EP 3 050 997 A1 (11)

(12)

EUROPEAN PATENT APPLICATION published in accordance with Art. 153(4) EPC

(43) Date of publication: 03.08.2016 Bulletin 2016/31

(21) Application number: 13894771.8

(22) Date of filing: 25.09.2013

(51) Int Cl.:

C23C 4/06 (2006.01) C21D 9/08 (2006.01) C23C 4/18 (2006.01)

C21D 1/34 (2006.01) C21D 9/50 (2006.01) C23C 26/00 (2006.01)

(86) International application number: PCT/JP2013/075927

(87) International publication number: WO 2015/045038 (02.04.2015 Gazette 2015/13)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

Designated Extension States:

BAME

(71) Applicant: The Chugoku Electric Power Co., Inc. Hiroshima-shi, Hiroshima 730-8701 (JP)

(72) Inventor: NISHIDA, Hidetaka Hiroshima-shi Hiroshima 730-8701 (JP)

(74) Representative: Osha Liang 2, rue de la Paix 75002 Paris (FR)

(54)METHOD FOR DIFFUSION COATING HEAT-RESISTANT METAL MEMBER WITH CREEP REINFORCEMENT MATERIAL, AND CREEP-STRENGTH-ENHANCED HEAT-RESISTANT **METAL MEMBER**

A creep reinforcement material containing one or a plurality of elements selected from B, W, Cr, Mo, Nb, V, Hf, Zr, Ti, Cu, and Co is coated or thermally sprayed onto a surface of a heat-resistant metal member manufactured using a heat-resistant metal material, and a section coated or thermally sprayed with the creep reinforcement material is covered by a heat-resistant covering member and secured so as to contact the section. The heat-resistant metal member covered by the heat-resistant covering member is heated to a temperature of 1000°C or greater, and thus compressive force accordingly acts on the heat-resistant metal member as it thermally expands in a direction toward the outer periphery, restraining thermal expansion of the heat-resistant metal member in the direction toward the outer periphery, and enabling the creep reinforcement material on the surface of the heat-resistant metal member to be efficiently diffused and permeated into the heat-resistant metal member.

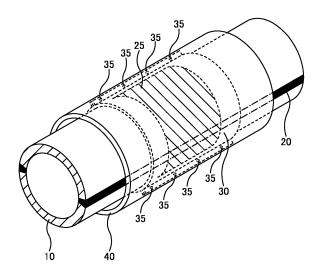


FIG. 1

15

20

25

30

35

40

45

Technical Field

[0001] The present invention relates to a method for diffusing and permeating a creep reinforcement material into a heat-resistant metal member, and to a heat-resistant metal member with creep strength enhanced by such a method.

1

Background Art

[0002] Hitherto, as a method for enhancing creep properties of a heat-resistant metal material, a method has been developed in which, for example, a grain boundary strengthening element that affects creep strength and/or fatigue strength is coated or thermally sprayed to form a film, and heated for a specific duration at a specific temperature (see Japanese Patent No. 3793966).

Summary of Invention

Technical Problem

[0003] An object of the present invention is to provide a method capable of efficiently diffusing and permeating a material that enhances creep strength (hereinafter referred to as a "creep reinforcement material") into a member manufactured using a heat-resistant metal material (hereinafter referred to as a "heat-resistant metal member"), and to provide a heat-resistant metal member with creep strength enhanced by such a method.

Solution to Problem

[0004] In order to address the above problem, according to the present invention, a method for diffusing and permeating a creep reinforcement material into a heat-resistant metal member, and a heat-resistant metal member with creep strength enhanced by such a method, include the following configuration. More specifically, the present invention includes:

(1) a method for diffusing and permeating a creep reinforcement material into a heat-resistant metal member, the method including: coating or thermally spraying a creep reinforcement material onto a surface of a heat-resistant metal member; covering, by a heat-resistant covering member, a section coated or thermally sprayed with the creep reinforcement material, and securing the heat-resistant covering member so as to contact the section; and heating the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000°C or greater, the creep reinforcement material containing one or a plurality of elements selected from B, W, Cr, Mo, Nb, V, Hf, Zr, Ti, Cu, and Co; (2) the method described in (1), wherein, after heat-

ing the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000° C or greater, the heat-resistant metal member covered by the heat-resistant covering member is cooled and re-heated to a temperature of an A_1 transformation point or greater;

(3) A heat-resistant metal member with enhanced creep strength, the heat-resistant metal member being obtained by coating or thermally spraying a creep reinforcement material onto a surface of a heat-resistant metal member, covering, by a heat-resistant covering member, a section coated or thermally sprayed with the creep reinforcement material, and securing the heat-resistant covering member so as to contact the section, and heating the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000 °C or greater; and the creep reinforcement material containing one or a plurality of elements selected from B, W, Cr, Mo, Nb, V, Hf, Zr, Ti, Cu, and Co; and (4) the heat-resistant metal member described in (3), wherein the heatresistant metal member is obtained by, after heating the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000°C or greater, cooling and re-heating to a temperature of an A₁ transformation point or greater.

Advantageous Effects of Invention

[0005] The present invention enables provision of a method capable of efficiently diffusing and permeating a creep reinforcement material into a heat-resistant metal member, and provision of a heat-resistant metal member with creep strength enhanced by such a method.

Brief Description of Drawings

[0006]

Fig. 1 is a schematic diagram illustrating a method to diffuse and permeate a creep reinforcement material into a heat-resistant metal member, to explain an embodiment of the present invention.

Fig. 2 is a schematic cross-section illustrating a cross-section of Fig. 1, to explain an embodiment of the present invention.

Description of Embodiments

[0007] Detailed explanation follows regarding preferable embodiments of the present invention, with reference to the appended drawings. Note that the objects, features, advantages, and ideas of the present invention will be clear to a person of ordinary skill in the art from the content of the present specification, and a person of ordinary skill in the art would easily be able to reproduce the present invention from the present specification. The following embodiments, drawings, and the like of the

20

25

40

45

present invention illustrate preferable embodiments of the present invention, and are there to give examples and for the purpose of explanation; however, the present invention is not limited thereto. It will be obvious to a person of ordinary skill in the art that various modifications may be implemented based on the content of the present specification within the intention and scope of the present invention disclosed in the present specification.

[0008] Fig. 1 is a schematic diagram illustrating a method for diffusing and permeating a creep reinforcement material into a heat-resistant metal member, to explain an embodiment of the present invention. Fig. 2 is a schematic cross-section illustrating a cross-section of Fig. 1, to explain an embodiment of the present invention. In the present embodiment, explanation is of an example of a case in which an already installed (including repaired cases thereof) or unused, or a degraded, high temperature pipe manufactured using a heat-resistant metal material, is employed as a heat-resistant metal member 10, however, there is no limitation thereto. The heat-resistant metal member 10 may be another high temperature member manufactured using a heat-resistant metal material, such as an already installed (including repaired cases thereof) or unused, or a degraded, turbine.

[0009] As illustrated in Fig. 1 and Fig. 2, in the method according to the present invention for diffusing and permeating a creep reinforcement material into a heat-resistant metal member 10, first the creep reinforcement material is coated or thermally sprayed onto a surface of the heat-resistant metal member 10. Then a section 25 onto which the creep reinforcement material has been coated or thermally sprayed is covered by a heat-resistant covering member 30, and the heat-resistant covering member 30 is secured so as to make contact with the section 25. Next, the heat-resistant metal member 10 covered by the heat-resistant covering member 30 is heated for a specific duration at a temperature of 1000°C or greater using a heater 40.

[0010] As mentioned above, the heat-resistant metal member 10 coated or thermally sprayed with the creep reinforcement material is covered by the heat-resistant covering member 30 and is heated to a temperature of 1000°C or greater, and thus compressive force acts on the heat-resistant metal member as it thermally expands in a direction toward an outer periphery, restraining thermal expansion of the heat-resistant metal member in the direction toward the outer periphery, and enabling the creep reinforcement material on the surface of the heatresistant metal member 10 to be efficiently diffused and permeated into the heat-resistant metal member 10. Thus, in cases in which the heat-resistant metal member 10 is a degraded member or an already installed member, by utilizing the force from thermal expansion in the direction toward the outer periphery of the heat-resistant metal member 10, creep voids and cracks in the heat-resistant metal member 10 and a weld 20 thereof are efficiently repaired, enabling regeneration of the heat-resistant

metal member 10 and the weld 20 thereof to be achieved. Moreover, structural strengthening of the heat-resistant metal member 10 and the weld 20 thereof can be achieved accompanying restoration of the structure of the heat-resistant metal member 10 and the weld 20 thereof. The creep strength is accordingly enhanced, enabling the lifespan to be extended to that of a new member or greater. On the other hand, in cases in which the heat-resistant metal member 10 is an unused member, structural strengthening of the heat-resistant metal member 10 and the weld 20 thereof can be achieved, thereby enhancing the creep strength and enabling the lifespan to be extended to that of a new member or greater.

[0011] In the method for diffusing and permeating a creep reinforcement material into the heat-resistant metal member 10 according to the present invention, etching treatment, or shot peening and etching treatment, may be performed on the section 25 to be coated or thermally sprayed with the creep reinforcement material prior to coating or thermally spraying the creep reinforcement material on the surface of the heat-resistant metal member 10. Such processing enables work hardening of the surface layer of the heat-resistant metal member 10 to be performed by plastic deformation, enables residual compressive stress to be imparted to the surface of the heat-resistant metal member 10, and enables any oxidized film on the surface of the heat-resistant metal member 10 to be removed.

[0012] In the method for diffusing and permeating a creep reinforcement material into the heat-resistant metal member 10 according to the present invention, processing to remove (reduce) residual stress, such as stress relief or tension annealing processing, may be performed after the heat-resistant metal member 10 covered by the heat-resistant covering member 30 has been heated to a temperature of 1000°C or greater using the heater 40. More specifically, after the heat-resistant metal member 10 covered by the heat-resistant covering member 30 has been heated to a temperature of 1000°C or greater using the heater 40, the heat-resistant metal member 10 may be first cooled to room temperature, then reheated to a temperature of an A₁ transformation point or greater (preferably from 10°C to 100°C above 1000°C) for a specific duration (for example, from approximately several hours to approximately 24 hours).

[0013] Moreover, in the method to diffuse and permeate a creep reinforcement material into the heat-resistant metal member 10 according to the present invention, in order to restrict thermal expansion of the heat-resistant metal member 10 toward the outside in the length direction thereof (in directions toward the ends of the heat-resistant metal member 10) occurring when the heat-resistant metal member 10, which has been coated or thermally sprayed with the creep reinforcement material, is covered by the heat-resistant covering member 30 and heated by the heater 40, the heat-resistant metal member 10 may be secured in sections not being heated by the heater 40, by, for example, two clamps so as to sandwich

25

30

35

40

45

50

55

the section being heated by the heater 40.

[0014] In cases in which the section heated by the heater 40 is small compared to the overall heat-resistant metal member 10, there is no need to secure the heat-resistant metal member 10 in sections not being heated by the heater 40 with clamps or the like, since thermal expansion toward the outside in the length direction of the heat-resistant metal member 10 in the section being heated by the heater 40 is restricted by the sections not being heated by the heater 40.

[0015] Examples of the heat-resistant metal of the member 10 include 0.3Mo steel, 0.5Mo steel, 0.5Cr-0.5Mo steel, 1Cr-0.2Mo steel, 1Cr-0.5Mo steel, 1.25Cr-0.5Mo steel, 2.25Cr-1Mo steel, 5Cr-0.5Mo steel, 7Cr-0.5Mo steel, 9Cr-1Mo steel, 0.3Cr-Mo-V steel, 0.5Cr-Mo-V steel, 9Cr-Mo-V steel, 12Cr-Mo-V steel, 1Cr-1.25Mo-0.25V steel, 9Cr-1Mo-W steel, SUS304, SUS304L, SUS316, SUS316L, SUS316TI, SUS317, SUS321, SUS347H, SUS310S, Super304, SUS904L, NCF600, NCF601, NCF800, and NCF800H; however, there is no limitation thereto. Any known material used for members employed in thermal or nuclear power generation units or other high temperature plants may be employed as the heat-resistant metal for the member 10.

[0016] There are no particular limitations to the creep reinforcement material, as long as it contains an element which has a melting point of 1000°C or greater and in which precipitation strengthening and solid solution strengthening occur upon heating to a temperature of 1000°C or greater so as to enable creep strength to be enhanced. Thus, for example, according to the substance of the heat-resistant metal member 10, the creep reinforcement material may contain any one or a plurality of elements appropriately selected from B (boron), W (tungsten), Cr (Chromium), Mo (molybdenum), Nb (niobium), V (vanadium), Hf (hafnium), Zr (zirconium), Ti (titanium), Cu (copper), and Co (cobalt). In cases in which the creep reinforcement material is coated on the surface of the heat-resistant metal member 10, powdered creep reinforcement material may be employed as it is, or a coating agent of the creep reinforcement material in a liquid form or paste form using a binder, solvent, adhesive or the like may be employed. In cases in which the creep reinforcement material is thermally sprayed on the surface of the heat-resistant metal member 10, for example, a known thermal spray method may be appropriately employed, such as a plasma spraying method using powdered creep reinforcement material. Note that coating or thermally spraying of the creep reinforcement material on the surface of the heat-resistant metal member 10 may be performed over the entire outer peripheral surface of the heat-resistant metal member 10 as in the present embodiment, or may be performed on a part of the surface of the heat-resistant metal member 10.

[0017] There are no particular limitations to the heat-resistant covering member 30, as long as it is capable of covering the section 25 coated or thermally sprayed with the creep reinforcement material so as to make contact

with the section 25, as long as it is made from a heatresistant material that restrains thermal expansion in the section 25 in the direction toward the outer periphery of the heat-resistant metal member 10 occurring when heated to the heating temperature mentioned above, and is able to maintain the approximate profile of the heat-resistant metal member 10 at the section 25. A material having a lower thermal expansion coefficient than the heat-resistant metal member 10 at temperatures of the heating temperature mentioned above or greater is preferably employed for the heat-resistant covering member 30. In cases in which the heat-resistant covering member 30 is configured from a heat-resistant material different from that of the heat-resistant metal member 10, yet having a thermal expansion coefficient of about the same as the heat-resistant metal member 10, or from a heat resistant material having a higher thermal expansion coefficient than the heat-resistant metal member 10, in order to restrain the thermal expansion of the heat-resistant covering member 30 occurring when heated to the heating temperature mentioned above, the outer periphery of the heat-resistant covering member 30 may be secured by a member of a heat-resistant material having a lower thermal expansion coefficient than the heat-resistant metal member 10 at or above the heating temperature mentioned above, so as to maintain the profile of the heat-resistant covering member 30.

[0018] Examples of the heat-resistant material of the heat-resistant covering member 30 include ceramics such as alumina, zirconia, aluminum nitride, silicon carbide, silicon nitride, cordierite, sialon, zircon, and mullite, and alloys such as Alloy 903, Alloy 909, and HRA 929. [0019] The heat-resistant covering member 30 is, for example, of a cord, plate, or clamp shape. Securing of the above may be performed by, for example, wrapping a cord-shaped or plate-shaped heat-resistant covering member 30 around the outer periphery of the heat-resistant metal member 10 at the section 25 coated or thermally sprayed with the creep reinforcement material, by attaching a clamp-shaped heat-resistant covering member 30 to the outer periphery of the heat-resistant metal member 10 at the section 25 coated or thermally sprayed with the creep reinforcement material, or by attaching a heat-resistant covering member 30 formed in a plate shape or the like to the outer periphery of a heat-resistant metal member 10 at the section 25 coated or thermally sprayed with the creep reinforcement material using fasteners, such as clamps or screws. In the present embodiment, the heat-resistant covering member 30 is made from fittings including two substantially semi-circular arc cross-section shapes. The heat-resistant covering member 30 is then secured to the surface of the heat-resistant metal member 10 using threaded members 35 attached to flanges of these fittings, such that the inner face of the fittings contact the outer periphery of the heat-resistant metal member 10 at the section 25 coated or thermally sprayed with the creep reinforcement material. The threaded members 35 are manufactured, for example,

15

20

25

30

35

40

from the same material as the heat-resistant covering member 30.

[0020] The heating temperature of the heat-resistant metal member 10 coated or thermally sprayed with the creep reinforcement material is not particularly limited, as long as it is a temperature of 1000°C or greater. Preferably the heat-resistant metal member 10 is heated at a temperature of, or greater than, an A₃ transformation point of the component of the heat-resistant metal material of the member 10 or the creep reinforcement material having the highest A₃ transformation point (preferably from 10°C to 100°C above 1000°C) for a specific duration (for example, from approximately several hours to approximately 24 hours). Note that although the present embodiment employs, as a heating device, the high frequency heater 40, which is capable of heating the heatresistant metal member 10 coated or thermally sprayed with the creep reinforcement material, from the outer periphery thereof, there is no particular limitation thereto, as long as a heating device capable of heating the heatresistant metal member 10 at the section 25 coated or thermally sprayed with the creep reinforcement material. [0021] The product of diffusing and permeating the creep reinforcement material into the heat-resistant metal member 10 by the method described above is useful as a heat-resistant metal member with enhanced creep strength due to the creep strength being enhanced as described above.

Reference Signs List

[0022]

- 10 heat-resistant metal member
- 20 weld
- 25 section coated or thermally sprayed with creep reinforcement material
- 30 heat-resistant covering member
- 35 threaded member
- 40 high frequency heater

Claims

- A method for diffusing and permeating a creep reinforcement material into a heat-resistant metal member, the method comprising:
 - coating or thermally spraying a creep reinforcement material onto a surface of a heat-resistant metal member;
 - covering, by a heat-resistant covering member, a section coated or thermally sprayed with the creep reinforcement material, and securing the heat-resistant covering member so as to contact the section; and
 - heating the heat-resistant metal member covered by the heat-resistant covering member to

a temperature of 1000°C or greater, the creep reinforcement material containing one or a plurality of elements selected from B, W, Cr, Mo, Nb V, Hf, Zr, Ti, Cu, and Co.

- 2. The method according to claim 1, wherein, after heating the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000°C or greater, the heat-resistant metal member covered by the heat-resistant covering member is cooled and re-heated to a temperature of an A₁ transformation point or greater.
- 3. A heat-resistant metal member with enhanced creep strength,

the heat-resistant metal member being obtained by

coating or thermally spraying a creep reinforcement material onto a surface of a heat-resistant metal member,

covering, by a heat-resistant covering member, a section coated or thermally sprayed with the creep reinforcement material, and securing the heat-resistant covering member so as to contact the section, and

heating the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000°C or greater; and

the creep reinforcement material containing one or a plurality of elements selected from B, W, Cr, Mo, Nb, V, Hf, Zr, Ti, Cu, and Co.

4. The heat-resistant metal member according to claim 3, wherein

the heat-resistant metal member is obtained by, after heating the heat-resistant metal member covered by the heat-resistant covering member to a temperature of 1000°C or greater, cooling and re-heating to a temperature of an A_1 transformation point or greater.

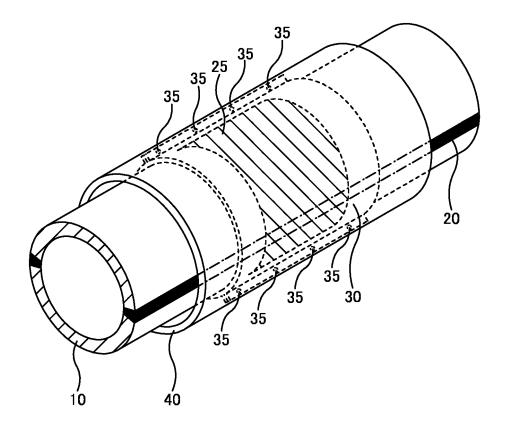


FIG. 1

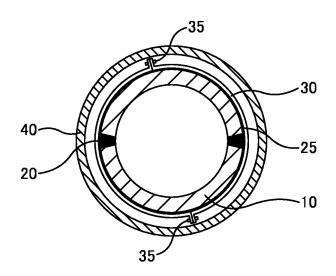


FIG. 2

EP 3 050 997 A1

INTERNATIONAL SEARCH REPORT International application No. PCT/JP2013/075927 A. CLASSIFICATION OF SUBJECT MATTER C23C4/06(2006.01)i, C21D1/34(2006.01)i, C21D9/08(2006.01)i, C21D9/50 5 (2006.01)i, C23C4/18(2006.01)i, C23C26/00(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C23C4/06, C21D1/34, C21D9/08, C21D9/50, C23C4/18, C23C26/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013 15 Toroku Jitsuyo Shinan Koho Kokai Jitsuyo Shinan Koho 1971-2013 1994-2013 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. JP 04-176856 A (NKK Corp.), 1 - 424 June 1992 (24.06.1992), claims 2, 3; examples 2, 3 25 (Family: none) Χ JP 11-037864 A (Aisin Seiki Co., Ltd.), 1 - 412 February 1999 (12.02.1999), claims 1, 5; paragraphs [0014], [0015], [0036], 30 (Family: none) 35 × Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: 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 document defining the general state of the art which is not considered to "E" earlier application or patent but published on or after the international filing 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 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) 45 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 referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 50 03 December, 2013 (03.12.13) 10 December, 2013 (10.12.13) Name and mailing address of the ISA/ Authorized officer Japanese Patent Office 55 Telephone No. Facsimile No.

Form PCT/ISA/210 (second sheet) (July 2009)

EP 3 050 997 A1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/075927

| C (Continuation | a). DOCUMENTS CONSIDERED TO BE RELEVANT | .0137 0 7 3 3 2 7 |
|-----------------|--|----------------------|
| ` | | Delegant 12 N |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages JP 08-176786 A (Praxair S.T. Technology, Inc.), | Relevant to claim No |
| A | O9 July 1996 (09.07.1996), claims 1 to 3; paragraphs [0001] to [0008], [0013], [0016], [0020] to [0022], [0027], [0028], [0034] & US 5652028 A | 1,3 |
| х | JP 02-277760 A (MTU Motoren-und Turbinen-Union Muenchen GmbH), 14 November 1990 (14.11.1990), claims 3, 6, 7; Industrial Field of Invention; Problems that the Invention is to solve; examples | 1,3 |
| | & US 5232789 A | |
| A | JP 2002-257163 A (Daido Seimitsu Kogyo Kabushiki Kaisha), 11 September 2002 (11.09.2002), paragraph [0004] (Family: none) | 1-4 |
| A | JP 04-002761 A (NKK Corp.), 07 January 1992 (07.01.1992), claims 1, 3, 4; examples (Family: none) | 2,4 |
| | | |
| | | |
| | | |
| | | |
| | | |

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

EP 3 050 997 A1

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

• JP 3793966 B **[0002]**