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Production of $CrSi_2$ and FGM Thick Coating by Instantaneous Sintering

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Abstract:

Nippon Steel Corp. has developed a new process in which coarse powders used as raw materials for ceramics and functionally gradient material are micronized to fine powders by vaporization/recondensation in a hybrid plasma system, the fine powders are transported by gas under air free conditions, and finally they are sintered instantaneously by high temperature gas while being sprayed at a high speed onto a substrate. This new method is capable of effectively utilizing the excellent properties of fine powders and proceeding only in densification of the fine powders without causing grain growth of micronized powders during instantaneous sintering. As a result, it is possible to manufacture densified ceramic thick coating with fine structures in an extremely short time. Furthermore, during proceses of manufacturing the functionally gradient material, since a sintering temperature can be varied sequentially depending on the composition changes, any part of functionally gradient material can be sintered at the most appropriate temperature, and a dense and fine structure can be obtained.

1. Introduction

For developing a highly functional ceramic thick coating or bulk, its structure and composition must be controlled to a high degree. However, in conventional processes using pulverized or atomized raw material powders such as the "mixing-molding-sintering" process, a high degree of structure/composition control is difficult. Active researches have been carried out into processes for synthesizing fine powders in gas phase and utilizing these synthesized fine powders. But most of the researches are into processes for taking out the fine powders in air after the synthesis and then molding and sintering the particles[1]. This method has many problems including contamination in air, aggregation of the fine powders during handling, and so on, and thus the properties of the fine powders thus produced in clean and dispersed states are not effectively utilized. Further, in general ceramics production, even for small parts, several days are necessary before sintering is completed, and thus good productivity is not provided.

For solving the above problems, Nippon Steel Corp. carried out research and development on processes for manufacturing fine powders by a hybrid plasma method and instantaneously sintering the powders simultaneously with the spraying process. The fine powders are transported in a closed system after manufacture, molded by spraying them onto a substrate at high speed (molding by spraying fine powder) and then sintered by spraying high temperature Ar gas on them. **Fig. 1** shows the entire process of the present development.

The present method enables the excellent sintered properties of fine powders produced in a plasma vapor phase to be made best use of without being contaminated. Accordingly, instantaneous sintering can be performed and, because of the shorter sintering time, the structure can be controlled precisely. Moreover, according to the present method, since formation of a ceramic thick coating

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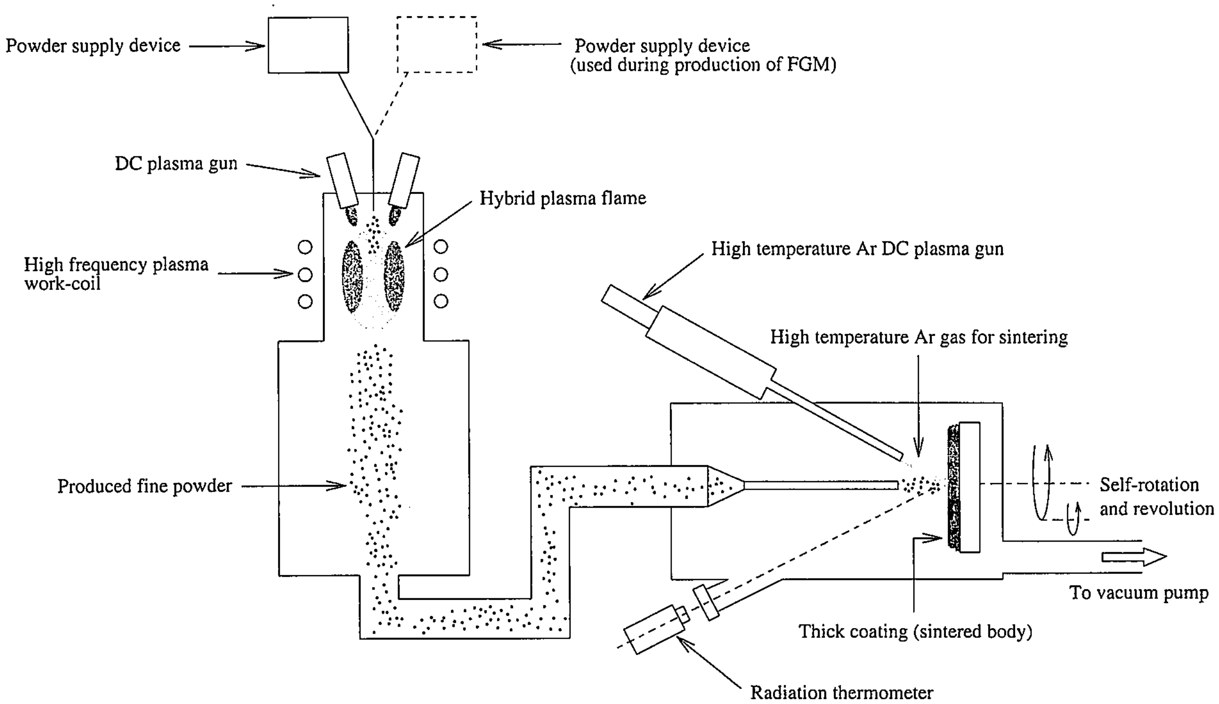

Fig. 1 Entire view of development process

is started at the same time coarse raw materials powders are introduced into hybrid plasma, and sintering is completed at the same time the introduction of the coarse raw materials powders is finished, manufacturing time is very short.

In addition, in the manufacture of a functionally gradient material (FGM), while changing the composition of the coarse raw materials powders introduced into the hybrid plasma, the temperature of high temperature Ar gas can be varied corresponding to the change of the composition. By utilizing the above, formation of densely sintered thick coating was tried for functionally gradient materials having different sintering temperatures.

This report describes the manufacture of fine powders by hybrid plasma system first and then thick coating manufacture by spraying the fine powders and instantaneous sintering. The report lastly describes FGMs made on an experimental basis.

2. Production of Fine Powders by Hybrid Plasma

2.1 Overview

Fine powders used as raw materials for spray-molding (referred to as molding by spraying finer powder, hereinafter) and instantaneous sintering (referred to as sequential sintering, hereinafter) must have good molding and sintering properties. Powders as fine as possible should preferably be used for providing good sintering. From the viewpoint of molding, however, since extremely fine powders have strong cohesion, small voids are easily formed in the mold and, if square particles are used, good filling property is not provided. Thus, powders needed for the present method may be spherical and have diameters near the submicron level. There are no particularly improper materials. Research was first conducted with emphasis placed on Cr compounds as ceramics having good corrosion resistance and wear resistance, especially $CrSi_2$.

In accordance with the above purpose, $CrSi_2$ fine powders were produced by a hybrid plasma system having three DC plasmas and one high frequency plasma in combination. In the present development, submicron powders were produced which were relatively large in size for the hybrid plasma system. As an example of generally produced fine powders, ZrB_2 powders are described at the end of this section[2].

2.2 Experimentation method

In the hybrid plasma system used for the experiment, the temperature of its peripheral portion is set higher than that of a normal high frequency plasma by superimposing the three DC plasmas on the high frequency plasma, and viscosity of this peripheral plasma is deliberately increased. Then, by means of this highly viscous plasma of the peripheral portion, raw materials introduced into a center axis are shielded and passing of the raw materials through the outer side of the plasma flame is prevented. As a result, the plasma is stabilized, the size of fine powders produced by evaporation and recondensation of the raw materials is relatively uniform and efficiency is increased.

Fig. 2 shows the specific structure of the hybrid plasma system, the gas introducing amount, and so on. Three DC plasma guns are symmetrically positioned on the upper part of a torch, and a high frequency plasma is positioned below them. The inner wall surface of a work coil is composed of a water cooled double quartz tube. The inner diameter of the inner quartz tube is 80 mm and its length is 150 mm. Portions other than the quartz tube are made mainly of copper. A nozzle inserted into the center axis of the high frequency plasma through the space between the DC plasma guns on the torch upper part is used to introduce raw material powders. It is normally inserted 40 mm into the torch. The plasma power of each of the three DC plasmas is around 8 kW, and the plate power of the high frequency plasma is between 120 and 180 kW. $CrSi_2$ raw material powders between several and several tens of μm were introduced through the raw-material-introducing nozzle at a rate of 5 to 20 g/min.

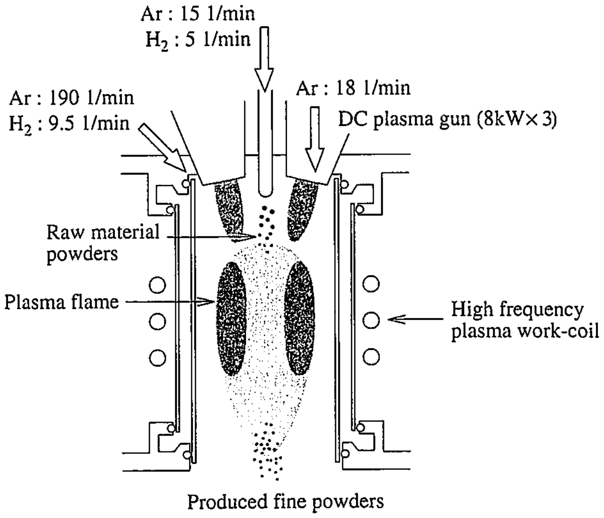

Fig. 2 Hybrid plasma torch structure and various conditions

2.3 Result

Photo 1 shows a plasma flame. It can be understood that as a result of superimposing the three DC plasmas on the high frequency plasma, the density of the plasma peripheral portion was increased.

Photo 2 shows a TEM photograph of the $CrSi_2$ fine powders obtained. It can be seen that fine powders have particle diameters of 300 nm or less. Considering the diameters of raw material powders, these fine powders may be the result of evaporation and recondensation of the raw material powders. Shapes are globular, and thus fine powders having the desired particle diameters and shapes were obtained. In addition, peaks of XRD patterns of the $CrSi_2$ fine powders obtained were all identified to be those of $CrSi_2$.

For reference, **Photo 3** shows ZrB_2 powders produced by the hybrid plasma system[2]. It can be seen that these are globular fine powders having particle size of around 50 nm. Generally, fine powders have this particle size in most cases.

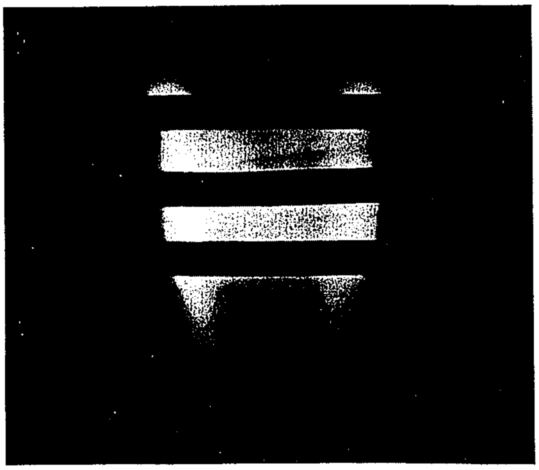

Photo 1 Hybrid plasma flame

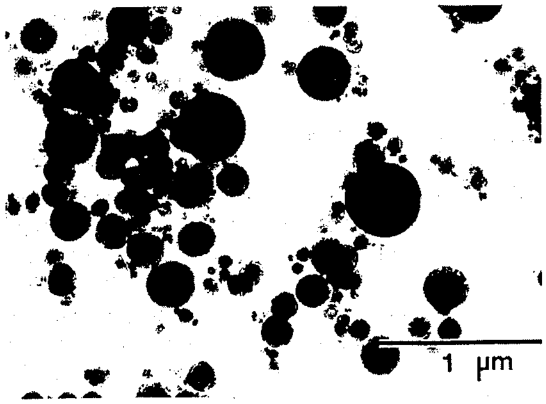

Photo 2 TEM photograph of produced $CrSi_2$ fine powders

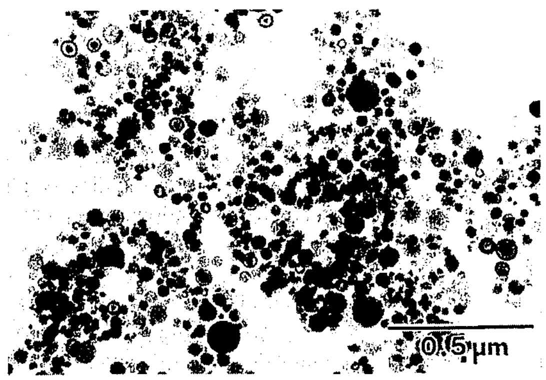

Photo 3 TEM photograph of produced ZrB_2 fine powders

3. Production of Thick Coating by Fine Powder Spraying Molding and Sequential Sintering

3.1 Overview

For the development of processes for molding $CrSi_2$ fine powders produced by the hybrid plasma system onto a substrate by spraying fine powders and simultaneously performing sequential sintering by high temperature Ar gas, it is important to mold fine powders highly densely by spraying fine powders without any defects and to obtain a sintered body having a highly dense micronized structure by instantaneous sintering.

Fig. 3 is a typical view showing molding by spraying fine powders and sequential sintering. By rotating the substrate at a constant speed of self-rotation and an angle-dependent revolution,

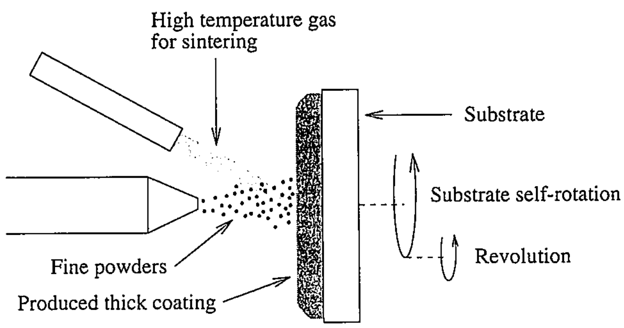

Fig. 3 Typical view of fine powder spray molding and sequential sintering

a thick coating having uniform thickness is obtained. Experimental molding by spraying fine powders was carried out by this device and, after optimization thereof, experimental sequential sintering was carried out.

3.2 Experimentation method

After $CrSi_2$ fine powders were produced by the hybrid plasma system, these fine powders were transported to the chamber of a fine powder spraying molding device together with gas, blown out from the tip of the cylindrical nozzle with plasma operation gas and then sprayed onto a stainless steel substrate. Its diameter was 80 to 150 mm, and the speed for spraying fine powders, distance from the nozzle to the substrate, and so on, were varied. The obtained mold was peeled off from the substrate and then its density was measured. Relative density was calculated by using the density of 4.98 g/cm^3 for $CrSi_2$. The mold was broken and its fracture surfaces were observed by SEM.

Then, high temperature Ar gas was sprayed simultaneously with the fine power spraying process, and sequential sintering was carried out simultaneously with the molding. The thick coating obtained were observed by SEM, TEM, and so on.

3.3 Result and consideration

Table 1 shows relative densities of $CrSi_2$ fine powder molds obtained under various fine powder spraying molding conditions while the substrate was maintained in a stationary state. Relative density is the average of three or more density values obtained, and error is a few percentage points at the maximum. If flow velocity is 23.2 m/s and the distance between the spray nozzle and the substrate is 55 mm, a fine powder mold having a very high relative density of 77% is obtained. There is a good dry molding method currently in general use which utilizes CIP (cold-isostatic-press). Normally, however, relative densities of molds are around 65%, and 70% or higher is a rare case. Thus, a relative density value of 77% is extremely large. If the flow velocity is 46.3 m/s or higher, the spraying velocity is too fast and the mold is blown away. Consequently, the amount of powder stuck to the substrate was small and measuring was impossible. But it can be seen that the mold has a relative density nearly equal to the relative density of 77%.

With the above in mind, 45-minute molding by spraying fine powders was carried out while self-rotating/revolving the substrate with the distance between the nozzle and the substrate set at 50 mm. **Photo 4** shows a state where the molded film is half-peeled off from the substrate. It can be understood that a relatively uniform film having a thickness of about 1 mm is formed. **Photo 5** shows an SEM photograph of the fracture surface of a mold formed by spraying fine powders with a flow velocity of 23.2 m/s and a distance of 20 mm between the nozzle and the substrate. The photograph shows the fine structure of the fine powder mold. It can be understood that the particles are supplied very uniformly and there are no large voids.

Table 1 Relative densities of $CrSi_2$ fine powders molds by fine powder spraying

Flow velocity (m/s)	Distance between spray nozzle and substrate 20mm	55mm
11.6	60.2%	36.2%
23.2	74.7%	77.0%
46.3	Measuring impossible due to thin coating	Measuring impossible due to thin coating

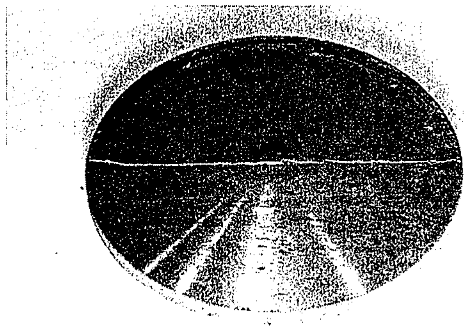

Photo 4 Mold (half peeled off) by fine powder spraying

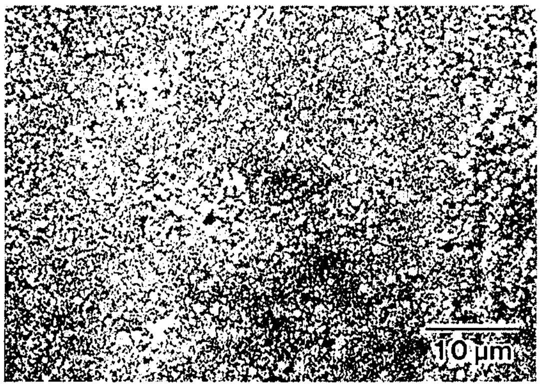

Photo 5 SEM observation of fracture surface of mold formed by fine powder spraying

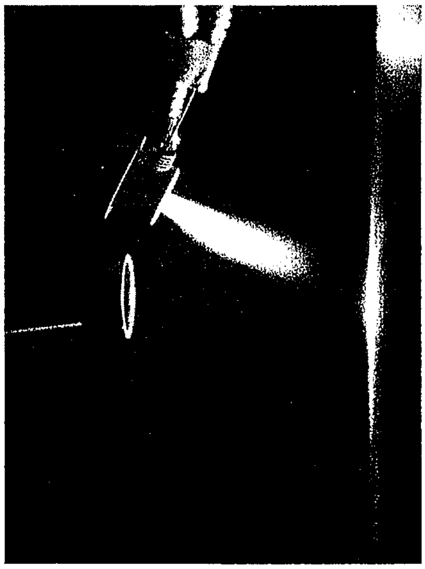

Photo 6 High temperature Ar flame for sequential sintering

From the foregoing, it is obvious that by means of the molding by spraying fine powders, a higher density and better quality mold than that obtained by the conventional dry molding method is possible.

Next, the result of high temperature Ar gas sequential sintering carried out simultaneously with the fine powder spray molding process is described. **Photo 6** shows the state of a high temperature

Ar gas flame. **Photo 7** shows the state of a $CrSi_2$ thick coating obtained. It can be seen that this thick coating has a smooth surface.

Photo 8 shows an SEM view of a section of a $CrSi_2$ sequential sintered body. It can be seen that there are no non-sintered parts left and good densification has occurred. **Photo 9** shows a view by TEM. The sintered body is composed of fine grains having grain sizes less than several hundred nm. Considering that the particle size of $CrSi_2$ fine powders produced by the hybrid plasma system is several hundred nm, it can be understood that progress is only made in densification without any grain growth of fine powders in the case of sequential sintering. Since sintering was carried out without contaminating the fine powders produced, this result may be attributed to the fact that sintering ability of the fine powders was fully utilized and accordingly sintering time was greatly shortened.

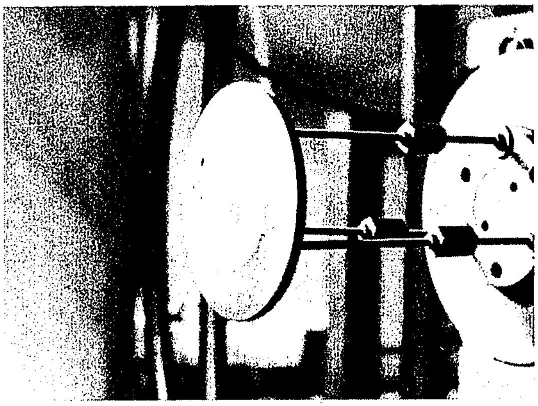

Photo 7 Entire $CrSi_2$ sequentially sintered thick coating

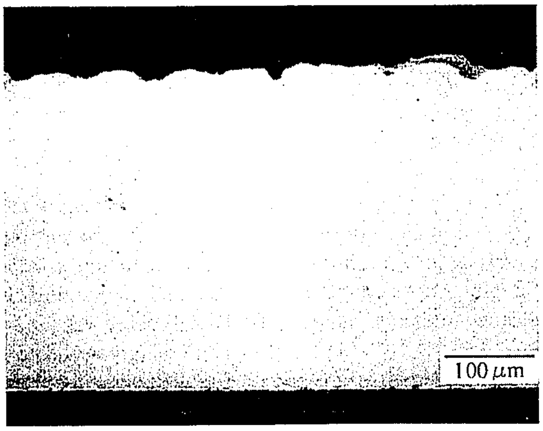

Photo 8 SEM observation of $CrSi_2$ sequentially sintered body

Photo 9 TEM observation of $CrSi_2$ sequentially sintered body

In the previous research, contrary to expectations, the use of fine powders often resulted in the deterioration of molding and sintering performance. In the present method, however, by carrying out processes from fine powder production to sintering in one closed system and using fine powder spray molding and sequential sintering, it was possible to obtain a ceramic thick coating having a fine and well-sintered structure.

4. Manufacture of FGM Thick Coating by Fine Powder Spray Molding and Sequential Sintering

4.1 Overview

As one application of the present development process, an FGM may be manufactured. Generally, a conventional method can be used for depositing and molding fine powders sequentially changed in composition, but changing of sintering temperature corresponding to the composition change is very difficult. On the other hand, in the present development process, while the composition of raw material powders introduced into the hybrid plasma system is changed, the temperature of the high temperature Ar gas for sintering can be changed according to the composition change. Thus, the present developing process is suited to the manufacture of an FGM coating. Therefore, a sample FGM thick coating ranging from Ni to $CrSi_2$ was manufactured.

4.2 Experimentation method

As an example of experimental conditions, two raw material supply devices were prepared, Ni raw material powders were introduced into the hybrid plasma at 5.8 g/min when starting the experiment, then the amount of the powders was gradually reduced and supply thereof was stopped after 11 minutes. Supply of $CrSi_2$ raw material powders was started 2 minutes after the start of the experiment, then the amount of the powders was gradually increased and, after 15 minutes, it was set to 8.3 g/min. Concerning the high temperature Ar flame of sequential sintering, experiments were made for two cases, i.e., one where the temperature was kept constant and the other where the temperature was gradually increased corresponding to the composition change.

4.3 Result

In the case where the temperature of the high temperature Ar flame was kept constant, only a thick coating containing many cracks and non-sintered portions was obtained. On the other hand, in the case where the temperature of the high temperature Ar flame was increased corresponding to the composition change, a densely sintered and good, thick coating was obtained. **Photo 10** shows an SEM photograph of a section of an FGM thick coating obtained and the results of observing each element distribution. It can be seen that the coating is densely sintered and the composition shows a functional gradient. Thus, the technology of the present development enabled a good FGM to be manufactured.

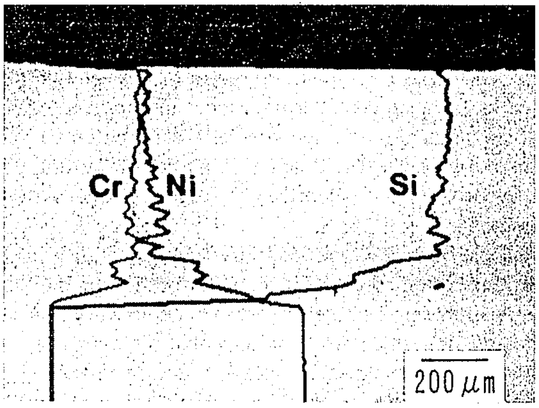

Photo 10 SEM photograph of FGM thick coating and element distribution

5. Conclusion

The development of the present process enabled a ceramic sintered body to be obtained within a much shorter time than was possible in the conventional case. A sintered body starts to be formed at the same time raw material powders are introduced into the hybrid plasma system, and the sintered body is completed when the introduction of the raw material powders is finished. Since fine powder spray molding and sequential sintering are carried out while spherical fine powders produced by the hybrid plasma system are maintained in a clean state, good molding performance is provided and no defects such as cracks or small voids occur after sintering. Concerning the structure of the sintered body, densification occurs without any grain growth of fine powders, and thus a fine structure can be realized. Further, it was found that the present process is suited to FGM manufacture.

This report includes details of the achievements obtained by work entrusted by New Energy and Industrial Technology Development Organization to the Advanced Function Technology Creation Machining Technology Research Cooperative, the work having been carried out as part of "Research and Development on Advanced Function Creation Machining Technology" executed based on MITI's Industrial Science and Technology Frontier Program.

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