EUROPEAN PATENT APPLICATION

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(54) Fabricating method of composite material, and heat conductive material and fabricating method of heat conductive material.

(57) In order to obtain a composite material excellent in the bonding strength (adhesion) of two materials and thermal conductivity, the invention presents a fabricating method of a composite material by compounding a high melting material W and a low melting material Cu, which comprises, a first step (1, 2, 3) of forming pores in the high melting material W, having the porosity distribution so that the porosity may be large at least in part of the surface thereof and that the porosity may gradually increase toward that part, and a second step (4) of infiltrating the low melting material Cu from the large porosity part of the material obtained in the first step (1, 2, 3), wherein the composition ratio of the high melting material and low melting material is in a gradient distribution.
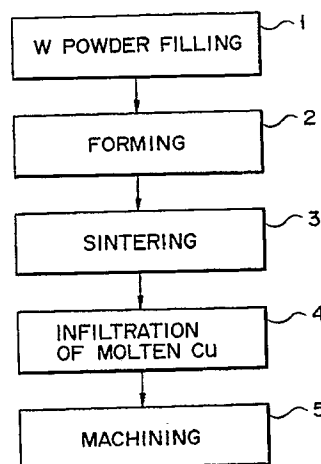
FIG. 1

The present invention relates to a fabricating method of a composite material for compounding two materials differing in melting point and not mixing with each other in solid solution, such as W (tungsten) and Cu (copper), and a heat conductive material and fabricating method of heat conductive material.

In the equipment possessing ultrahot molten metal field as represented by active metal melting crucible and heat receiving plate, it is often indispensable to use a material withstanding electron beam or plasma having high temperature and high energy density, that is, the beam target material.

Since the beam target material is used in rugged condition, it is required to satisfy the following two characteristics: (1) sufficient resistance to heat directly beneath heat source rising in temperature, (2) excellent heat conductivity and cooling characteristic. The second point is needed because the opposite side of the heat source is generally cooled by some means.

In a single material, however, the heat resistance and heat conductivity cannot be considered separately, and when either one is determined, the other is automatically determined, of course, within a limited range. Accordingly, hitherto, in order to enhance the both characteristics together, it is attempted to composite materials. One of such attempts is to fabricate a composite material excellent in both heat resistance and heat conductivity, by combining W which is high in melting point among metals and Cu which is excellent in heat conductivity.

When compounding W and Cu, however, since they are not mixed with each other in solid solution, the bonding method is limited, and simple gluing or brazing or other mechanical bonding methods are mainly employed.

If such compound of W and Cu is used in high temperature field, the difference in thermal expansion between the two is very large. Specifically, W has thermal expansion factor of $4.5 \times 10^{-6}/K$, while Cu has that of $17.1 \times 10^{-6}/K$, and the generated thermal stress is extremely large. Accordingly, when W and Cu are merely brazed and compounded, cracks are likely to be formed in W which has the smaller thermal expansion factor, due to tensile stress when heating, as well as peeling due to thermal stress caused in the interface of W and Cu. Such cracking and peeling will lower the total thermal conductivity, which may lead to temperature rise of materials, or meltdown accident in worst cases.

It is therefore attempted to obtain gradient materials with structure control (hereafter referred to as "gradient material" recently by mixing two powders, laminating by varying their mixing ratio, and sintering the laminates.

This technique is capable of obtaining gradient materials if the melting points of two powders to be mixed are similar to each other, but when extremely different, only one material is molten while the other is not, and it is difficult to fabricate a gradient material with structure control.

It is hence a primary object of the invention to present a fabricating method of a composite material excellent in thermal conductivity and bonding strength at the interface of two materials to be bonded together, a heat conductive material, and a fabricating method of a heat conductive material.

According to the invention there is provided a fabricating method of composite material compounding a high melting material and low melting material comprising: a first step of forming pores in the high melting material to obtain a material having a porosity distribution, with the porosity large at least in a part of the surface and gradually increasing in the porosity toward that part, and a second step of infiltrating the low melting material from the large porosity part of the material obtained in the first embodiment, wherein the composition ratio of the high melting material and low melting material is in a gradient distribution.

According to the invention, since the composition changes continuously in the gradient composition region (interface) of high melting material and low melting material, that is, the composition is sloped, the bonding strength (adhesion) of the interface of two materials and thermal conductivity are superior.

Besides, when the position with a large generation of thermal stress is made of the high strength material, it is possible to withstand more rugged conditions, such as high thermal load condition in the case of beam target, for example.

In addition, since the sintering process is varied by using thermal spraying, a gradient composition is made of a three-dimensional surface such as cylinder.

According to the second invention, grain boundary likely to cause grain boundary brittleness can be eliminated, so that the heat conductive material can withstand both stationary and nonstationary thermal loads.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a process chart showing a first embodiment of fabricating method of a composite material of the invention;

Figs. 2A and 2B show a schematic diagram of a composite metallic material gradient in composition at the interface of W and Cu of Fig. 1;

Fig. 3 is a schematic diagram of stress generated on the interface of W and Cu of Fig. 1;

Fig. 4 is a diagram showing the thermal conductivity in the mixed layer of W and Cu in the composition gradient part of Fig. 1;

Figs. 5A and 5B show, respectively, a sectional view of an active metal melting crucible and a diagram schematically showing the fine texture of part A of the material obtained in the embodiment in Fig. 1; .

Fig. 6 is a process chart showing a second embodiment of fabricating method of a composite material of the invention;

Fig. 7 is a diagram for explaining the effect of particle size of W powder or forming pressure on the relative density of the sintered body in the second embodiment;

Fig. 8 is a process chart showing third and fourth embodiments of fabricating method of composite material of the invention;

Fig. 9 is a diagram for explaining the mechanical strength of the material obtained from the third embodiment;

Fig. 10 is a diagram showing candidate examples of dispersion reinforcing material of the third embodiment and their principal properties;

Fig. 11A shows a perspective view of an electron beam target including the material obtained in the third embodiment;

Fig. 11B shows a sectional view of the electron beam target along an A-A line;

Fig. 12 is a diagram for explaining the infiltration method of Cu when fabricating the electron beam target material of Fig. 11;

Figs. 13A to 13D show, respectively, the results of analysis of temperature distribution and mechanical stress distribution when electron beam is emitted to the electron beam target in Fig. 11;

Fig. 14 is a diagram for showing the relation of the input heat density of electron beam, maximum principal stress (thermal stress) and maximum reaching temperature when electron beam is emitted to the electron beam target in Fig. 11;

Fig. 15 is a process chart showing a fifth embodiment of fabricating method of composite material of the invention;

Fig. 16 is an approximate sectional view of the material obtained in the fifth embodiment;

Fig. 17 is a process chart showing a sixth embodiment of fabricating method of composite material of the invention;

Fig. 18 is a process chart showing a seventh embodiment of fabricating method of composite material of the invention;

Fig. 19 is a process chart showing an eighth embodiment of fabricating method of composite material of the invention; and

Fig. 20 is an approximate sectional view of the material obtained in the eighth embodiment.

Referring now to the drawings, some of the

preferred embodiments of the invention are described in detail below. Fig. 1 is a process chart for explaining the first embodiment of the fabricating method of composite material of the invention. At step 1, in order to form W powder in specified shape, it is charged into a pattern (not shown). At step 2, the W powder obtained at step 1 is formed. At step 3, the form obtained at step 2 is sintered to form pores, and a sintered W body increased in the porosity toward the infiltrating side (the side where the infiltrated material becomes 100% as a result of infiltration) is obtained. At step 4, Cu is melted in a container (not shown), and it is infiltrated in the pores of the sintered W body obtained at step 3. At step 5, the material obtained at step 4 is machined and a finally desired product shape is obtained.

From thus obtained composite metallic material, the following effects are obtained.

1) The composition at the interface of W and Cu varies almost continuously, that is, the composition becomes gradient. Fig. 2 is a schematic diagram of compound metal material fabricated as described above, in which Fig. 2A is a composition distribution diagram and Fig. 2B is a distribution characteristic diagram relating to the ratio by weight of W and Cu. As evident from this diagram, since the composition is sloped in the gradient composition region of W and Cu, the composite metal material of the invention is, as compared with the conventional composite metal material making use of mechanical bonding such as gluing and thermal spraying of simple materials, increased in the contact area of W and Cu because a microscopic network structure is formed between W and Cu, so that the contact is notably enhanced.

2) In the embodiment, the coefficient of thermal expansion stress in the mixed layer of W and Cu changes almost in proportion to the mixing ratio. The thermal stress of the layer (i.e., a combination of compression stress and tensile stress) is relatively small and gently changes as is indicated by the solid curve shown in Fig. 3. By contrast, the thermal stress of the composite layer made by the conventional mechanical bonding method is great and changes much as is evident from the dot-dash line shown in Fig. 3.

3) The material of the embodiment can eliminate the gap between materials as seen in the simple gluing (the prior art), as the contact area of W and Cu increases. Accordingly, the thermal resistance is reduced at the interface of the gradient composition of W and Cu, and an excellent thermal conductivity as in W alone or Cu alone may be obtained. Fig. 4 is a characteristic diagram of thermal conductivity to explain this, and

as evident from this diagram, it is possible to obtain an excellent thermal conductivity on the whole, exceeding that of the W alone, by making use of the characteristic that the thermal conductivity of the portion gradient in composition depends greatly on Cu which is greater in the conductivity.

Referring now to Fig. 5, an example of applying the composite material obtained in the first embodiment into a crucible for melting active metal or heat receiving plate is explained below. Fig. 5A is a sectional view showing a crucible for melting active metal main body 11 and water-cooled hearth 13, and Fig. 5B is a schematic diagram of fine texture of part A of Fig. 5A. The crucible main body 11 side is exposed to high temperature and is hence made of high melting metal W, the water-cooled hearth 13 is made of Cu which is excellent in thermal conductivity, and the gradient composition region 14 of W and Cu is a so-called gradient composition varying continuously in composition. Numeral 12 is a water cooling hole.

To manufacture such structure, the process is as shown in Fig. 6. That is, at the first step 21, W fine powder is prepared, and it is laminated in the shape of the crucible main body 11 in Fig. 5. At the second step 22, the laminate obtained in the first step 21 is formed, for example, by CIP (cold isostatic pressing) to produce a W form. At the third step 23, the W form obtained in the second step 22 is held in H_2 or other reducing high-temperature atmosphere for about several hours to produce a W sinter. At the fourth process 24, the sintered W body obtained in the third step 23 is machined to finally finish into a crucible shape. In this case, it is machined including the gradient portion of the interface.

In the first to fourth processes 21 to 24, the density becomes 95% or more at the inside of the crucible main body 11. Besides, the manufacturing conditions such as material powder, forming pressure, sintering temperature and others are controlled so that the density may change continuously to about 50% at the outside of the crucible main body 11.

At the fifth step 25, Cu is melted by some means, and the sintered W obtained in the third process 23 is infiltrated into this molten bath of W, and after holding until the molten Cu is sufficiently penetrating into the pores of the sintered W, it is cooled. The fifth process 25 is conducted in reducing high temperature atmosphere of H_2 or the like, and in the sixth process 26, after sufficiently cooling, it is taken out into the atmosphere, and is machined to the specified dimensions of the crucible main body 11 and water-cooled hearth 13.

The crucible made of such composite metal material manufactured in such fabricating method

(Fig. 5) is wide in the contact area of the gradient composition region 14 with W and Cu, and hence the adhesion and thermal conductivity are excellent. Moreover, since the composition of the gradient composition region 14 is gradient, it is effective to reduce the peak value of the thermal stress caused when heating due to the difference in the coefficient of thermal expansion between W and Cu.

On the other hand, the crucible of the embodiment is characteristic in that a sintered W crucible continuously varying in the porosity at the outside of the crucible main body 11 is fabricated. As for the effect of the material powder on the density of sintered body as shown in Fig. 7, by varying the powder particle size within a range of 1 μm to 10 μm, it is possible to fabricate a W sinter possessing the relative density of 60% to 95%. By making use of this property, by continuously varying the particle size of the W powder used in lamination of W powder, the sintered W crucible varying continuously in density from 95% to 60% can be manufactured. Meanwhile, although the effect is not so great as to change the powder particle size, it is also a method to vary the forming pressure and sintering temperature for changing the density of the sinter, and by combining them, it is possible to fabricate the sintered W crucible main body 11 more effectively. Besides, in impregnation of sintered W crucible main body 11 into molten Cu, since the molten Cu is very likely on a solid W to wet, and it penetrates into the closed pores in the sintered W body. Since the boundary of the closed pores and open pores of the sintered W body is about 90%, the majority is infiltrated into the low density area of the outside of the sintered W crucible main body 11. Therefore, since the density of the outside of the sintered W crucible main body 11 changes continuously, a crucible of gradient composition of W and Cu is completed in this way.

According to the second embodiment described so far, the interface composition of W and Cu is gradient, and the contact area of W and Cu is increased, so that the following effects are brought about.

a) The adhesion at the gradient composition region 14 is strengthened, and the thermal stress at the gradient composition region 14 during high-temperature use is alleviated, and hence cracks and peeling at the gradient composition region 14 are decreased, so that the life is extended.

b) The thermal resistance at the gradient composition region 14 is reduced and the total thermal conductivity is enhanced, so that the water-cooling effect of the water-cooled hearth 13 may be sufficiently utilized. As a result, the temperature gradient of the molten metal in the crucible

main body 11 is increased, and the internal wall temperature of the crucible main body 11 may be lowered, which also contributes to extension of the life.

The second embodiment relates to an active metal melting crucible or heat receiving plate, but it may be also applied in other high temperature devices that require the combination of W and Cu. In the embodiment, as the materials for compounding, the combination of W and Cu is presented, but it is not limitative, and it may be applied to any other two materials as far as they differ in melting point and are not mutually miscible in solid solution. Anyway, it is necessary to comprise a step of sintering the high melting material and a step of impregnation of the sintered body into the low melting molten material, and after these steps, a gradient material at the interface of the composite metal material is obtained.

The third and fourth embodiments of the fabricating method of the composite material of the invention are explained below while referring to Figs. 8 to 10. In the first embodiment described above, since the change of the coefficient of thermal expansion at the interface of W and Cu is reduced, as compared with the conventional brazed material, the thermal stress can be alleviated significantly. However, in the first embodiment, the mechanical strength is not fully satisfactory because it requires a step of manufacturing a sintered W body having a porosity distribution in the plate thicknesswise direction, and a step of sintering and infiltrating of molten Cu into pores of the sintered W body. That is, since the W which is responsible for mechanical strength undergoes a step of sintering, the grain boundary is particularly weak in the recrystallized grains. Furthermore, since this sintered W body is required to have a porosity distribution in the plate thicknesswise direction, hot forging cannot be applied as the post-processing for enhancing the mechanical strength. Therefore, even if the thermal stress is alleviated by sloping the composition at the interface of W and Cu, since the mechanical strength is low, cracks may be formed in the W.

Accordingly, in the third embodiment, in order to enhance the mechanical strength of the first embodiment, in a combination of two materials of single composition such as W/Cu gradient material, by adding a second element which is miscible in solid solution, for example, powder of Re (rhenium), Ta (tantalum), Nb (niobium) or Hf (hafnium), the solid solution composition is sloped, so that only the mechanical strength is enhanced while holding the same functions.

More practically, as shown in the process chart in Fig. 8, at the first step 31, Re powder is added to the W powder differing in particle size. At the

second step 32, powders are laminated sequentially from the smaller particle size. At the third step 33, the laminate laminated in the second step 32 is formed by die press forming or CIP forming method. At the fourth step 34, the form obtained in the third step 33 is sintered, and the solid-solution element is alloyed with W, thereby obtaining a W alloy sintered body having a porosity distribution in the plate thicknesswise direction (W-HIP material in Fig. 9). At the fifth step 35, the W alloy sintered body obtained in the fourth step 34 is impregnated in molten Cu and Cu is infiltrated in pores, and it is cooled. At the sixth step 36, the infiltrated material obtained in the fifth step 35 is machined and finished to a desired product shape.

The fourth embodiment is, similar to the third embodiment, a fabricating method of composite material enhanced only in the mechanical strength, while maintaining the functions, in which, in order to enhance the mechanical strength of the first embodiment, in a combination of two materials of single composition such as W/Cu gradient material, a second element or compound not miscible in solid solution, such as ThO_2 (thoria) powder is added, and the dispersion is intensified to slope the composition.

More practically, the four embodiment is same as the third embodiment except that, as shown in the process chart in Fig. 8, ThO_2 powder is added to the W powder differing in particle size in the first step 31.

The materials obtained by the third and fourth embodiments feature the following points.

1) The W which is responsible for the mechanical strength of the material is greatly enhanced in the bending strength by alloying as shown in Fig. 9.

2) Since the interface of the W alloy and Cu is gradient in composition, there is not abrupt change in the coefficient of thermal expansion, and the thermal stress is alleviated as compared with the bond by the conventional brazing or other method.

3) Since the thermal conductivity of W alloy mainly depends on W which is superior in heat conduction, the thermal conductivity on the whole is hardly lowered although the thermal conductivity of ThO_2 is a low 10 W/m,k.

5) As evident from the process of the material obtained in the fourth embodiment, since the Cu with excellent thermal conduction is in network structure, the total thermal conduction is very good.

In the fourth embodiment, ThO_2 is used as the dispersion reinforcing agent, but basically any other material may be used as far as it is stable chemically and high in melting point, and any of the dispersion reinforcing agents shown in Fig. 10,

that is, TaB_2, TiB_2, HfB_2, Y_2O_3, ZrO_2, may be used.

Hence, according to the third and fourth embodiments, peeling at the interface of W and Cu and cracks in material may be eliminated, and finally rise of material temperature and melting accident derived from the increase of thermal stress due to peeling or cracking may be eradicated.

An example of application of the material obtained in the third embodiment as electron beam target is explained below while referring to Figs. 11 to 14. Fig. 11A, Fig. 11B relate to an example of application of the composite material obtained in the third embodiment in the beam target for active metal melting crucible or the like, in which Fig. 11A is a schematic diagram of a target for electron beam (EB), and Fig. 11B is a sectional view showing the section cut in the direction of the arrow along the line A-A in Fig. 11A. Since the C side of the beam target 121 is exposed to the EB 116 and high in temperature, it is made of W alloy of high melting point and high strength.

On the other hand, the D side on the opposite side of the beam target 121 is made of Cu which is excellent in thermal conductivity and machinability, and it is cooled in water with water cooling pipe 117. Between the C side and D side, the composition ratio of W alloy and Cu changes continuously, that is, the so-called gradient composition is made.

The composite material used in Fig. 11A, Fig. 11B is manufactured in the following procedure. In the first place, the W alloy sintered body 118 is fabricated same as shown in Fig. 8, from the first to the fourth steps. However, when infiltrating Cu 119 into pores of the W alloy sintered body 118, as shown in Fig. 12, in a slightly large graphite crucible 120, the low porosity side is set at the upper side, and the build-up part of Cu is disposed at the opposite side. In this state, after completion of infiltration of Cu, it is machined and finished to desired size, and a hole is drilled for the water cooling pipe 117. Finally, the water-cooling pipe 117 is brazed by using Ag-Cu solder or the like, thereby completing the beam target 121.

In thus fabricated beam target 121, the W alloy and Cu are in gradient composition, and the Cu of excellent thermal conductivity is in network structure, and therefore the temperature reached during use may be lowered, and the thermal stress may be alleviated.

Fig. 13 shows the result of analysis of temperature distribution and thermal stress (principal stress) distribution when the electron beam target shown in Fig. 11 is exposed to electron beam. Specifically, Fig. 13A and Fig. 13C are to compare the result of analysis by finite element method of temperature distribution when heated by linear EB

of 5 kW/cm^2 each, between the W alloy/Cu gradient material, and W alloy/Cu brazed material. Fig. 13B and Fig. 13D are to compare the thermal tress distribution when heated by linear EB of 5 kW/cm^2 each by the same finite element method, between the W alloy/Cu gradient material and W alloy/Cu brazed material. It is known from the result that the maximum reaching temperature may be lowered by about 80 K by composing gradient material. Besides immediately, beneath the EB where the temperature gradient is the greatest, the maximum thermal stress is known to be reduced to about 1/3.

Incidentally, since the beam target 121 is heightened in strength by alloying W, the EB input until breakdown may be increased. Fig. 14 shows the EB input heat density, generated maximum thermal stress, and maximum reaching temperature as analyzed by finite element method. As shown in Fig. 13, the maximum thermal stress is generated in the W alloy layer immediately beneath the heat source, and since the degree of lowering of strength of each part does not seem to be so great owing to compounding with Cu, the breakdown of beam target 121 is considered to be induced when the stress generated in the alloy layer becomes larger than its strength.

The dot-dash lines shown in Figs. 13A to 13D are central lines of distribution diagrams. Only right half of each distribution diagram is, hence, illustrated, since the left half if symmetrical to the right half.

Here, on the basis of the result of measurement of strength of W or W alloy at ordinary temperature, it is estimated how much the input heat can be increased by alloying. In the case of pure W, the strength is about 0.4 Gpa, and the maximum applicable input heat density is about 4 kW/cm^2 at most, but in the case of W-5Re alloy adding 5% Re, the strength is increased about twice to 0.8 Gpa, so that an EB input of about 8 kW/cm^2 is possible. Furthermore, when the input heat density is 9 kW/cm^2 the maximum reaching temperature exceeds the melting point of W alloy, and it is meaningless if the Re content is increased to raise the strength, which is the application limit for the beam target 121.

In the third and fourth embodiments described so far, the beam target 121, especially linear EB heating, is mentioned, but it may be also applied to all other high temperature equipment parts requiring heat resistance and thermal conductivity, and the beam form is not limited to EB, but it may be applied to all heat sources.

The fifth embodiment is described below by reference to Figs. 15, 16. The fabricating method of the fifth embodiment comprises the first step 41 through fourth step 44. At the first step 41, a high strength substrate 45 is prepared by rolling, forging

or other plastic processing. At the second step 42, the high strength substrate 45 fabricated in the first step 41 is sprayed by a known vacuum plasma spraying apparatus as mentioned below, On the heating surface in the case of EB irradiated beam target, or a material producing a large stress locally, and the sprayed film with gradient porosity is made of two materials. At the third step 43, the material obtained in the second step 42 is applied to a capsule-free HIP (hot isostatic pressing) device to remove the closed pores (defects) which may initiate breakdown. At the fourth step 44, by infiltrating the second material into the open pores existing in the material obtained in the third step 43, a composite material having a gradient composition layer 46 is completed as shown in Fig. 16.

The vacuum plasma spraying (VPS) apparatus is briefly described below. A high pressure container is filled with inert gas reduced to about tens to hundreds of Torr, and the work to be sprayed is put in this atmosphere, and the powder from the powder feeder is sprayed therein together with the plasma from the plasma control unit.

The capsule-free HIP (open HIP) is a process of conducting hot isostatic pressing on the material not contained in a capsule, and is different from the ordinary HIP in which no pressure is applied to the inner part of the material which is contained in a capsule which collapses at high temperatures.

Thus obtained composite material using the high strength substrate 45 manufactured by plastic processing, and the mechanical strength can be reinforced. Besides, since the porosity by spraying method depends greatly on the particle size of the powder to be used, in other words, a spray film with gradient porosity is formed only by varying the particle size of the powder to be used. Still more, since the vacuum plasma spraying method is to spray in a reduced inert atmosphere of about tens to hundreds of Torr, it is possible to form a film less in oxide coating, strong in bonding force among particles, and tight in contact with the high strength substrate. Besides, by a capsule-free HIP, it is possible to eliminate causes of increase of thermal resistance, or closed pores where stress is concentrated. In this case, by performing infiltration at ordinary pressure or high pressure with inert gas or in reducing atmosphere, the open pores may be filled up with the second material.

Thus, according to the fifth embodiment, cracks and other defects in electron beam heating may be reduced, while the input heat density may be increased.

Reference is them made to Figs. 17, 10 to explain the sixth embodiment of the invention. As shown in the process chart in Fig. 17, this method comprises the first step 51 through the fifth step 55. At the first step 51, substrate surface is cleaned at the first step. At the second step 52, the substrate cleaned in the first step 51 and the same material are sprayed, for example by vacuum plasma spraying, to slope the composition continuously. At the third step 53, by the open HIP, leaving the open pores (communicating with outside) formed in the second step 52, the closed pores (not communicating with outside) are destroyed. At the fourth step 54, a low melting metal, for example, Cu is infiltrated into the pores obtained in the third step 53. The fifth step 55 is for machining.

The sixth embodiment brings about the following effects. Since the vacuum plasma spraying in the second step 52 is to spray in an inert gas atmosphere at tens of Torr, the material is not oxidized. By using powder material of large particle size for spraying, the internal unmolten particles drift and deposit, and a film of a relatively large porosity may be formed.

Furthermore, in the open HIP treatment in the third step 53, the closed pores can be eliminated while leaving the open pores formed by vacuum plasma spraying in the second step 52. By infiltrating the low melting material Cu into the material W possessing only open pores and having gradient pores obtained in this way, it is possible to spray in a relatively wide area, and a large and continuous gradient material may be fabricated.

Accordingly, also on the three-dimensional curved surface which was difficult to obtain in the first embodiment, a gradient structure may be formed, and the gradient is continuous, while it was stepwise in the first embodiment, so that the thermal stress may be alleviated furthermore. Consequently, the thermal stress alleviation on the interface of different materials such as coating and joint may function effectively, so that the heat cycle characteristic and heat resistance may be improved.

As the substrate in the sixth embodiment, any one of W, Mo, Ta, Nb, Re, V, ZrO_2, MgO, Al_2O_3, Y_2O_3, SiC, Si_3N_4, BN, AlN may be used, and the low melting material may be selected from Cu, Ag, Fe, Ni, Co or their alloys.

The vacuum plasma spraying in the sixth embodiment is not limitative, but as far as the material is excellent in oxidation resistance, any atmospheric spraying method such as plasma spraying, gas spraying and arc spraying method may be applied, and same effects will be obtained.

The seventh embodiment is explained by reference to the process chart in Fig. 18. This embodiment is characterized by the HIP infiltration to treat at high pressure, when infiltrating the second material into the pores of the first material in the fourth step of the first embodiment. That is, after obtaining the sintered body in the third step 63, infiltra-

tion by open HIP is conducted at the fourth step 64, and then HIP infiltration is carried out at the fifth step 65.

For example, in order that a fluid with a surface tension δ enters in a circular pore with radius r, supposing the contact angle to be θ, the pressure P must satisfy the following relation.

$$P \geq (2\delta \cos\theta) \div r$$

Therefore, once the material system is determined, θ and δ are automatically decided, and if desired to permeate liquid into tiny holes, the pressure P must be increased. In other words, when pressure P is applied more, liquid can penetrate into smaller holes.

Hence, by infiltrating by means of HIP apparatus capable of creating high temperature, high pressure field, the second material can be securely infiltrated into open pores. As the type of gas, meanwhile, when inert gas such as Ar and He is used, the problem of oxidation of material may be eliminated.

On the other hand, when the temperature is raised, generally, the contact angle θ becomes smaller. In consequence, cos θ becomes smaller, and therefore provided the pressure P be constant, the radius r may be reduced, but it gives rise to the problem of material reaction.

Accordingly, by HIP infiltration in high pressure field, open pores are not left over, and it is possible to fabricate a gradient material with small reaction between materials. As the pores are eliminated, the mechanical strength is enhanced, and the thermal conductivity is improved.

In the seventh embodiment, in order to reduce the contact angle θ, an active element may be added in the liquid to promote infiltration into the fine pores.

Referring then to Figs. 19, 20, the fabricating method of heat conductive material by the invention, and the heat conductive material obtained by this method (hereinafter called the eighth embodiment) are explained. Fig. 19 is a process chart for explaining the fabricating method, and at the first step 71, the dope rolled material is fabricated to make the heat receiving side with single crystals of W, Mo. At the step 72, the surface of the rolled material obtained in the first step 71 is roughened by blasting or the like, and W powder is laminated in gradient. At the third step 73, sintering and bonding the W rolled material and W powder obtained in the second step 72, the materials are sent to the fourth step 74, in which, simultaneously with the third step 73, by making use of secondary recrystallization, the minimum surface doped W, Mo rolled materials of W, Mo are grown into giant

crystal grains to prepare a skeleton of W or Mo. In this case, the heat receiving side is the single crystal. Later, at the fifth step 75, Cu is infiltrated into the pores sloped at the fourth step 74, and it is machined and finished at the sixth step 76.

The heat receiving material 77 made in such process is shown in Fig. 20. In this case, the large thermal stress receiving unstationarily is borne by the single crystal W Or Mo excelling in ductility on the heat receiving surface 78, while the stationary thermal stress is alleviated by the W/Cu gradient composition beneath it. By eliminating the grain boundary of W and Mo where grain boundary brittleness is likely to occur, a heat receiving material having W, Mo extremely excellent in ductility disposed at the heating side is obtained. Aside from superior heating performance, the thermal impact property by quick heating is improved.

This embodiment for manufacturing the heat receiving material also avoids the following points. That is, in fabrication of sintered body of W, Mo and giant crystal grain growth, sintering of W, Mo powder is sometimes promoted too much, and a porosity gradient region may not be fabricated sufficiently. Accordingly, in this embodiment, by using particles of about 10 microns, this problem is avoided. Besides, by vacuum plasma spraying, it is possible to form a gradient region 80 of W, Mo on the rear side of the single crystal plate. Moreover, by executing the giant crystal growth in the first place, the powder may be laminated in gradient on the surface of the single crystal material, and then the sintered bond Cu is infiltrated, so that a similar heat receiving plate may be manufactured.
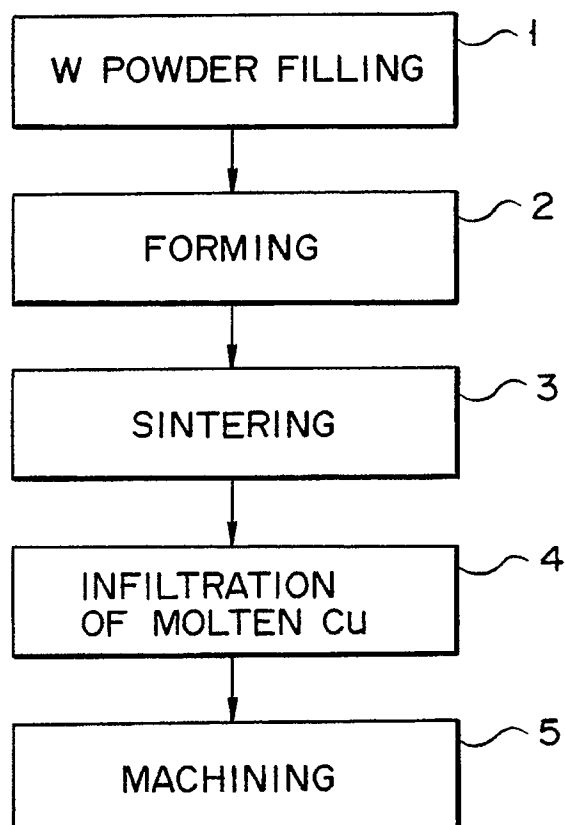
In the eighth embodiment for fabricating the heat receiving material 77, the heat receiving side 78 is W, or Mo, but this heat receiving side may be also made of Re or V, or an alloy mainly comprising W, Mo, Re or V. Besides, on the opposite side of the heat receiving side 78 in Fig. 20 (for example, the water cooling surface) 79, a high thermal conductive material such as Cu, Ag, Fe or their alloy may be formed, and the composition may be sloped from the heat receiving side 78 to the opposite side.

In the foregoing embodiments, when forming pores in the high melting material or low melting material, either sintering method or vacuum plasma spraying method is employed, but it may be also possible to employ other methods, including chemical deposition method and physical deposition method.
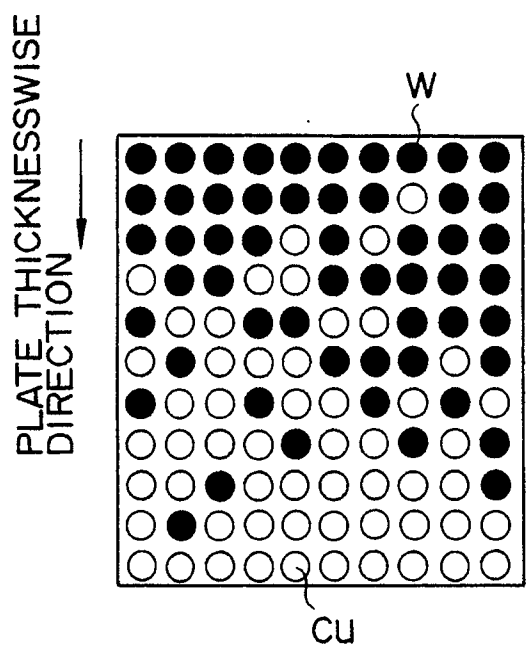
Claims

1. A fabricating method of composite material compounding a high melting material and low melting material characterized by comprising:
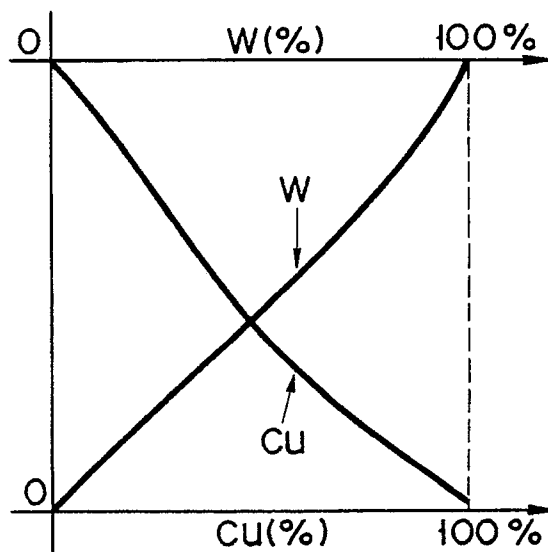
a first step of forming pores in the high melting material to obtain a material having a porosity distribution, with the porosity large at least in a part of the surface and gradually increasing in the porosity toward that part, and

a second step of infiltrating the low melting material from the large porosity part of the material obtained in the first embodiment, wherein

the composition ratio of the high melting material and low melting material is in a gradient distribution.

2. A fabricating method of claim 1, characterized in that the method of forming pores in the high melting material is any one of sintering method, vacuum plasma spraying method, chemical deposition method and physical deposition method.

3. A fabricating method of claim 1, characterized in that the first step comprises:

a) a step of adding and mixing a powder of high melting material and a powder of a second element miscible with this powder in solid solution, and

b) a step of forming the mixture obtained in step a) to obtain a reinforced form in solid solution.

4. A fabricating method of claim 1, characterized in that the first step comprises:

c) a step of adding and mixing a powder of high melting material and a powder of a second element or a compound not reacting to this powder, and

d) a step of forming the mixture obtained in step c) to obtain a dispersed and reinforced form.

5. A fabricating method of claim 1, characterized in that the first step comprises:

e) a step of obtaining a substrate having the high melting material reinforced in mechanical strength by any one of the methods of rolling, forging, other plastic processing, and alloying, and

f) a step of spraying a common material to the substrate obtained in step e) by vacuum plasma thermal spraying to form pores, thereby obtaining a spraying film increased in the porosity to the infiltrating side.

6. A fabricating method of claim 1, characterized in that the first step is to form pores by spraying a similar material to the substrate by thermal spraying.

7. A fabricating method of claim 1, characterized in that the first step comprises:

g) a step of spraying a similar material to the substrate by thermal spraying to obtain a material having pores, and

h) a step of treating the material obtained in step g) by hot isostatic pressing.

8. A fabricating method of claim 7, characterized in that the hot isostatic pressing treatment is a capsule-free method of treating without putting material in capsule.

9. A heat receiving material used in ultrahigh temperature field, possessing heat receiving side and anti-heat receiving side, characterized by forming a material layer high in melting point and capable of forming single crystals at the heat receiving side, and distributing the composition ratio in gradient from the heat receiving side to the anti-heat receiving side.

10. A fabricating method of heat receiving material compounding a low heat conductive material and a high heat conductive material, characterized by comprising:

a first step of using a substrate made of plastic material such as doped rolled material and forged material as the low heat conductive material, and laminating a material powder of the same kind as the substrate on one side of the substrate to form a laminate,

a second step forming a sintered body by of heating and sintering the laminate obtained in the first step, thereby forming single crystal on the surface to be used as the heat receiving side, by forming pores in the side opposite to this heat receiving side, and by controlling the porosity distribution so that the porosity is large at least in part of the surface and that the porosity increases gradually toward that part, and

a third step of infiltrating the high heat conductive material into the pores of the sintered body obtained in the second step, wherein

the composition ratio of the low heat conductive material and high heat conductive material is in a gradient distribution.

11. A fabricating method of claim 10, characterized in that the first step is to obtain a laminate by using a substrate made of plastic material such as doped rolled material and forced material as the low heat conductive material, and laminating the material powder of the same kind as this substrate on one side of the substrate by vacuum plasma thermal spraying.

```
┌─────────────────────┐
│  W POWDER FILLING   │╮ 1
└─────────────────────┘╯
          │
          ▼
┌─────────────────────┐
│      FORMING        │╮ 2
└─────────────────────┘╯
          │
          ▼
┌─────────────────────┐
│     SINTERING       │╮ 3
└─────────────────────┘╯
          │
          ▼
┌─────────────────────┐
│    INFILTRATION     │╮ 4
│   OF MOLTEN Cu      │╯
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│     MACHINING       │╮ 5
└─────────────────────┘╯
```

F I G. 1

F I G. 2A   F I G. 2B

F I G. 3

F I G. 4

F I G. 5A

F I G. 5B

LAMINATION OF W POWDER (CRUCIBLE SHAPE)	21

↓

PREPARATION OF W FORM (CIP)	22

↓

PREPARATION OF W SINTER (ATMOSPHERIC REDUCING ATMOSPHERE)	23

↓

MACHINING (CRUCIBLE SHAPE)	24

↓

INFILTRATION OF MOLTEN Cu	25

↓

MACHINING (CRUCIBLE MAIN BODY AND WATER-COOLING HEARTH)	26

F I G. 6

FIG. 7

| W POWDER | | SECOND ELEMENT, COMPOUND |

```
        ┌──────────────────┐
        │     MIXING       │── 31
        └──────────────────┘
        ┌──────────────────┐
        │    LAMINATING    │── 32
        └──────────────────┘
        ┌──────────────────┐
        │     FORMING      │── 33
        └──────────────────┘
        ┌──────────────────┐
        │    SINTERING     │── 34
        └──────────────────┘
        ┌──────────────────┐
        │   INFILTRATION   │── 35
        └──────────────────┘
        ┌──────────────────┐
        │    MACHINING     │── 36
        └──────────────────┘
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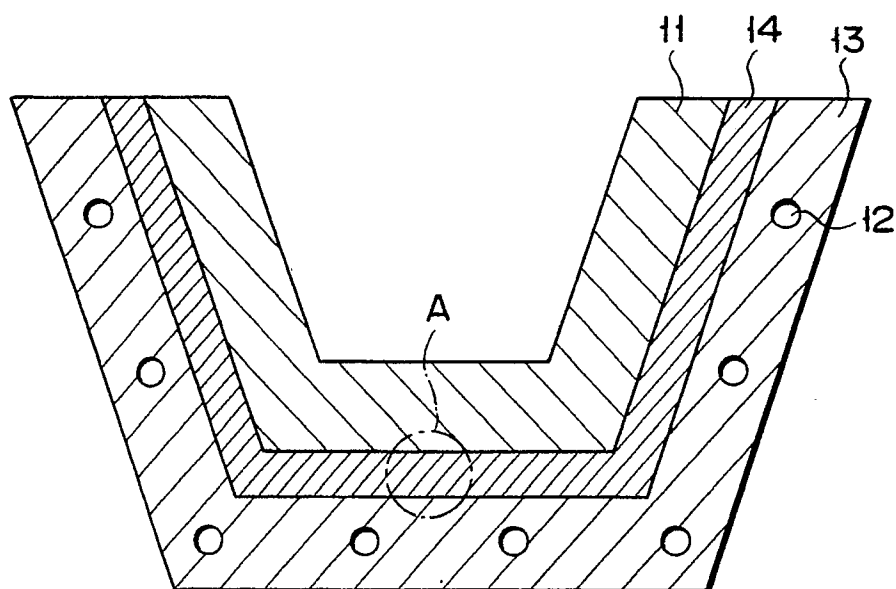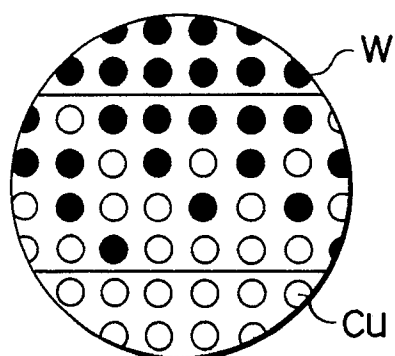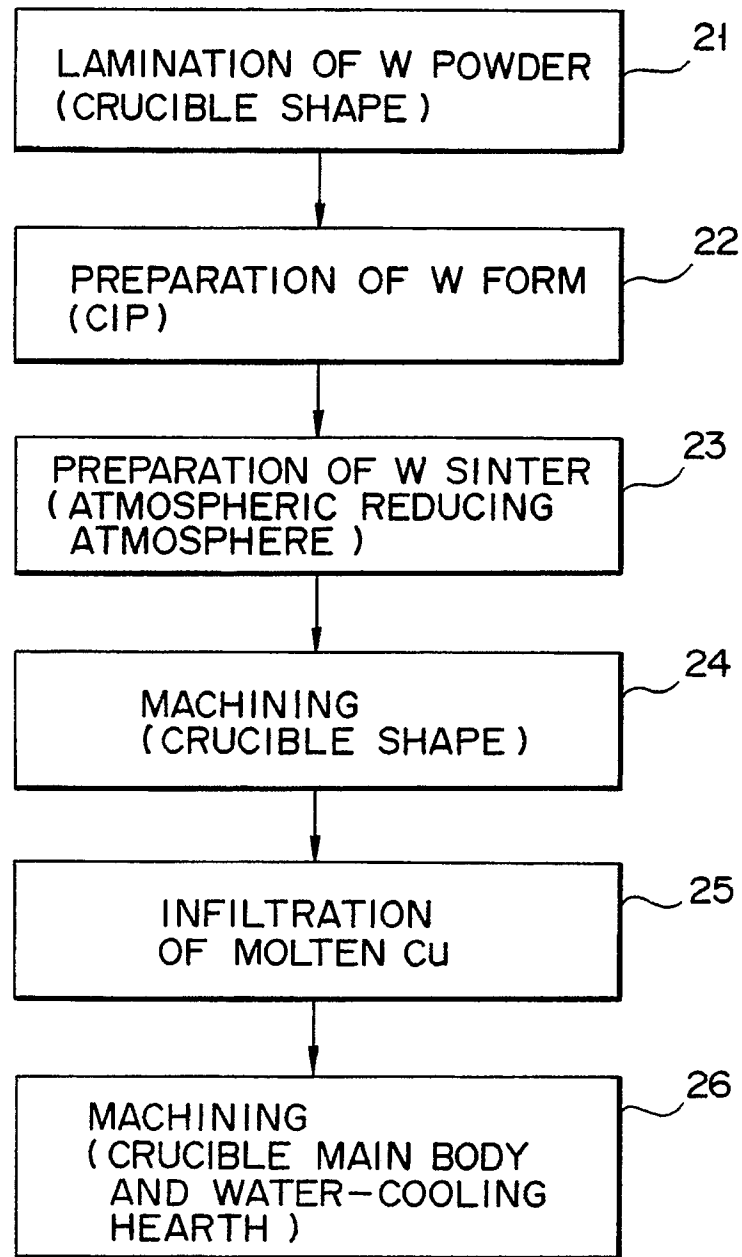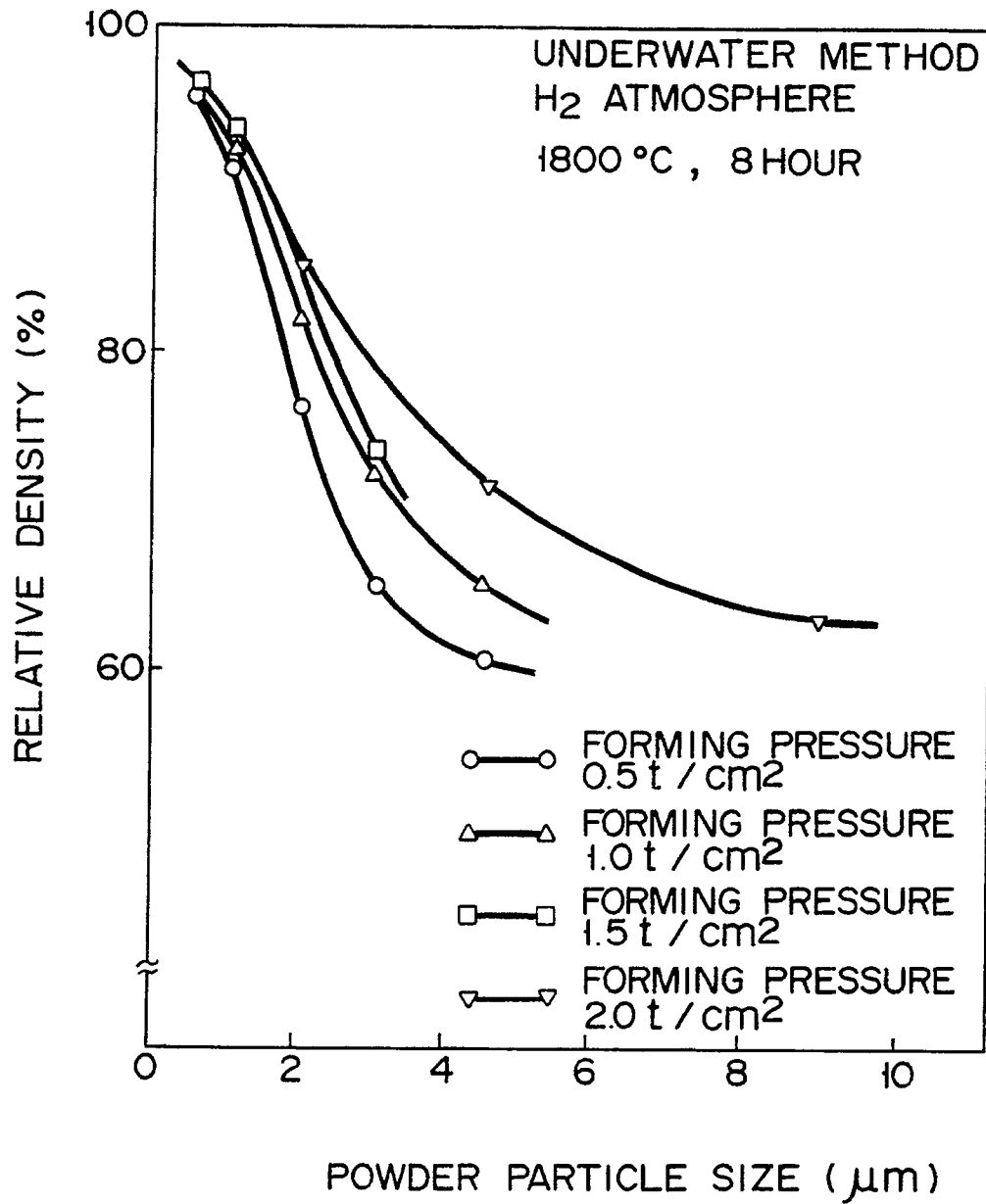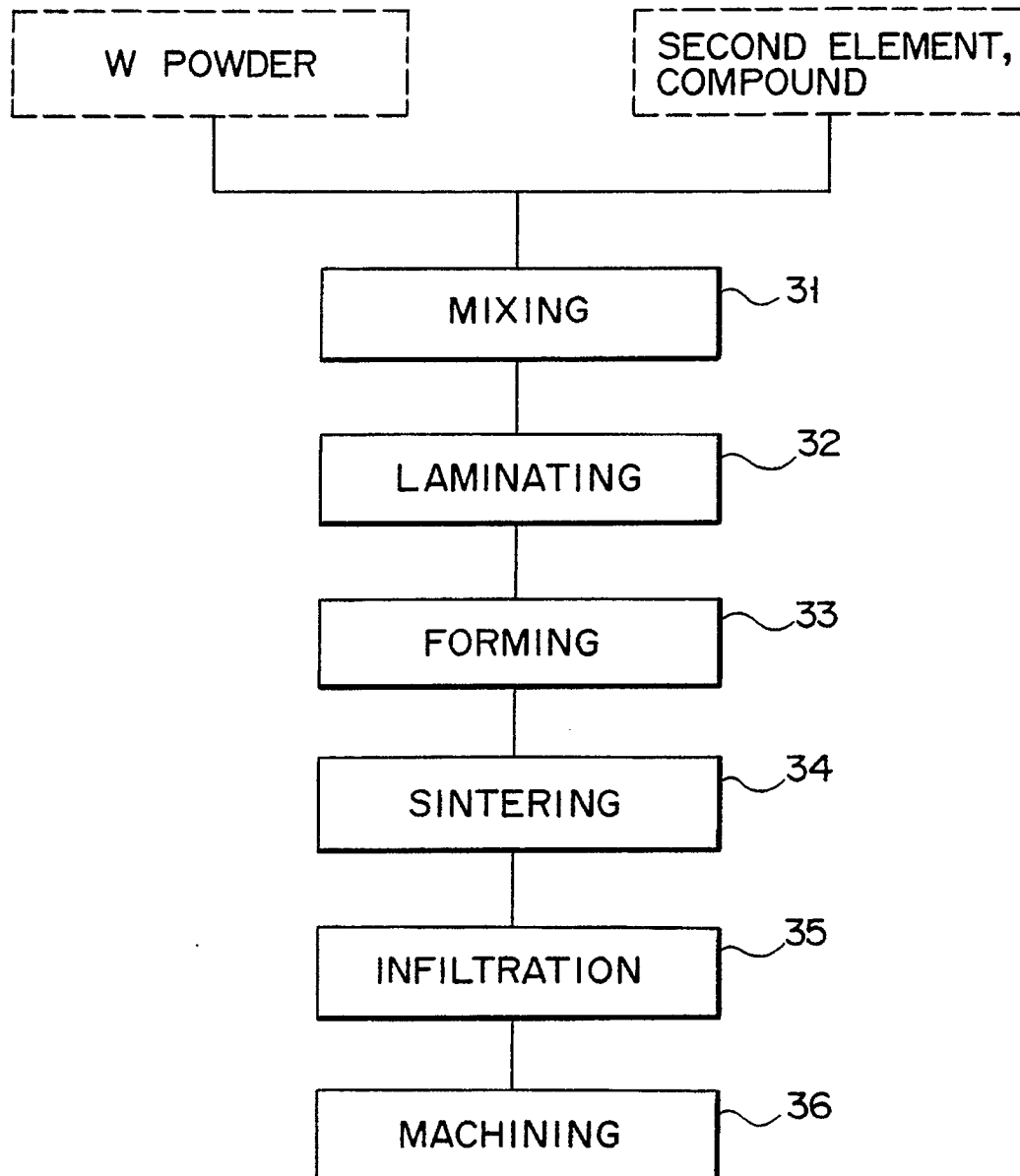
F I G. 8
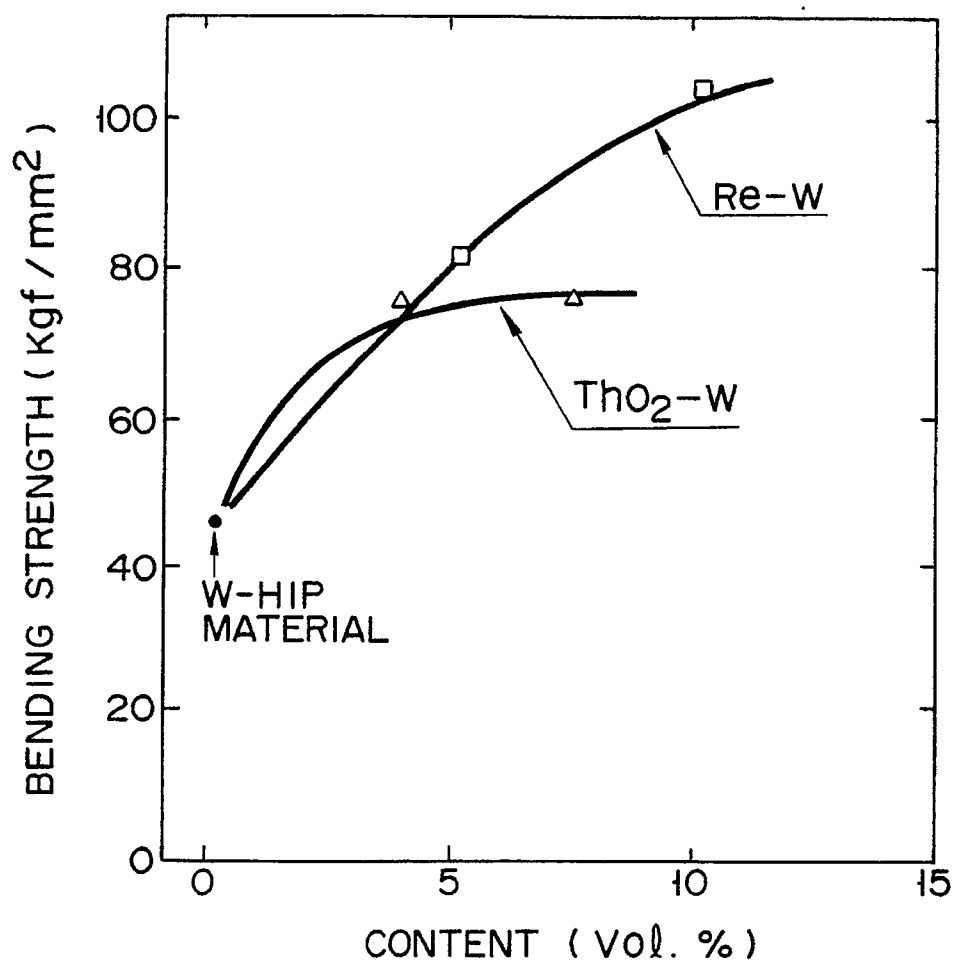
FIG. 9

MATERIAL	CHEMICAL STABILITY	MELTING POINT(K)	THERMAL CONDUCTIVITY (W/m,K)
TaB_2	STABLE	3370	40
TiB_2	STABLE	3190	38
HfB_2	STABLE	3520	85
Y_2O_3	STABLE	2713	3
ZrO_2	STABLE	2950	2

FIG. 10

116
116
C SIDE
W ALLOY
A
A
Cu
D SIDE
121
118
117
117

F I G. 11A

116
118
W ALLOY
121
Cu
117
117

F I G. 11B

POROSITY
LARGE

POROSITY
SMALL

119

120

118

F I G. 12

HEATING (5kw/cm²)

2300 ~1900 700

1500

1100

INTERFACE
UNIT : K

TEMPERATURE DISTRIBUTION

F I G. 13A

HEATING (5kw/cm²)

2300 ~1900 700

1500

1100

INTERFACE
UNIT : K
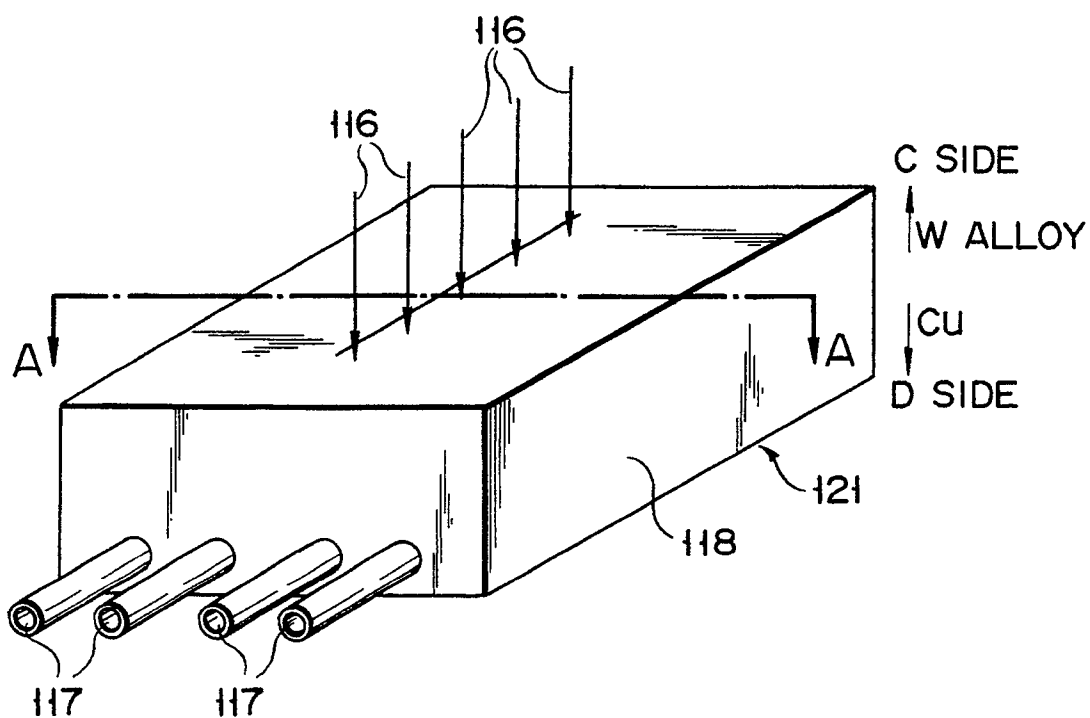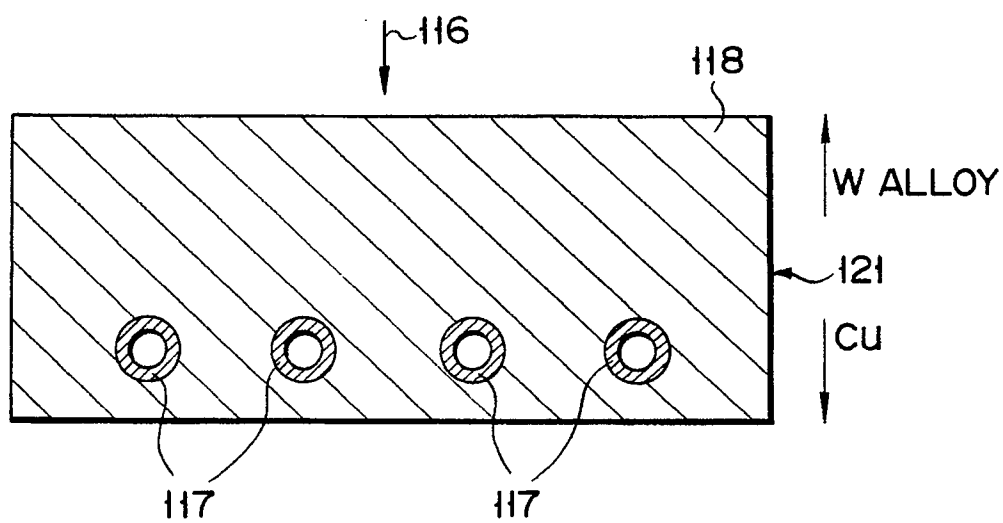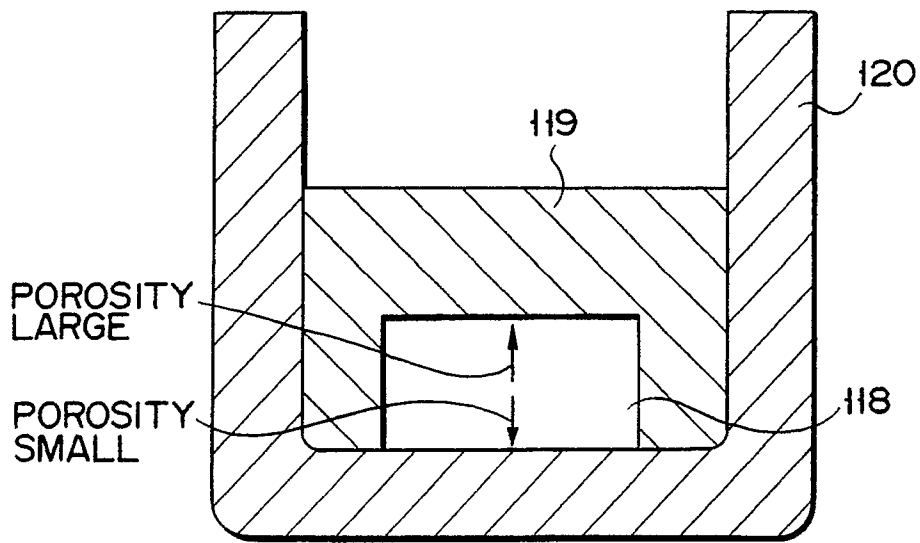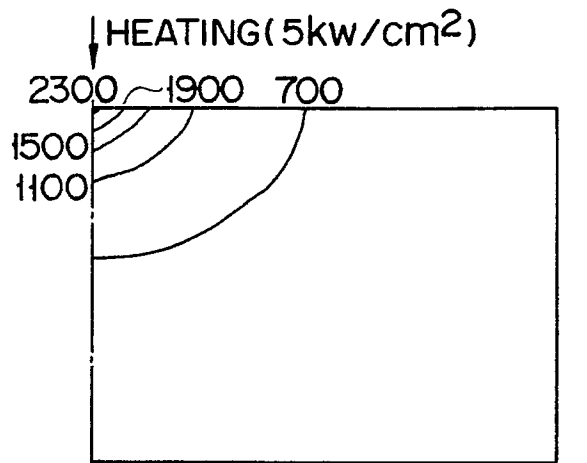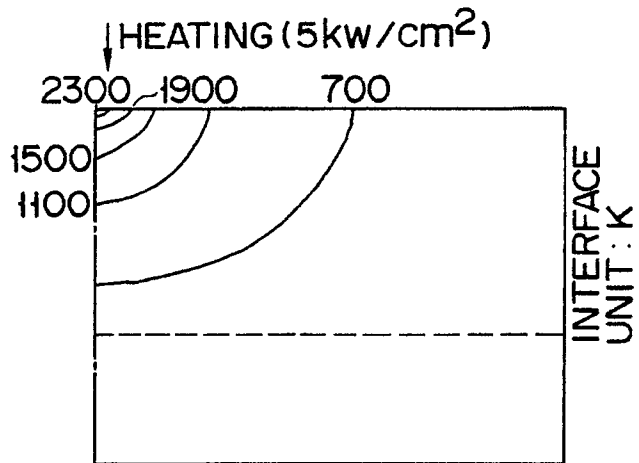
TEMPERATURE DISTRIBUTION
OF BRAZING MATERIAL

F I G. 13C

0.4 0.3 0.1

0.2

0

THERMAL STRESS
DISTRIBUTION

F I G. 13B

1.3 1.1 0.8 0.5

0.8

0.5

0.5

0.1

INTERFACE
UNIT : GPa
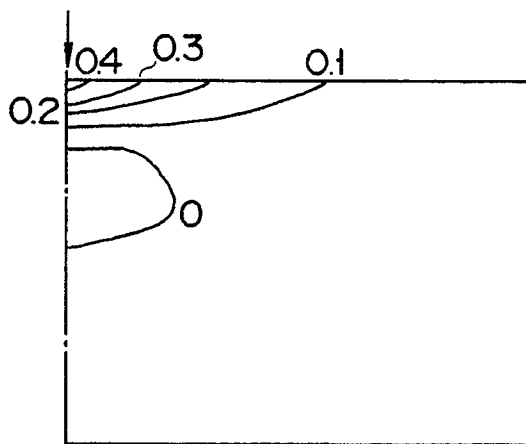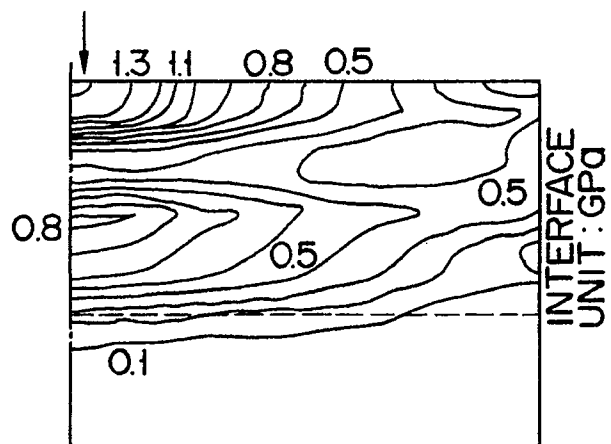
THERMAL STRESS
DISTRIBUTION OF
BRAZING MATERIAL

F I G. 13D

F I G. 14

```
┌─────────────────────┐
│ PREPARATION OF      │  ← 41
│ HIGH STRENGTH       │
│ MATERIAL            │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│ VACUUM PLASMA       │  ← 42
│ SPRAYING            │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│ OPEN  HIP           │  ← 43
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│ INFILTRATION        │  ← 44
└─────────────────────┘
```

F I G. 15

45 HIGH STRENGTH
   SUBSTRATE

46 GRADIENT
   COMPOSITION
   LAYER

F I G. 16

```
┌─────────────────────┐
│   SUBSTRATE         │ ～51
│ SURFACE CLEANING    │
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│   VPS SPRAYING      │ ～52
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│    OPEN HIP         │ ～53
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│   INFILTRATION      │ ～54
└─────────────────────┘
          │
          ▼
┌─────────────────────┐
│    MACHINING        │ ～55
└─────────────────────┘
```

F I G. 17

```
┌─────────────────────────┐
│   LAMINATION OF          │──╮ 61
│   POWDER                 │  
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│   ONE-BODY FORMING       │──╮ 62
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│   SINTERING              │──╮ 63
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│   OPEN HIP               │──╮ 64
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│   HIP INFILTRATION       │──╮ 65
└─────────────────────────┘
            │
            ▼
┌─────────────────────────┐
│   MACHINE FINISHING      │──╮ 66
└─────────────────────────┘
```

F I G. 18

```
┌─────────────────────────┐
│  PREPARATION OF         │  ⌐71
│  DOPED W ROLLED         │
│  MATERIAL               │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐  ⌐72
│  W POWDER LAMINATION    │
│  ON ROLLED  MATERIAL    │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐  ⌐73
│  SINTERING , BONDING    │
└─────────────────────────┘        ⎫
             │                     ⎬  SIMULTANEOUSLY
             ▼                     ⎭
┌─────────────────────────┐
│  GIANT CRYSTAL          │
│  GROWING                │
└─────────────────────────┘  ⌐74
             │
             ▼
┌─────────────────────────┐  ⌐75
│  INFILTRATION           │
└─────────────────────────┘
             │
             ▼
┌─────────────────────────┐  ⌐76
│  MACHINING              │
└─────────────────────────┘
```

F I G. 19

HEAT RECEIVING SURFACE

```
┌──────────────────────────┐
│  GIANT                   │
│  CRYSTAL                 │
│  GRAIN  W , M            │
│──────────────────────────│  �
│ ///////////////////////// │  ⌐ 80 GRADIENT
77 ─→ ///////////////////////  │     COMPOSITION
│ ///////////////////////// │     REGION
│  ○    ○    ○    ○         │
└──────────────────────────┘
```
           79   WATER COOLED PORTION

F I G. 20