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(54) **THERMAL SPRAY MATERIAL AND METHOD FOR MANUFACTURING SAME, THERMAL SPRAYING METHOD AND THERMAL SPRAY PRODUCT**

(57) Thermal spraying may be readily carried out using fine particles which were difficult to be handled in the conventional art by using particles of a resin containing the fine particles of a ceramic or a metal as a material for thermal spraying. To produce a material for thermal spraying, the fine particles are dispersed in a liquid resin, and a cured material obtained by curing the mixture is pulverized to obtain a material for thermal spraying which contains particles having a particle diameter within a target particle diameter range, and these operations are repeated. In the second or later time production of a material for thermal spraying, over-pulverized particles which were obtained in a completed pulverization step of a cured material and have a particle diameter below the target particle diameter range are also added to a liquid resin and are dispersed in the step for dispersing fine particles in a liquid resin. Accordingly, the yield rate of a material for thermal spraying produced from the fine particles and the resin may be improved by recycling the over-pulverized particles which are too small to be used as a material for thermal spraying in a next time or later production of a material for thermal spraying.

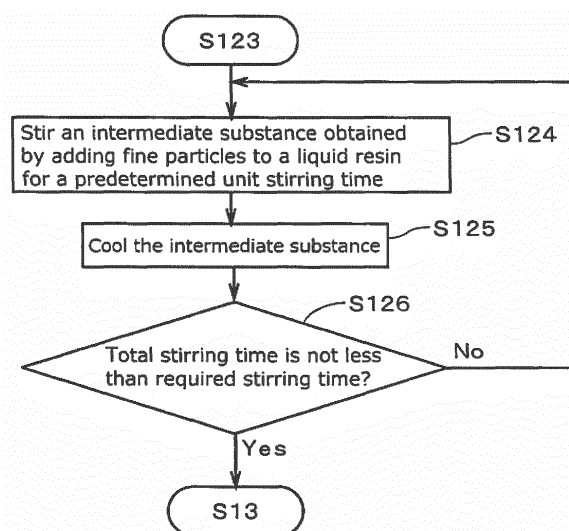


Fig. 7

Description**TECHNICAL FIELD**

5 **[0001]** The present invention relates to the technology for forming a coating on a substrate by plasma thermal spraying, flame thermal spraying, or laser thermal spraying.

BACKGROUND ART

10 **[0002]** In plasma thermal spraying, flame thermal spraying, and laser thermal spraying, a powder material, such as a metal and a ceramic, is introduced into a hot plasma flow, a hot flame flow, and a concentrated laser beam, and then a melted particle material is sprayed and deposited on a surface of a substrate to thereby form a coating. These thermal spraying methods have been established as industrial production technologies. These thermal spraying methods have no need to locate a subject in a closed space and are applicable to a large area and to a long object.

15 **[0003]** Meanwhile, the layered structural bodies using fine particles which are called nanoparticles have been applied in various field and products, such as a coating, an element, etc. Usually, those may form a dense composition or a structure by methods, such as aerosol deposition method (AD method) and chemical vapor deposition (CVD method). However, as of now, these methods may not be used under an atmosphere environment and are not suitable for a continuous production, an application to a large or long object, or their mass productions.

20 **[0004]** Thus, if nanoparticles may be used in the existing thermal spraying methods, a coating, such as a dense coating layer, will be able to be formed in a short time on a larger number of produced subjects or on a longer large object. In addition to the formation of a dense coating, the thermal spraying technology using nanoparticles enables the production of a coating having performance and functions which were not achieved by the conventional thermal spraying, such as formation of a layer in which two or more kinds of particle materials are uniformly mixed at a nanosized level or a heat insulation function having nanosized pores.

25 **[0005]** However, the lower limit of the particle diameter of a powder material which is introduced into a hot section which serves as a heat source of thermal spraying, such as plasma and flame, is about 1-5 micrometers. When the particle diameter of the powder material is smaller than the lower limit, a conveying tube for introducing the powder material into a hot section may be blocked. Further, usually, nanoparticles are aggregated and exist as particles each having a size of several ten micrometers under an atmosphere at a room-temperature. If such aggregated particles are introduced into a plasma flow, the particles become an aggregated droplet when the particles are melted in a hot plasma part and thus do not reach a substrate as nanoparticles. As a result, the properties of the nanoparticles may not be effectively utilized.

30 **[0006]** Japanese Patent Application Publication No. 2011-256465 (Document 1) discloses a flame thermal spraying. In the flame thermal spraying, slurry is obtained by preliminarily dispersing ceramic particles each having a particle diameter of 0.1-5 micrometers in a solvent which is an alcohol or kerosene. And then thermal spraying is carried out by spraying the slurry in a flame. However, in the method of Patent document 1, it is not easy to disperse the ceramic particles uniformly in a solvent when the particle diameter of the ceramic particles is too small.

35 **[0007]** Also, "Soshu Kirihaara, et al, 'ceramic dense coating on a practically used alloy substrate by plasma thermal spraying using a nanoparticle narrow line,' Japan Welding Society national conference summary, the 91st collection, September 3, 2012, p.372-373" (Document 2) discloses that a line material is obtained by dispersing nanoparticles in a light curing acrylic resin solvent and then curing it on a line using an ultraviolet ray. The nanoparticles are dispersed uniformly in the line material. Then the line material is introduced into plasma, and thus plasma thermal spraying is carried out. Thereby a high quality coating may be formed on a substrate.

40 **[0008]** By the way, in the method of Document 2, a feeding apparatus for feeding the line material is needed. Also, the optimizations of the cross-sectional area and feeding speed, etc., of the line material are needed. Further, it is not easy to use two or more materials by changing a material to another one during one step of thermal spraying.

SUMMARY

50 **[0009]** The present invention is directed to a method for producing a material for thermal spraying used for plasma thermal spraying, flame thermal spraying, or laser thermal spraying. The purpose of the present invention is to readily carry out thermal spraying using fine particles which were difficult to be handled in the conventional art. Further, the present invention is also directed to a material for thermal spraying which is produced by the method, a method for thermal spraying using the material for thermal spraying, and a product obtained by thermal spraying comprising a substrate and a coating which is formed on the substrate by the method for thermal spraying.

55 **[0010]** A method for producing a material for thermal spraying according to the present invention comprises the steps of: a) dispersing fine particles of a ceramic or a metal in a liquid resin; b) pulverizing a cured material from a mixture

obtained in the step a) to obtain a material for thermal spraying having a particle diameter which is larger than that of the fine particles and is within a predetermined target particle diameter range; and c) repeating the step a) and step b), wherein over-pulverized particles having a particle diameter below the target particle diameter range obtained when the cured material is pulverized in a completed step b) are also added to the liquid resin and are dispersed in a second or later time step a). According to the production method, thermal spraying may be readily carried out using particles which were difficult to be handled in the conventional art.

[0011] In a preferable embodiment of the present invention, the over-pulverized particles are added to the liquid resin in a second or later time step a) after the fine particles are dispersed in the liquid resin.

[0012] In another preferable embodiment of the present invention, time for pulverizing the cured material in the step b) is determined in advance based on percentages of the material for thermal spraying and the over-pulverized particles obtained in a step b).

[0013] In another preferable embodiment of the present invention, the material for thermal spraying is obtained using a sieve from the cured material after the cured material is pulverized in the step b), and the over-pulverized particles added to the liquid resin in a second or later time step a) are separated from the material for thermal spraying by a sieve in a completed step b) and are aggregated.

[0014] In another preferable embodiment of the present invention, the over-pulverized particles added to the liquid resin in the second or later time step a) are all of the over-pulverized particles obtained in a previous step b).

[0015] In another preferable embodiment of the present invention, the fine particles have an average particle diameter of not less than 25 nm and not more than 1000 nm when the average particle diameter is measured by a laser diffraction scattering method or a dynamic-light-scattering method.

[0016] In another preferable embodiment of the present invention, the liquid resin has room-temperature curing properties and wherein the step a) comprises the steps of: a1) stirring an intermediate substance obtained by adding the fine particles to the liquid resin for a predetermined unit stirring time; a2) cooling the intermediate substance after the step a1); and a3) repeating the step a1) and the step a2) until a total stirring time of the intermediate substance amounts to not less than a required stirring time.

[0017] Above-described purpose, other purposes, features, modes, and advantages will be clarified by following detailed explanations of this invention with reference to the attached figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

Fig. 1 shows a configuration of a thermal spraying apparatus.

Fig.2 shows the flow of the production of a material for thermal spraying.

Fig. 3 shows a part of the flow of the production of a material for thermal spraying.

Fig. 4 shows a cross-section of a cured material

Fig. 5 shows a part of the flow of the production of a material for thermal spraying.

Fig. 6 shows the flow of a thermal spraying operation.

Fig. 7 shows a part of the flow of the production of a material for thermal spraying.

Fig. 8 shows a cross-section of a cured material

Fig. 9 shows a cross-section of a cured material

Fig. 10 shows a cross-section of a cured material

Fig. 11 shows a cross-section of a cured material

Fig. 12 shows another example of a thermal spraying apparatus.

Fig. 13 shows the flow of a thermal spraying operation.

DESCRIPTION OF EXAMPLE EMBODIMENTS

[0019] Fig. 1 shows a configuration of a thermal spraying apparatus 1. The thermal spraying apparatus 1 is an apparatus which carries out plasma thermal spraying on a substrate 9 and comprises a thermal spraying gun 11, a gas supplying part 12, a material storing part 13, an air supplying part 14, and a material conveying part 15. The thermal spraying gun 11 generates plasma flare 8. The gas supplying part 12 supplies argon gas to the thermal spraying gun 11. The gas supplied by the gas supplying part 12 is not limited to argon gas, but may be helium gas or other gas. The material storing part 13 stores a material for thermal spraying used for thermal spraying. The air supplying part 14 supplies air to the material conveying part 15. The material conveying part 15 supplies a material for thermal spraying into the plasma flare 8 by using the air from the air supplying part 14. The gas used for the conveyance (hereinafter referred to as "carrier gas") is not limited to air.

[0020] The thermal spraying gun 11 is a spraying nozzle which carries out thermal spraying. The thermal spraying

gun 11 internally comprises a flow path 21 of argon gas. A cathode 22 is located in the center of the flow path 21. An anode 23 is located at a downstream position relative to the cathode 22 such that the flow path is surrounded by the anode 23. The plasma flare 8 blows out from a spraying hole 24 by an electrical discharge between the cathode 22 and the anode 23.

[0021] The material conveying part 15 comprises a constant-amount supplying part 31 and a conveying pipe 32. The constant-amount supplying part 31 brings out a material for thermal spraying at a constant amount per unit time from the material storing part 13 and merges the material and the carrier gas. The end of the conveying pipe 32 serves as a spraying hole 33. The material for thermal spraying blows out together with carrier gas from the spraying hole 33. The material for thermal spraying is vertically introduced from the side of the advancing direction of the plasma flare 8 toward the center of the plasma flare 8.

[0022] The material for thermal spraying is a powder. Each of the powder particles has a size which does not block the conveying pipe 32. As described later, each of the powder particles is a resin containing finer particles. The fine particles contained in the material for thermal spraying are ceramic particles or metal particles. The resin of the material for thermal spraying is burned down by the plasma flare 8, and the fine particles in a molten state or in a semimolten state flow together with the plasma flare 8 toward the substrate 9. As a result, the fine particles are deposited on the substrate 9, and thereby a coating is formed.

[0023] Next, with reference to an example of a material for thermal spraying which was actually produced (hereinafter referred to as a "production example"), the production of a material for thermal spraying will be explained. Fig. 2 shows the flow of the production of a material for thermal spraying. First, ceramic particles or metal particles are prepared as the fine particles. Also, a resin having room-temperature curing properties is prepared as the liquid resin. The resin having room-temperature curing properties is a resin whose curing naturally proceeds at a room temperature (for example, an environment at a temperature of 15 to 35°C).

[0024] The fine particles used in the production example are zirconia particles having an average particle diameter of 200 nm (a product of KCM Corporation, brand name "KZ-8YF"). The average particle diameter here is a median size (d50) calculated from a particle size distribution calculated by a laser diffraction scattering method. In the following explanation, the zirconia fine particles will be referred to merely as "particles."

[0025] The raw material of the fine particles is not limited to above-described zirconia (ZrO_2), but may be variously changed. For example, one or two or more kinds selected from the group consisting of oxides and compound oxides, including aluminum oxide, silicon oxide, mullite ($Al_2O_3-SiO_2$), zirconium dioxide, zircon (ZrO_2-SiO_2), forsterite ($2MgO-SiO_2$), steatite ($MgO-SiO_2$), barium titanate ($BaTiO_3$), lead zirconium titanate ($Pb(Zr, Ti)O_3$), titanium oxide, zinc oxide, calcium oxide, magnesium oxide, chromic oxide, manganese oxide, iron oxide, nickel oxide, copper oxide, gallium oxide, germanium oxide, yttrium oxide, silver oxide, cobalt oxide, tungstic oxide, vanadium oxide, barium oxide, etc.; nitrides, including aluminum nitride, silicon nitride, etc.; carbides, including silicon carbide, etc.; cermets, including WC/C, WC/Ni, WC/CrC/Ni, WC/Cr/Co, CrC/NiCr, sialon ($SiN_4-Al_2O_3$), etc., may be used as a ceramic material of the fine particles.

[0026] Various metals, such as aluminum and copper, may be used as a material for the fine particles when the particles comprise a metal. The raw material of the fine particles may comprise two or more kinds of mixed metals. Further, a ceramic and a metal may be mixed as a raw material of the fine particles.

[0027] The average particle diameter of the fine particles may also be changed variously. However, the average particle diameter of the fine particles is so small that the particles are difficult to be handled directly by air conveyance in the thermal spraying apparatus 1. That is, the average particle diameter of the fine particles is a size of so-called nanoparticles. In detail, the average particle diameter of the fine particles according to a laser diffraction scattering method or a dynamic-light-scattering method is not less than 25 nm and not more than 1,000 nm (not less than 25×10^{-9} m and not more than $1,000 \times 10^{-9}$ m). If the average particle diameter of the fine particles is less than 25 nm, it will be difficult to supply the fine particles to the central part of the plasma flare because the amount of the fine particles which may keep a monodispersion state in the resin decreases, and thus the specific gravity of the material for thermal spraying will be too small. If the average particle diameter of the fine particles exceeds 1,000 nm, the fine particles will precipitate easily when the fine particles are mixed with a resin, and thus it will be difficult to keep a monodispersion state of the fine particles. Preferably, the average particle diameter is not less than 50 nm and not more than 500 nm, which is easily available. The measurement may be carried out by a dynamic-light-scattering method when the measurement by a laser diffraction scattering method is difficult to carry out. A particle diameter indicated by the manufacturer of the fine particles may also be used as the average particle diameter.

[0028] In the production example, a multicomponent-type resin (so-called a two-component resin) whose curing proceeds at a room temperature when a base resin and a curing agent (so-called a catalyst) are mixed is used as a liquid resin having room-temperature-curing-properties. The curing of the two-component resin is accelerated by raising the temperature within a range from a room temperature to a temperature higher to some extent than the room temperature (for example, a temperature range from a room temperature to a temperature higher by about 10 degrees than the room temperature). The specific resin used in the production example is a polyester two-component resin (a product of Marumoto Struers, Inc., brand name "REIKAN UMEKOMI JUSHI No. 105"). Various resins may be used as the resin

having room-temperature curing properties as long as the resin mainly contains an organic material. An acrylic resin and an epoxy resin may be used. A moisture-curable resin and a solvent-volatilizing type resin may also be used as the resin having room-temperature curing properties.

[0029] In the production of a material for thermal spraying, first, a liquid resin having room-temperature curing properties is generated by mixing and stirring a curing agent and a base resin which has room-temperature curing properties in a container (Step S11). The temperature of the liquid resin is about 32 degrees (°C), for example. In the liquid resin, the base resin and the curing agent are mixed approximately uniformly, and thereby the curing of the resin is initiated. The stirring of the mixture of the base resin and the curing agent is manually carried out using a stirring rod in a plastic container having a diameter of a 50 mm and a depth of 80 mm, for example.

[0030] Then the above-mentioned fine particles are dispersed in the liquid resin generated in Step S11 (Step S12). Fig. 3 shows the detailed flow of Step S12. Step S12 comprises Steps S121-S123 shown in Fig. 3. In Step S12, first, the fine particles are added to the liquid resin having room-temperature curing properties in the container. Thereby an intermediate substance is obtained. The percentage of the fine particles contained in the intermediate substance is about 40 volume %, for example. Then the intermediate substance in the container is stirred for a predetermined unit stirring time (Step S121).

[0031] The stirring of the intermediate substance in Step S121 is carried out, for example, by a stirring and defoaming apparatus which may rotate and revolve. The rotation is at 350 rpm and the revolution is at 1060 rpm in the condition of stirring and defoaming in the stirring and defoaming apparatus. The unit stirring time is 30 seconds, for example. In Step S121, the temperature of the intermediate substance increases due to the friction between the fine particles, the heat resulting from the stirring and defoaming apparatus, etc. The temperature of the intermediate substance after Step S121 is completed is, for example, about 45 to 50 degrees. Even while Step S121 is carried out, the curing of the resin having room-temperature curing properties in the intermediate substance proceeds and is accelerated by increasing the temperature.

[0032] After Step S121 is completed, the container which stores the intermediate substance is ejected from the stirring and defoaming apparatus, and then the intermediate substance is cooled (Step S122). In Step S122, the intermediate substance is cooled, for example, by a coolant which is colder rather than a room temperature. In the production example, quick cooling of the intermediate substance is carried out by contacting the container which stores the intermediate substance with running water or ice which is colder than a room temperature. In other words, the intermediate substance indirectly contacts the running water or ice which is colder than a room temperature via the container. Thereby, the curing of the resin having room-temperature curing properties in the intermediate substance is prevented.

[0033] The cooling of the intermediate substance in Step S122 is carried out, for example, until the temperature of the intermediate substance is lowered to a predetermined temperature for resuming stirring. The temperature for resuming stirring is, for example, not more than a temperature which is about 10 degrees higher than a room temperature. In detail, the temperature for resuming stirring is about 40 to 45 degrees. The cooling of the intermediate substance in Step S122 may be carried out, for example, for a predetermined cooling time. The cooling time is about 60 seconds, for example.

[0034] When Step S122 is completed, a total of the stirring time of the intermediate substance after the fine particles are added to the liquid resin (hereinafter referred to as a "total stirring time") is compared with a predetermined required stirring time (Step S123). The required stirring time is longer than the unit stirring time. The required stirring time is 600 seconds, for example. If the total stirring time is less than the required stirring time, the process returns to Step S121, and the stirring of the intermediate substance for the unit stirring time and the cooling of the intermediate substance after the stirring are carried out (Steps S121 and S122).

[0035] In Step S12, Steps S121 and S122 are repeated until the total stirring time of the intermediate substance amounts to not less than the required stirring time. Thereby, nano-slurry comprising fine particles which are so-called nanoparticles and are uniformly monodispersed is obtained. The required stirring time is about 600 seconds, for example. The required stirring time is determined based on an experimentally calculated time-course change of the viscosity property of the intermediate substance, for example. In detail, for example, the relation between the stirring speed and the shearing stress while changing the total stirring time is experimentally calculated, and a total stirring time until when the state of the hysteresis which appears in a viscosity curve shows almost no change or a time obtained by adding a predetermined margin time to the total stirring time may be adopted as the required stirring time. Alternatively, another total stirring time until when the time-course change of the thixotropic property of the intermediate substance does not appear or a time obtained by adding a predetermined margin time to the other total stirring time may be adopted as the required stirring time.

[0036] The volume percentage of the fine particles in the nano-slurry may be variously changed. However, if the volume percentage is too low, the film forming speed by thermal spraying will be slow, and thus the film forming efficiency will decrease. The upper limit of the volume percentage is dependent on the particle diameter and the size of the solvent molecule which enters between the particles. That is, for example, the maximum filling rate is about 51%, in a case where the particles each have an ideal spherical body having a particle diameter of 150 nm, and the solvent molecule has a thickness of 15 nm, and each of the particles is located on the lattice point of a hexagonal close-packed lattice.

Thus, the maximum value of the filling rate changes depending on the conditions of the fine particles and the solvent. However, the actual filling rate differs from the theoretical value because the fine particles actually have a particle size distribution which is not within an ideal distribution in a significant range.

[0037] A nano-slurry which is a mixture obtained in Step S12 is ejected from the container. In the nano-slurry, the curing of the resin having room-temperature curing properties has already proceeded to some extent, and the nano-slurry has a shape of soft rice cake. Thus, the nano-slurry in the container may be integrally handled. If a thermosetting resin was used instead of the resin having room-temperature curing properties, it would not be easy to integrally handle a mixture obtained in Step S12 because the mixture would be like whipped cream. In contrast, if a resin having room-temperature curing properties is used as the liquid resin, a nano-slurry may be integrally handled, and the nano-slurry may be easily ejected from the container. Further, the yield rate of a material for thermal spraying may also be improved because a part of the nano-slurry may be prevented (or inhibited) from adhering to and remaining in the container when the nano-slurry is ejected.

[0038] The nano-slurry ejected from the container is thinly stretched, for example, on a piece of paraffin paper and is shaped. Then the nano-slurry becomes a cured material while keeping a monodispersion state of the fine particles due to the curing of the resin having room-temperature curing properties with the lapse of time (Step S13). Fig. 4 shows a cross-section of the cured material observed by a scanning electron microscope. It is confirmed from Fig. 4 that the fine particles do not contact each other and are independently dispersed in a monodispersed state in the cured material.

[0039] The cured material (namely, the cured material obtained by curing the mixture obtained in Step S12) is pulverized using, for example, a hand-worked fracturing apparatus or an oscillating mill. The cured material after it is pulverized (hereinafter referred to as a "pulverized material") is fractionated using a sieve. Thereby, a material for thermal spraying comprising particles having a particle diameter larger than the above-described fine particles is obtained (Step S14). In this embodiment, the pulverized material is fractionated into a range of a particle diameter of not less than 45 micrometers and not more than 106 micrometers (not less than 45×10^{-6} m and not more than 106×10^{-6} m) which is a predetermined target particle diameter range, and into other fractions.

[0040] The particle diameter range may be variously changed as long as the particles may be used in the thermal spraying apparatus 1. The particle diameter range may be defined by the opening of the sieve used for the fractionation. The particle diameter of the particles obtained by pulverizing a cured material may be variously determined as long as the particle diameter is larger than that of the fine particles contained in the particles. Preferably, the particle diameter range of the pulverized particles may be suitably determined between 1 micrometer and 120 micrometers (not less than 1×10^{-6} m and not more than 120×10^{-6} m). More preferably, the particle diameter of the pulverized particles is more than 5 times of the particle diameter of the fine particles, and is not less than 5 micrometers and not more than 120 micrometers from a viewpoint that the thermal spraying apparatus readily carries out air conveying.

[0041] Fig. 5 shows an example of the detailed flow of Step S14. Step S14 comprises Steps S141-S145 shown in Fig. 5. In Step S14, first, the cured material obtained in Step S13 is roughly pulverized by a hand-worked fracturing apparatus and thereby becomes a pulverized material having a particle diameter below 400 micrometers (Step S141). The pulverized material obtained in Step S141 is supplied on a sieve having an opening of 106 micrometers and then is fractionated in a vibration sieving process using a sieve shaker (Step S142). Preferably, together with the pulverized material, a tapping component, such as a tapping ball and a tapping block, is added on the sieve. Thereby, the sieve is prevented from being blocked, and thus the fractionation of the pulverized material may be efficiently carried out. The particles which each have a particle diameter of not less than 106 micrometers and remained on the sieve (namely, a residue) are pulverized again using a mill (Steps S143 and S144), and then are fractionated again using the sieve (Step S142). Then the pulverization by a mill and the fractionation by a sieve are repeated until the particle diameters of all the pulverized materials become less than 106 micrometers (Steps S142-S144).

[0042] Then, the pulverized material obtained in Steps S142-S144 is supplied on a sieve having an opening of 45 micrometers and is fractionated in a vibration sieving process using a sieve shaker. Similarly as described above, a tapping component is preferably added on the sieve along with the pulverized material. Thereby, the sieve is prevented from being blocked, and thus the fractionation of the pulverized material may be efficiently carried out. The particles which each have a particle diameter of not less than 45 micrometers (and less than 106 micrometers) and remain on the sieve are obtained as a material for thermal spraying having a particle diameter within the target particle diameter range (Step S145). The over-pulverized particles which pass the sieve and have a particle diameter of less than 45 micrometers (namely, the particles each having a particle diameter below the target particle diameter range) are collected and used in the after-mentioned second or later time production of a material for thermal spraying. The particle diameter of the over-pulverized particles is not less than the particle diameter of the fine particles and is usually larger than the particle diameter of the fine particles. The fine particles are dispersed uniformly in the over-pulverized particles. The over-pulverized particles separated from the material for thermal spraying by the sieve in Step S145 are collected in an aggregational state.

[0043] Incidentally, in Step S14, in order to confirm that the particle diameter of the pulverized material obtained in the above-mentioned step S141 is less than 400 micrometers, the pulverized material may be supplied on a sieve having

an opening of 400 micrometers and then be fractionated in a vibration sieving process using a sieve shaker between Step S141 and Step S142. If the pulverized material remains on the sieve, the remaining pulverized material is pulverized by a mill, etc., until the particle diameter of it becomes less than 400 micrometers.

[0044] The pulverization by a mill in Step S144 is carried out, for example, for a predetermined pulverization time. The pulverization time of a cured material is determined in advance based on the percentages of the material for thermal spraying and the over-pulverized particle obtained in Step S144 (namely, their percentages to the cured material supplied to a mill in Step S144). In detail, the pulverization of a cured material is repeatedly carried out while changing the pulverization time, and thus the particle size distributions of the pulverized material which each correspond to two or more pulverization times may be calculated. Thereby, the rates of the material for thermal spraying and the over-pulverized particles which each correspond to the two or more pulverization time may be calculated. The longer the pulverization time is, the more the percentages of the material for thermal spraying and the over-pulverized particle increase. The shorter the pulverization time is, the more the percentages of the material for thermal spraying and the over-pulverized particle decrease.

[0045] In the production of a material for thermal spraying, the improvement in efficiency of the producing operation needs to be achieved by increasing the amount of the material for thermal spraying obtained in one time of step S144 and thereby decreasing the number of times to repeat Step S144. Further, the percentage of a material for thermal spraying obtained at Step S14 to an entire cured material (namely, the yield rate of the material for thermal spraying) needs to be increased by suppressing the amount of the over-pulverized particles generated at one time of step S144. The appropriate pulverization time which satisfies these requirements is determined as the pulverization time in Step S144. The pulverization time in Step S144 is 40 seconds, for example.

[0046] Fig. 6 shows the flow of the thermal spraying by the thermal spraying apparatus 1. The material for thermal spraying is produced by the production method according to the above-mentioned steps S11-S14 (Step S21). Then the material storing part 13 is filled with the material for thermal spraying (Step S22). Then, plasma thermal spraying is carried out using the material for thermal spraying. Thereby, the heated fine particles are fused together on the substrate 9, and a coating is formed on the substrate 9 (Step S23). On the substrate 9, the fine particles are melted and fused together to thereby form a dense coating. The conditions may be determined such that the fine particles reach the substrate 9 while the fine particles are in a semimolten state. In this case, a porous coating is formed.

[0047] As described above, by using particles of a resin containing the fine particles of a ceramic or a metal as a material for thermal spraying, thermal spraying may be readily carried out even when a thermal spraying apparatus having a structure similar to conventional one is used and even when fine particles each having a size of so-called a nanoparticle which were difficult to be handled in the conventional art are used. As a result, the cost required for thermal spraying may be prevented from increasing. Also, the efficiency of the thermal spraying operation is prevented from decreasing. That is, a high production speed may be achieved by the thermal spraying technology even when a subject is long and large. Further, the use of a material having dramatically improved physicochemical properties, such as nano composite material and a nano porous material which take advantage of nanoparticles, as an industrial material may also be achieved.

[0048] As described above, in the production of a material for thermal spraying, in Step S12 (the dispersion of fine particles in a resin), the intermediate substance obtained by adding the fine particles to the liquid resin having room-temperature curing properties is stirred for the predetermined unit stirring time, and then the intermediate substance is cooled (Steps S121 and S122). Then Steps S121 and S122 are repeated until the total stirring time of the intermediate substance amounts to not less than the required stirring time (Step S123).

[0049] If the above-described intermediate substance is continuously stirred for the required stirring time (namely, one time stirring is carried out for the required stirring time), the resin would be cured in a state where the fine particles are insufficiently dispersed because the temperature of the intermediate substance would increase excessively during the stirring. If particles obtained by pulverizing a cured material comprising the fine particles which are insufficiently dispersed are used as a material for thermal spraying, it would be difficult to form a uniform coating on the substrate. In contrast, by carrying out Steps S121-S123 in Step S12 in the above-mentioned production of a material for thermal spraying, the liquid resin having room-temperature curing properties may be prevented from curing before the fine particles are dispersed, and a material for thermal spraying comprising the fine particles which are dispersed in a monodispersion state in the resin having room-temperature curing properties may be readily produced. Further, a material for thermal spraying may be produced more readily because it is not necessary to heat the intermediate substance or to irradiate the intermediate substance due to the use of the resin having room-temperature curing properties as the liquid resin, when the intermediate substance comprising the fine particles which are dispersed in a monodispersion state is cured.

[0050] In Step S122, the quick cooling of the intermediate substance may be readily achieved by cooling the intermediate substance using a coolant (for example, running water or ice) colder than a room temperature. Thereby, the curing of the intermediate substance after it is stirred for the unit stirring time may be prevented from developing. Further, the intermediate substance may be cooled more quickly by indirectly contacting the intermediate substance to the coolant, and thereby the curing of the intermediate substance after it is stirred may be further suppressed. In Step S122, the

cooling of the intermediate substance is carried out until the temperature of the intermediate substance decreases to a temperature for resuming stirring. Therefore, excessive increase of the temperature of the intermediate substance and excessive progress of the curing may be suppressed when the intermediate substance is again stirred after it is cooled

[0051] In the above-described production of a material for thermal spraying, in advance of the addition of the fine particles to the resin in Step S12, a liquid resin having room-temperature curing properties is generated by mixing and stirring a base resin having room-temperature curing properties and a curing agent (Step S11). Accordingly, by stirring the base resin and the curing agent to generate a liquid resin prior to the addition of the fine particles, the fine particles may be dispersed approximately uniformly in a resin having room-temperature curing properties whose components are approximately uniform.

[0052] In the actual production of a material for thermal spraying, Steps S11-S14 are repeated. Fig. 7 shows a part of the flow of the second or later time production of a material for thermal spraying. In the second or later time production of a material for thermal spraying, the over-pulverized particles obtained when a cured material is pulverized in a completed Step S14 for producing a material for thermal spraying are also added to and dispersed in the liquid resin in Step S12. The other flow of the production is approximately the same as that of Steps S11-S14 shown in Figs. 2, 3, and 5.

[0053] In detail, in the second time or later time production of the material for thermal spraying, first, a liquid resin having room-temperature curing properties is generated by mixing and stirring a base resin having room-temperature curing properties and a curing agent in a container (Step S11). Then, fine particles and over-pulverized particles are dispersed in the liquid resin generated in Step S11 (Step S12).

[0054] In detail, in Step S12, as shown in Fig. 3, first, the above-mentioned fine particles are added to a liquid resin having room-temperature curing properties to obtain an intermediate substance, and then the intermediate substance is stirred for a unit stirring time (Step S121). The percentage of the fine particles contained in the intermediate substance is the about 40 volume % as in the first time production of a material for thermal spraying. After Step S121 is completed, the intermediate substance is cooled (Step S122). Then Steps S121 and S122 are repeated until the total stirring time of the intermediate substance amounts to not less than the required stirring time while comparing them (Step S123).

[0055] After the total stirring time amounts to not less than the required stirring time, and thereby the dispersion of the fine particles in the intermediate substance is completed, the over-pulverized particles obtained in a completed production of a material for thermal spraying is added to the intermediate substance (namely, to a mixture of a liquid resin and fine particles). The added over-pulverized particle is in an aggregational state as described above. In the second or later time production of a material for thermal spraying, the over-pulverized particles added to the intermediate substance are preferably all of the over-pulverized particles obtained in Step S14 in a previous production of a material for thermal spraying (for example, in Step S14 in the first time production of a material for thermal spraying when the second time production of a material for thermal spraying is carried out). The percentage of the over-pulverized particles to the intermediate substance after the over-pulverized particle is added is, for example, about 30 weight % or less, and is about 20 weight % in this embodiment.

[0056] Then, the intermediate substance obtained by adding the fine particles and the over-pulverized particles to the liquid resin is stirred for a predetermined unit stirring time (Step S124). The unit stirring time in Step S124 may be the same as or different from the above-mentioned unit stirring time in the step S121. The stirring of the intermediate substance in Step S124 is carried out, for example, by the same stirring and defoaming apparatus as that used in Step S121.

[0057] After Step S124 is completed, the intermediate substance is cooled (Step S125). As in Step S122, the cooling of the intermediate substance in Step S125 is carried out, for example, by a coolant (running water or ice) which is colder than a room temperature until the temperature of the intermediate substance decreases to a predetermined temperature for resuming stirring. The cooling of the intermediate substance in Step S125 may be carried out, for example, for a predetermined cooling time. The temperature for resuming stirring and the cooling time in Step S125 may be the same as the temperature for resuming stirring and the cooling time in Step S122, respectively, or may be different from them.

[0058] In the second or later time production of a material for thermal spraying, Steps S124 and S125 are repeated until the total stirring time of the intermediate substance in Step S124 amounts to not less than the required stirring time while comparing them (Step S126). The total stirring time in Step S124 and the required stirring time in Step S126 may be the same as the total stirring time in Step S121 and the required stirring time in Step S123, respectively, or may be different from them.

[0059] As shown in Fig. 2, the nano-slurry which is a mixture generated in Step S12 (namely, in steps S121-S126) becomes a cured material due to the curing of the resin having room-temperature curing properties with the lapse of time (Step S13). In the cured material, the fine particles and the over-pulverized particles are in a monodispersion state. Fig. 8 shows a cross-section of the cured material observed by a scanning electron microscope. Also, Fig. 9 shows a cross-section of the cured material which is generated in the first time production of a material for thermal spraying (namely, a cured material which does not contain over-pulverized particles) observed similarly as in Fig. 8. The parts having a deeper color than the other parts in Fig. 8 comprise the over-pulverized particles. It has been confirmed from Fig. 8 that the over-pulverized particles do not contact each other and are dispersed separately and independently in a

mono dispersion state in the cured material generated in the second or later time production of a material for thermal spraying.

[0060] Figs. 10 and 11 show enlarged views of a part of Figs. 8 and 9, respectively. Fig. 10 shows an area including a part of one over-pulverized particle. The solid line 71 in Fig. 10 shows a boundary between the over-pulverized particle and the surrounding part. The lower left part relative to the solid line 71 corresponds to the over-pulverized particle. Fig. 10 shows that both the fine particles contained in the over-pulverized particle and the fine particles located in the other part surrounding the over-pulverized particle are dispersed approximately uniformly in a similar manner. Further, Figs. 10 and 11 show that, even when the over-pulverized particles are added to a liquid resin, the fine particles are dispersing uniformly and approximately similarly as in the case where the over-pulverized particles are not added

[0061] The cured material obtained in Step S13 is pulverized, for example, by a hand-worked fracturing apparatus or an oscillating-type mill. The cured material after it is pulverized is fractionated using a sieve. Thereby, a material for thermal spraying having a particle diameter within the target particle diameter range (for example, not less than 45 micrometers and not more than 106 micrometers) is obtained (Step S14).

[0062] In the second or later time production of a material for thermal spraying, the weight percentages of the material for thermal spraying and the over-pulverized particles obtained in Step S14 to the cured material obtained in Step S13 (that is, a cured material containing over-pulverized particles) are the almost same as the weight percentages of the material for thermal spraying and the over-pulverized particles which are obtained in Step S14 from a cured material which does not contain over-pulverized particles, respectively. In detail, the weight percentages of the material for thermal spraying and the over-pulverized particles when the cured material does not contain over-pulverized particles are about 64% and about 29%, respectively. In contrast, the weight percentages of the material for thermal spraying and the over-pulverized particles when the cured material contains over-pulverized particles are about 67% and about 27%, respectively. Accordingly, it has been confirmed that there hardly occurs a phenomenon that the over-pulverized particles are not appropriately pulverized by exfoliating from the cured material containing over-pulverized particles when the cured material is pulverized in Step S14.

[0063] Similarly as shown in Fig. 6, the material for thermal spraying obtained by the second or later time production is also used for the thermal spraying in the thermal spraying apparatus 1. That is, a material for thermal spraying produced by the production method of the steps of S11-S14 is prepared (Step S21). Then the material for thermal spraying is filled into the material storing part 13 (Step S22). Then plasma thermal spraying is carried out using the material for thermal spraying. Thereby, the heated fine particles are fused together on the substrate 9, and thus a coating is formed on the substrate 9 (Step S23). Accordingly, thermal spraying may be readily carried out while using nano-level fine particles which were difficult to be handled in the conventional art and while using a thermal spraying apparatus which has the same structure as that of a conventional apparatus. As a result, the increase of the cost required for thermal spraying may be suppressed, and the decrease in the efficiency of the thermal spraying operation may also be prevented. Further, the use of a material having dramatically improved physicochemical properties, such as nano composite material and a nano porous material which take advantage of nanoparticles, as an industrial material may also be achieved

[0064] As explained above, in the second or later time production of a material for thermal spraying, in Step S12, in addition to dispersing the fine particles in a liquid resin, the over-pulverized particles obtained when a cured material is pulverized in a completed step S14 are also added and dispersed in the liquid resin. Thus, the yield rate of the material for thermal spraying produced from the fine particles and the resin may be improved by recycling the over-pulverized particles which are too small to be used as a material for thermal spraying in the next or later time production of a material for thermal spraying in the thermal spraying apparatus 1.

[0065] In the production of a material for thermal spraying which does not recycle over-pulverized particles, only the particles of a cured material other than over-pulverized particles and lost particles (namely, particles which have been lost by scattering the particles due to air-conditioning, etc., in the room for the production) are used as a material for thermal spraying. In contrast, in the production of a material for thermal spraying which recycles the above-mentioned over-pulverized particles, the particles of a cured material other than lost particles are used as a material for thermal spraying. Therefore, the yield rate of a material for thermal spraying after the production of a material for thermal spraying is repeated two or more times is greatly improved to about 95%, when the weight percentage of the lost particles is about 5%.

[0066] By the way, as another method for recycling over-pulverized particles in the production of a material for thermal spraying, for example, it is conceivable that the fine particles contained in over-pulverized particles (nanoparticles of zirconia in this embodiment) are collected and recycled as the fine particles which are mixed with a liquid resin in Step S121. In this case, a step for heating over-pulverized particles or melting over-pulverized particles in a solvent is required. Therefore, much work is required to collect the particles. Further, it is difficult to prevent foreign substances from adhering to and contaminating in the particles in the collecting step. Further, as another method for recycling over-pulverized particles, for example, it is also conceivable that over-pulverized particles are collected and pelletized into particles each having a particle diameter within the target particle diameter range. However, the over-pulverized particles are required to be melted to be pelletized, and re-curing of a resin after it is melted is technically difficult.

[0067] In contrast, in the above-mentioned production of a material for thermal spraying, the recycle of over-pulverized particles may be readily carried out because the fine particles and the over-pulverized particles are dispersed in a liquid resin in Step S12, and therefore a step for heating or melting over-pulverized particles, etc., is made unnecessary. Further, in the step for recycling over-pulverized particles, the adhesion and contamination of foreign substances to the fine particles in the over-pulverized particle may also be prevented. Further, the ratio of the fine particles to the resin in the over-pulverized particles is substantially the same as the ratio of the fine particles to the liquid resin in Step S121. Thus, the percentages of the fine particles in the cured material and in the material for thermal spraying which are obtained by the second or later time production which recycles over-pulverized particles are substantially equal to the percentages of the fine particles in the cured material and the material for thermal spraying which are obtained by the first time production in which over-pulverized particles are not recycled, respectively. For this reason, whenever a material for thermal spraying is produced and used, a uniform coating may be formed on the substrate 9 by the thermal spraying using the thermal spraying apparatus 1.

[0068] As described above, in the second or later time production of a material for thermal spraying, in Step S12, the addition of over-pulverized particles to the liquid resin (Step S124) is carried out after the fine particles are dispersed in the liquid resin (Step S121). Thereby, the over-pulverized particles are prevented from affecting the dispersion of the fine particles in the resin. Further, the fine particles may be prevented from affecting the dispersion of the over-pulverized particles in the resin because the fine particles are dispersed in a monodispersion state in the resin when the over-pulverized particles are added. As a result, both the fine particles and the over-pulverized particles may be readily dispersed uniformly in the liquid resin.

[0069] As described above, the pulverization time of a cured material in Step S144 is determined in advance based on the percentages of the material for thermal spraying and over-pulverized particles which are obtained in Step S14. Thereby, the production efficiency may be improved by increasing the amount of a material for thermal spraying obtained at one time of step S144. In addition, the yield rate of the material for thermal spraying obtained in Step S14 may also be efficiently improved by reducing the amount of over-pulverized particles generated at one time of step S144.

[0070] In the second or later time production of a material for thermal spraying, the over-pulverized particles to be added to the liquid resin in Step S12 are separated from a material for thermal spraying by a sieve in a completed step S14 and are in an aggregational state. Thereby, the handling of the over-pulverized particles during the collection of the over-pulverized particles or the addition of the over-pulverized particles to a liquid resin may be made easier. Further, the scattering and loss of the over-pulverized particles obtained in Step S14 due to air-conditioning, etc., are suppressed. As a result, the yield rate of a material for thermal spraying may be further improved.

[0071] As described above, the over-pulverized particles added to a liquid resin in Step S12 are all of the over-pulverized particles obtained in a previous step S14. Thereby, it is not necessary to store and use the over-pulverized particles generated at one time production of a material for thermal spraying, over two or more subsequent productions of a material for thermal spraying. Therefore, the production of a material for thermal spraying may be simplified. At the same time, a material for thermal spraying may also be efficiently produced.

[0072] In the second or later time production of a material for thermal spraying, as in the first time production of a material for thermal spraying, in Step S12, an intermediate substance obtained by adding the fine particles to a liquid resin having room-temperature curing properties is stirred for the unit stirring time, and then the intermediate substance is cooled (Steps S121 and S122). Then Steps S121 and S122 are repeated until the total stirring time of the intermediate substance amounts to not less than the required stirring time (Step S123). Thereby, the liquid resin having room-temperature curing properties may be prevented from curing before the fine particles are dispersed, and thus a material for thermal spraying comprising the fine particles dispersed in a resin having room-temperature curing properties in a monodispersion state may be readily produced. Further, due to the use of a resin having room-temperature curing properties as the liquid resin, a material for thermal spraying may be produced more readily because it is unnecessary to heat the intermediate substance or to irradiate the intermediate substance when the intermediate substance comprising the fine particles dispersed in a monodispersion state is cured.

[0073] Further, in the second or later time production of a material for thermal spraying, in Step S12, an intermediate substance obtained by adding the fine particles and the over-pulverized particles to a liquid resin having room-temperature curing properties is stirred for the unit stirring time, and then the intermediate substance is cooled (Steps S124 and S125). Then Steps S124 and S125 are repeated until the total stirring time of the intermediate substance amounts to not less than the required stirring time (Step S126). Thereby, the liquid resin having room-temperature curing properties may be prevented from curing before the over-pulverized particles are dispersed, and thus a material for thermal spraying comprising over-pulverized particles dispersed in a resin having room-temperature curing properties in a monodispersion state may be readily produced.

[0074] Fig. 12 shows another example of a thermal spraying apparatus 1a. The thermal spraying apparatus 1a has two material storing parts 13 and two constant-amount supplying parts 31. The conveying pipes 32 extending from the two respective constant-amount supplying parts 31 join together on the way. The materials for thermal spraying which are stored in the two material storing parts 13 are different from each other. That is, in the two kinds of materials for

thermal spraying, the raw materials of the fine particles contained in resin particles are different from each other. The two kinds of materials for thermal spraying are produced by the above-described production method of a material for thermal spraying. In each of the productions of the two kinds of materials for thermal spraying, the recycle of over-pulverized particles (Steps S124-S126) is preferably carried out. Which of the material storing parts 13 supplies a material for thermal spraying to a thermal spraying gun 11 is determined by controlling two valves 34 which are installed on the conveying pipes 32 and an air supplying part 14. Other configurations of the thermal spraying apparatus 1a are the same as those of the thermal spraying apparatus 1 in Fig. 1. The same numbers are given to the same components.

[0075] Fig. 13 shows the flow of the operation when thermal spraying is carried out by the thermal spraying apparatus 1a of Fig. 12. Two kinds of materials for thermal spraying are prepared by the above-described production method (Step S31). Then they are filled into the two material storing parts 13 (Step S32). Then a coating is formed by carrying out thermal spraying using one of the materials for thermal spraying to fuse the fine particles on a substrate 9 (Step S33). Next, another coating is formed by carrying out thermal spraying using the other of the materials for thermal spraying to fuse the different kind of fine particles on the existing coating formed in Step S33 (Step S34).

[0076] Accordingly, due to the use of different raw materials for the fine particles contained in the materials for thermal spraying, the change of a material for thermal spraying may be readily achieved only by changing its supply route. In the thermal spraying apparatus 1a, three or more material storing parts 13 may be installed, and three or more coating layers may be stacked using three or more kinds of materials for thermal spraying. Further, two or more kinds of coatings may be stacked repeatedly. That is, in the thermal spraying apparatus 1a, two or more kinds of coatings may be readily stacked on the substrate 9.

[0077] The above-described production of a material for thermal spraying and the thermal spraying apparatus 1, 1a may be variously changed

[0078] The stirring of the intermediate substance in Steps S121 and S124 may be carried out by any of various apparatuses or may be manually carried out by an operator using a stirring rod, etc. The unit stirring time may be suitably changed as long as the curing of the resin having room-temperature curing properties in the intermediate substance does not excessively proceed. The cooling of the intermediate substance in Steps S122 and S125 may be carried out by any of various methods. For example, the intermediate substance may be cooled by blowing gas at a room temperature or a temperature lower than the room temperature toward the intermediate substance. Further, the cooling of the intermediate substance may be carried out by leaving the intermediate substance in the atmosphere at a room temperature. The temperature for resuming stirring and the cooling time may be changed suitably as long as the curing of the resin having room-temperature curing properties in the intermediate substance does not excessively proceed.

[0079] In the second or later time production of a material for thermal spraying, the over-pulverized particles added to a liquid resin in Step S124 may not necessarily be all of the over-pulverized particles obtained in a previous production of a material for thermal spraying and may be a part of the over-pulverized particles. Further, the over-pulverized particles added to a liquid resin may be over-pulverized particles obtained in a second last or former time production of a material for thermal spraying. Further, in Step S124, the over-pulverized particles which are in an aggregational state may be disintegrated and then added to a liquid resin.

[0080] In the second or later time production of a material for thermal spraying, Steps S124-S126 (dispersion of over-pulverized particles) may be carried out in Step S12 in parallel with Steps S121-S123 (dispersion of fine particles). In this case, first, the fine particles and the over-pulverized particles are mixed in a liquid resin approximately at the same time, and an intermediate substance which is a liquid resin containing the fine particles and the over-pulverized particles is stirred for the unit stirring time. Then, the intermediate substance is cooled for the predetermined cooling time or until the temperature of the intermediate substance decreases to the temperature for resuming stirring. The stirring and cooling of the intermediate substance are repeated until the total stirring time of the intermediate substance amounts to not less than the required stirring time. Alternatively, Steps S124-S126 may be carried out prior to Steps S121-S123. In any case, the yield rate of a material for thermal spraying may be improved by recycling over-pulverized particles to produce a material for thermal spraying.

[0081] In the above-described production method, the fine particles are added to a liquid resin after the liquid resin is generated by mixing a curing agent and a base resin which has room-temperature curing properties. However, the addition of the fine particles may be carried out in parallel with the mix of a base resin and a curing agent. In the second or later time production of a material for thermal spraying, the addition of fine particles and over-pulverized particles may be carried out in parallel with mixing a base resin and a curing agent.

[0082] The liquid resin used in the above-mentioned production method of a material for thermal spraying may not necessarily be a room-temperature-curing resin which naturally cures at a room temperature. The liquid resin may be, for example, a thermosetting resin which starts to cure by heat or a photocurable resin which starts to cure by the irradiation with light. When a thermosetting resin or a photocurable resin is used as the liquid resin, Steps S122, S123, S125, and S126 may be skipped in the above-mentioned step S12.

[0083] The thermal spraying in the above-mentioned embodiment is applicable to the production of various products of thermal spraying which comprise a substrate and a coating formed on the substrate. Further, only a coating portion

may also be used as a product. When a nanoporous structure is formed by stopping fusing the fine particles by thermal spraying within a stage of sintering, the thermal spraying is applicable to the production of carriers for a catalyst, various battery electrodes, additive agents, filters, functional inks, semiconductor devices, thermal barrier coatings, insulation covers, etc. When a dense structure is formed by melting and fusing the particles, the thermal spraying is applicable to the production of, for example, anticorrosion coatings, machining parts (such as a cutter), and heat-resistant parts (a crucible, a boiler tube, etc.).

[0084] The thermal spraying apparatus 1, 1a may also be an apparatus for carrying out flame thermal spraying or laser thermal spraying. The thermal spraying gun 11 may be a thermal spraying gun of another type. In other words, the material for thermal spraying produced by the above-mentioned production method may also be used for flame thermal spraying or laser thermal spraying. When flame thermal spraying or laser thermal spraying using the material for thermal spraying are carried out, the heated fine particles are fused to form a coating on a substrate. Using any method for thermal spraying, almost or completely without changing an existing apparatus, so-called nanoparticles may be readily used for thermal spraying.

[0085] The configurations in the above-mentioned embodiments and the modifications may be suitably combined as long as they are consistent with each other.

[0086] The invention has been described and explained in detail. However, the explanations as stated above are exemplary and are not restrictive. Therefore, a lot of modifications and embodiments are possible as long as they do not deviate from the scope of the present invention.

DESCRIPTION OF THE REFERENCE NUMERALS

[0087]

1, 1a	Thermal Spraying Apparatus
9	Substrate
S11-S14, S21-S23, S31-S34, S121-S126, S141-S145	Step

Claims

1. A method for producing a material for thermal spraying, used for plasma thermal spraying, flame thermal spraying, or laser thermal spraying, the method comprising the steps of:

- a) dispersing fine particles of a ceramic or a metal in a liquid resin;
- b) pulverizing a cured material from a mixture obtained in the step a) to obtain a material for thermal spraying having a particle diameter which is larger than that of the fine particles and is within a predetermined target particle diameter range; and
- c) repeating the step a) and step b),

wherein over-pulverized particles having a particle diameter below the target particle diameter range obtained when the cured material is pulverized in a completed step b) are also added to the liquid resin and are dispersed in a second or later time step a).

2. The method for producing a material for thermal spraying according to claim 1, wherein the over-pulverized particles are added to the liquid resin in a second or later time step a) after the fine particles are dispersed in the liquid resin.

3. The method for producing a material for thermal spraying according to claim 1 or 2, wherein time for pulverizing the cured material in the step b) is determined in advance based on percentages of the material for thermal spraying and the over-pulverized particles obtained in a step b).

4. The method for producing a material for thermal spraying according to any one of claims 1 to 3, wherein, in the step b), the material for thermal spraying is obtained using a sieve from the cured material after the cured material is pulverized, and

Wherein the over-pulverized particles added to the liquid resin in a second or later time step a) are separated from the material for thermal spraying by a sieve in a completed step b) and are aggregated.

5. The method for producing a material for thermal spraying according to any one of claims 1 to 4, wherein the over-pulverized particles added to the liquid resin in the second or later time step a) are all of the over-pulverized particles

obtained in a previous step b).

6. The method for producing a material for thermal spraying according to any one of claims 1 to 5, wherein the fine particles have an average particle diameter of not less than 25 nm and not more than 1000 nm when the average particle diameter is measured by a laser diffraction scattering method or a dynamic-light-scattering method

7. The method for producing a material for thermal spraying according to any one of claims 1 to 6, wherein the liquid resin has room-temperature curing properties and wherein the step a) comprises the steps of:

- a1) stirring an intermediate substance obtained by adding the fine particles to the liquid resin for a predetermined unit stirring time;
- a2) cooling the intermediate substance after the step a1); and
- a3) repeating the step a1) and the step a2) until a total stirring time of the intermediate substance amounts to not less than a required stirring time.

8. A material for thermal spraying, wherein the material is produced by the method according to any one of claims 1 to 7 and is used for plasma thermal spraying, flame thermal spraying, or laser thermal spraying.

9. A method for thermal spraying comprising the steps of:

- d) preparing a material for thermal spraying by the method according to any one of claims 1 to 7; and
- e) carrying out plasma thermal spraying, flame thermal spraying, or laser thermal spraying using the material for thermal spraying to fuse the fine particles by heat and thereby form a coating on a substrate.

10. The method for thermal spraying according to claim 9, further comprising the steps of:

- f) preparing another material for thermal spraying, wherein the other material is produced by the method according to any one of claims 1 to 7 and contains other fine particles which are formed from a raw material different from that of the fine particles dispersed in the step a);
- g) carrying out plasma thermal spraying, flame thermal spraying, or laser thermal spraying using the other material for thermal spraying after the step e) to fuse the other fine particles and thereby form another coating on the coating formed in the step e).

11. A product obtained by thermal spraying, comprising a substrate and a coating formed on the substrate by the method for thermal spraying according to claim 9 or 10.

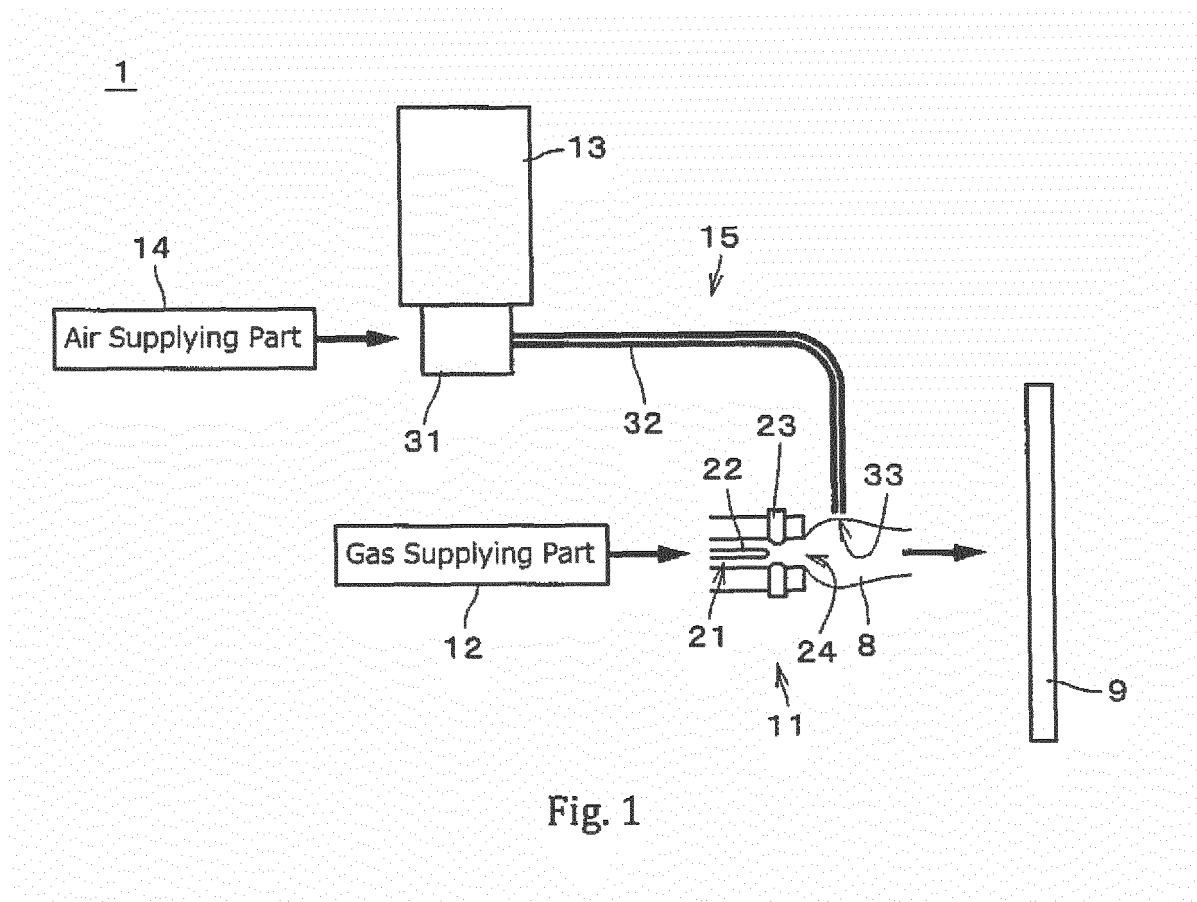
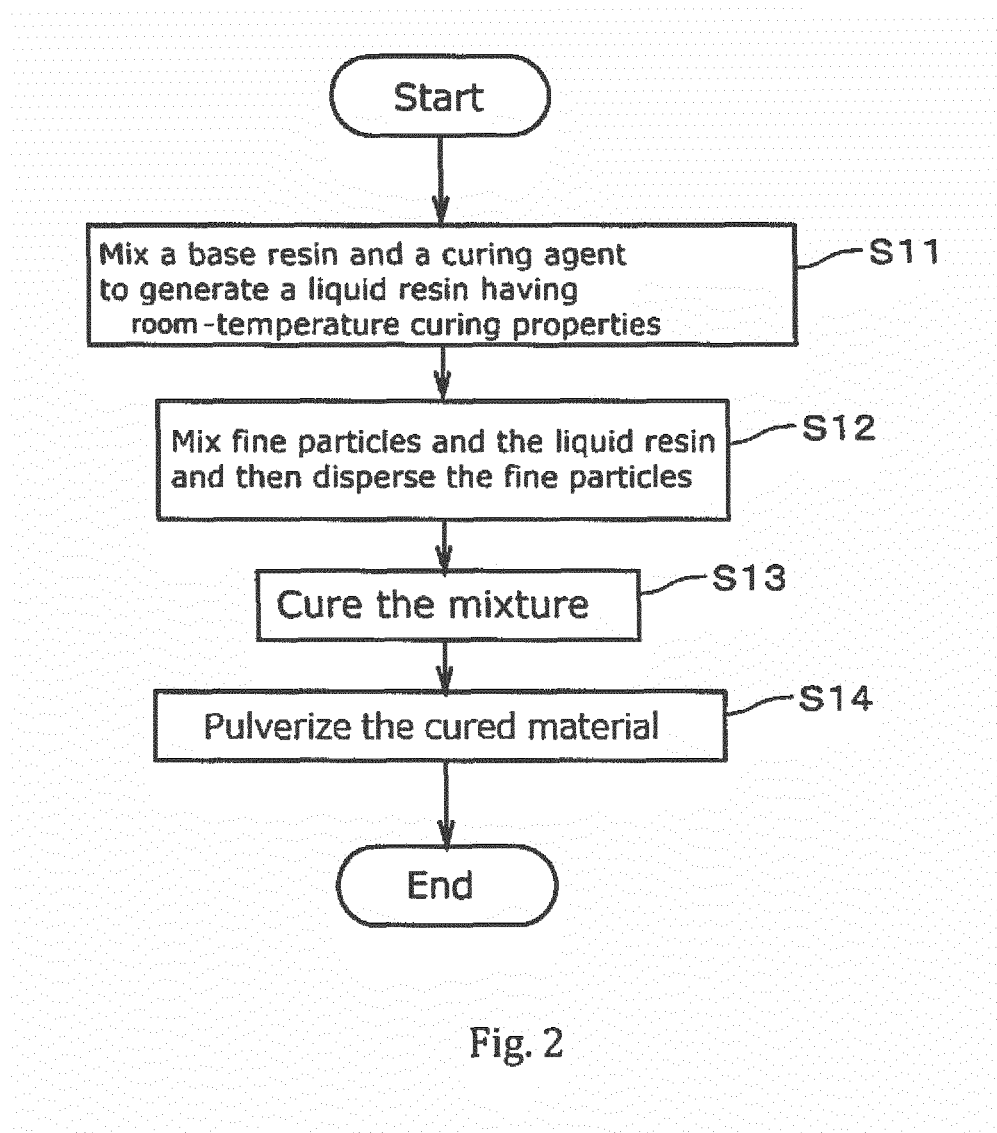


Fig. 1



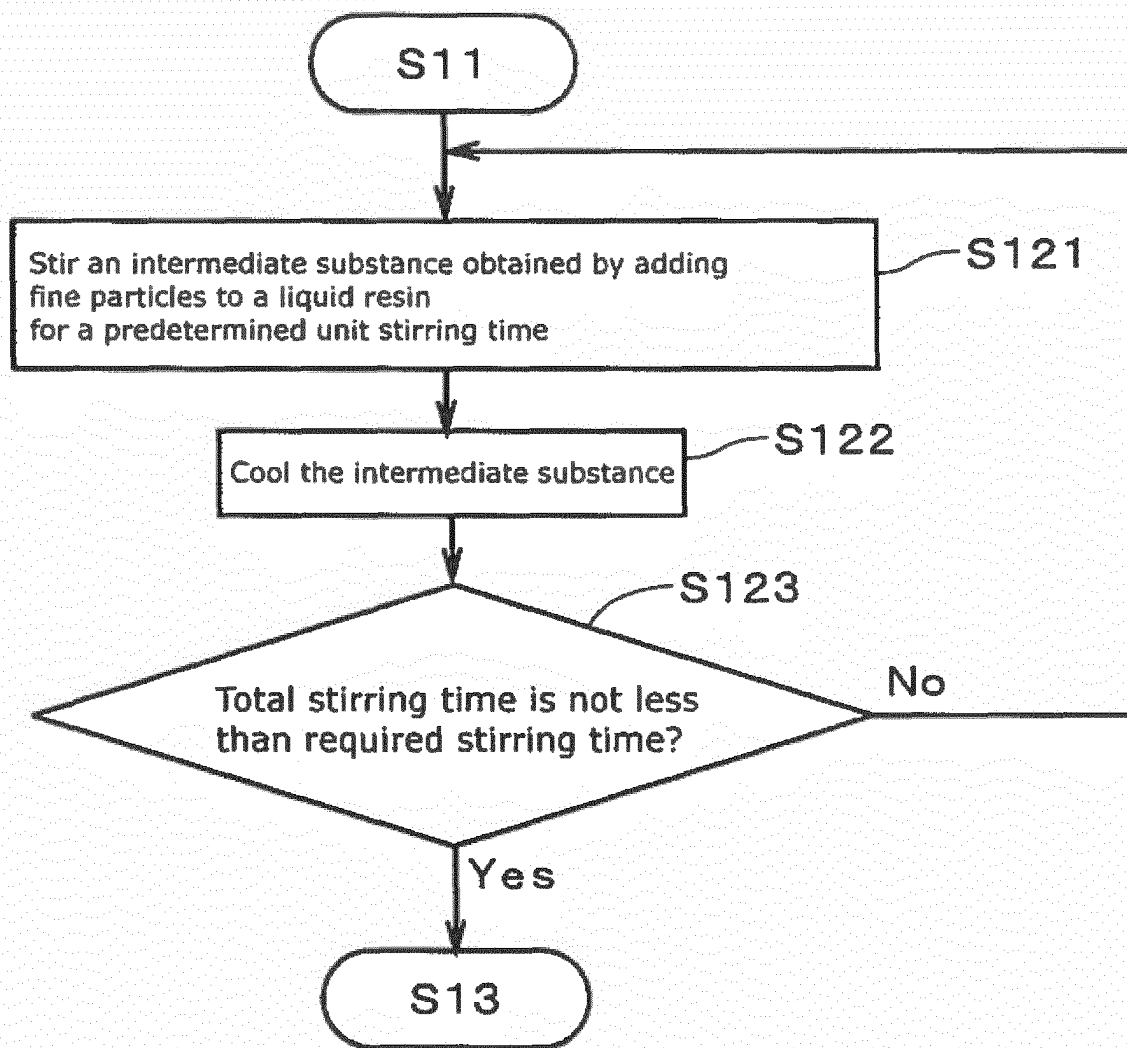


Fig. 3

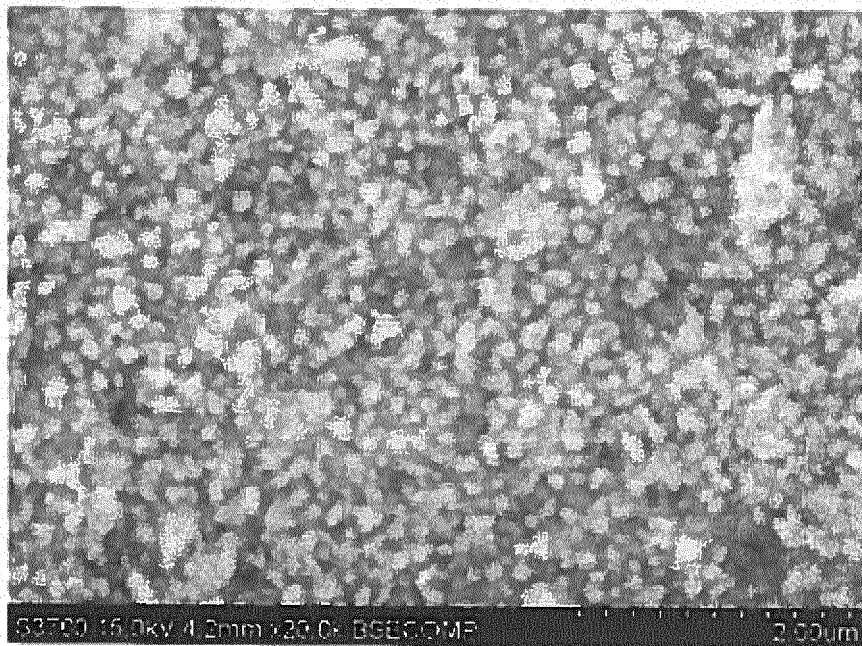


Fig. 4

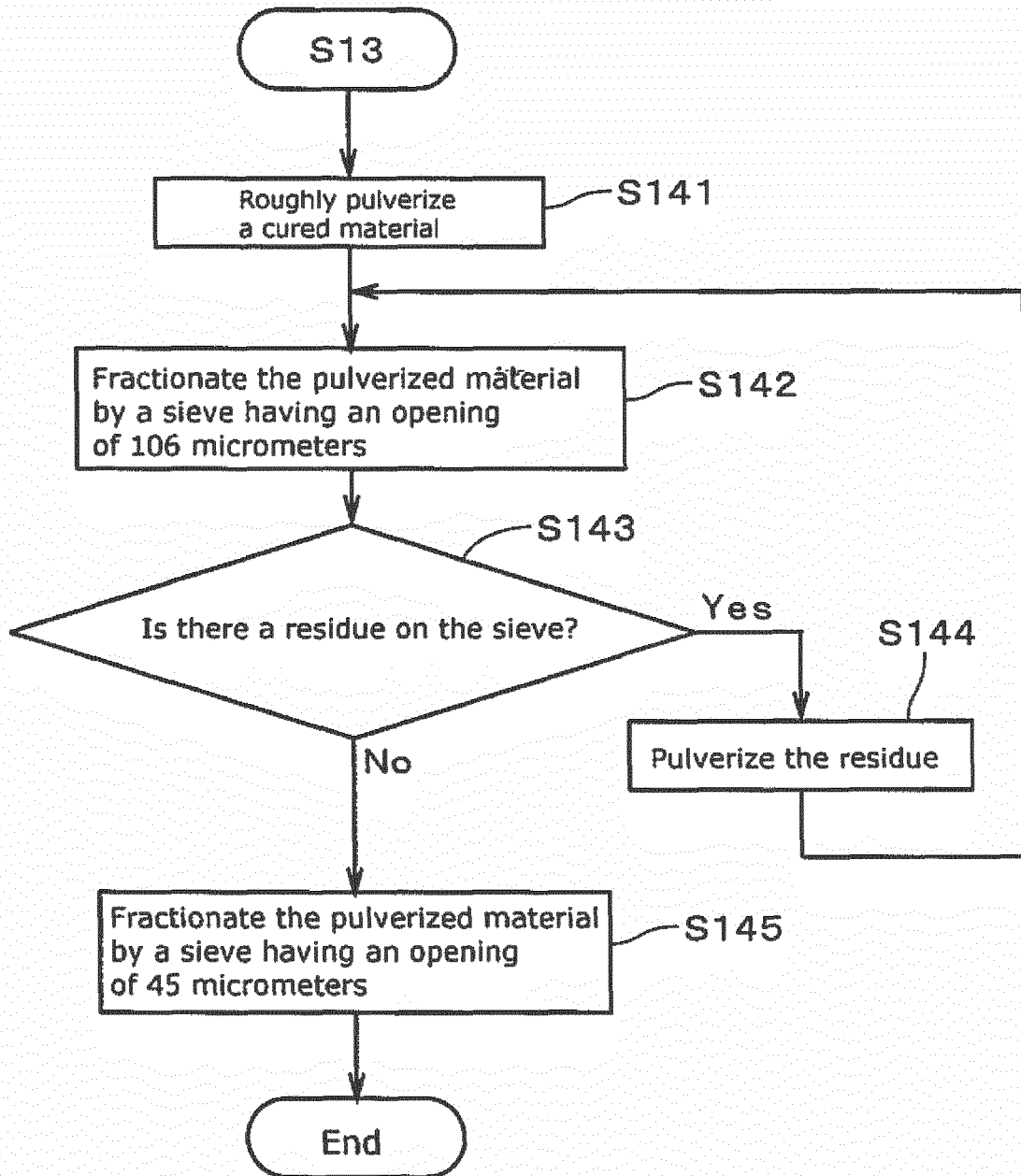
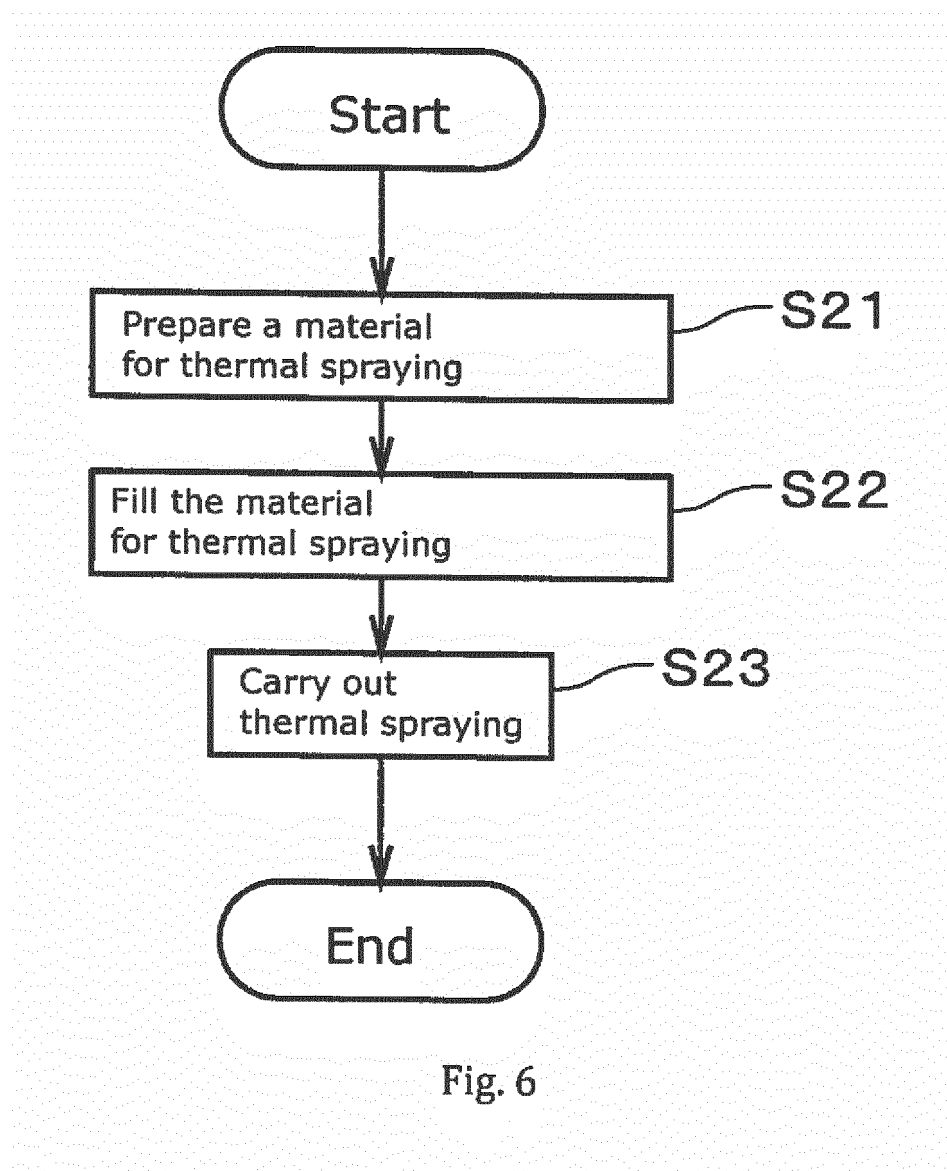


Fig. 5



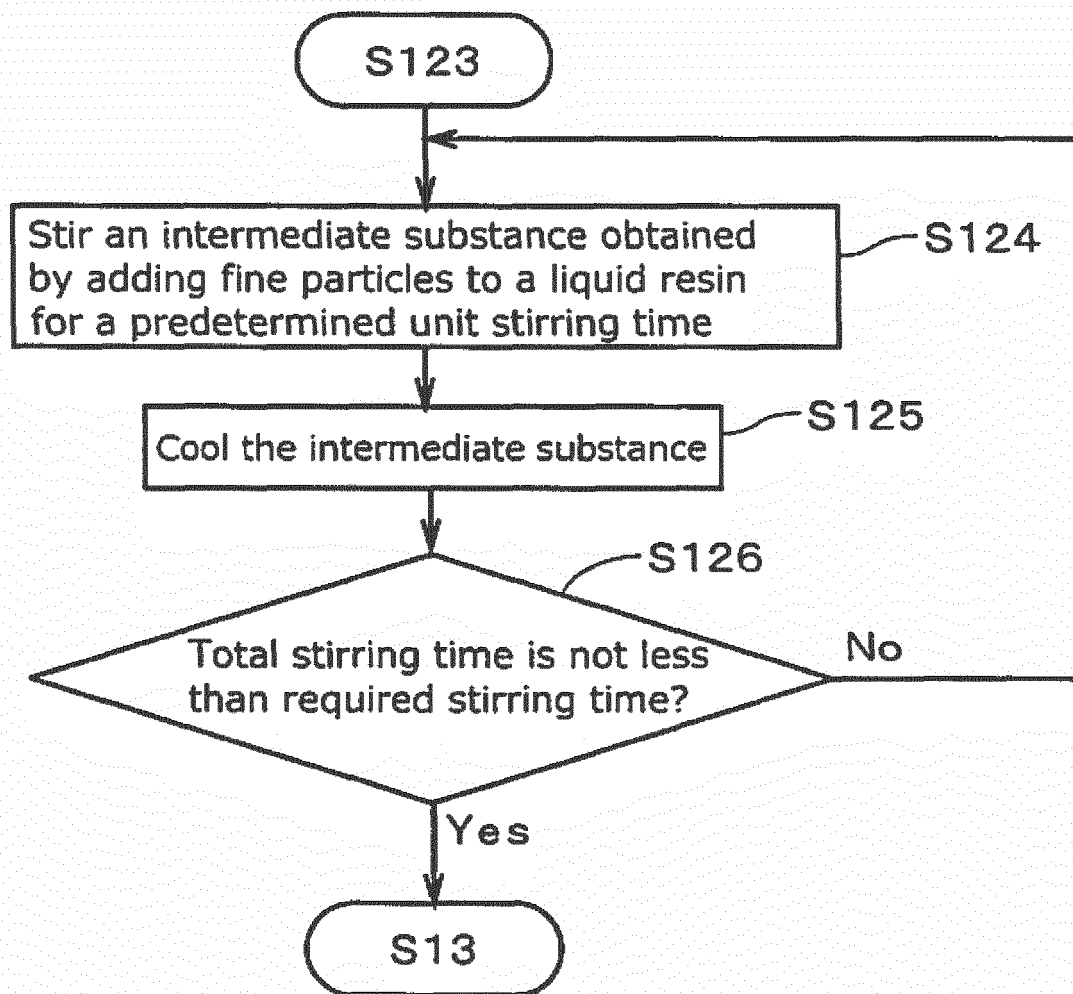


Fig. 7

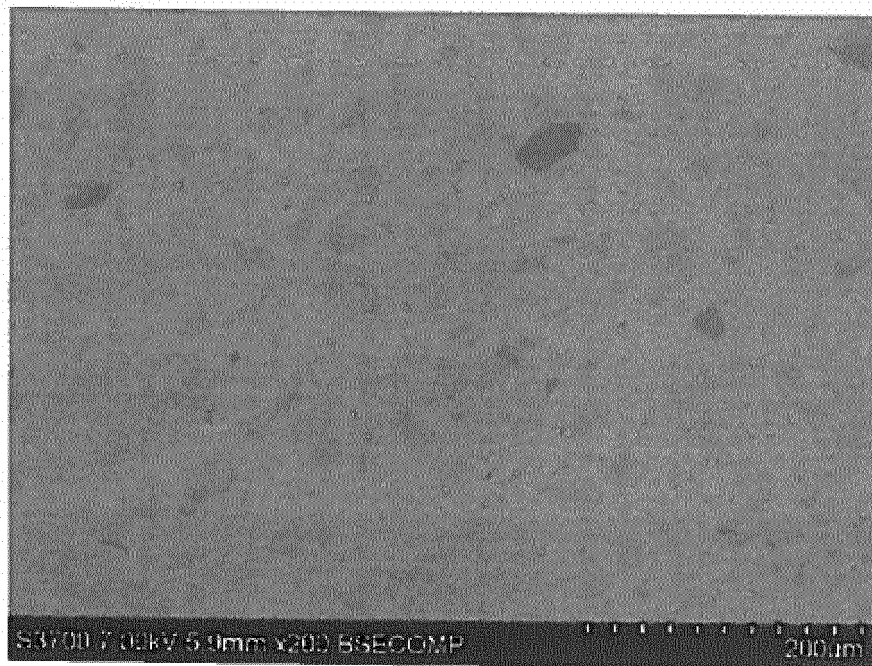


Fig. 8



Fig. 9



Fig. 10

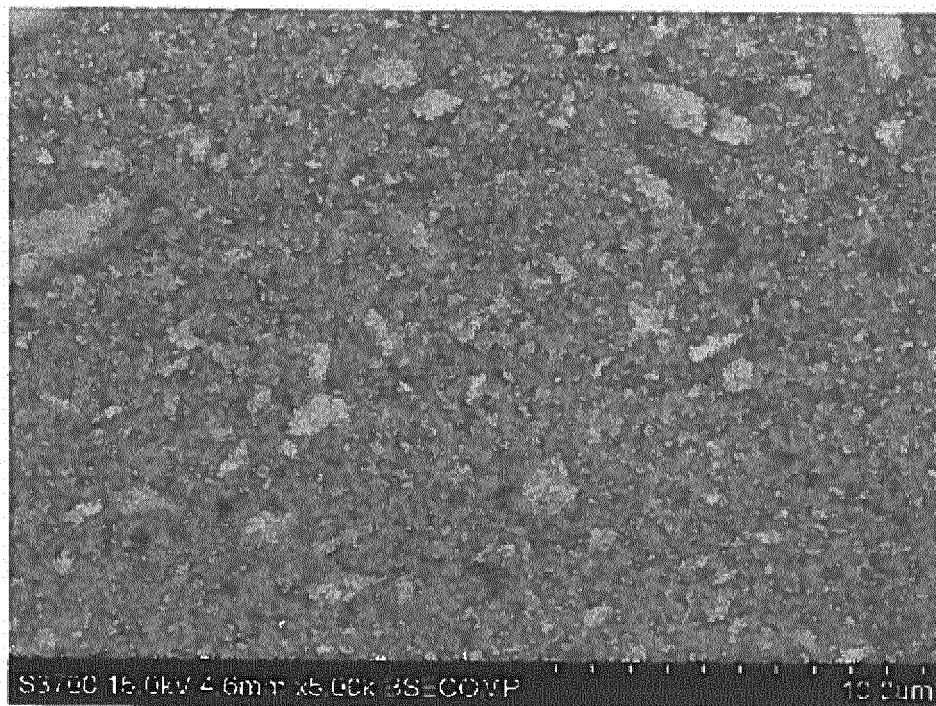
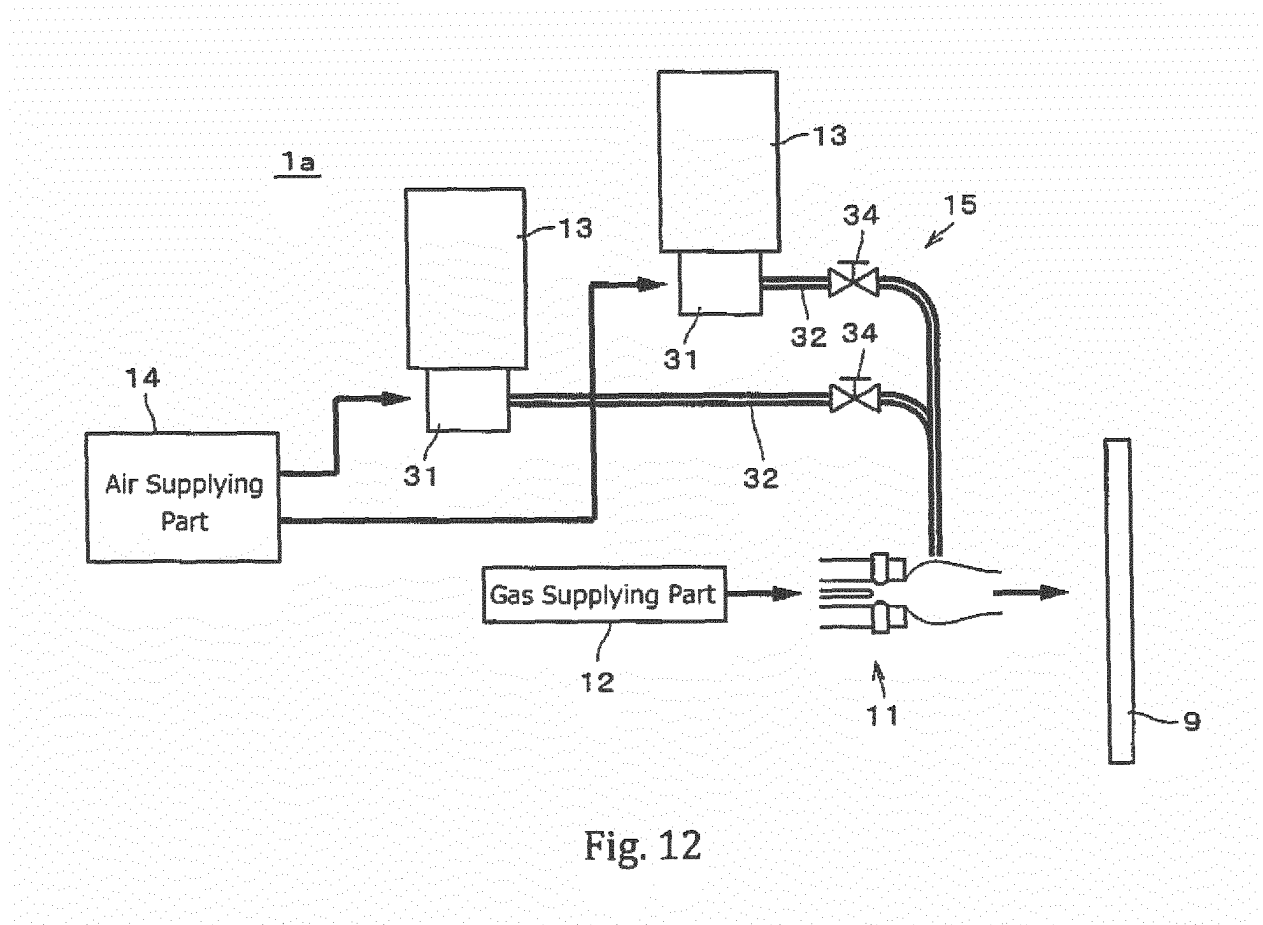


Fig. 11



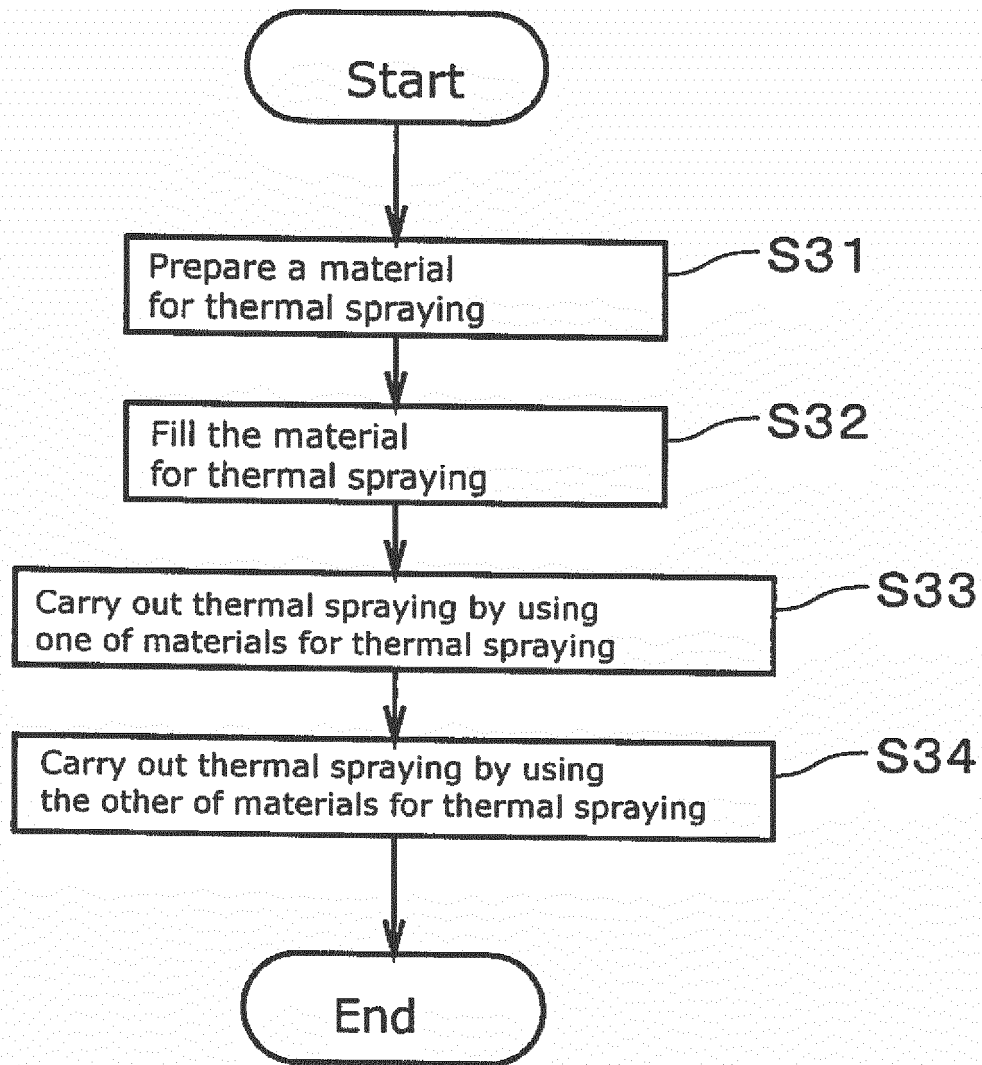


Fig. 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/051077

A. CLASSIFICATION OF SUBJECT MATTER

C23C4/10(2016.01)i, C23C4/06(2016.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C4/10, C23C4/06

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 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-207282 A (The Kansai Electric Power Co., Inc.), 25 October 2012 (25.10.2012), paragraphs [0019] to [0020], [0024] (Family: none)	1-11
A	JP 2010-133021 A (Topy Industries Ltd.), 17 June 2010 (17.06.2010), paragraphs [0019] to [0041] (Family: none)	1-11

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
27 January 2016 (27.01.16)Date of mailing of the international search report
09 February 2016 (09.02.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/051077

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-332558 A (Shin-Etsu Chemical Co., Ltd.), 22 November 2002 (22.11.2002), paragraphs [0021] to [0024], [0039] & US 2002/0160189 A1 paragraphs [0039] to [0044] & EP 1239055 A2 paragraphs [0037] to [0042]	1-11
A	JP 5-33113 A (Tocalo Co., Ltd.), 09 February 1993 (09.02.1993), paragraphs [0009], [0016], [0026] (Family: none)	1-11

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2011256465 A [0006]

Non-patent literature cited in the description

- **SOSHU KIRIHARA et al.** ceramic dense coating on a practically used alloy substrate by plasma thermal spraying using a nanoparticle narrow line. *Japan Welding Society national conference summary, the 91st collection*, 03 September 2012, 372-373 [0007]