Rapid Prototyping of Mg/SiC Composites by a Combined SLS and Pressureless Infiltration Process

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Introduction

The expanding market for metal matrix composites (MMCs) presents a unique niche application for rapid prototyping / manufacturing. MMCs are well suited to RP for two reasons. First, these relatively new high performance materials are largely used in high cost, low production applications which are easily accommodated by RP techniques. Second, the hard and brittle ceramic reinforcement phases used in MMCs add cost and complexity to traditional production methods. Special tools or processes are required to machine these materials, and the cost and design limitations imposed by the production of a mold limit the competitiveness of casting [1,2]. In comparison, the additive nature of Selective Laser Sintering (SLS) avoids the problems associated with machining of the ceramic phase, and the wide range of geometries which can be produced ensures the versatility of the process.

Process Description

The new RP process consists of three steps: the production of a porous ceramic preform by SLS of polymer coated powder, a polymer debinding / firing cycle, and the infiltration of the metal matrix into the preform. A schematic of these steps is shown if Figure 1.

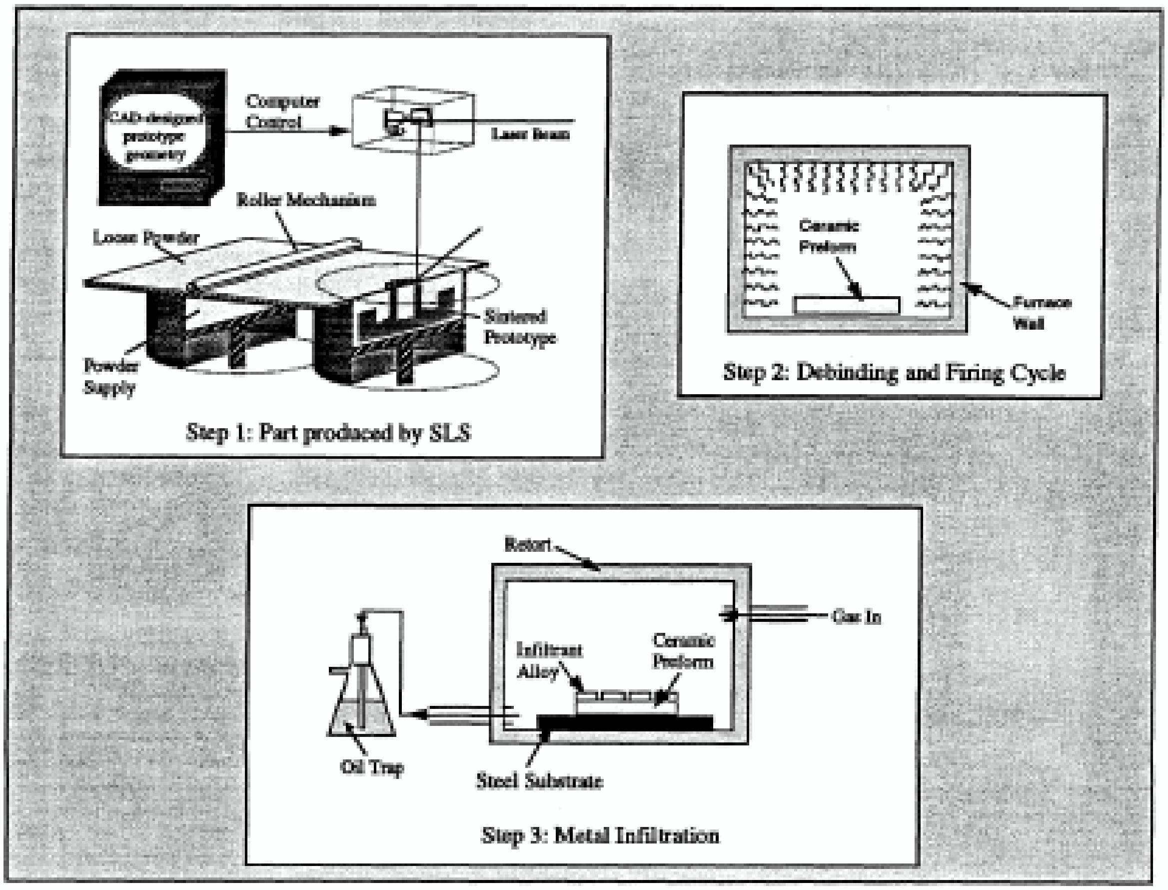

Figure 1. Schematic showing the three steps of the new production process.

SLS of Ceramic Preforms

The production of a porous ceramic preform by SLS is central to the new process. The part geometry is established at this stage and will remain unchanged throughout the remaining processing steps. The production of the preforms did not pose any substantial problems; however, the use of a new proprietary polymer binder formulation did prompt a series of short investigations to establish the optimal coating thickness and scanning parameters to provide maximum density and strength. It was established that a 4.5 wt% polymer coating and fluence of approximately 4 cal/cm^2 provided optimal properties [3]. The density of the preforms was typically 40 vol%. The production of higher density preforms was prevented by the poor packing behavior exhibited by the angular SiC particles. Use of a bimodal particle size distribution or the availability of more spherical particles should substantially increase this value. A micrograph of the fracture surface of a scanned preform is shown in Figure 2. The average particle size is 50 μm (280 mesh).

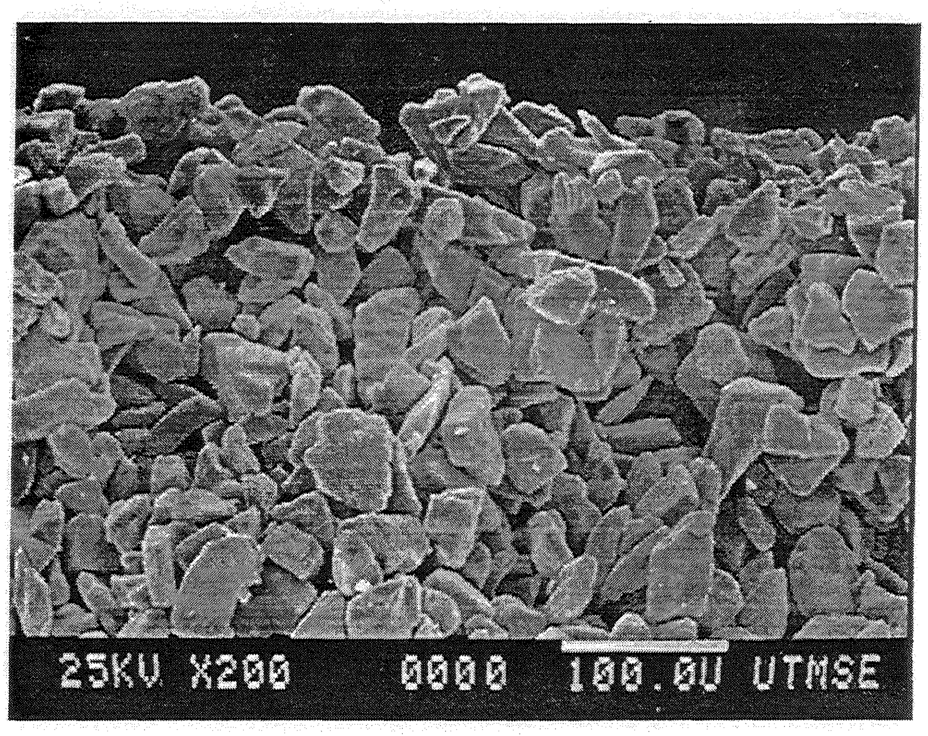

Figure 2. Scanning electron micrograph of a preform fracture surface transverse to the build direction.

The selection of SiC as the ceramic reinforcement phase was based on its wide availability and its high thermal conductivity, which makes it useful in electronics packaging applications (discussed later). In theory, any ceramic reinforcement phase can be selected which is available in powdered form, compatible with the polymer binder, and stable under the laser beam. Previous work done with alumina suggests that it would be a suitable alternative.

Debinding and Firing

Before the metal matrix can be infiltrated into a preform, the polymer binder remaining on the surface of the SiC must be removed. This is accomplished by heating the preform to 400 °C in air. At this temperature, the polymer is volatilized and leaves the surface as a vapor. The preforms are now quite fragile, and further handling or attempts at infiltration typically result in damage to the preform. The addition of a firing step greatly improves the strength and handleability of the preforms. By holding the preforms at 1100 °C for 2 hours, a thin layer of the SiC is converted to SiO_2. The formation of the silica layer allows light bonding between the individual particles; however, no real sintering or densification of the preform occurs at this stage. Sintering of the SiC directly was not attempted because of the high temperature and inert atmosphere which are required. Even with the addition of boron and free carbon as sintering aids, processing temperatures of 2150 °C are typically used during commercial processing of SiC powders [4]. Such processing conditions would have added substantially to the cost of the production process. Future work may be directed toward the elimination of the polymer debinding and perform oxidation step by directly sintering the SiC under the laser beam. Preliminary experiments have indicated that such processing is possible.

Pressureless Infiltration

Infiltration of the porous preforms with the metallic matrix is the final step in the production process. This process is not as readily achieved with a metal-ceramic material system as it is with the more common metal-metal systems such as the iron-copper and copper-solder systems used in other RP processes. The obstacles associated with this process are due to the relative surface energies required to drive the infiltration process. In a spontaneous or pressureless infiltration process, the surface tension of the liquid infiltrant must be lower than the surface energy of the solid matrix. Because the surface energies of ceramic materials tend to be quite low, this situation rarely occurs. As the table below shows, the surface energies of typical ceramics are lower than the surface tensions of common metals and alloys.

Surface Energies of Common Alloys and Ceramic Materials [5-8].

Material	Temperature (°C)	Surface Energy (mN/m)
$Pt_{(l)}$	1770	1865
$Fe_{(l)}$	1120	1835
$Cu_{(l)}$	1120	1270
$Al_{(l)}$	660	914
$Mg\text{-}8Al_{(l)}$	600	571
$SiC_{(s)}$	RT	3800
$TiC_{(s)}$	1100	1190
$Al_2O_{3(s)}$	1850	905
$ZrO_{2(s)}$	RT	770
$SiO_{2(s)}$	1300	310

For the magnesium-SiC material system which we are considering, the values shown in the table suggest that infiltration should not be difficult because of the relatively high surface energy of SiC. This high value is misleading. The surface energy for SiC listed in the table was established for a perfectly clean surface of SiC at room temperature. The exposed surfaces of most SiC, including the particles in the preform, are no longer SiC, instead they have formed a surface layer of SiO_2. As can be seen, the surface energy of silica is among the lowest of the common ceramic materials. It is the surface layer of silica which effectively prevents the infiltration of most alloys.

Because of the unfavorable surface energies of these materials, processes such as squeeze casting have been developed which use an externally applied pressure to overcome the surface energy considerations and force the liquid into the matrix. Such a process is not suitable for this application because it requires the production of a mold. An alternative approach to pressure infiltration is the incorporation of a reactive species such as magnesium, lithium, or titanium into the infiltrant alloy [9-11]. It has been shown that the presence of these elements promotes wetting. Sessile drop experiments with SiC and aluminum have recorded a change in contact angle from 112° to 83° with the addition of 5 wt% Mg to the aluminum [9]. It has been proposed that the change in wetting behavior is due to reactions between the magnesium and the oxide layer present on the surface of the SiC [12]. The Al-Mg-O and Mg-Si-O ternary phase diagrams are shown in Figure 3. As can be seen, the system is fairly complex with many possible stable phases. Fosterite (Mg_2SiO_4), Spinel ($MgAl_2O_4$), and Mullite ($3Al_2O_3 \cdot SiO_2$) were suggested as the most likely reaction products. The exact nature of the reaction at the interface has not been definitively established, but the experimental evidence for superior wetting behavior provided by magnesium suggested that a magnesium based alloy would make a suitable infiltrant. For the infiltration experiments, a common die casting alloy AZ91D was selected. Aside from its ability to wet the SiC, this alloy provides low weight and high thermal conductivity.

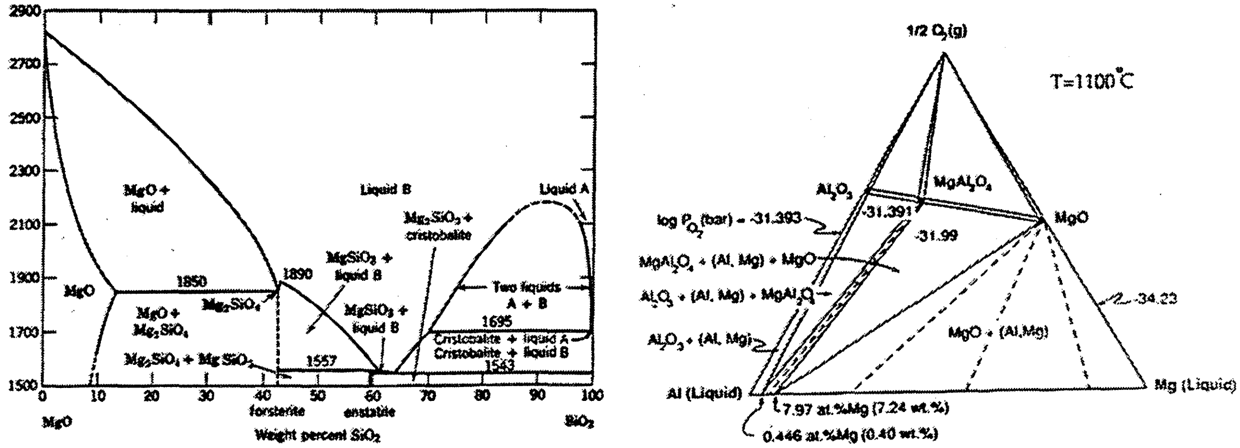

Figure 3. Phase diagrams for the Mg-Si-O and Al-Mg-O systems [13,14].

Infiltration Experiments

To prevent oxidation of the preform and infiltrant alloy, the infiltration process must be performed in a controlled atmosphere. A sealed retort capable of being evacuated and backfilled with inert gas was required for successful infiltration. A purge cycle consisting of evacuation to approximately 100 mTorr followed by a backfill with inert gas to atmospheric pressure was repeated twice before the heating cycle was begun. The purge gas was allowed to flow through the retort during the entire experiment. The gas was vented through an oil trap which provided a slight positive pressure in the retort. Strips of the infiltrant alloy approximately 3 mm thick were placed directly on top of the SiC preforms. This arrangement ensured the shortest infiltration distance for the part geometry used in these experiments. A steel substrate was used to support the preform and prevent reactions between the magnesium alloy and the retort. A schematic of the experimental set up is labeled as Step 3 in Figure 1. Following the purging of the retort atmosphere, the process cycle consisted of a one hour ramp to the infiltration temperature, a one hour hold, and a slow cool to room temperature.

Previous research conducted by Aghajanian et al, indicated that a nitrogen based atmosphere is required for spontaneous infiltration [15,16]. The preforms manufactured by SLS behaved similarly, with no infiltration occurring in helium or argon atmospheres. When a nitrogen atmosphere was used, the infiltration proceeded readily, if somewhat slower than is observed with other materials systems. A processing temperature of 670 °C was sufficient to infiltrate a 1 cm thick preform in one hour. Typical microstructures are shown in Figure 4. As can be seen, the

SiC is well distributed throughout the sample, with no clustering or layering evident. The level of porosity is also quite low. It was observed that two factors must be controlled to limit porosity. First, the infiltration time must be sufficient to allow complete infiltration; short infiltration times (30 minutes) frequently resulted in incomplete infiltration. Second, no large pores may be present in the preform prior to infiltration. Pre-existing pores will be retained after infiltration, presumably due to the lack of capillary action to draw the liquid into the pores.

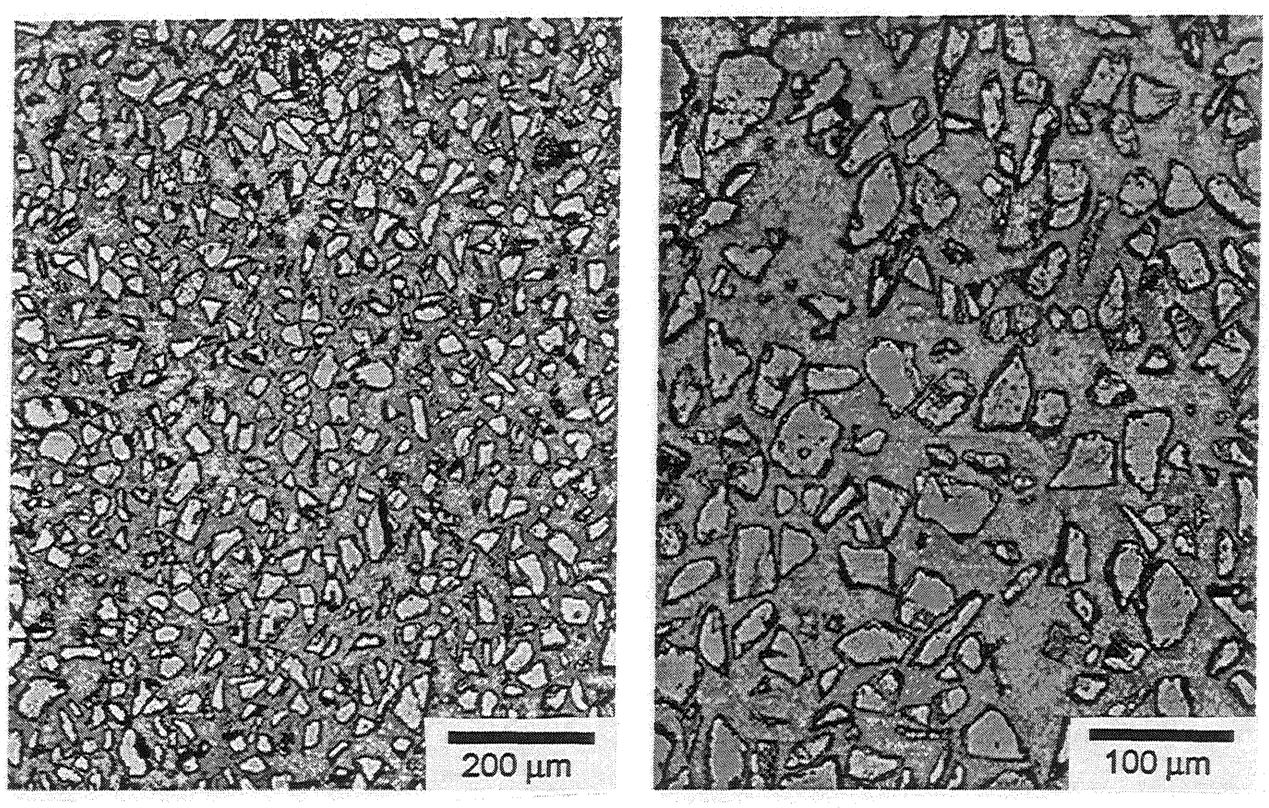

Figure 4. Micrographs of the infiltrated preforms. a)100X b)200X

Thermal Properties

The use of MMCs for electronic packaging materials has been suggested because of their high thermal conductivity and low thermal expansion. To prevent thermal stresses from arising at the interface between the chip and the packaging, the coefficients of thermal expansion (CTEs) must be matched. For this application a CTE equivalent to that of silicon 6.7 ppm/°C is required. Because the magnesium alloy has a relatively high CTE (27.2 ppm/°C) [17] a large volume fraction of SiC is required to achieve the desired value. Theoretical models indicate that as much as 80 vol% SiC may be required. In practice, concentrations of SiC somewhat less than this value appear to be adequate [18]. For the approximately 40 vol% SiC present in the samples produced by SLS, average CTE values of 11.9 ppm/°C were obtained with TMA testing. It was noted that the CTE values were similar in directions parallel and transverse to the SLS build direction, which was expected based on the uniform microstructure.

Clearly, a higher volume fraction of SiC is required to obtain the desired CTE value. Due to time constraints, the production of preforms with a bimodal powder size distribution was not possible; however, a similar structure was produced by infiltrating existing preforms with additional SiC. A slurry consisting of 79.7 wt% water, 20 wt% 1200 mesh SiC, and 0.3 wt% sodium dedocyl sulfate (a surfactant) was infiltrated into the preforms. The preforms were then processed with a debinding, firing, and metal infiltration process identical to that used with the previous samples.

The addition of the 1200 mesh powder increased the volume fraction of SiC to approximately 48%. The increased SiC content resulted in a decrease in CTE to 7.1 ppm/°C. A value which closely approaches the desired 6.7 ppm/°C. The presence of the additional SiC provided the added benefit of improving the strength and handleability of the preforms after the firing cycle. The one problem associated with this process is the nonuniform distribution of the SiC. As can be seen in the micrographs in Figure 5, the smaller SiC tends to form clusters around the larger particles. This fact, coupled with a decreasing concentration gradient away from the surface of the sample, led to occasional warping of the preforms during the firing stage. This problem should be alleviated by producing the preforms directly from a bimodal particle mixture.

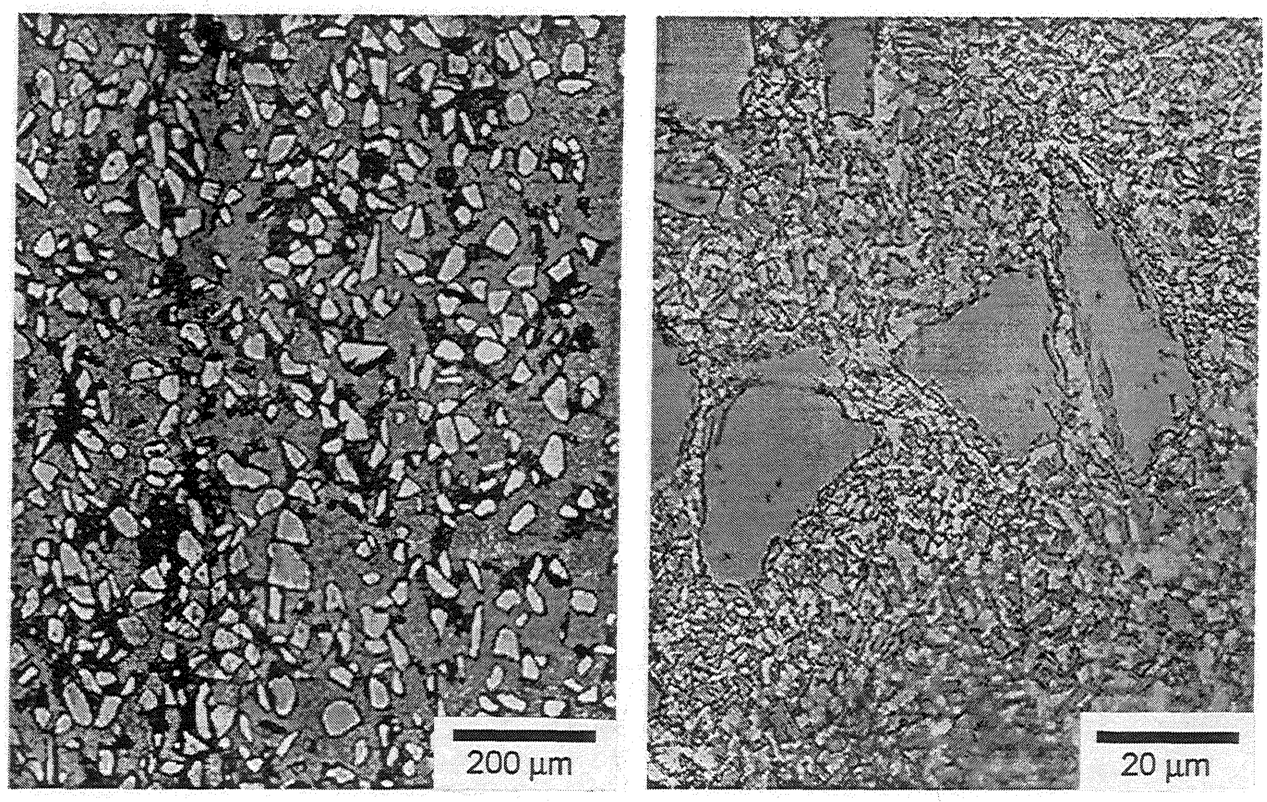

Figure 5. Micrographs showing clusters of 1200 mesh SiC particles. a)100X b)1000x

Geometry

After the processing procedure had been demonstrated with simple rectangular test coupons, several more complex geometries were infiltrated to determine if accurate dimensions could be retained. Two of the test geometries are shown in Figure 6. Three different parameters were considered. First, the thin walls and small features of the test pieces are far more delicate than the simple rectangular bars. These areas are prone to damage or collapse during handling of the preform or during the infiltration process itself. Optimization of the binder coating thickness to improve green part strength, and a firing cycle of sufficient length and temperature ensured that these features were accurately retained.

Second, holes of varying dimensions were present in the test geometry to determine if over-infiltration would occur. It was determined that the surface tension effects which drive the infiltration process are quite weak and close particle spacing is required for infiltration. Holes as small as 2 mm in diameter were still too large to provide a sufficient capillary force with which to draw in the infiltrant and remained uninfiltrated. A related concern is the small amount of excess infiltrant which must be provided in any infiltration process to ensure that the part will be

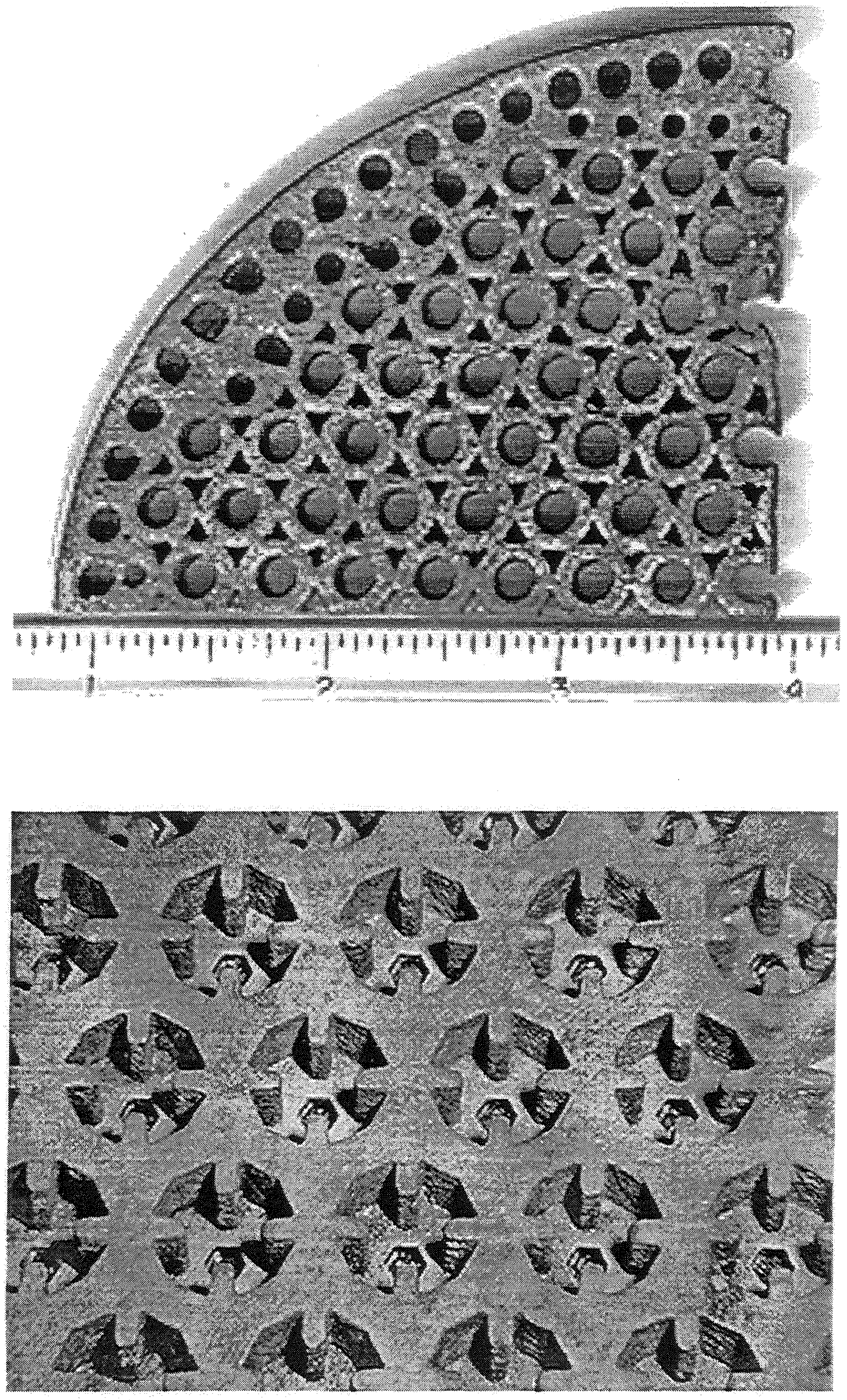

Figure 6. Fully infiltrated test parts. Parts were finished by bead blasting following the infiltration step. (Top scale in inches)

completely infiltrated. This excess material collects at the bottom of the preform along the surface of the substrate such that it would occasionally block through holes in the parts. The presence of Second, holes of varying dimensions were present in the test geometry to determine if over-infiltration would occur. It was determined that the surface tension effects which drive the infiltration process are quite weak and close particle spacing is required for infiltration. Holes as small as 2 mm in diameter were still too large to provide a sufficient capillary force with which to draw in the infiltrant and remained uninfiltrated. A related concern is the small amount of excess infiltrant which must be provided in any infiltration process to ensure that the part will be

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the excess magnesium does not cause substantial difficulties in the processing of the parts because it is very easily removed. The great difference in hardness between the excess magnesium alloy and the composite part allows abrasive bead blasting or tumbling processes to quickly remove the excess material. The high hardness of the ceramic phase effectively limits any additional material removal once the surface of the composite is reached.

The third concern is warping or large scale distortion of the preform. Warpage was observed in some of the test pieces. It appears that the infiltration process disrupts the light bonding which exists between the SiC particles. The weakened structure of the preform tends to conform to the shape of the substrate. This distortion suggests that parts with overhanging features may present problems during infiltration. Two possible methods to alleviate this problem include packing the preform in a supporting powder bed which is not infiltrated by the magnesium, or using a ceramic binding agent such as a preceramic polymer [19] which can be decomposed to provide a SiC "glue" to hold the individual particles together.

Conclusions

A process has been established for the rapid manufacturing of MMCs based on Selective Laser Sintering. Parts with complex geometries, containing between 40 and 50 vol% SiC were successfully produced. The low thermal expansion and high thermal conductivities provided by these materials may make them suitable for applications such as electronic packaging. Future work on this process will focus on direct SLS processing of the SiC which would allow the removal of the polymer binder along with the current debinding / firing stage. Additionally, the incorporation of a ceramic precursor to the preform may provide higher SiC content and improved preform strength and stability during the infiltration process.

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