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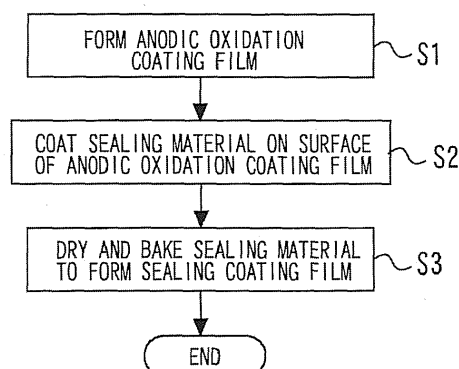
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(54) **METHOD FOR FORMING HEAT INSULATING FILM, AND STRUCTURE OF HEAT INSULATING FILM**

(57) A method for forming a heat insulating film includes: a step of subjecting an aluminum alloy constituting a surface of a base material to an anodic oxidation treatment (S1) to form an anodic oxidation coating film having pores formed in the surface thereof; a step of coating on the surface of the anodic oxidation coating film (S2) a sealing material that includes a silicon-based poly-

mer solution and particles of a heat insulating material that are dispersed in the silicon-based polymer solution and are particles having an average particle diameter that is larger than an average pore diameter of the pores; and a step of drying and baking (S3) the sealing material to form a sealing coating film.

*Fig. 1*



## Description

### BACKGROUND

#### Field of the Invention

[0001] This invention relates to a method for forming a heat insulating film, and a structure of a heat insulating film.

#### Background Art

[0002] A method for forming a heat insulating film in an umbrella portion of an engine valve has already been disclosed in Japanese Patent Laid-Open No. 2013-014830. Specifically, the aforementioned conventional method includes a first step of forming an aluminum plating film over the entire circumference of an engine valve, a second step of, after formation of the aluminum plating film, subjecting the entire circumference of the engine valve to an anodic oxidation treatment to form an anodic oxidation coating film, and a third step of, after formation of the anodic oxidation coating film, subjecting an umbrella portion of the engine valve to a sealing treatment to form a sealing coating film. According to this conventional method, a heat insulating film can be obtained that has a structure in which a sealing coating film is formed on an anodic oxidation coating film. Further, according to the engine valve on which the above described heat insulating film is formed, in addition to improving the heat resistance and a heat insulating property of a combustion chamber of the engine, a heat radiation property can also be improved.

[0003] Other prior arts include Japanese Patent Laid-Open No. 2012-047110, Japanese Patent Laid-Open No. 2013-060620, and Japanese Patent Laid-Open No. 2012-172619.

[0004] In this connection, when performing anodic oxidation treatment of an aluminum alloy, there is the problem that because the formation of the anodic oxidation coating film is affected by inclusions that are included in the aluminum alloy, the surface of the anodic oxidation coating film that is formed is not smooth, and minute concavities and convexities arise thereon. This problem can also arise in a similar manner in the aforementioned first and second steps in a case where an aluminum alloy plating film is formed on the surface of the engine valve and the plating film is thereafter subjected to an anodic oxidation treatment.

[0005] When concavities and convexities arise on the surface of an anodic oxidation coating film, a heat transfer area thereof increases. If the heat transfer area increases, an effect of improving the heat insulating property that is obtained by the anodic oxidation coating film is weakened. If concavities and convexities have arisen on the surface of the anodic oxidation coating film, the fluidity of a flame that arises inside the combustion chamber decreases, and the combustion efficiency deteriorates.

In this respect, by forming the sealing coating film in the above described third step, the surface of the heat insulating film having a structure in which the anodic oxidation coating film and the sealing coating film are formed can be made smooth to a certain extent. Ideally, it is desirable for the surface of the heat insulating film to be made as smooth as the surface of the aluminum alloy prior to the anodic oxidation treatment.

[0006] In this connection, the sealing coating film is formed by subjecting a sealing material that is the raw material of the sealing coating film to a drying and baking process. Consequently, in order to make the surface of the heat insulating film smooth by means of the sealing coating film, it is necessary to provide a large amount of the sealing material in concave portions of the surface of the anodic oxidation coating film to thereby make the sealing material thick at such concave portions. However, because the sealing material contains a solvent, the thicker the sealing material, the more difficult it becomes for a gas of the solvent that is generated at the time of drying and baking to escape to the outside. Therefore, there is the problem that cracks are liable to arise in the sealing coating film. Consequently, there is a trade-off relationship between thickening the sealing material to smoothen the surface of the heat insulating film, and reducing cracks in the sealing coating film, and it is difficult to achieve both a smooth surface and a reduction in the amount of cracks in a compatible manner.

### SUMMARY

[0007] The present invention has been conceived in view of the above described problem. That is, an object of the present invention is, with respect to a heat insulating film having a structure in which a sealing coating film is formed on the surface of an anodic oxidation coating film, to smooth the surface of the heat insulating film and also reduce the occurrence of cracks in the sealing coating film in a compatible manner.

[0008] A first aspect of the present invention is a method for forming a heat insulating film, including:

a step of subjecting an aluminum alloy constituting a surface of a base material to an anodic oxidation treatment to form an anodic oxidation coating film having a surface in which pores are formed;  
a step of coating on the surface of the anodic oxidation coating film a sealing material that includes a silicon-based polymer solution and particles of a heat insulating material that are dispersed in the silicon-based polymer solution and are particles having an average particle diameter that is larger than an average pore diameter of the pores; and  
a step of drying and baking the sealing material to form a sealing coating film.

[0009] A second aspect of the present invention is in accordance with the first invention, wherein the particles

may be particles that have a hollow structure.

[0010] Further, in a third aspect of the present invention, an average primary particle diameter of the particles may be greater than 30 nm.

[0011] A fourth aspect of the present invention is a structure of a heat insulating film that is formed by a formation method according to any one of the first to third inventions, and may include:

an aluminum alloy constituting a surface of a base material;

an anodic oxidation coating film that is formed on a surface of the aluminum alloy, and that has a surface in which pores are formed; and

a sealing coating film that is formed so as to cover an opening portion of the pores, and that includes particles of a heat insulating material having an average particle diameter that is larger than an average pore diameter of the pores.

[0012] A fifth aspect of the present invention is in accordance with the fourth invention, wherein:

the particles may be particles that have a hollow structure; and

a porosity of the sealing coating film may be from 27.3 to 57.7%.

[0013] According to the first aspect of the present invention, a sealing treatment can be performed using a sealing material that includes a silicon-based polymer solution and particles of a heat insulating material that are dispersed in the silicon-based polymer solution and are particles having an average particle diameter that is larger than an average pore diameter of pores of an anodic oxidation coating film. In the case of using a sealing material including particles of a heat insulating material of the aforementioned size, the occurrence of cracks in a drying and baking process can be suppressed in comparison to when using a sealing material that does not include the particles. Therefore, the occurrence of cracks can be suppressed even when a sealing material is made thicker by providing a large amount thereof on concave portions of the surface of an anodic oxidation coating film. Further, the surface of the heat insulating film can be made smooth by means of a thick sealing coating film that is formed by drying and baking of the sealing material.

[0014] According to the second aspect of the present invention, since a heat insulating function of air inside particles that have a hollow structure can be utilized, a heat insulating film can be formed that has a high heat insulating property in comparison to a heat insulating film that does not include particles that have a hollow structure.

[0015] According to the third aspect of the present invention, a heat insulating film that has a high heat insulating property can be formed by using particles which

have an average primary particle diameter that is greater than 30 nm.

[0016] According to the fourth aspect of the present invention, since a sealing coating film is provided that is formed so as to cover an opening portion of pores of an anodic oxidation coating film, a structure of a heat insulating film having a high heat insulating property can be provided that utilizes a heat insulating function of air inside the pores that is located at a deeper place than the opening portion.

[0017] According to the fifth aspect of the present invention, a structure of a heat insulating film having a high heat insulating property that is obtained by means of a sealing coating film in which the porosity is between 27.3 and 57.7% can be provided.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

Fig. 1 is a flowchart for describing an embodiment of a method for forming a heat insulating film of the present invention;

Fig. 2 is a vertical cross-sectional view of an anodic oxidation coating film;

Fig. 3 is a partially enlarged schematic view of the anodic oxidation coating film shown in Fig. 2;

Fig. 4 is a vertical cross-sectional view of a heat insulating film formed by the formation method of the embodiment;

Fig. 5A is a cross-sectional view of a heat insulating film formed using a sealing material that does not include hollow silica particles;

Fig. 5B is a cross-sectional view of a heat insulating film formed using a sealing material that does not include hollow silica particles;

Fig. 6A is a view illustrating a process for forming a sealing coating film shown in Fig. 5;

Fig. 6B is a view illustrating a process for forming a sealing coating film shown in Fig. 5;

Fig. 6C is a view illustrating a process for forming a sealing coating film shown in Fig. 5;

Fig. 7 is a view for describing the periphery of a combustion chamber to which a structure of a heat insulating film of the present invention is applied;

Fig. 8 is a partially enlarged schematic view of the heat insulating film shown in Fig. 7;

Fig. 9 is a view showing results of measuring a thermal conductivity  $\lambda$ ;

Fig. 10 is a view showing results of measuring a volumetric heat capacity  $C$ ; and

Fig. 11 is a view showing results of measuring a surface roughness  $R_a$ .

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] Hereunder, an embodiment of a method for

forming a heat insulating film and of a structure of a heat insulating film according to the present invention will be described referring to Fig. 1 to Fig. 11. Note that, for each of the drawings, the same or corresponding portions are denoted by the same reference numerals, and a description of such portions is simplified or omitted.

[Method for forming heat insulating film]

**[0020]** First, an embodiment of the method for forming a heat insulating film of the present invention will be described. Fig. 1 is a flowchart for describing the embodiment of the method for forming a heat insulating film. In the present embodiment, first, an anodic oxidation coating film is formed on the surface of an aluminum alloy by subjecting a base material to an anodic oxidation treatment (step S1). In the present step, a treatment apparatus (not illustrated) that includes a flow channel through which an electrolytic solution is circulated and a pair of electrodes is used. Further, in the present step, a base material is used that is made of aluminum alloy. However, instead of a base material made of aluminum alloy, a base material may be used in which an aluminum alloy plating film is formed on a surface such as heat-resisting steel, carbon steel, or a titanium material.

**[0021]** In step S1, specifically, the aforementioned base material is placed in the aforementioned treatment apparatus, and a voltage is applied between the aforementioned pair of electrodes while circulating an electrolytic solution through the aforementioned flow channel. By this means, an anodic oxidation coating film is formed on the surface of the base material. The anodic oxidation coating film is a coating film of porous alumina that has a large number of pores that open at the surface thereof (described in detail later). By means of this porous structure, the anodic oxidation coating film realizes a low thermal conductivity and a low heat capacity per unit volume (described in detail later).

**[0022]** However, the surface of the anodic oxidation coating film is rough in comparison to the surface of the base material before the anodic oxidation treatment. Fig. 2 is a vertical cross-sectional view of the anodic oxidation coating film. As shown in Fig. 2, concavities and convexities have arisen on the surface of an anodic oxidation coating film 10, and a surface roughness (arithmetic mean roughness) Ra thereof is an average of 4 to 5  $\mu\text{m}$ . The reason concavities and convexities arise on the surface of the anodic oxidation coating film 10 is that inclusions that are contained in the aluminum alloy affect the formation of the anodic oxidation coating film 10. One object of steps S2 and S3 that are described hereunder is to smooth the surface of a heat insulating film in which the anodic oxidation coating film 10 is a constituent element.

**[0023]** The description of the present embodiment will now be continued referring again to Fig. 1. After step S1, a sealing material is coated onto the surface of the anodic oxidation coating film (step S2). In the present step, a

sealing material is used that includes a silicon-based polymer solution that includes silicon in a main chain backbone (more specifically, a polymer solution including polysilazane or polysiloxane and an ether-based solvent), and silica particles that are dispersed in the silicon-based polymer solution. The polymer solution may include an additive as necessary. A dispersant that enhances the dispersibility of the particles, a leveling agent, a surfactant, a viscosity modifier and the like may be mentioned as examples of the additive. The silica particles used in the present step have an average primary particle diameter (average particle diameter before the particles agglomerate and become secondary particles) that is larger than an average pore diameter of pores of the anodic oxidation coating film, and the silica particles also have a hollow structure. However, silica particles with a solid structure may be used instead of the silica particles with a hollow structure (hereunder, referred to as "hollow silica particles"), and particles of a heat insulating material other than silica (for example, alumina ( $\text{Al}_2\text{O}_3$ ), zirconia ( $\text{ZrO}_2$ ), or titania ( $\text{TiO}_2$ ) particles) may also be used. Further, two or more kinds among the aforementioned three kinds of particles may be used at the same time.

**[0024]** The average pore diameter of the pores of the anodic oxidation coating film is approximately 30 nm. Therefore, in the present step, hollow silica particles for which the average primary particle diameter is greater than 30 nm (preferably, 50 nm) are used. However, a target value of the surface roughness Ra of the heat insulating film that is formed by the present embodiment is approximately 1  $\mu\text{m}$ , and therefore in the present step hollow silica particles are used with respect to which an average secondary particle diameter is less than 1  $\mu\text{m}$  (preferably 500 nm, more preferably 150 nm).

**[0025]** Here, the term "average pore diameter" refers to an arithmetic mean diameter that is determined by photographing sectional images at a plurality of magnifications using a scanning electron microscope and digitalizing the obtained images by a scanner input method, and thereafter calculating a distribution of diameters of circles having an area that is equal to the area of respective pores extracted by computer image analysis. Further, the term "average primary particle diameter" refers to an arithmetic mean diameter that is determined by photographing transparent particle images at a plurality of magnifications using a transmission electron microscope and digitalizing the obtained images by a scanner input method, and thereafter calculating a distribution of diameters of circles having an area that is equal to a projected area of respective pores extracted by computer image analysis. Furthermore, the term "average secondary particle diameter" refers to an average particle diameter (D50 value) that is obtained by a dynamic scattering method, and is a diameter that can be simply measured by a commercially available particle size analysis and measurement apparatus.

**[0026]** The mixing ratio of the hollow silica particles in the sealing material is appropriately adjusted in accord-

ance with the target value (for example, a value in a range from 27.3% to 57.7%) of the porosity of the sealing coating film to be formed after drying and baking of the sealing material (after step S3).

**[0027]** The surface of the anodic oxidation coating film after application of the sealing material will now be described referring to Fig. 3. Fig. 3 is a partially enlarged schematic view of the anodic oxidation coating film 10 shown in Fig. 2. As shown in Fig. 3, the anodic oxidation coating film 10 is constituted by alumina 10a having a nonuniform length in a perpendicular direction relative to the surface of the aluminum alloy, and pores 10b. Further, a sealing material 12 constituted by a silicon-based polymer solution 14 and hollow silica particles 16 is provided so as to cover an opening portion 10c of the pores 10b. A large amount of the sealing material 12 is provided at concave portions of the surface of the anodic oxidation coating film 10, and a small amount of the sealing material 12 is provided at protruding portions of the anodic oxidation coating film 10.

**[0028]** The description of the present embodiment will now be continued referring again to Fig. 1. A method for coating the sealing material in step S2 is not particularly limited, and examples thereof include a spray method, a blade coating method, a spin coating method, and a brush application method.

**[0029]** After step S2, the sealing material is dried and baked to form a sealing coating film (step S3). The conditions (temperature, time period and the like) at the time of drying and baking are appropriately adjusted in accordance with the thickness of the sealing material that was coated onto the surface of the anodic oxidation coating film. A heat insulating film is formed by performing the present step. Fig. 4 is a vertical cross-sectional view of a heat insulating film that is formed by the formation method of the present embodiment. As shown in Fig. 4, a sealing coating film 20 constituted by hollow silica particles 16 and silica 18 derived from a silicon-based polymer is formed on the surface of the anodic oxidation coating film 10. A heat insulating film 22 is constituted by the anodic oxidation coating film 10 and the sealing coating film 20. A surface roughness Ra of the heat insulating film 22 is equal to or less than 1  $\mu\text{m}$ . The details of the structure of the heat insulating film 22 as well as the effects obtained by the structure of the heat insulating film 22 will be described later.

**[0030]** The effects of the present embodiment will now be described referring to Figs. 5A to 6C. Heat insulating films 30a and 30b shown in Figs. 5A and 5B are heat insulating films that were formed for the purpose of comparison with the heat insulating film 22. The heat insulating film 30a is constituted by a sealing coating film 32a that does not include hollow silica particles, and the anodic oxidation coating film 10. The heat insulating film 30b shown in Fig. 5B is constituted by a sealing coating film 32b that does not include hollow silica particles, and the anodic oxidation coating film 10. The thickness of the sealing coating film 32b is greater than the thickness of

the sealing coating film 32a, and is approximately equal to the thickness of the sealing coating film 20 in Fig. 4. However, cracks 34 have arisen in the sealing coating film 32b.

**[0031]** Fig. 6A is a view illustrating a process for forming the sealing coating film 32a. Fig. 6B and Fig. 6C are views illustrating a process for forming the sealing coating film 32b. In a case where a sealing material 36a that does not include hollow silica particles is thinly coated (Fig. 6A), a drying rate of an upper part (surface part) of the sealing material 36a at the time of drying and baking is approximately equal to a drying rate of an inner part of the sealing material 36a. Consequently, gas of a solvent that is generated during drying and baking is released from the inner part of the sealing material 36a to the outside thereof. In contrast, in a case where a sealing material 36b that does not include hollow silica particles is thickly coated (Fig. 6B), the upper part of the sealing material 36b hardens before the inner part of the sealing material hardens. Consequently, gas of a solvent that is generated during drying and baking cannot escape from the inner part of the sealing material 36b, and cracks 34 arise in the sealing coating film 32b (Fig. 6C).

**[0032]** As will be understood from Figs. 5A to 6C, in the case of using a sealing material that does not include hollow silica particles, there is the problem that the thicker the coating of the sealing material, the easier it is for cracks to arise in the sealing coating film during drying and baking (Fig. 5B, Fig. 6B and Fig. 6C). Further, when the sealing material is thinly coated, since a thin sealing coating film is formed, the surface of the heat insulating film cannot be smoothed sufficiently (Fig. 5A and Fig. 6A). In contrast, according to the present embodiment, since the sealing material including hollow silica particles of the above described size is used, the gas of a solvent that is generated during drying and baking can be released from inside the sealing material to the outside. The fact that it is easy for the gas of the solvent that is generated inside the sealing material to flow along the surface of the hollow silica particles to move to the upper part of the sealing material may be mentioned as one of the reasons why the gas of the solvent can be released. Accordingly, in a case where the sealing material is thickly coated also, the generation of cracks can be favorably suppressed. Hence, a thick sealing coating film can be formed and the surface of the heat insulating film can be smoothed.

[Structure of heat insulating film]

**[0033]** Next, an embodiment of the structure of a heat insulating film according to the present invention will be described. The structure of a heat insulating film of the present invention is applied to an inner wall of a combustion chamber of an engine. Fig. 7 is a view for describing the periphery of a combustion chamber to which the structure of a heat insulating film of the present invention is applied. Note that although Fig. 7 is described on the

premise that the engine is a spark-ignition type engine, the structure of a heat insulating film of the present invention can also be applied to a compression-ignition type engine.

**[0034]** A cylinder 42 of an engine 40 is formed inside a cylinder block 44. A cylinder liner 46 is provided at an inner circumferential face of the cylinder 42. Further, inside the cylinder 42, a piston 48 is slidably disposed with respect to the cylinder liner 46. A cylinder head 50 is installed at an upper portion of the cylinder block 44. An intake port 52 and an exhaust port 54 are formed in the cylinder head 50. An intake valve 56 is provided in the intake port 52, and an exhaust valve 58 is provided in the exhaust port 54.

**[0035]** A space that is surrounded by an inner circumferential face of the cylinder liner 46, a top face of the piston 48, a bottom face of the cylinder head 50, a bottom face of an umbrella portion of the intake valve 56 and a bottom face of an umbrella portion of the exhaust valve 58 corresponds to a combustion chamber 60. That is, an inner wall of the combustion chamber 60 is constituted by the inner circumferential face of the cylinder liner 46, the top face of the piston 48, the bottom face of the cylinder head 50, the bottom face of the umbrella portion of the intake valve 56 and the bottom face of the umbrella portion of the exhaust valve 58. The heat insulating film 22 formed by the above described method is provided on the inner wall of the combustion chamber 60.

**[0036]** Fig. 8 is a partially enlarged schematic view of the heat insulating film 22 shown in Fig. 7. As shown in Fig. 8, the heat insulating film 22 has a structure that includes the anodic oxidation coating film 10 and the sealing coating film 20. The anodic oxidation coating film 10 is constituted by the alumina 10a and the pores 10b. The sealing coating film 20 is constituted by the hollow silica particles 16 and the silica 18, and is formed so as to cover the opening portions 10c.

**[0037]** The silica 18 has a lower thermal conductivity than the aluminum alloy, and has a lower heat capacity per unit volume (volumetric heat capacity) than the aluminum alloy. Further, the alumina 10a has a lower thermal conductivity and a lower volumetric heat capacity than not only the aluminum alloy, but also than a conventional ceramic-based heat insulation material. Therefore, by applying the structure of the heat insulating film 22, in addition to improving the heat resistance and the heat insulating property of the combustion chamber 60, a heat radiation property thereof can also be improved.

**[0038]** Further, according to the structure of the heat insulating film 22 including the hollow silica particles 16 of the above described size, the heat insulating property of the combustion chamber 60 can be further improved. The reason for this will now be described in detail referring to Fig. 9 to Fig. 11. Fig. 9 is a view showing results of measuring a thermal conductivity  $\lambda$  of two kinds of heat insulating films. Fig. 10 is a view showing results of measuring a volumetric heat capacity C of the two kinds of heat insulating films. The thermal conductivity  $\lambda$  and the

volumetric heat capacity C were calculated based on the following equations after measuring a specific heat capacity Cp and a thermal diffusivity  $\alpha$  with respect to two kinds of samples (a sample containing hollow silica particles and a sample that did not contain hollow silica particles).

$$\lambda = C_p \times \rho \times \alpha$$

$$C = C_p \times \rho$$

**[0039]** Where, Cp represents specific heat capacity,  $\rho$  represents density, and  $\alpha$  represents thermal diffusivity.

**[0040]** The sample containing hollow silica particles (hereunder, referred to as "sample A") was prepared as follows. First, a base material (test piece of aluminum alloy) was subjected to an anodic oxidation treatment to form an anodic oxidation coating film. Next, hollow silica particles (hollow silica particles manufactured by GRANDEX Co., Ltd (primary particle diameter 90 to 110 nm)) were mixed in a polysilazane solution (ingredients and percentages: diethyl ether 72%, poly(perhydrosilazane) 20%, and anisole 8%) and stirred adequately using a stirrer to thereby prepare a sealing material. Thereafter, the sealing material was applied five times onto the anodic oxidation coating film using a brush, and then dried and baked for 8 hours in a constant temperature oven at 180°C to thereby prepare the sample A. The sample that did not contain the hollow silica particles (hereunder, referred to as "sample B") was prepared in the same manner as the sample A except that the polysilazane solution was used as the sealing material.

**[0041]** The measurement conditions and the like for the specific heat capacity Cp and the thermal diffusivity  $\alpha$  were as follows.

#### (1) Specific heat capacity Cp

**[0042]** Measurement method: DSC method

**[0043]** Measurement apparatus: DSC Q1000 manufactured by TA Instruments

**[0044]** Reference sample: Sapphire

**[0045]** Measurement atmosphere: N<sub>2</sub> atmosphere

**[0046]** Measurement sample: After processing each sample to  $\Phi 6$  mm, the base material was dissolved in hydrochloric acid to prepare samples that were constituted only by film (2) Thermal diffusivity  $\alpha$

**[0047]** Measurement method: Laser flash method

**[0048]** Measurement apparatus: LFA 457 manufactured by NETZSCH

**[0049]** Temperature measurement method: Noncontact temperature measurement using InSb sensor Surface treatment: Graphite spray

**[0050]** Measurement atmosphere: N<sub>2</sub> atmosphere

**[0051]** Calculation technique: Base material and film were measured in an integrated state, and the thermal diffusivity of only the film was calculated by multilayer analysis including pulse width correction and heat loss.

**[0052]** The measurement results in Fig. 9 and Fig. 10 are shown as percentages based on the sample B as 100%. As shown in Fig. 9 and Fig. 10, the thermal conductivity  $\lambda$  of the sample A (with particles) is low in comparison to the sample B (without particles), and the volumetric heat capacity  $C$  of the sample A is also lower than the sample B. These results indicate that the heat insulating property of the sample A is superior to that of the sample B. The fact that the sample A includes hollow silica particles and the air in the internal space of the hollow silica particles functions similarly to the air inside the pores 10b may be mentioned as one of the reasons why the heat insulating property of the sample A is superior to that of the sample B.

**[0053]** The fact that the surface roughness  $R_a$  of the sample A is small may be mentioned as another reason why the sample A has an excellent heat insulating property. Fig. 11 is a view illustrating results of measuring the surface roughness  $R_a$ . The surface roughness  $R_a$  was measured with respect to both the sample A and the sample B that were prepared in the same manner as described above. However, with respect to the sample A, three different kinds of samples were prepared using three kinds of sealing materials that were prepared by changing the mixing ratio of the hollow silica particles. The porosity (= volume of internal space of hollow silica particles/volume of sample  $\times$  100) after drying and baking the three kinds of sealing materials was as follows.

Sample A1: 27.3% (porosity: low)

**[0054]** Sample A2: 46.3% (porosity: medium)

**[0055]** Sample A3: 57.7% (porosity: high)

**[0056]** The surface roughness  $R_a$  was measured in accordance with JIS B601 (2001). The measurement results in Fig. 11 are shown as percentages based on the sample B as 100%. As shown in Fig. 11, the surface roughness  $R_a$  of the samples A1 to A3 (with particles) was less than that of the sample B (without particles). Further, the surface roughness  $R_a$  of the sample A3 was less than that of the sample A1 and the sample A2. The fact that the surface roughness  $R_a$  is small means that the surface of the relevant sample is smooth and a heat transfer area is small. Accordingly, it was found that the heat insulating property of the sample A is superior to that of the sample B. Further, it was found that the heat insulating property of the sample A3 is superior to that of the sample A1 and the sample A2.

## Claims

1. A method for forming a heat insulating film, comprising:

a step of subjecting an aluminum alloy constituting a surface of a base material to an anodic oxidation treatment to form an anodic oxidation coating film having a surface in which pores are formed;

a step of coating on the surface of the anodic oxidation coating film a sealing material that includes a silicon-based polymer solution and particles of a heat insulating material that are dispersed in the silicon-based polymer solution and are particles having a primary particle diameter that is larger than an outer diameter of the pores; and

a step of drying and baking the sealing material to form a sealing coating film.

2. The method for forming a heat insulating film according to claim 1, wherein the particles are particles that have a hollow structure.
3. The method for forming a heat insulating film according to claim 1, wherein the primary particle diameter of the particles is greater than 30 nm.
4. A structure of a heat insulating film that is formed by a formation method according to claim 1, comprising:

an aluminum alloy constituting a surface of a base material;

an anodic oxidation coating film that is formed on a surface of the aluminum alloy, and that has a surface in which pores are formed; and  
a sealing coating film that is formed so as to cover the surface of the anodic oxidation coating film, and that includes particles of a heat insulating material having a primary particle diameter that is larger than an outer diameter of the pores.

5. The structure of a heat insulating film according to claim 4, wherein:

the particles are particles that have a hollow structure; and  
a porosity of the sealing coating film is from 27.3 to 57.7%.

Fig. 1

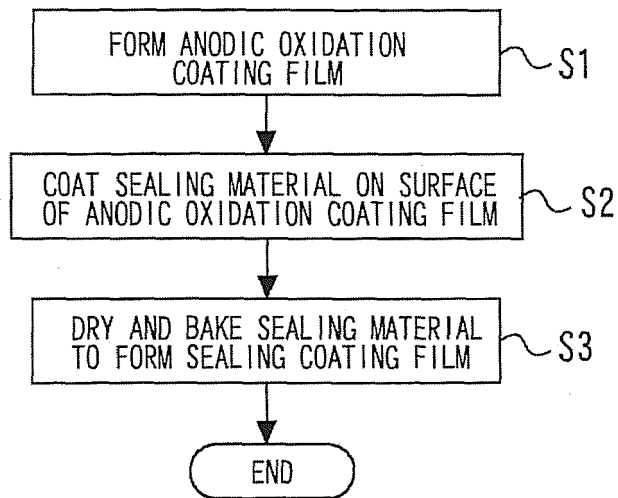


Fig. 2

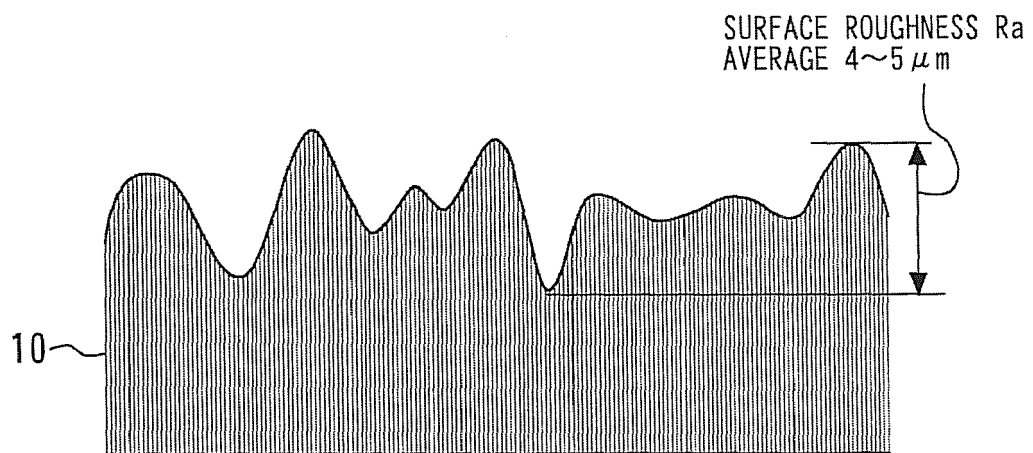


Fig. 3

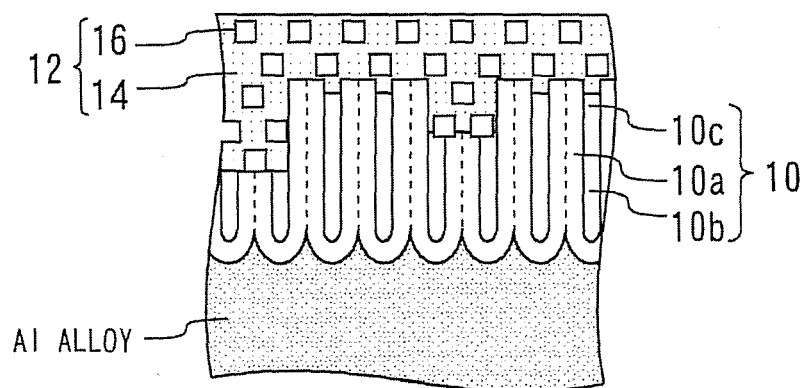
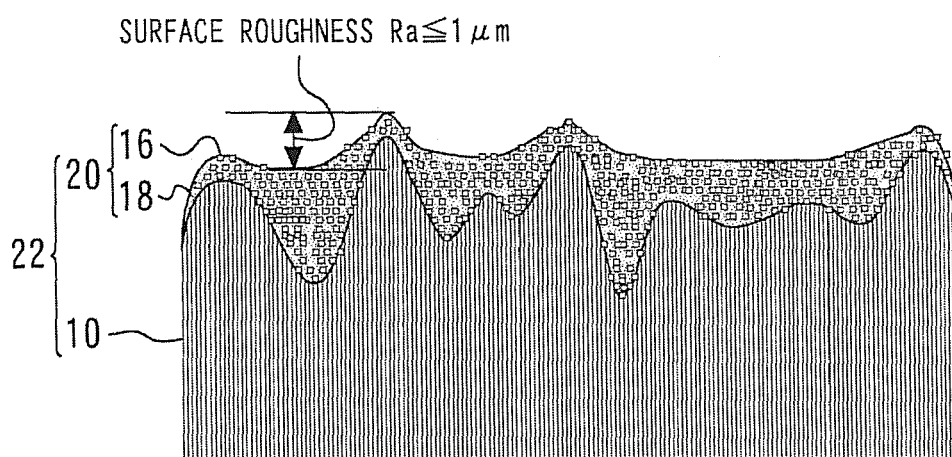
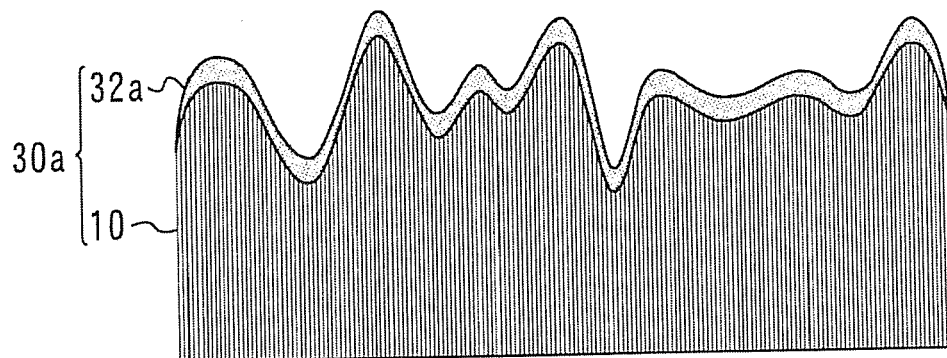


Fig. 4



*Fig. 5A*



*Fig. 5B*

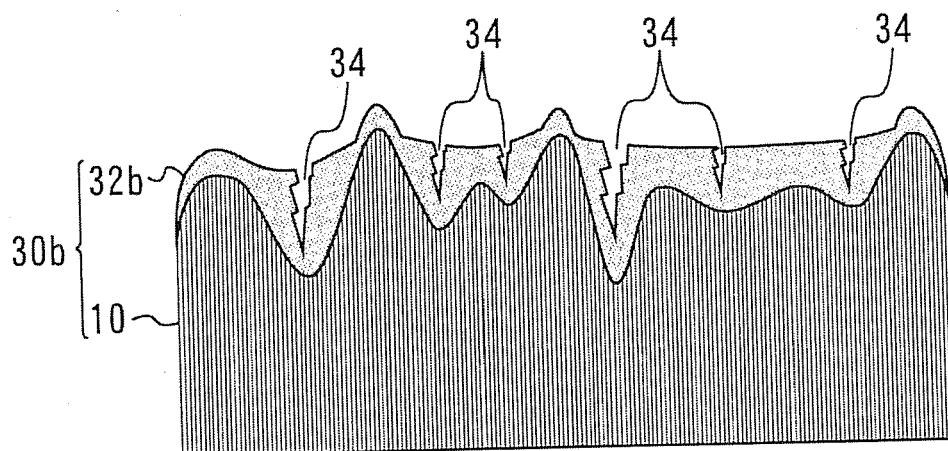


Fig. 6A

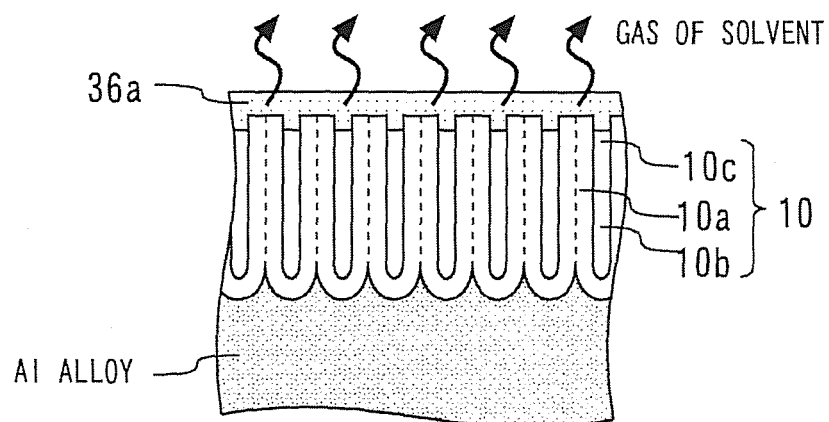


Fig. 6B

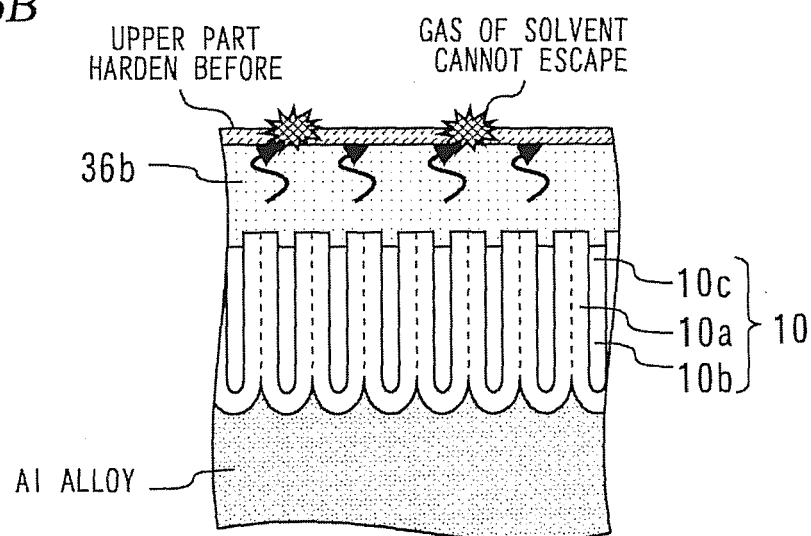


Fig. 6C

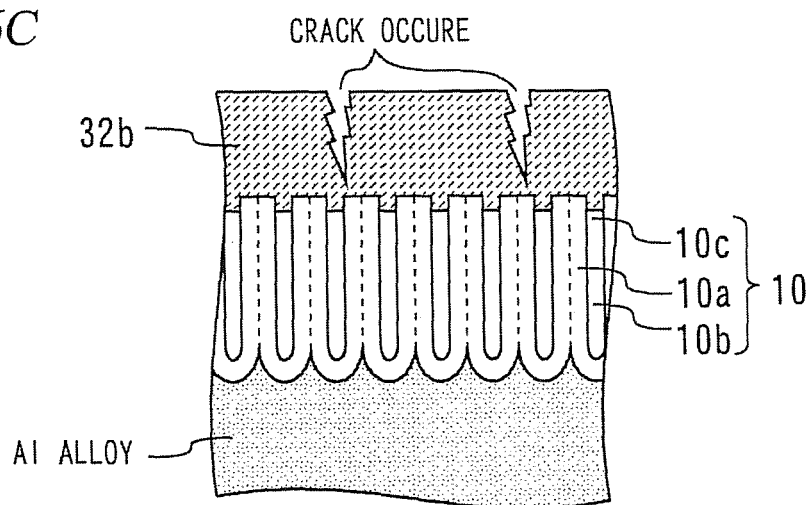


Fig. 7

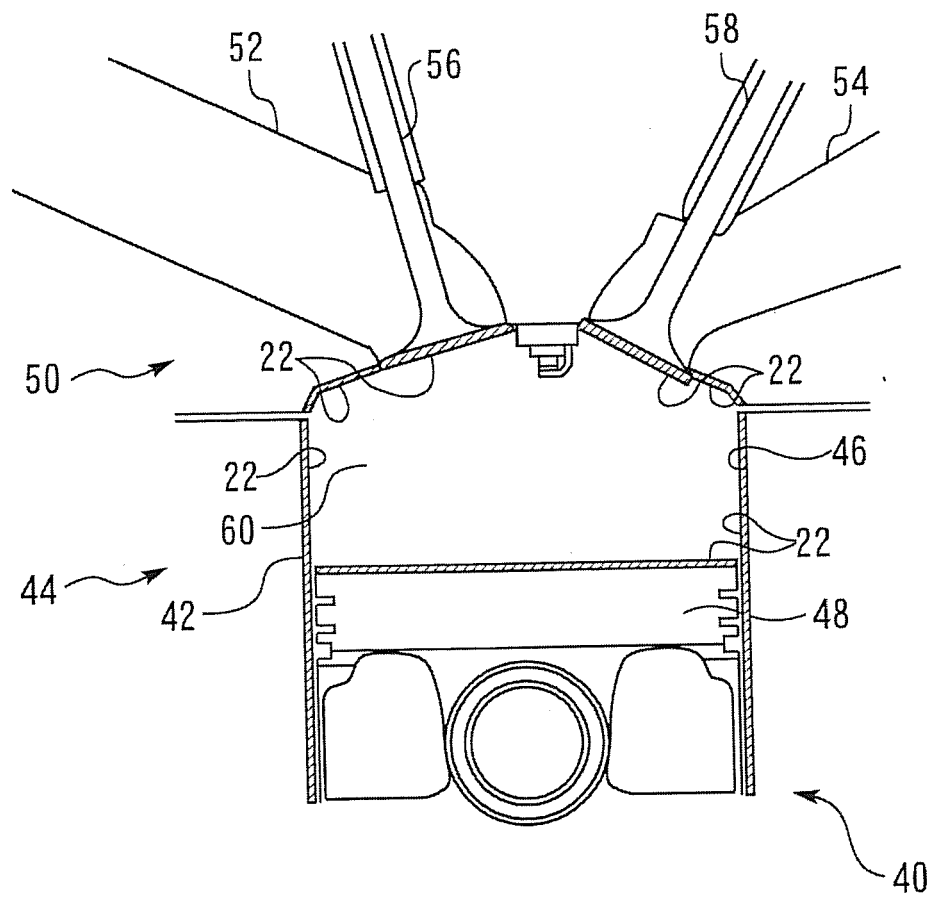
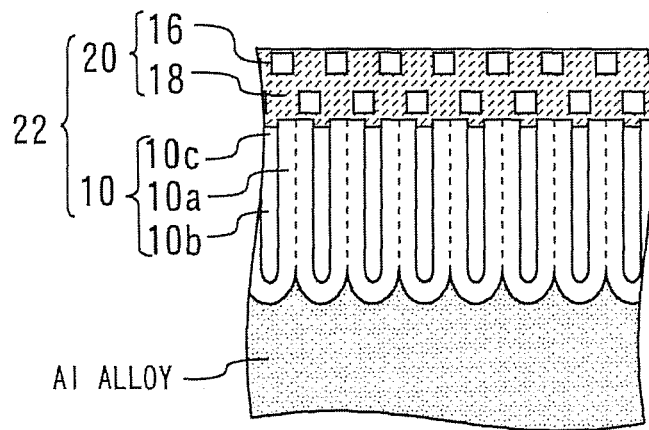
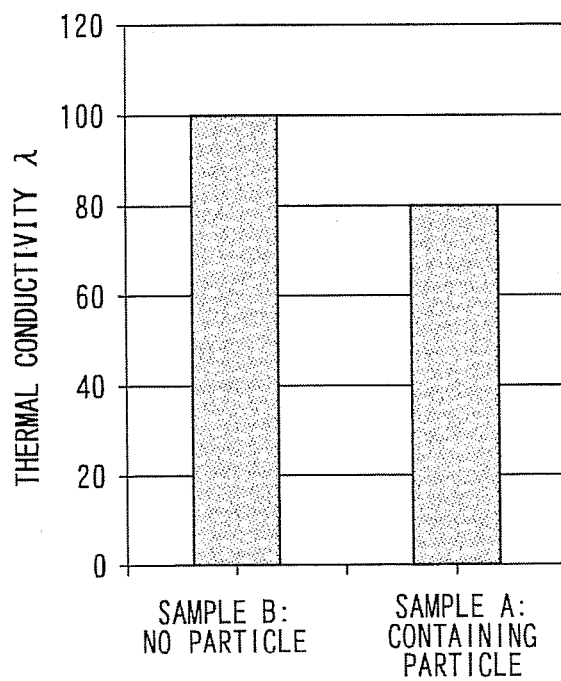


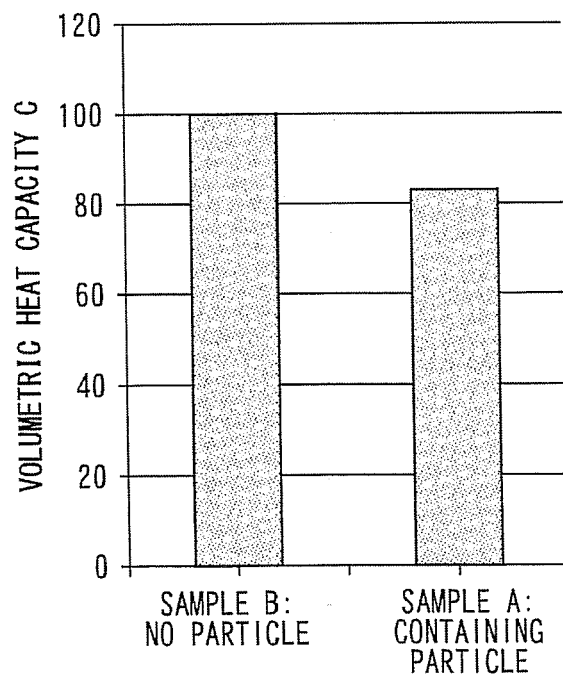
Fig. 8



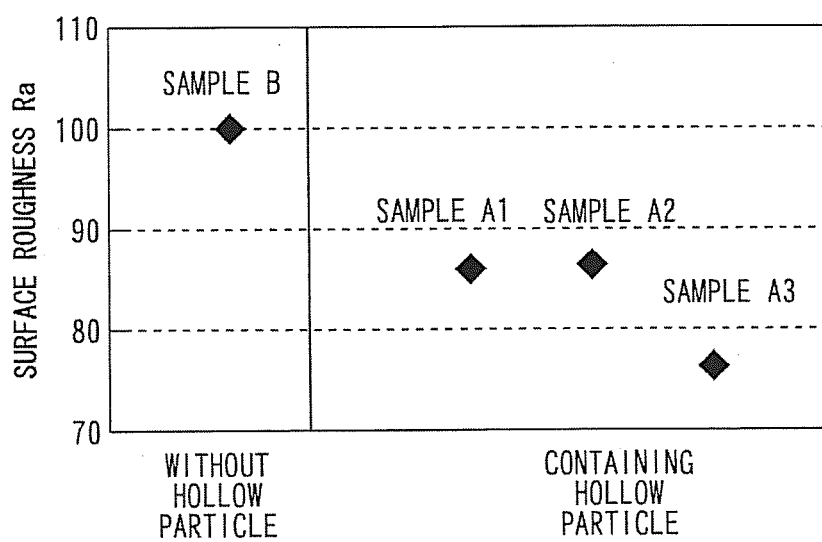
*Fig. 9*



*Fig. 10*



*Fig. 11*





## EUROPEAN SEARCH REPORT

Application Number  
EP 15 17 0930

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2014/030297 A1 (MAZDA MOTOR [JP]) 27 February 2014 (2014-02-27) * abstract * & DE 11 2013 004121 T5 (MAZDA MOTOR [JP]) 30 April 2015 (2015-04-30) * abstract * * examples 1, 2 * * table 1 * * paragraphs [0058], [0090] *	1-5	INV. C25D11/04 C25D11/24
X	CA 2 847 549 A1 (NBC MESHTEC INC [JP]) 14 March 2013 (2013-03-14) * abstract * * figures 2, 3 * * claims 1-3, 7 * * paragraph [0049] *	1,3,4	
X	WO 2007/048513 A2 (CLARIANT INT LTD [CH]; BRAND STEFAN [DE]; DIERDORF ANDREAS [DE]; LIEBE) 3 May 2007 (2007-05-03) * abstract * * page 5, line 11 - page 6, line 7 * * page 9, lines 12-22 *	1,4	TECHNICAL FIELDS SEARCHED (IPC) C25D
A	WO 2014/024494 A1 (AISIN SEIKI [JP]; AKROS CO LTD [JP]) 13 February 2014 (2014-02-13) * abstract * & US 2015/204269 A1 (HIRATSUKA ICHIRO [JP] ET AL) 23 July 2015 (2015-07-23) * abstract * * paragraphs [0003], [0007], [0100], [0117] *	2,5	
A	EP 2 679 791 A1 (AISIN SEIKI [JP]; AKROS CO LTD [JP]) 1 January 2014 (2014-01-01) * abstract * * paragraphs [0010], [0015], [0032] *	2,5	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 15 October 2015	Examiner Lange, Ronny
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 15 17 0930

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-10-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014030297 A1	27-02-2014	DE 112013004121 T5	30-04-2015
		JP 2014040820 A	06-03-2014
		US 2015204233 A1	23-07-2015
		WO 2014030297 A1	27-02-2014
CA 2847549 A1	14-03-2013	AU 2012305805 A1	20-03-2014
		CA 2847549 A1	14-03-2013
		CN 103781945 A	07-05-2014
		EP 2754734 A1	16-07-2014
		JP W02013035343 A1	23-03-2015
		KR 20140057622 A	13-05-2014
		US 2014367263 A1	18-12-2014
		WO 2013035343 A1	14-03-2013
WO 2007048513 A2	03-05-2007	AR 057561 A1	05-12-2007
		CA 2627399 A1	03-05-2007
		DE 102005051755 A1	10-05-2007
		EP 1943375 A2	16-07-2008
		JP 2009513824 A	02-04-2009
		KR 20080059468 A	27-06-2008
		US 2009220806 A1	03-09-2009
		WO 2007048513 A2	03-05-2007
WO 2014024494 A1	13-02-2014	CN 204572181 U	19-08-2015
		US 2015204269 A1	23-07-2015
		WO 2014024494 A1	13-02-2014
EP 2679791 A1	01-01-2014	CN 103328797 A	25-09-2013
		EP 2679791 A1	01-01-2014
		JP 2012172619 A	10-09-2012
		US 2013327289 A1	12-12-2013
		WO 2012114676 A1	30-08-2012

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- JP 2013014830 A [0002]
- JP 2012047110 A [0003]
- JP 2013060620 A [0003]
- JP 2012172619 A [0003]