y-TZP).
- Zirconia toughened ceramics (ZTC) which comprise tetragonal t-ZrO<sub>2</sub> particles or  
25 monoclinic m-ZrO<sub>2</sub> particles dispersed in another ceramic material (e.g. alumina [ZTA], mullite, or spinel).

It is known that reduction of zirconia results in a darkening of the ceramic from its normal white colour, and this has been attributed, at least in part, to the presence of

zirconia sub oxides [ZrO<sub>2-x</sub>] and (where yttria is present) yttria sub-oxides [Y<sub>2</sub>O<sub>3-x</sub>].

[*“Origin of Darkening in 8wt% Yttria-Zirconia Plasma-Sprayed Thermal Barrier Coatings”*,

Gabriel Maria Ingol, J. Am Ceram. Soc. **74**(2), 381-86 (1991)]. Stronger coloration has

5 been attributed to the presence of impurities such as iron [*“Reply to “Comment on ‘Black Color in Partially Stabilized Zirconia’”*], Javier Soria et al, J. Am Ceram. Soc. **74**(7), 1747-48 (1991)]. Whatever the source, such darkening has been seen as a cosmetic disadvantage.

Darkening of a dense Y-TZP monolith and its fracture toughness has been reported in

*“Mechanical and Magnetic properties of Novel Yttria-Stabilized Tetragonal Zirconia/Ni*

10 *Nanocomposite prepared by the Modified Internal Reduction Method”*, Kondo et al, J. Am Ceram. Soc. **88**(6), 1468-1473 (2005)]. No significant change in fracture toughness was shown following heat treating in a pure hydrogen atmosphere at 1300°C for 2.5 hours.

### Brazing

Brazing and soldering are processes in which a molten filler metal (frequently referred

15 to as a filler) is used to wet facing surfaces of a joint, and is then solidified on cooling to form a joint between the facing surfaces. Reaction or alloying at the junction between the brazing material and the articles to be joined may occur to a limited extent.

Conventionally, brazing takes place above 450°C and soldering at or below that temperature.

20 Brazing can also be used to provide a metallized surface to an article, or to provide electrically conductive pathways through articles.

According to “Principles of Brazing” by Jacobson and Humpston, (ASM International, ISBN 0-87170-812-4), brazing has been known since about 3200BCE for joining metals, and so for some materials it could be considered a mature technology. However the

25 range of materials that can be successfully brazed has been extended over recent years as methods have been developed to deal with such widely different materials as ceramics, glasses and composite materials. For example “active brazes” incorporate in otherwise conventional brazing alloys a small amount of metals such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, or silicon, to improve wetting and spread on ceramic materials.

30

For brazing to occur, the brazing material normally has a liquidus temperature below the solidus temperature of the materials to be brazed, and the temperatures used for brazing must not detrimentally affect the materials to be joined.

5 A significant factor in assessing the quality of a brazed joint to ceramic is the shear strength at the joint. If the joint shears within the ceramic rather than in the braze, or at the braze-ceramic interface, then the braze does not represent a region of weakness.

#### Brazing zirconia ceramics

When brazing zirconia ceramics, it is known to use active brazes, however such active brazes have some drawbacks:-

- 10 • they tend to cause discoloration to the ceramic surrounding the braze, which is not only unsightly, it also makes it difficult to visually assess the presence of any surface contamination, or indeed the discoloration may be seen as a surface contamination;
- 15 • the discoloration caused in brazing is hard to control, resulting in variability of appearance between brazed products – this variability in appearance casts doubt in the mind of users of the brazed products;
- the active brazes work in part through reaction with the ceramic surface, which can sometimes cause problems in the strength of the braze if the reaction zone is too thick;
- 20 • to produce a good bond, high levels of vacuum or a pure argon atmosphere is required.

Brazing zirconia ceramics, with a brazing alloy other than active brazes, does not work as the alloys do not wet to the zirconia ceramics.

#### Scope of the disclosure

25 The present disclosure provides improved zirconia materials providing improved brazing, and can avoid the use of active braze alloys.

The inventors have found that providing a reduced surface to sintered zirconia ceramic bodies assists wetting of the bodies to metals, such that optionally brazing materials other than active braze alloys may be used.

5 The inventors have further found that such sintered zirconia ceramic bodies having a reduced surface (in particular, although not exclusively, by the use of reduction in a hydrogen atmosphere at an elevated temperature) have improved shear strength over sintered zirconia ceramic bodies exposed to the same elevated temperature under vacuum.

10 The scope of the invention is as set out in the claims, and in any new and inventive features described herein with reference to the following non-limitative description.

### Background

At this time metallizing does not exist to permit the brazing of yttria stabilised TZP (YTZP) so the only way to braze is to use active brazing (ABA Alloys) in a vacuum furnace.

15 As part of a study into the brazing of zirconia materials, the inventor observed that exposing Y-TZP to a temperature of 1550°C in a hydrogen atmosphere resulted in a uniformly darkened material having a shear strength more than 50% higher than a sample of the same material exposed to the same temperature, for the same time, in vacuum.

20 In looking more closely, the inventor realised that the material exposed to the hydrogen atmosphere had a surface that was more easily wetted by brazing alloys, including brazing materials other than active brazing alloys.

While the particular Y-TZP used in the following examples is uniformly darkened, under other conditions, the zirconia ceramics may only exhibit darkening at the surface.

### 25 Examples

#### The zirconia ceramic

The following examples illustrate but do not limit the invention and each use an injection moulded and sintered dense (>90% dense) material made from yttria

stabilised TZP (YTZP) [made from TZ-3YSE-E grade zirconia powder supplied by Tosoh Corporation which had an analysed composition in weight percent:-  $Y_2O_3$  5.23%,  $Al_2O_3$  0.252%,  $SiO_2$  at most 0.002%,  $Fe_2O_3$  at most 0.002%,  $Na_2O$  0.007%, ignition loss of 0.45%, balance zirconia].

- 5 The material, prior to brazing, had been fired in dry hydrogen (dew point  $-60^\circ C$  or better) at  $1500^\circ C$  for 30 min and then cooled in dry hydrogen to  $150^\circ C$ .

This heat treatment turned the YTZP dark (material changing from white to black). The YTZP did not become electrically conductive.

- Heat treatment temperatures that may be used include (without limitation)  $>1350^\circ C$ ,  
10  $>1400^\circ C$ ,  $>1500^\circ C$ ,  $>1550^\circ C$ .

#### Example 1

- The inventors have brazed articles to titanium, using a  $50\mu m$  (2 thousandth of an inch) thick foil of Ticuni ® active brazing alloy (15 Cu, 15 Ni, 70 Ti) placed between the YTZP  
15 and the titanium. Brazing took place at  $980^\circ C$  in vacuum.

A good joint resulted that did not pull apart with significant force and that was hermetic.

Figure 2 shows an SEM micrograph of the braze, with the dense ceramic 1 joined to titanium 2 at joint 3

#### Example 2

- 20 The heat treated YTZP of example 1 was brazed to titanium using a  $50\mu m$  (2 thousandth of an inch) thick pure gold foil as brazing material.

A good joint resulted that did not pull apart with significant force and that was hermetic.

#### Example 3

- The heat treated YTZP of example 1 was brazed to stainless steel using a  $50\mu m$  (2  
25 thousandth of an inch) thick foil of copper-gold brazing alloy.

A good joint resulted showing good wetting of the YTZP.

#### Example 4

The heat treated YTZP of example 1 was brazed to another piece of the heat treated YTZP of example 1 using a copper-silver alloy as brazing material.

A good joint resulted showing good wetting of the YTZP.

#### 5 Prospective examples

Although exemplified with respect to TZP, improved wetting properties resulting from reduction of zirconia are predicted to apply to other zirconia containing ceramics such as PSZ and ZTC.

10 In light of the zirconia content, the improved strength is expected to apply at least to PSZ.

Optionally the zirconia ceramic may comprise other oxides that darken when exposed to reducing conditions (for example, and without limitation, one or more of: iron oxide, titanium oxide, cerium oxide, chromium oxide, nickel oxide, cobalt oxide) to enhance the uniformity and darkness of colour. Such elements need not be present in high quantities  
15 to provide such effect [e.g. <1%; <0.5%; <0.1%; <0.05%; <0.01%; or <0.005%] although if appropriate may be at higher levels.

#### Typical processing steps

Fig. 1 shows typical processing steps in brazing according to the present invention.

#### Industrial applicability

20 The invention is not limited to any particular brazing materials (other than that they are compatible both with the zirconia ceramic and any other article to which the ceramic is brazed), nor to any particular form of brazing material, and encompasses, for example, foils, pastes, powders, wires.

Brazed zirconia ceramics will have a variety of uses including (without limitation) in:  
25 medical implants, electrical feedthroughs, surgical equipment, analytical equipment, aerospace applications, oxygen sensors, fuel cell components.

The above description is illustrative only and the person skilled in the art will recognise that many variants may fall within the scope of the appended claims.

CLAIMS

1. A method of brazing a sintered zirconia ceramic body, comprising:-
  - providing a sintered zirconia ceramic body having a surface;
  - chemically reducing the sintered zirconia ceramic body in whole or in part to  
5 form a reduced surface to the sintered zirconia ceramic body;
  - applying a brazing material to at least part of the reduced surface to form an assembly comprising said brazing material and sintered zirconia ceramic body;
  - heating said assembly to a temperature sufficient to at least partially melt the  
10 brazing material such that the brazing material wets the reduced surface ; and
  - cooling the assembly to solidify the brazing material.
2. A method of preparing a sintered zirconia ceramic body for brazing, comprising:-
  - providing a sintered zirconia ceramic body having a surface comprising at least in part a region adapted to be brazed; and
  - chemically reducing the sintered zirconia ceramic body in whole or in part to  
15 form a reduced surface to the sintered zirconia ceramic body.
3. A method as claimed in Claim 1 or Claim 2, in which chemically reducing the sintered zirconia ceramic body comprises exposing the sintered zirconia ceramic body to a reducing atmosphere.
- 20 4. A method as claimed in any of Claims 1 to 3, in which the reducing atmosphere comprises hydrogen.
5. A method as claimed in any of Claims 1 to 4 in which the sintered zirconia ceramic body comprises greater than 50wt% zirconia.
6. A method as claimed in Claim 5, in which the sintered zirconia ceramic body is a  
25 tetragonal zirconia polycrystal ceramic.
7. A brazed article comprising a sintered zirconia ceramic body comprising a chemically reduced surface.

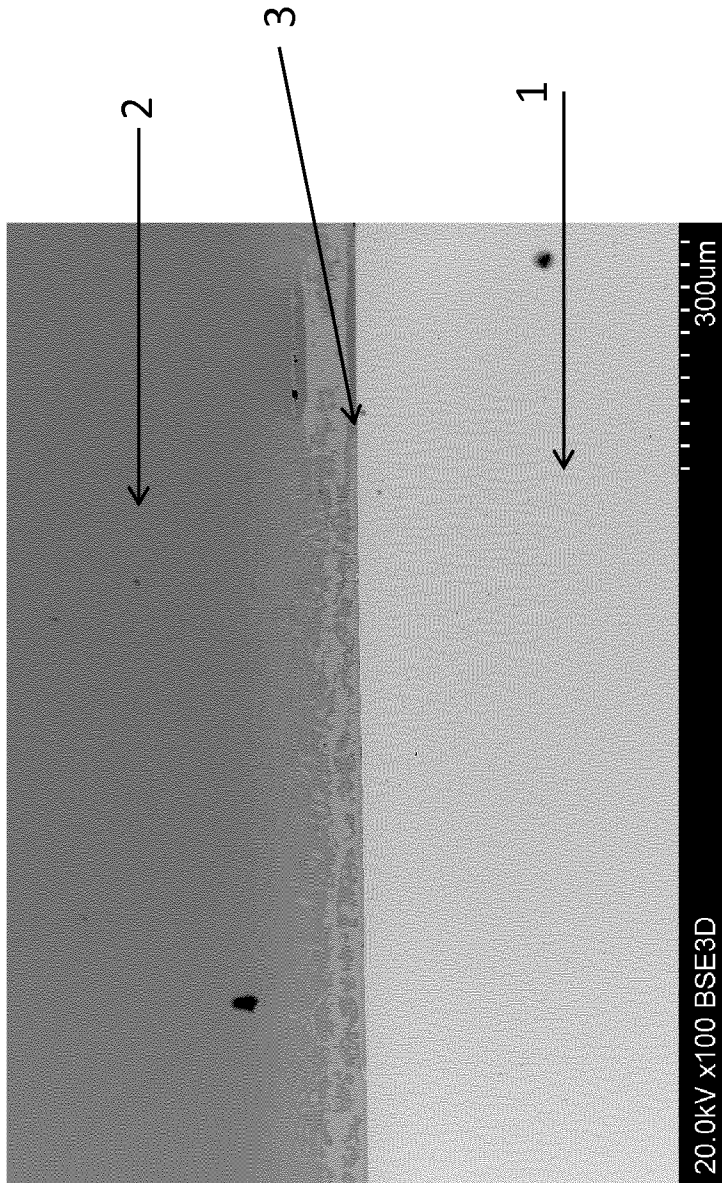


Fig. 1

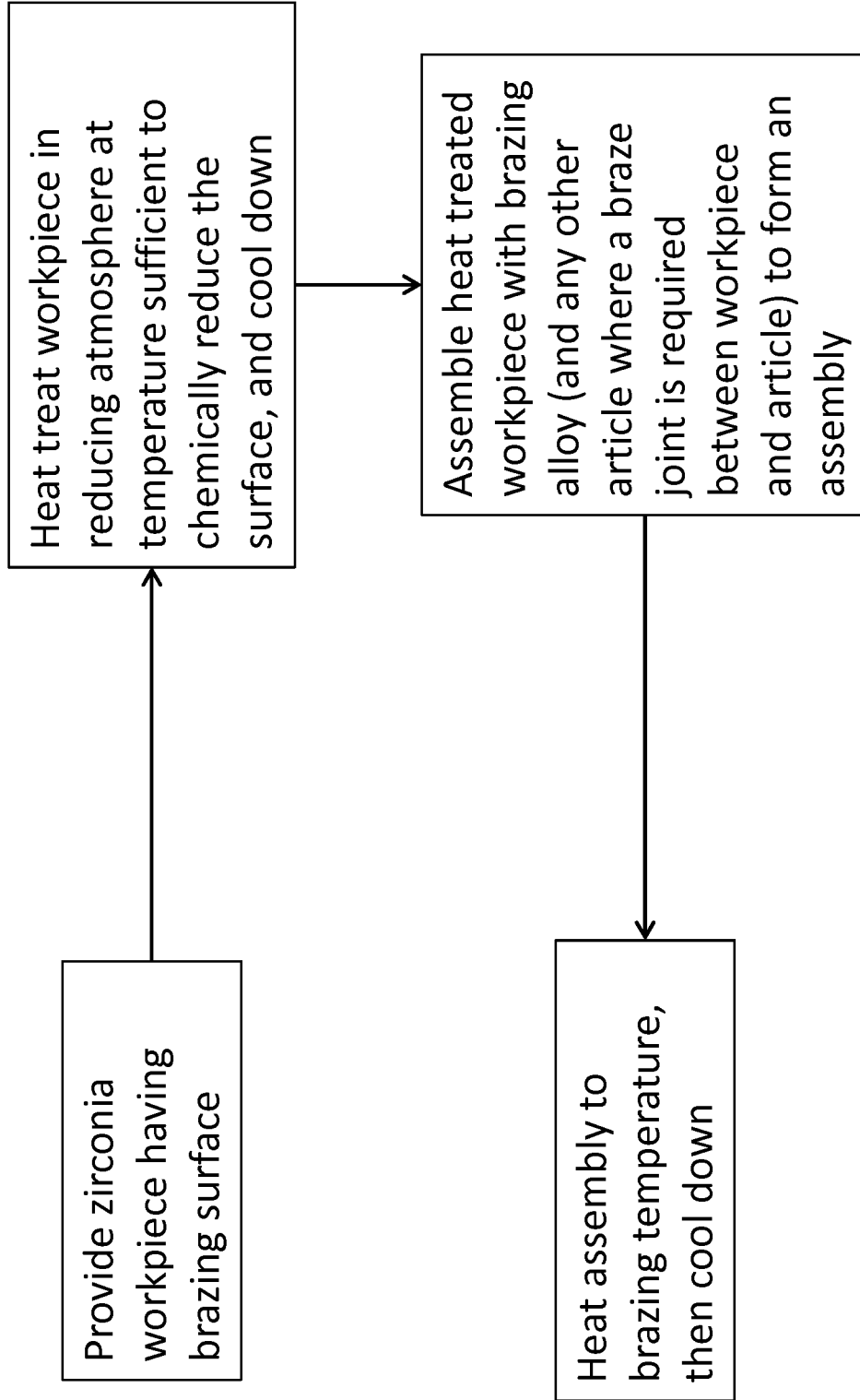


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/051692

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C04B37/00 C04B37/02  
ADD.  
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)  
C04B

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)  
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2004 146130 A (TOKYO GAS CO LTD) 20 May 2004 (2004-05-20)	1-4,7
Y	figures 1-7; example 1	5,6
X	Jean S Pimenta ET AL: "Brazing of Zirconia to Titanium using Ag-Cu and Au-Ni Filler Alloys (Brasagem da Zircônia ao Titânio usando Ligas de Adição Ag-Cu e Au-Ni)", 31 December 2013 (2013-12-31), pages 4349-357, XP055366634, Retrieved from the Internet: URL:http://www.scielo.br/pdf/si/v18n4/07.pdf [retrieved on 2017-04-24]	7
Y	Section 3.1;	5,6
A	page 355; figures 5-7; tables 1, 4	1-4
	----- -/--	

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search <b>25 April 2017</b>	Date of mailing of the international search report <b>03/05/2017</b>
---	---

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <b>Süzük, Kerem Güney</b>
--	---

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/051692

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 3 736 648 A (SPIELBERG D ET AL) 5 June 1973 (1973-06-05)	7
A	column 3, line 3 - line 12; claims 1-13; examples 1, 2	1-6
	-----	
X	MRITYUNJAY SINGH ET AL: "Brazing of yttria-stabilized zirconia (YSZ) to stainless steel using Cu, Ag, and Ti-based brazes", JOURNAL OF MATERIALS SCIENCE, KLUWER ACADEMIC PUBLISHERS, BO, vol. 43, no. 1, 8 November 2007 (2007-11-08), pages 23-32, XP019552970, ISSN: 1573-4803	7
A	page 30, right-hand column; figures 3-8; table 5	1-6
	-----	
A	M. SINGH ET AL: "Brazing of Stainless Steel to Yttria-Stabilized Zirconia Using Gold-Based Brazes for Solid Oxide Fuel Cell Applications", INTERNATIONAL JOURNAL OF APPLIED CERAMIC TECHNOLOGY, vol. 4, no. 2, 31 March 2007 (2007-03-31), pages 119-133, XP055366897, US ISSN: 1546-542X, DOI: 10.1111/j.1744-7402.2007.02126.x Introduction; figures 3-8	1-7
	-----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/051692

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
JP 2004146130	A	20-05-2004	JP 4087216 B2	21-05-2008
			JP 2004146130 A	20-05-2004
-----				
US 3736648	A	05-06-1973	NONE	
-----				