



(11) **EP 1 111 091 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
23.06.2010 Bulletin 2010/25

(51) Int Cl.:
C23C 28/02 (2006.01) **C23C 28/00** (2006.01)
C23C 10/02 (2006.01)

(21) Application number: **00311496.4**

(22) Date of filing: **20.12.2000**

(54) **Method of forming an active-element containing aluminide as stand alone coating and as bond coat and coated article**

Verfahren zur Herstellung eines Aluminid-Überzugs mit einem aktiven Element als Beschichtung und Verbindungsschicht und beschichteter Gegenstand

Procédé de formation d'une couche d'aluminure renfermant un élément actif comme revêtement et couche de liaison et article revêtu

(84) Designated Contracting States:
CH DE FR GB LI NL

(30) Priority: **21.12.1999 US 172824 P**
12.12.2000 US 735223

(43) Date of publication of application:
27.06.2001 Bulletin 2001/26

(73) Proprietor: **United Technologies Corporation**
Hartford, CT 06101 (US)

(72) Inventors:
• **Bose, Sudhangsu**
Manchester, Connecticut (US)

• **Olson, Walter E.**
Vernon, Connecticut 06066 (US)
• **Duhl, David N.**
Newington, Connecticut 06111 (US)

(74) Representative: **Hall, Matthew Benjamin**
Dehns
St. Bride's House
10 Salisbury Square
London EC4Y 8JD (GB)

(56) References cited:
EP-A- 0 386 386 EP-A- 0 587 341
EP-A- 0 845 547 US-A- 3 692 554
US-A- 3 979 273 US-A- 4 962 005
US-A- 5 427 866 US-A- 5 658 614

EP 1 111 091 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates generally to oxidation and corrosion resistant coatings, and relates more particularly to aluminide coatings containing one or more active elements and improved oxidation and corrosion resistance.

[0002] Overlay coatings are widely used in high temperature and/or corrosive environments, for example in gas turbine engines, as a stand alone coating, e.g., to provide high temperature corrosion and oxidation resistance to the underlying substrate, and also as an adherent bond coat for a subsequently-applied ceramic thermal barrier coatings. A typical overlay coating is an MCr, MCrAl or MCrAlY coating, such as a coating disclosed in commonly-owned U.S. Pat. No. 4,585,481 and Reissue No. 32,121, both to Gupta et al. The M is selected from the group including nickel, cobalt and iron or combinations of these elements. The Y typically indicates yttrium but may also include silicon and/or other active elements such as hafnium. Overlay coatings are generally, although not necessarily, applied by plasma spraying. See, e.g., U.S. Pat. Nos. 4,321,311 and 4,585,481 and Reissue No. 32,121. Application of overlay coatings by other applications, including but not limited to, electron-beam physical vapor deposition, chemical vapor deposition, cathodic arc and electroplating are also possible. While the bond coat thickness may vary depending upon the particular component and application, the illustrated bond coat typically has a thickness of less than about 5 mils (125 μm), although thicker or thinner coatings are also used.

[0003] Aluminide coatings are also used in high temperature and/or corrosive environments, for example in gas turbine engines, as a stand alone coating, e.g., to provide high temperature corrosion and oxidation resistance to the underlying substrate, and as an adherent bond coat for a subsequently-applied ceramic thermal barrier coating. Some aluminide coatings also include one or more noble metals, which enhance erosion and/or corrosion resistance. See, e.g., U.S. Pat. No. 5,856,027 to Murphy. Aluminide coatings, including those containing noble metal(s), are traditionally applied by a pack process or by chemical vapor deposition (CVD). In a typical "in pack" process, the article to be coated is usually initially electroplated with a noble metal, and is then placed in a pack containing a source of aluminum, an activator, e.g., halide, and inert materials, e.g., alumina. The pack and article are then heated, forming vapors of the aluminum, which reacts with the nickel or cobalt in the article to form the aluminide. The coatings may be further heat treated to obtain desired coating properties. In a typical CVD process, individual generators produce aluminum vapors, and the vapors are conveyed into a chamber to a heated article to be coated where the vapors condense and react with the nickel or cobalt in the article to form the aluminide.

[0004] It is generally accepted that it is difficult to produce active element containing aluminides of consistent quality. It is also generally accepted that it is at least as difficult to consistently produce aluminide coatings containing more than one active element.

[0005] Numerous patents describe various overlay and aluminide coating compositions and processes. Exemplary patents are identified below.

[0006] U.S. Pat. No. Re 32,121 describes forming an MCrAlY (M including nickel, cobalt or a combination) bond coat by plasma spraying, with the MCrAlY composition including about 0.1 - 0.7 % silicon, and 0.1 - 2 % hafnium.

[0007] U.S. Pat. No. 4,897,315 describes a plasma sprayed NiCoCrAlY overlay, which is then aluminized to form an aluminide coating on the substrate.

[0008] U.S. Pat. No. 5,658,614 describes a platinum aluminide (without an MCrAlY) coating formed by electroplating the platinum onto the substrate, and then aluminizing by CVD.

[0009] It is a general object of the present invention to provide a coating having improved properties. It is another object to provide an aluminide coating, and a process for applying an aluminide, having improved durability.

[0010] It is still another object to provide a repeatable process for forming active element(s) containing aluminide coatings that produces high quality coatings more consistently.

[0011] According to the invention, a method is disclosed for improving the corrosion and oxidation resistance of a substrate. The method includes providing a superalloy substrate, and an overlay coating including at least one oxygen active element which is applied onto the substrate by an overlay step. Platinum is applied onto the overlay coating, by electroplating. The overlay coating and metal is then aluminized by chemical vapor deposition. A ceramic thermal barrier coating may also be applied. A coated article is also disclosed.

[0012] Certain preferred embodiments of the present invention will now be described by way of example only and with reference to the accompanying drawings, in which:

FIG. 1 is a photomicrograph of a coating of a preferred embodiment, including a ceramic coating.

FIG. 2 is a flow diagram illustrating a preferred process for fabricating the coating of the present invention.

[0013] Turning now to FIG. 1, a substrate having an aluminide coating in accordance with the present invention is illustrated by the reference numeral 10. The coating may serve as a stand alone coating, e.g., for high temperature oxidation resistance, or as an adherent bond coat for a subsequently-applied thermal barrier such as a layer of ceramic material, e.g., stabilized zirconia. In the embodiment illustrated in FIG. 1, a ceramic layer is applied over the aluminide

to form a thermal barrier. The ceramic layer may be a stabilized zirconia, such as is disclosed in commonly owned U.S. Pat. 4,321,311 to Strangman or Ser. No. 09/164,700 to Maloney both of which are commonly owned with the present invention and are expressly incorporated by reference herein.

[0014] A substrate 12 is typically composed of nickel, cobalt and /or iron base superalloy material. As described further below with reference to FIG. 2, an overlay coating 14 such as an MCrAl type coating is first applied to the substrate, by low pressure plasma spray and together with one or more oxygen active elements such as hafnium, yttrium and silicon or other oxygen active element. Platinum is then deposited by electroplating, and is aluminized to form an adherent alumina layer 16. The article is also heat treated to provide the coating with desired properties, e.g., improved mechanical properties. As indicated in FIG. 3, the present invention provides coatings having improved properties, e.g., corrosion and oxidation resistance and durability relative to prior coatings. While the invention illustrated below is used with a nickel base, cobalt base or iron base superalloy material, the invention is not limited to use with these materials.

[0015] Typical compositions of such alloys are shown in Table 1. Exemplary U.S. Patents describing columnar and single crystal and directionally solidified alloys include 4,209,348; 4,643,782; 4,717,432; 4,719,080 and 5,068,084, each of which is expressly incorporated by reference herein. Cooling holes, which may be positioned on one or more portions of a turbine blade, may be provided for flowing cooling air over the specific portions of the airfoil during operation, as is known generally in the art.

TABLE 1: COMPOSITION OF COLUMNAR AND SINGLE CRYSTAL ALLOYS

| Alloy | Type | Ni | Co | Cr | Al | Mo | Ta | W | Re | Hf | Ti | Nb |
|----------|------|------|-----|-----|------|-----|-----|-----|----|------|-----|----|
| PWA 1422 | DS | Bal. | 10 | 9 | 5 | - | - | 12 | - | 1.6 | 2 | 1 |
| DS R80H | DS | Bal. | 9.5 | 14 | 3 | 4 | - | 4 | - | 0.75 | 4.8 | - |
| CM247LC | DS | Bal. | 9.2 | 8.1 | 5.6 | 0.5 | 3.2 | 9.5 | - | 1.4 | 0.7 | - |
| PWA 1480 | SC | Bal. | 5 | 10 | 5 | - | 12 | 4 | - | - | 1.5 | - |
| PWA 1484 | SC | Bal. | 10 | 5 | 5.65 | 1.9 | 8.7 | 5.9 | 3 | 0.1 | - | - |
| Rene' N5 | SC | Bal. | 7.5 | 7 | 6.2 | 1.5 | 6.5 | 5 | 3 | 0.15 | - | - |
| CMSX-4 | SC | Bal. | 9 | 6.5 | 5.6 | 0.6 | 6.5 | 6 | 3 | 0.1 | 1 | - |

[0016] Other alloys include, for example, Rene N4 and CMSX-2, which are described in the prior art.

[0017] Generally, the active element(s) is applied by a conventional overlay process, and may or may not contain other elements, e.g., as part of an MCr or MCrAl overlay coating. In accordance with the present invention, an overlay coating such as an MCrAl is applied to the substrate surface by low pressure plasma spray. As is known, M indicates nickel, cobalt, iron and mixtures thereof. The bond coat also includes at least one oxygen active element, e.g., yttrium, hafnium, silicon or others. As applied, the present invention includes an overlay coating having a thickness of between about 1 - 5 mils (0.001 - 0.005 inches, (25.4-127 μm)).

[0018] The overlay coating (described further in an example below) according to the invention which we have used successfully is a NiCoCrAl coating with added Y, Hf and/or Si. In broad terms, the coating is composed in weight percentage of about 5 - 40 Cr, 8 - 35 Al, up to 2 Y, 0.1 - 7 Si, 0.1 - 5.5 Hf, balance Ni and/or Co.

[0019] Platinum is then deposited on the MCrAl coating. We believe that the final coating should contain in weight percent 10 - 11 Pt as described below we have obtained good results. Platinum is deposited by electroplating, in a known manner. Plating the platinum to a thickness of about 0.05 - 0.15 mils (1.3-3.8 μm) should provide a final coating with the above-desired transition metal content. Plating processes are known generally and are not described here in detail.

[0020] Aluminum is then applied to the part by chemical vapor deposition to aluminize the part. While CVD aluminizing processes are known generally and are not described here in detail, a coating gas has a composition including some amount, in vol. % of a carrier gas, such as hydrogen, and an amount, in vol. %, of an aluminum containing gas. The coating gas may be formed by passing a carrier gas over a source of aluminum. The above process is adjusted as desired to provide a given quantity of aluminum on the part surface. The coating gas is then impinged upon the heated substrate, at a given delivery rate, with the substrate typically being heated to between about 1800 - 2200 F (982 - 1204°C) and preferably about 1950 - 2000F (1065 - 1093°C)

[0021] After aluminizing, the coated part is diffusion heat treated. The diffusion heat treatment includes heating the component to a temperature of about 1975 F (1079°C) for a sufficient time, of about 3 hours, followed by a precipitation heat treatment, at about 1600 °F (871°C) for about 16 hours. A resulting coating is illustrated in FIG. 1, which includes a subsequently applied, columnar grain, ceramic thermal barrier layer.

[0022] As noted above, coatings in accordance with the present invention may be employed to provide stand alone coatings or bond coats for subsequently-applied ceramic thermal barrier coating. Typical ceramics are zirconia based, and may be partially or fully stabilized with additions of yttria or other appropriate stabilizer. Exemplary ceramic coatings composed of yttria stabilized zirconia (YSZ) are described, for example, in commonly-owned U.S. Pat. Nos. 4,321,311, 5,262,245. The ceramic may be applied by EB-PVD, by plasma spray or by another suitable method.

[0023] Samples were prepared using superalloy substrates in accordance with preferred embodiments and some were also coated with a standard, zirconia based columnar ceramic thermal barrier coating. The overlay coating as described above was applied by low pressure plasma spray, and then plated with platinum in a known manner. The samples were aluminized using a coating gas included about 80 vol. % of a carrier gas, such as hydrogen, and about 20 vol. %, of an aluminum containing gas, in this case AlCl_3 . The coating gas was formed by passing HCl over a source of aluminum at about 600 C. The coating gas was impinged upon the heated substrate, at a delivery rate of about 224 standard cubic feet per minute, with the substrate heated to a nominal temperature of between about 1950-2000 F (1065-1093°C). Some of the samples were then coated with a ceramic thermal barrier coating composed of yttria stabilized zirconia, as taught for example in the above referenced '311 patent to Strangman, while other samples were tested without such a ceramic coating.

[0024] Coated articles in accordance with the present invention have been tested in a burner rig apparatus. Testing indicated that the present invention coatings, which tests included samples having a subsequently applied thermal insulating layer, are about 2 - 3 times more durable than current TBC's. The inventive coated articles were also tested as stand alone coatings, e.g., no overlying ceramic layer, and also demonstrate improved protection and durability.

[0025] The samples were tested in high temperature burner rigs. The test cycles comprised 117 minute exposure at 2150 degree F (1176°C) followed by 3 minute air cooling per cycle together with standard platinum aluminides. The samples prepared in accordance with the present method exhibited improved lives over the samples including the standard aluminides by a factor of about 2.5.

[0026] As a result of the testing, we believe that the composition of the final coating is, in weight percent, 10 - 11 Pt, 2.6 - 4.2 Si, 13.4 - 13.6 Al, 3.9 - 5.3 Hf, remainder Ni, Co, and Cr.

[0027] The present invention provides significant advantages over prior processes. The improved process enables the production of active element containing aluminide coatings having significantly more consistent compositions, and thus significantly more consistent properties and improved durability. The quality of the resulting coatings are thus similarly improved.

Claims

1. A method of improving the corrosion and oxidation resistance of a substrate, comprising the steps of:

providing a superalloy substrate (44);
 applying an MCrAl overlay coating including at least one oxygen active element onto the substrate by low pressure plasma spray;
 electroplating platinum onto the overlay coating (48);
 aluminizing the MCrAl overlay coating and platinum (50) by chemical vapour deposition at a temperature of between 1950-2000°F (1065-1093°C) to form an aluminide coating;
 diffusion heat treating; and precipitation heat treating,

characterised in that: the overlay coating is composed in weight percent of 5-40 Cr, 8-35 Al, up to 2 Y, 0.1-7 Si, 0.1-5.5 Hf, balance Ni and/or Co;
 the diffusion heat treating is at a temperature of 1975°F (1079°C) for 3 hours;
 the precipitation heat treating is at 1600°F (871°C) for 16 hours;
 the overlay coating is applied to a thickness of 1-5 mils (25.4-127 μm);
 the platinum is electroplated to a thickness of 0.05-0.15 mils (1.3-3.8 μm); and
 the aluminide coating has a nominal composition in weight percent of 10-11 Pt, 2.6-4.2 Si, 13.4-13.6 Al, 3.9-5.3 Hf, balance Ni, Co, and Cr.

2. A method as claimed in claim 1, further comprising the step of depositing a thermally insulating ceramic on the aluminide (54).

3. A method as claimed in claim 2, wherein the ceramic coating is composed of a stabilized zirconia.

4. A method as claimed in claim 3, wherein the zirconia is stabilized by yttria or by gadolinia

Patentansprüche

1. Verfahren zur Verbesserung der Korrosions- und Oxidationsbeständigkeit eines Substrats, folgende Schritte aufweisend:

5
 Bereitstellen eines Superlegierungs-Substrats (44);
 Auftragen einer MCrAl-Deckschicht-Beschichtung, die mindestens ein Sauerstoffaktives Element enthält, auf das Substrat durch Niederdruckplasmaspritzen;
 10 Elektroplattieren von Platin auf die Deckschicht-Beschichtung (48);
 Aluminieren der MCrAl-Deckschicht-Beschichtung und des Platins (50) durch chemische Dampfabscheidung bei einer Temperatur von zwischen 1950 bis 2000 °F (1065 bis 1093 °C), um eine Aluminid-Beschichtung zu bilden;
 Diffusionswärmebehandeln; und
 Ausscheidungswärmebehandeln,

dadurch gekennzeichnet, dass:

20 die Deckschicht-Beschichtung, in Gew.%, besteht aus 5-40 Cr, 8-35 Al, bis zu 2 Y, 0,1-7 Si, 0,1-5,5 Hf, Rest Ni und/oder Co;
 die Diffusionswärmebehandlung bei einer Temperatur von 1975 °F (1079 °C) 3 Stunden lang stattfindet;
 die Ausscheidungswärmebehandlung bei 1600 °F (871 °C) 16 Stunden lang stattfindet;
 die Deckschicht-Beschichtung in einer Dicke von 1-5 mil (25,4-127 µm) aufgetragen wird;
 das Platin in einer Dicke von 0,05-0,15 mil (1,3-3,8 µm) elektroplattiert wird; und
 25 die Aluminid-Beschichtung eine Sollzusammensetzung, in Gew.%, von 10-11 Pt, 2,6-4,2 Si, 13,4-13,6 Al, 3,9-5,3 Hf, Rest Ni, Co, und Cr hat.

- 30 2. Verfahren wie in Anspruch 1 beansprucht, außerdem aufweisend den Schritt des Abscheidens einer thermisch isolierenden Keramik auf dem Aluminid (54).
 3. Verfahren wie in Anspruch 2 beansprucht, bei dem die Keramikbeschichtung aus einem stabilisiertem Zirconiumdioxid besteht.
 4. Verfahren wie in Anspruch 3 beansprucht, bei dem das Zirconiumdioxid durch Yttriumoxid oder durch Gadoliniumoxid stabilisiert wird.

Revendications

- 40 1. Procédé d'amélioration de la résistance à la corrosion et à l'oxydation d'un substrat, comprenant les étapes suivantes :

fournir un substrat en superalliage (44) ;
 appliquer une couche de recouvrement MCrAl comprenant au moins un élément actif oxygène sur le substrat par pulvérisation par plasma basse pression ;
 45 galvaniser du platine sur la couche de recouvrement (48) ;
 électroplaquer la couche de recouvrement MCrAl et le platine (50) par dépôt chimique en phase vapeur à une température comprise entre 1 065 et 1 093 °C (1 950 et 2 000 °F) pour former un revêtement d'aluminure ;
 traiter thermiquement par diffusion ; et traiter thermiquement par précipitation ;

50 **caractérisé en ce que** : la couche de recouvrement est composée en pour cent en poids de 5 à 40 de Cr, de 8 à 35 de Al, jusqu'à 2 Y, de 0,1 à 7 Si, de 0,1 à 5,5 Hf, le reste étant Ni et/ou Co ;
 le traitement thermique par diffusion a lieu à une température de 1 079 °C (1 975 °F) pendant 3 heures ;
 le traitement thermique par précipitation a lieu à 871 °C (1 600 °F) pendant 16 heures ;
 la couche de recouvrement est appliquée à une épaisseur de 25,4 à 127 µm (1 à 5 mils) ;
 55 le platine est électroplaque à une épaisseur de 1,3 à 3,8 µm (0,05 à 0,15 mils) ; et
 le revêtement d'aluminure a une composition nominale en pour cent en poids de 10 à 11 de Pt, de 2,6 à 4,2 de Si, de 13,4 à 13,6 de Al, de 3,9 à 5,3 de Hf, le reste étant Ni, Co et Cr.

EP 1 111 091 B1

2. Procédé selon la revendication 1, comprenant en outre l'étape de dépôt d'une céramique thermiquement isolante sur l'aluminure (54).
3. Procédé selon la revendication 2, dans lequel le revêtement de céramique est composé d'une zircone stabilisée.
4. Procédé selon la revendication 3, dans lequel la zircone est stabilisée par de l'oxyde d'yttrium ou par de l'oxyde de gadolinium.

5

10

15

20

25

30

35

40

45

50

55

FIG. 1

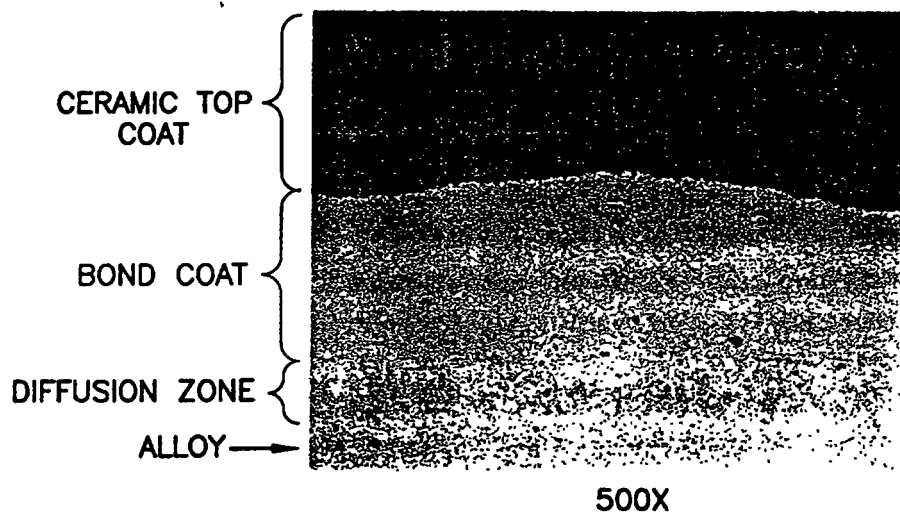
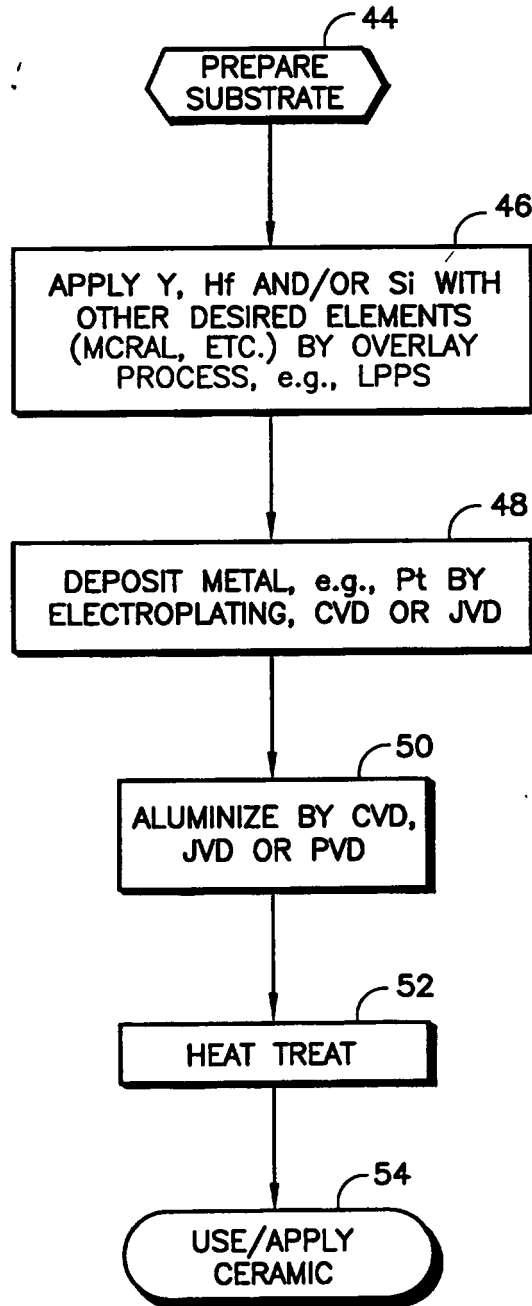


FIG.2



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4585481 A [0002]
- US 32121 A, Gupta [0002]
- US 4321311 A [0002] [0013] [0022]
- US 5856027 A, Murphy [0003]
- US RE32121 E [0006]
- US 4897315 A [0007]
- US 5658614 A [0008]
- US 09164700 B, Maloney [0013]
- US 4209348 A [0015]
- US 4643782 A [0015]
- US 4717432 A [0015]
- US 4719080 A [0015]
- US 5068084 A [0015]
- US 5262245 A [0022]