Fabrication of Inorganic Material Models with Local Chemical Reaction Heat by Laser Scanning

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ABSTRACT

In this paper, we propose a new method of fabricating 3-D models of the inorganic materials having high melting points such as ceramics and intermetallic compounds by laser scanning. To save the laser energy, we adopted the combustion synthesis which is the exothermic reaction between the raw materials. By adding chemical reaction heat to laser heat, the particles of the products of the reaction were bonded together by relatively low laser energy. The combinations of the raw materials and the laser scanning conditions for solidifying the products of the reaction and laminating the solidified layers were investigated experimentally. By mixing the powdered binder with the reactive raw materials, the simple layered models were fabricated. Since burning in the furnace is unnecessary in the proposed method, it is possible to fabricate the models in a short time.

1. INTRODUCTION

Metal and ceramics are widely used in the mechanical parts required the strength and the heat resistance. Ceramics are also used as the casting molds. Metal models are generally fabricated by cutting, milling, electrical discharge machining (EDM), casting, etc. Ceramics models are mostly fabricated by pouring the ceramics slurry into the molds and sintering at high temperature.

In recent years, selective laser sintering (SLS)[1], three dimensional printing (3DP)[2], fused deposition modeling (FDM)[3], and laminated object manufacturing (LOM)[4] have been developed as the methods of fabricating 3-D models of the ceramics and the metal directly from CAD data like the stereolithography.

In any of these methods, since the powders or the sheets of the materials are connected temporarily by the binder, sintering at high temperature near the melting points above 1000°C is required to connect the materials together firmly. Therefore, the fabrication takes for a long time and a high degree of skill about burning process is required.

There is the method of fabricating the models directly by heating and fusing the metal powder sprayed on the laser beam spot. However, laser power of more than 500W is necessary even in the case of Co alloy having the melting point of 1200°C[5]. It is difficult to apply this method to the ceramics models which has to be sintered by keeping the materials at high temperature for a long time.

In this paper, we propose a new method of fabricating the 3-D models of high-temperature structual materials by using combustion synthesis[6] induced by laser heating. In this method, the synthesis of the compounds and the fabrication of the 3-D models progress simultaneously. By adding the chemical reaction heat to laser heat, the fabrication of the 3-D models of the heat-resistant inorganic materials such as the ceramics and the intermetallic compounds can be realized with low laser energy. Since the proposed method dispenses with sintering in the furnace, the knowledge and the skill about the process are unnecessary and the models can be fabricated in a short time. The principle of this method and the experiments are described in the following chapters.

2. COMBUSTION SYNTHESIS

Generally, combustion means the chain-reacting chemical reaction between an element and oxygen with the generation of heat and luminescence. In the case of using the element near the oxygen in the periodic table instead of the oxygen, similar reaction often occurs. The former which is the oxidation reaction and the latter are known as oxidative combustion and nonoxidative combustion, respectively.

The method of producing the compounds as the condensate by these combustion reaction is called combustion synthesis[6]. The Combustion synthesis is a highly efficient method of obtaining the compounds, because it advances to spontaneously after the ignition and the compounds are synthesized in a few seconds. In the oxidative combustion, ceramics such as Al_2O_3 is obtained. The nonoxidative combustion by using N, C, B, and Si produce the nonoxide ceramics which are nitride, carbide, boride, and silicide, respectively. In the case where Al is used, the intermetallic compound termed alminide is produced. In this study, we adopted the reaction heat of the combustion synthesis to solidify the materials having high melting points with low laser energy.

3. EXPERIMENT OF SOLIDIFICATION AND LAMINATION OF POWDERED MATERIALS

3.1 Tested materials

Cermet of Cu and Al_2O_3, intermetallic compound TiAl, and ceramics $MoSi_2$ were used as the structural materials of the models. TiAl and $MoSi_2$ are known as the promising high-temperature structural materials. Tested materials and their chemical reaction formulas are shown in Table1. Particle sizes of the raw materials were CuO: 1-2 μm, Cu: 15 μm, Al: 27.6 μm, Ti: 45 μm, TiAl: 40 μm, Mo: 1.5 μm, and Si: 2-3 μm.

Table1 Combinations of the tested materials and their chemical reaction formulas.

No.	Raw materials (molar ratio)	Chemical reaction formula	Calorific power	Products	Melting point of the products
①	CuO: 10%, Cu: 84%, Al: 6%	$0.3CuO+2.7Cu+0.2Al=3.0Cu+0.1Al_2O_3$	38.8kJ/mol	Cu Al_2O_3	Cu: 1084°C Al_2O_3: 2054°C
②	Ti: 33%, Al: 33%, TiAl: 34%	0.5Ti+0.5Al+0.5TiAl=TiAl	37.7kJ/mol	TiAl	TiAl: 1460°C
③	Ti: 43%, Al: 43%, TiAl: 14%	0.75Ti+0.75Al+0.25TiAl=TiAl	56.5kJ/mol	TiAl	TiAl: 1460°C
④	Ti: 50%, Al: 50%	Ti+Al=TiAl	75.3kJ/mol	TiAl	TiAl: 1460°C
⑤	Mo: 33%, Si: 67%	$Mo+2Si=MoSi_2$	118.4kJ/mol	$MoSi_2$	$MoSi_2$: 2027°C

In the combustion synthesis, the product which is inert substance is sometimes added to the raw materials for the purpose of controlling the calorific power[6]. The inert materials in Table1 are Cu of ①, and TiAl of ② and ③.

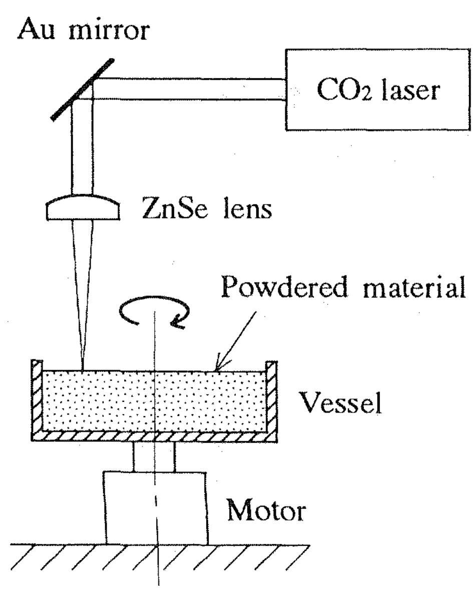

Fig.1 Experimental system.

3.2 Experimental apparatus

Fig.1 shows the experimental apparatus. Output beam of CO_2 laser (SYNRAD Co.: Model 48-1-28, wave length: 10.6μm, TEM00 mode) is focused on the raw materials by ZnSe lens (lens aperture: 30mm, focal length: 50mm) and then scans the surface of the raw materials. To simplify the scan, the vessel is rotated by a motor. Spot size of the laser is 117μm at the calculated value.

The selective laser sintering which solidifies the spread powdered materials selectively by laser heating is used as the method of forming the solidified layers. By repeating the spread of the powders and the beam scan alternately, a 3-D model is fabricated. In this method, it is necessary that the material only in the scanned area solidifies stably and the layers are connected firmly.

3.3 Experiment of solidification and lamination with only reactive materials

Firstly, several materials were investigated whether or not the combustion reaction was limited in the scanned area. The raw material was spread with the thickness of 3 mm and scanned from the above by the laser. Fig.2 shows the state of the material during laser scanning. The material in the irradiated area incandesced and sparked, and turned black after the irradiation.

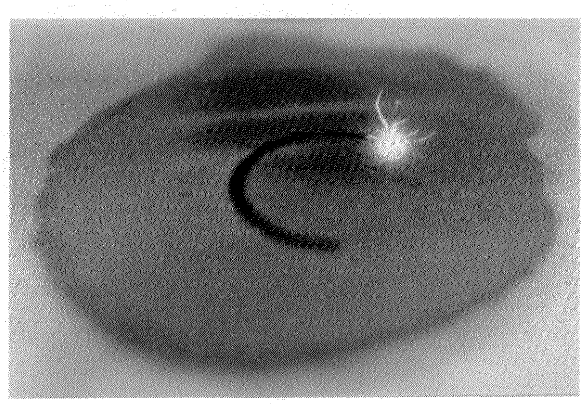

Fig.2 Material during laser scanning.
(material ③, laser power: 4W, scanning speed: 1.65mm/sec)

Fig.3 shows the experimental results. Reactions are classified into the next 3 states by the scanning condition of the laser and the constitution of the raw material.

(1) The material only in the scanned area were solidified.
(2) The whole material were burned out by the chain reaction.
(3) The powders in the irradiated area were scattered by the excess laser power.

Increment of the supplied energy [W/mm/sec] makes the reaction move from (1) to (3). Material ④Ti+Al is easy to burn out by the chain reaction. Solidified object made from material ② and ③ that the product TiAl was mixed previously is significantly brittle. Accordingly, ① Cu+Al+CuO and ⑤Mo+Si are in prospect as the raw materials.

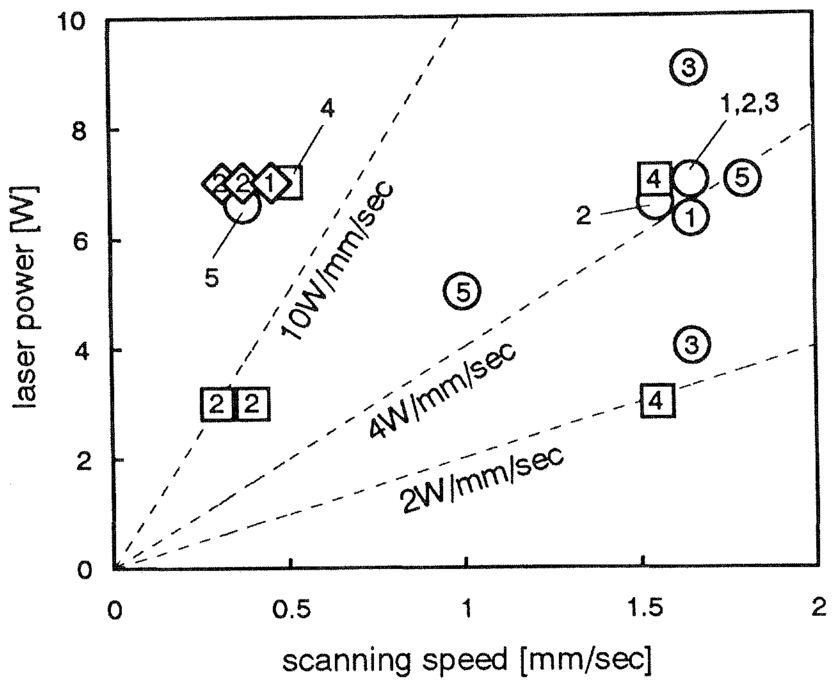

Fig.3 Relationship between the scanning condition and the stability of the solidification.
(The numbers in the symbols show the material numbers.
○: The material only in the scanned area were solidified.
□: The whole material were burned out.
◇: The powders in the irradiated area were scattered.)

To know the effect of the reaction heat, the same solidification experiment as the above was done by using Fe powder (particle size: 50μm, melting point: 1535°C). In the case of the reactive materials, the materials could be solidified with the laser power of a few W. On the other hand, to solidify the Fe powders with the scanning speed of 1mm/sec, not less than 10W was required. Thus the combustion reaction plays a part which reduces the external energy required for the solidification.

Next, lamination experiment was done by using material ① and ⑤. Since the solidified depth was not less than 0.3mm in the above solidification experiment, the experimental condition was set as the following:

laser power: 7W
scanning speed: 1.65mm/sec
layer thickness: 0.2mm

However, in this condition, the layers did not connect each other and unified object could not be fabricated. On the other hand, when the supplied energy [W/mm/sec] was increased, burning out by the chain reaction was occurred.

3.4 Experiment of solidification and lamination by addition of binder

We attempted to add an inorganic inert binder to the raw reactive materials and connect the reactive material particles with the combustion synthesis and the help of the binder. In this case, it is thought that the binder materials restrain the calorific power same as the inert materials and reduce the reactivity of the total system. For this reason, we considered that the reactivity of the raw materials themselves have to be high in the case of using the binder. ④Ti+Al was selected as the reactive raw materials and the glass powder (particle size: 100μm, softening point: 550°C) which was easy to obtain was used as the binder. The mixed material was spread with the thickness of 3 mm as paragraph 3.3. In the case that the material ④ : glass powder weight ratio was 1:1, even if the laser power was 3W and the scanning speed was 1.55mm/sec, the materials burned out by the chain reaction. To reduce the reactivity further, the ratio was changed to be 1:2. In this ratio, the solidification reaction stabilized, but the solidified object was porous and fragile. To strengthen the solidified object, the ratio was chosen to be 1:3. As a result, the solidified object became dense and rigid. The materials could be solidified with the laser power of not less than 2W.

On the other hand, in the case of only the glass powder, not less than 3W was needed for the solidification. Thus, it is clear that the reaction heat assists the melting of the binder.

Next, to confirm the connectivity between the layers, lamination experiment was done by using the above mixed material of 1:3 weight ratio. Experimental condition is maintained as the following based on the above solidification data.

laser power: 3W
scanning speed: 0.5mm/sec
layer thickness: 0.2mm
the number of layers: 15 layers

Fig.4 shows an example of the layered model. In this example, the center of the circular solidified objects are shifted from the fifth layer. Contact area between the fourth layer and the fifth is significantly narrow, but the connectivity between the layers is firm enough.

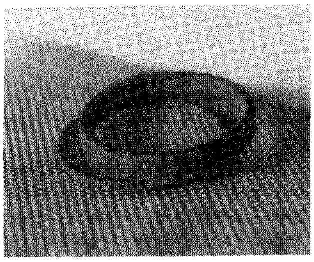

Fig.4 An example of the layered model.

4. CONCLUSIONS

We have proposed the new method for fabricating 3-D models of the inorganic materials with low laser energy by using the exothermic reaction and have done some fundamental experiments. Since the combinations of the tested materials were significantly reactive, the top of the solidified layers could not be heated to the melting point by the laser to avoid burning out by the chain reaction. Thus, it is not easy to connect the layers only the reactive materials.

We are planning to try to melt the top of the solidified layers through the use of the raw materials having a slightly lower reactivity than the tested materials. In the case, the required laser energy becomes larger than that of this time, but it is expected that the laminated models can be fabricated without the binder.

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