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Preparation of SiC Compacts by the Rapid Prototyping Machine

A.A.M. Abdelrahman, A.Z. Ahmed, M.A.A. Elmasry[1]
[1]Metallurgy Dept., NRC, Atomic Energy Post office 13759, Abo Zabal, Egypt.

ABSTRACT

The preparation of ceramic green bodies from powders by the rapid prototyping is a promising technique. In this work SiC green bodies were prepared from black SiC powder mixed with 10 wt% organic binder namely Avebe SP G20 starch. Different liquid binders were investigated and were successful in producing strong green bodies such as NH_4OH in the pH range 9-10 or 1 % HCl solution in water and or a mixture of 1% NH_4Cl and NH_4OH in the pH range of 8.5 to 9. The green bodies were then preheated at 200 C to eliminate the starch by thermal decomposition. After that these parts were infiltrated using molten silicon at 1450 ^{o} C in Argon atmosphere. Unfortunately it was impossible to infiltrate the green bodies using liquid silicon. Another technique was followed which is dipping of the green bodies in liquid silicon. This method was successful. The densities of the green and dipped bodies were determined and they were examined under the metallograph and SEM. It was found that no SiC dissolved in the silicon after dipping. This was concluded from the presence of sharp corners of SiC grains.

Key Words: Rapid Prototyping/ Silicon Carbide /3D Printing /Infiltration/Dipping

INTRODUCTION

The Rapid Prototyping technologies are rapidly developing and finding tremendous applications in industry. It is a free forming technique, in which prototypes of complex 3D data are manufactured. It is based on the same principle of building 3D models layer by layer. In contrast to abrasive or subtractive processes such as lathing, milling, drilling, grinding, and eroding, in which the form is shaped by removing material. In rapid prototyping the component is formed by joining volume elements. These processes are 2½ processes strictly in X,Y but not continuously in Z- coordinate. The extrusion processes are in principle the only 3D processes, in which the incremental volume elements can be added at any chosen point of the model. In reverse engineering, from 3D measuring device, the data can be converted into 3D CAD model.

Numerous rapid prototyping techniques are under investigation such as Stereo Lithography, Fused Layer Modeling /FLM, Deposition /FDM, Deposition Ceramics /FDC, Extrusion Free Form Fabrication /EFF, Selective Laser Sintering /SLS, 3D printing /3DP, Layer Laminate Manufacturing /LLM, Object /LOM, Computer Aided Manufacturing of Laminated Engineering Materials /CAM-LEM, Ballistic Particle Modeling /BPM, Direct Photo Shaping /DPS, Sanders prototype, Shape Deposition Manufacturing /SDM. The most feasible techniques are stereo lithography, fused deposition modeling, selective laser sintering, and 3D printing. Prototype models are mainly used for engineering tests and evaluation issues [1,2,3].

The 3D printing is strictly rapid prototyping technique that has the feature of building the specimen by adding process i.e. building layer by layer in fast process. The 3D printers use a combination of powder and binder. In this process, the binder liquid is injected into a powder layer using the normal standard ink-jet print head. After which a new powder bed is spread over the previous one and the process is repeated until the prototype is built. The main advantage in this technique is obtaining neat shape with high complexity. On the other hand, it needs a suitable powder and adjustment of printing parameters; such as binder type and quantity in order to have a green body with suitable strength to be handled safely.

It is theoretically proposed that 3D printer can work with any combination of powder- binder materials such as polymer, metal or ceramic. The use of ceramic powder binder combinations are still under investigation. The two main approaches used in fabricating ceramic parts are the dry powder bed 3DP and slurry base 3DP processes. The machine is commercially available in Stratasys 3-D modeller retrofitted with modified extrusion heads suitable for extruding ceramic materials [4)]. The dry powder bed approach, which was developed first, builds parts by selective printing binder into a powder bed. To build another layer a new layer of powder is spread over the surface of the build area. The binder is then printed into the powder bed using a process similar to inkjet printing. The printed areas become the part material and the unprinted areas function as support during the build process. After all the layers have been built, the part is left to dry, then depowdered and removed, followed by binder removal and sintering [5)].

The 3 DP Technique was used by many investigators. Suns et al. [(6)] used the 3D printing technique to form Ti3SiC2 using a water soluble binder which was followed by drying, depowdering and finally sintering at 1600 C. It was used also by Evans [(7)] to print TiO_2 water based PZT suspensions in ethanol. An array of PZT pillars made by drop on demand ink jet printing was obtained. Wang et al.[(8)] used the 3DP to print PZT in paraffin wax, polyester dispersion system. Small actuators for microelectronics were produced in this way. Zhao et al.[(9)] used the 3D printing technique to print ZrO_2 in wax, octane alcohol mixture. Ceramic pillars with sufficient height 2mm were created and sintered without deformation. Ceram Res. Group [(10)] used the 3D printer Z-Corp for the formation of Al2O3, SiO2, ZrO2 and SiC green bodies with colloidal silica binder. Monolithic Al_2O_3 components with densities of over 99.3% theoretical and average flexural strength of 360 MPa, sintered Si_3N_4 parts could be prepared by this way. Materials with controlled or graded microstructures such as zirconia toughened alumina (ZTA) were prepared by depositing ZrO_2 slurry onto an Al_2O_3 bed. Seitz et al.[(11)] applied the 3D printing technique for the forming of material modified hydroxy apatite (HA), powder polymer based binder. Porous ceramic scaffolds for bone tissue engineering were printed and the green bodies were consolidated at 1250 C in air.

The layer object manufacturing technique (LOM) was applied using Javelin´s Steam Roller by many investigators. The materials used in this machine were Ce-ZrO_2 and two phase mixture of Al_2O_3/Ce-ZrO_2, Si_3N_4, stainless steel 316 sheet, alumina, zirconia, and silicon nitride. In NASA this technique was used for the fabrication of Si_3 N_4 green bodies [(12)]. Holly Shulman et al.[13)] adopted the LOM technique for the formation of Si3N4 green bodies. A green flexible ceramic tape was used to create the part instead of the LOM paper, i.e. single sheet feed system. The resulting prototype was sintered in a microwave furnace. Xuemin Cui et al. [(14)] adopted the LOM technique to fabricate Al2O3 objects from its powder using styrene-acrylic latex as a binder that has low foam and viscosity. The median size of powder used in that work was 0.8 μm. This method allows lamination at room temperature under low or slight pressures and without any adhesive on the surface of green tapes. Fritz and Weisset [(15)] used shape deposition manufacturing technique (SDM), for the formation of Si3N4. The Sintering was carried out at 1750 C in N2 atmosphere. Vaidyanathan et al.[(4)] used fused deposition ceramic technique (FDC) for the formation of Si3N4 green bodies.

EXPERIMENTAL

Materials:

Two types of commercial SiC powder supplied by Shunk were used in this work. The first one is a grey grade containing 90 wt% SiC, 1 wt% B_4C and 9 wt% organic binder. The average particle size for this powder is 1 μm and its specific surface area is $5m^2\ g^{-1}$. The second one is a black grade containing 80 wt% SiC, 10 wt% colloidal C and 10 wt% organic binder.

A 32 μm sieve was used to remove the SiC powder finer than 32 μm. After that the powder was mixed with the required amount of starch. Two types of starch were used in this work. These were Avebe SPG20 and Ca lignin sulfonate powders.

The humidity level injected by the 3D print head is controlled to get the required amount of liquid. The amount of liquid coming out from the print head for each standard powder type was measured. The maximum and minimum amounts of liquid were determined. This was achieved by making a print for each case on a weighed blank paper and the change was calculated.

Rapid prototyping of SiC:

The 3D printer, Z402C 3D, from Z-Corporation Technology was used in this work. The printer has 3D print setup[15], including, the binder to volume ratio, the saturation level, the saturation and the anisotropic scaling factor. These parameters are linked to the choice of powder type and the layer thickness.

The 3D printing jobs were performed in the spread mode to increase the amount of liquid injected into the powder layer. After printing the printed parts were left to dry, then depowdered and removed.

Strength evaluation:

The strength of the green bodies was examined using an instrument by which the load at failure is determined.

Pre-firing and infiltration:

The SiC green parts were pre-fired at 300 C to remove the binder and its decomposition products from the green bodies. After the pre-firing process, a trial to infiltrate green SiC printed parts using liquid Si at 1450 C, in argon atmosphere was carried out.

Density measurement:

The densities of green and dipped SiC printed parts were measured using the submersion technique and xylene as a liquid.

Metallography and SEM:

The metallograph and the SEM were used to identify the phases present.

RESULTS AND DISSCUSSION

Investigation of different liquid binders:

20 ml of the liquid binders, given in Table 1, were poured on 2g of SiC powder in a porcelain dish and dried at 80 C. After drying each sample was tested under a static load to determine its strength. The results are given in Table 1.

Table1. Strength of green bodies prepared using different liquid binders.

No.	Liquid Binder	Load (Kg)	
		(Grey Powder)	(Black Powder)
1	H_2O	0.9	1.9
2	NH_4OH (2 m /l)	0.8	1.8
3	32% HCL	0.5	1.5
4	CH_3OH (M= 32.04 g/mol)	<0.1	<0.1
5	50v% H_2O + 50v% CH_3OH	0.4	1.2
6	50v% H_2O + 50v% NH_4OH	0.8	1.7
7	25v% H_2O + 25v% NH_4OH + 25v% HCL + 25v% CH_3OH	0.4	2.0
8	33.3v% H_2O + 33.3v% NH_4OH+ 33.3v% CH_3OH	0.4	2.0
9	80v% H_2O+ 10v% NH_4OH+ 5v% HCL+ 5v% CH_3OH	0.3	2.0
10	H_2O + 1% HCL	0.3	2.3
11.	H_2O + 5% HCL	0.3	2.2
12	H_2O + 1% NH_4OH	0.3	2.0
13	H_2O + 5% NH_4OH	0.6	2.0
14	H_2O + 1% HCL + 1% C_2H_5OH	0.3	2.2
15	H_2O + 3% HCL + 3% C_2H_5OH	0.6	2.1
16	H_2O + 1% NH_4OH + 1% C_2H_5OH	0.5	2.0
17	H_2O + 3% NH_4OH + 3% C_2H_5OH	0.4	2.1

From these results it is clear that the green bodies with the highest strength were obtained from the black powder and 1% HCl. For this reason the black powder was considered in the following work.

3D Printing using black SiC powder:

Green bodies with the dimensions 45x10x5mm in size were prepared using black SiC powder and 1%HCl as a binder. Some printed parts were broken during handling which may be due to the inefficient packing of the powder or the insufficient amount of starch. The 3D printer was checked the next day and the print head was found damaged. It was noticed also that the humidity level coming out from the print head was low. Therefore, it was necessary to increase the humidity level, and this can be achieved by increasing the amount of binder injected from the print head into the SiC powder layers. The knowledge of the amount of humidity is thus important to adjust the required amount necessary for printing.

The damage in the print head was investigated under the optical microscope and a new and a used print head were compared. The technologies of the ink-jet print head were also reviewed and two types were found available in the market. One of these types uses the piezoelectric technology in which the mechanical motion pushes the drop of liquid out. Whenever a drop is required, an electrical current is sent through the crystal; this causes a flex and pushes the liquid out of nozzle. The other type, which is used in the 3D printer Z-402, is the thermal technology in which the chamber holding the liquid bubble is heated and the bubble bursts due to the heat and the liquid drop shoots out of the nozzle. Finally the vacuum caused by the drop leaving the chamber draws the next bubble into the chamber. The manufacturer reported that silicon element is used as a heating element; and recommended alkaline liquids to be used to avoid the reaction with the heating element.

Optimization of starch addition to SiC powder:

10 % by weight of the two kinds of starch was added separately to the black SiC powder. The strength of the resulting green bodies are given in Table 2.

Table 2, Strength of printed SiC green bodies containing 10 wt % starch.

No.	Liquid binder	Load (Kg)	
		Avebe SPG20	Ca lignin sulfonate
1	H_2O + 1% NH_4OH	9.0 – 9.5	4.5
2	H_2O + 5% NH_4OH	9.5	4.5 – 5.0
3	H_2O + 1% HCL	14.5	6.5
4	H_2O + 5% HCL	14.0	6.5 – 6.7

From Table 2, it is clear that the strength of the green bodies is much higher than the corresponding ones in Table 1. This is due to increasing the percentage of starch. It is obvious also that the starch Avebe SPG20 is more effective in binding SiC black powder than Ca lignin sulfonate. The binding strength of the former is more than two times higher than the latter whatever the liquid binder used.
The results reveal also that the acidic solutions are more effective than the alkaline ones. This may be due to the idea that the decomposition efficiency of the starch molecule by HCl is higher than that with ammonium hydroxide.

To optimize the amount of starch, 5 wt % of Avebe SG20 starch was mixed with black SiC powder using the same procedure. The results are given in Table 3.

Table3. Strength of printed green bodies which containing 5wt % Avebe SG20 starch.

No.	Liquid binder	Load (Kg)
1	H_2O + 1% NH_4OH	5.5
2	H_2O + 5% NH_4OH	6.5
3	H_2O + 1% HCL	6.0
4	H_2O + 5% HCL	5.0

From Table 3, it is clear that the strength of green bodies prepared using the acidic solutions and 5 wt**%** Avebe SPG20 starch is nearly one third that prepared using 10 wt%. From the previous result, it can be concluded that 10 wt% starch is optimum to get the highest possible green strength.

Measurement of liquid amount injected by the 3D print head:

The amount of humidity level is to be controlled to get dense and strong SiC green body. The results of measurements are given in Tables 4 and 5. From these Tables, it is clear that the amount of liquid is inversely proportional to the layer thickness of SiC powder. The parameter binder to volume ratio expresses volume of liquid injected to the volume of powder. Practically, the choice of smaller layer thickness leads to a problem during printing on a real powder. That is, when the machine spreads the second layer; the gantry removes the already built previous layer and destroys it. So the layer thickness should be optimized.

Table 4, Humidity level measurements.

powder	Δω (g)	Binder/Volume ratio		Saturation level		Saturation		Layer thickness (mm)
		Shell %	Core %	Shell %	Core %	Shell	Core	
ZP14	0.17585	40	40	333	667	2	2	0.088
	0.0400	10	10	83	167	0.5	0.5	0.088
ZP15e	0.31585	40	40	333	667	2	2	0.088
	0.0713	10	10	83	167	0.5	0.5	0.088
ZP100	0.30225	40	40	114	229	2	2	0.088
	0.0276	10	10	29	57	0.5	0.5	0.088

Table5. Amount of liquid injected to the powder layer.

Powder	Δw (g)	(max/min) ratio
ZP14	0.17585	4
	0.0400	
ZP15e	0.31585	4.5
	0.0713	
ZP100	0.30225	11
	0.0276	

Calculations are carried out to clarify the concept of binder to volume ratio. The ZP15e powder was taken as an example, (layer thickness 0.088 mm, Table 4). The amount of liquid measured is 0.315839 and the volume to binder ratio is 40% [16].

The printed parts so produced were weak and friable may be, due to the less humidity injected into the powder layers. The injection was done manually using the same binder. Because of this reason the 3D printing jobs were performed in the spread mode to increase the amount of liquid injected into the powder layer. The resulting green parts enjoyed good strength.

In all the 3D printing technology, the bottom surface of the part is concave and the upper surface is flat. The reason for this is due to the difference in drying rates at different parts of the green body and the coming down of the liquid to the bottom by gravity. A simple technique was followed up to avoid this and it was successful.

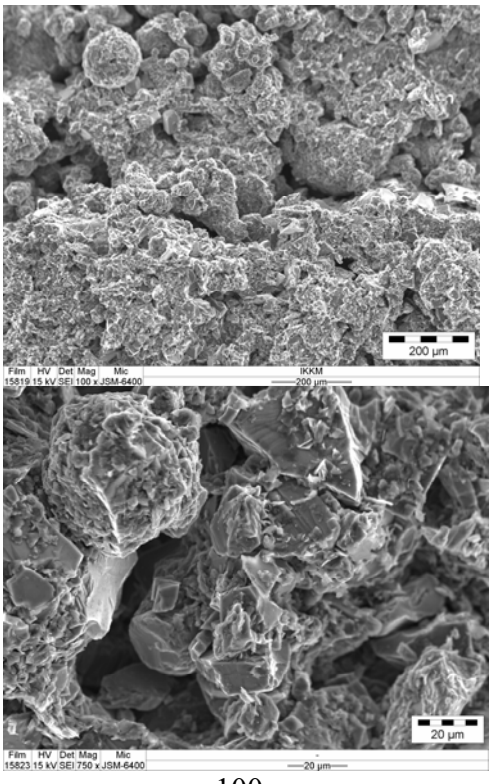
Printing using 1% NH_4Cl and NH_4OH:

A solution containing 1% NH_4Cl and NH_4OH was used as a binder the pH of which was 8.5–9.0. The resulting green parts showed high strength, with flat top and bottom surfaces. So, it is necessary to withdraw the humidity from the green bodies evenly during drying before depowdering. It was found that the print head was out of service after printing. This may be due to the presence of Cl^- ions. The Chlorine ions react with the Si heating element of the print head which damages it and makes it out of use just after one run.

A SEM section for the printed green part is shown in Figs. 1a and 1b. It is clear that the starch particles surround the SiC particles and the second phase, dark black areas, is porosity.

Density measurement:

The density of some green parts is determined using the submersion technique and xylene as a liquid. The results are given in Table 6.



a 100x b 750x

Fig. 1 SEM section for a printed part with 1% NH_4 Cl and NH_4 OH.

Table 6, the relative density of some SiC printed green bodies.

Sample (Print job)	Binder	ρ, gCm^{-3}	% relative density
A	1% NH_4OH	1.411595	58.9
B	1% NH_4 Cl and NH_4OH	1.362935	56.8
C	1% HCl	1.439615	60

The infiltration of SiC printed parts by Si:

A trial to infiltrate the green bodies using elemental Si at 1450 C was conducted. This trial failed and the reason is unknown till now. So it was necessary to use another technique. So the dipping technique was followed.

Dipping in liquid Si:

The green parts were dipped in liquid Si at 1450 C. A photomicrograph for some of the resulting dipped parts is shown in Fig. 2, where A, B and C are the print jobs given in Table 6.

A C C B

Fig.2 Photomicrograph for SiC printed parts dipped in liquid Si.

Density measurement of dipped samples:

The density of some samples after dipping in liquid Si at 1450 C is measured and the results are given in Table 7.

From this table it is clear that the highest density that could be reached is 2.96 gcm^{-3}.

Table7, density of SiC dipped in liquid Si.

No.	Specimen (Print job)	Density (gcm^{-3})
1	A	2.96
2	A	2.83
3	B	2.85
4	B	2.75
5	B	2.85
6	B	2.87
7	B	2.83
8	C	2.83
9	C	2.82
10	C	2.83

SEM and metallographic examination of SiC dipped samples

Fig. 3 shows a SEM photomicrograph for a printed sample after dipping in liquid Si at 1450 C with magnification 750x. The sharp corners of SiC particles are still present and clear, which indicates that the SiC is not soluble in molten Si or, it has very limited solubility.

Fig. 4 is a metallographic section for SiC printed part print job after dipping in liquid Si. The sharp corners of SiC particles are still present and clear, which is the same as obtained from the SEM. This is another proof which indicates that the SiC is not soluble in molten Si or it has very limited solubility.

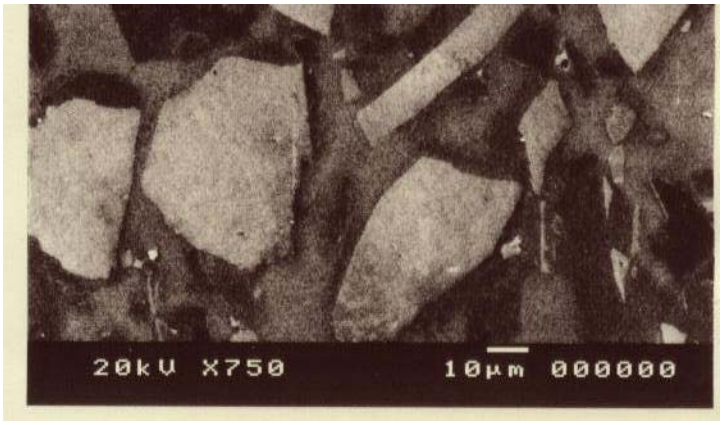


Fig. 3. SEM section for a printed part dipped in liquid Si,750x .

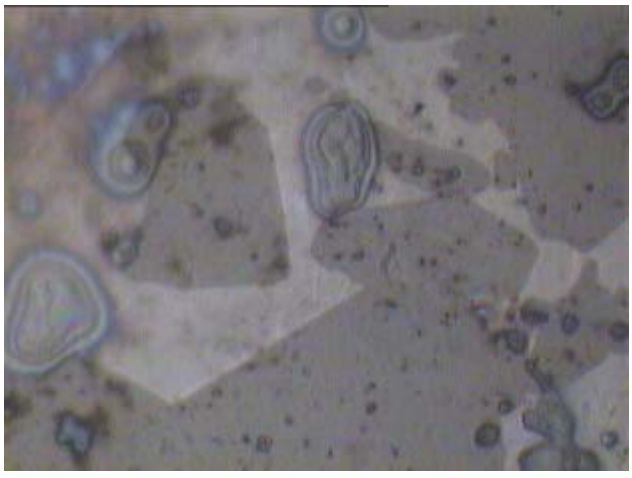


Fig. 4 Metallographic section for SiC printed part dipped in liquid Si, (1000x)

Conclusions:

From the results of the experimental work that has been done it may be concluded that:

- The green bodies produced from the black powder enjoyed higher strength than those produced from the grey powder.
- It was found that some printed parts were broken during handling. This may be due to the inefficient binder content or the insufficient amount of starch which added as a binder.
- The amount of humidity level is to be controlled to get dense and strong SiC green body.
- Avebe SP G20 starch gave higher green body strength than Ca lignin sulfonate.
- The optimum amount of Avebe SP G20 starch was found to be 10 wt%.
- The use of NH_4OH in the pH range 9-10 or, 1 % HCl solution in water and or a mixture of 1% NH_4Cl and NH_4OH in the pH range of 8.5 to 9 as a binder gave the highest possible strength of the green bodies.
- It was impossible to infiltrate the SiC printed parts with Si and the reason was unknown .
- The SiC printed parts were dipped in molten Si and pore free parts were obtained.
- From the SEM and Metallographic examinations for the dipped SiC parts, it was found that no SiC dissolved in the silicon after dipping. This was concluded from the presence of sharp corners of SiC grains.

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