RAPID MANUFACTURING OF SILICON CARBIDE COMPOSITES

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Abstract

From the earliest days of SFF technology development, a viable technique for the direct manufacture of fully-functional parts has been a major technology goal. While direct metal methods have been demonstrated for a variety of metals including aluminum, steel and titanium, they have not reached wide commercial application due to processing speed, final material properties and surface finish. In this paper the development of an SLS-based rapid manufacturing (RM) platform is reviewed. The core of this platform is a thermosetting binder system for preform parts in contrast to the thermoplastic materials currently available for SLS. The preforms may include metal and/or ceramic powders. A variety of fully functional parts can be prepared from different combinations of materials and post processing steps including binder pyrolysis, free-standing alloy infiltration, room temperature polymer infiltration and machining. The main issues of these steps are reviewed followed by a discussion about the support of RM. This paper is an intermediate report additional materials, applications, process models and product design strategies will be incorporated into the project in the next year.

A Manufacturing Context

Indirect SLS and the SLS processing of thermosetting polymers are not new. 3D's Castform is infiltrated with wax before it is used for metal casting, a flexible resin, Somos 201, is infiltrated with polyurethane for toughness and strength and several commercial metal systems involve steel powder and bronze infiltration. Work at Fraunhofer-Gesellschaft in Germany demonstrated SLS preforms for SiC ceramic prototypes. Their work also involved multiple infiltrations of phenolic to increase carbon yield, and SiC formation during subsequent furnace operations. Binder systems developed for the DTM Rapid Steel process (now 3D Systems) have contained phenolic as a high-temperature reinforcing agent. Phenolic-coated sand and a phenolic-zirconia system have been previously explored in industry, but have not been made commercially available. Most relevant to the current work, Lanxide Corporation pursued a variety of Metal Matrix Composite Materials formed from SLS preforms [Deckard and Claar, 1993]. These previous efforts suggest the capability of indirect methods to support freeform fabrication in a variety of materials.

Previous work at UT established a method for creating Reaction- Bonded Silicon Carbide (RBSiC) [Wang, 1999]. This involved first forming an SLS preform from SiC powder mixed with a binder. This part was then placed in a furnace where the binder was ashed and liquid silicon was infiltrated into the part forming RBSiC. The current project drives this basic method toward a more general rapid manufacturing process which requires consideration of powder processing, finish machining and a more generally applicable binder system. In addition, there is an integrated low-temperature polymer infiltration step. Figure 1 is a diagram of that process.

The potential variety of materials supported by the current work is also shown. Each of the main processes shown in Figure 1, establish capabilities and limitations of the overall process. One output of this process is a fully-dense polymer matrix composite – a 'functional prototype.' After furnace processing and infiltration a metal and/or ceramic matrix part is formed. The characteristics of matrix composites support fully functional parts.

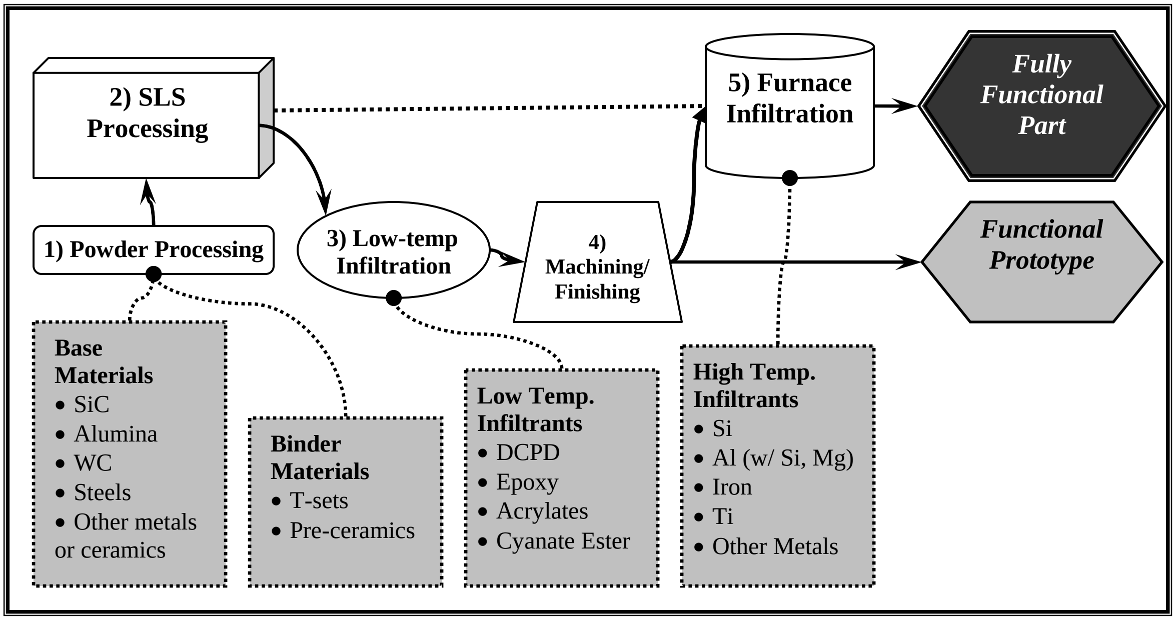

Figure 1 : Manufacturing Process Diagram

Fabrication Process Overview

Powder processing includes the preparation of individual powders as well as the mixing and appropriate dispersion of powder constituents. The influence of particle size, size distribution, shape and bulk density on the powder density and flow of powdered materials is reviewed by German, 1989. Each of these parameters must be matched to the capabilities of the SLS machine and to the infiltration steps that follow. During this project, base powders with average particle sizes from 20 to 80 microns have been examined, with various distributions. The sizes for binder powders ranged from below 1 micron to about 20 microns. Various grinding, ball milling and attritor milling operations were tested on the base/ binder systems. The purpose of these tests was to ensure proper powder dispersion and in the case of friable powder, appropriate particle sizes. Attritor milling was found to be the most effective as it combined grinding and mixing, but with longer cycles ball milling achieved similar results although finished parts were produced from simply rolled powder.

Binders and SLS

The operation of the binders themselves is of particular interest. The main functionality of binders for SLS has traditionally been carried by thermoplastic resins and waxes. A previous binder system for 3D Systems' Rapid Steel product was a mixture of wax, nylon and phenolic.

Bhandari, 2004, examined the behavior of this binder system and the function of each component. Partly based on the results of that work, single-component thermoset binders were explored. The draw of working with thermosets was the potential for greater adhesion strength, higher temperature performance (many cured thermosets do not melt) and finally precursors to high-temperature materials (such as carbon ash or silica). Several types of thermosets were examined during this project including polyester, phenolic, polyamide-imide and hybrid resins. The curing characteristics of these resins were analyzed using a differential scanning calorimeter (DSC). None of the thermoset systems evaluated reached a full cure under the laser. A model of the thermal curing of thermoset materials is being matched with a model for the heat transfer associated with laser scanning over a powder bed. This coupled model will support additional development of thermosetting materials for SLS and will be published separately. Empirically, increasing laser power increases adhesion, but also increases part growth due to heat flowing beyond the regions scanned by the laser. The key problems presented by thermosets lie in the melt flow and adhesion variations which affect the recycling of powder similar to the solid-state polymerization observed during the SLS processing of nylon powder. Figure 2 shows well distributed binder with good flow, distribution and obvious binding. Figure 3, is an SEM micrograph of the same binder showing lower binder distribution (especially of smaller particles), higher melt flow and ultimately lower particle-to-particle adhesion.

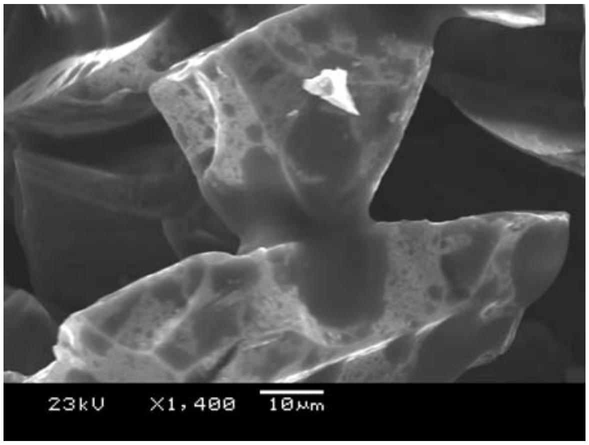

Figure 2 : Thermosetting Binder Attaching SiC Particles

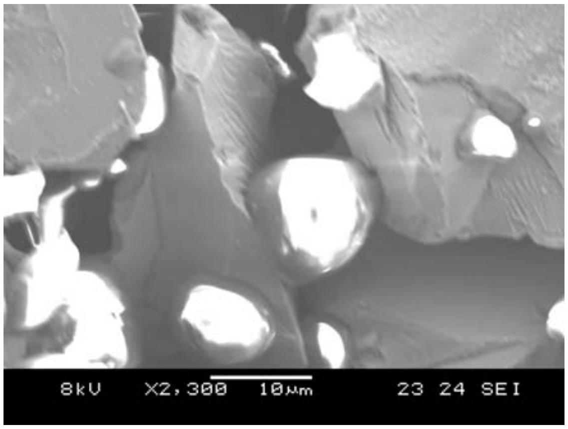

Figure 3 : Lower flow binder

The research has focused on glass and SiC base powders as they are readily available, inexpensive, support the use of several binders and infiltrants, and finally represent many base powders. The parts produced from base and binder powders are called green parts and are porous.

Polymer Infiltration

Porous green parts may be infiltrated with a variety of thermosetting materials. This is a relatively inexpensive path to a fully dense, stiff, net shape, polymer matrix composite part. In addition this is a very useful intermediate step for fully functional materials as critical surfaces and tolerances may be achieved easily at this stage. The ash from these types of materials represents further support during furnace processing and additional precursors for final material.

Polymer matrix solder masks for electronics manufacturing have been made and sent to a potential customer for review. A closely related research project examining SLS fabrication of fuel-cell components has demonstrated a polymer-matrix graphite material and is described in concurrent publication.

Furnace Processes

Commercially processed Rapid Steel parts are infiltrated in a nitrogen-inerted kiln at 1200°C. These parts are supported by alumina powder during infiltration. One of the targets of the current work is to pursue a free-standing infiltration and higher temperatures. A graphite vacuum furnace with several process gases was used for several types of experiments. This type of furnace allows higher temperature (to 2000°C) materials including iron, silicon, titanium. Argon and Argon/ Hydrogen (forming gas) were the process gases during materials processing. There are three basic phases to the furnace process; polymer curing, polymer ashing and finally infiltration. Each of these phases determines a section of the temperature cycle used to form the final parts.

Without a full cure under the laser, it is important to facilitate curing in the furnace to maximize the strength of the parts, dimensional stability and final part properties. This is accomplished by a slow ramp to an appropriate curing temperature which is held to unsure curing before moving into decomposition and ashing. The temperatures and holds were determined from DSC analysis of heat aged samples.

Decomposition involves outgassing, chemical bond reorganization, shrinkage and the formation of structural ash. Typically the critical temperature region for this process is 300-500°C and the appropriate ramp through this temperature range is relatively slow [Choe and Lee, 1992]. This is to retain structural integrity during outgassing and the reorganization of chemical bonds. Above this temperature the formation of chemical bonds continue to be important, but ramp rates can be raised. In the case of phenolic with its high carbon yield (40-70% by weight), the ashed resin can be stronger than the base resin. Figure 4 is an SEM micrograph of phenolic ash showing shrinkage in bulk resin. If the SiC particles are interconnected this shrinkage is a micro-scale feature and does not represent significant dimensional changes in the final part.

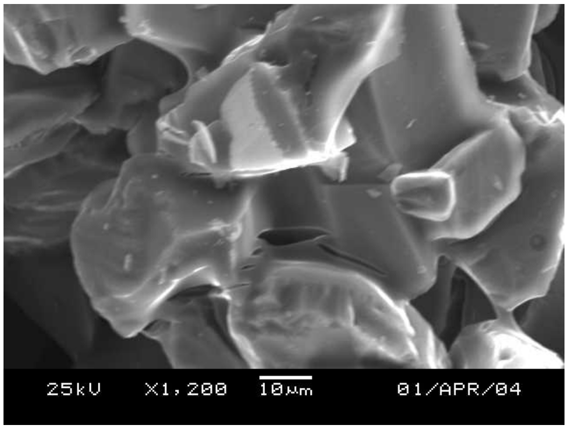

Figure 4 : Phenolic Ash (bonding SiC particles)

The metal infiltration in this project is the spontaneous wicking of a molten metal material into a porous, free-standing part. Capillary action driven by surface energy differences allows the metal to fill the parts. The mechanism of infiltration was explored during the previous SiC research at UT [Wang, 1999]. For silicon infiltration into SiC preforms, the theoretical maximum wicking height was calculated by Wang, 1999, to be 2 meters. A test part, shown in Figure 5, illustrates the loss of part shape caused by over-infiltration from a long temperature cycle and presence of extra infiltrant.

Figure 5 : Metal Infiltrated Part

It is difficult to examine the furnace processes because the parts cannot be observed during the ashing and infiltration processes. The test part designed to analyze the process is shown in Figure 6. This part allows the examination of the SLS process in terms of part accuracy, surface detail and the ability to break fine features out of the machine. The nozzle-like features on the part allow it to stand during the furnace infiltration and test the limits of the process. It was expected that the thinnest wall and cylinders would be very difficult to form into final parts, but the increasing sizes of the features on the part would establish aspect ratios that could be produced using this manufacturing process.

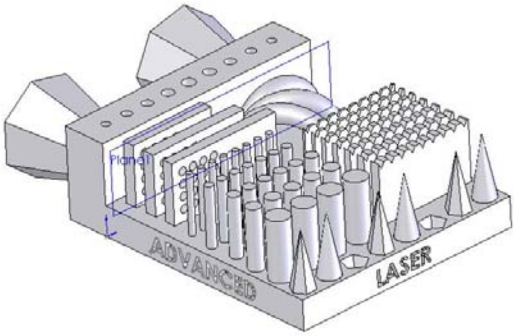

Figure 6 : Breakout/ Infiltration Parts

RM Support

In addition to material properties, economics and applications must be examined to establish rapid manufacturing. It is also critical to tie RM to actual manufacturing to help target the research and also assess commercial potential. One of the key elements of this project has been the collaboration with SLS, polymer and manufacturing industries to support and guide the research. A cost model was prepared that covers polymer and furnace infiltration processes. This model showed that the economic viability of this process was dominated by avoiding post processing (machining, finishing, etc.). Within the SLS process build time and base material are the main cost centers. In terms of applications, the greatest advantage comes in high value, high complexity parts made from difficult materials. As an example, SiC is used to make pump seals which are relatively simple 1-2 inch tube shaped parts. However, an indirect SLS process is capable of making these parts for about $40.00 each while they are sold for $150-200. Pump seal test parts have been made and will be reviewed by a chemical manufacturer. Another interesting application follows the extensive work in rapid tooling and represents a much larger opportunity. With the ability to make complex, high-temperature MMC parts, fully functional metal casting dies are within reach. A 2-part die measuring a few inches across could be sold for approximately 7 times the manufacturing cost estimated for the process discussed in this paper.

Next Steps

The tasks for this research project are the completion of the curing/ SLS processing model and the mechanical testing of parts from aluminum and iron matrix composites. At the same time additional test parts will be prepared for review by potential customers. Other thermoset binders and infiltrants will be explored.

Conclusion

By tying together the findings of several previous research projects with current research involving thermoset binders and infiltration, a platform for rapid manufacturing materials is being developed. This project includes process modeling, example materials and the analysis of applications and economics. In this paper the basic material sets being pursued and the main processes of the manufacturing process have been reviewed. A more technical discussion of this project will follow the final phases of research and intellectual property protection to be completed during the following year.

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