THREE – DIMENSIONAL PRINTING, 3DP™, OF ELECTRONIC CERAMIC COMPONENTS

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Abstract

Products which incorporate ceramic components frequently demand properties and shapes that challenge contemporary forming techniques. The Three-Dimensional Printing, 3DP™, process has been modified to incorporate colloidal science for the fabrication of these fine ceramic parts. Dielectric components were built using a sequential layering process of a ceramic powder bed followed by ink jet printing of a binder. A well-dispersed slurry and optimized printing parameters are required to form a uniform powder bed with a high green density. Slurry-powder bed interactions affect the geometry of the component and produce structural and inter-layer defects ("differential slip casting"); the correct choice of binder system and slurry chemistry has, however, eliminated these defects. Removal of the printed components is an important processing step in 3DP™ since the part retrieval process plays a key role in the resulting shape and properties of the ceramic parts. Part retrieval is achieved through the redispersion of the powder bed. This technology has been used for the fabrication of dielectric radio frequency (RF) components with good dimensional tolerances. The dielectric characterization of RF filters was performed on dry-pressed and 3DP™ formed components in order to examine the effects of processing technique on performance.

Introduction

Dielectric ceramic components have made a large impact on the growth of the communications industry. The current technology has evolved to include pagers, automobile collision avoidance, global positioning systems and other frequency sensing devices. The growth was facilitated by the development of a unique class of ceramic dielectrics. These materials combine a high dielectric constant and low dielectric loss enabling new design possibilities. Conventional forming processes, such as die pressing, extrusion and tape casting are currently used to form such components. These processes restrict the geometry of the components to very simple shapes. Additional processing steps are required to meet the strict dimensional tolerances while machining is needed in order to produce components with more complex geometries. The macrostructure and microstructure of the components are non-uniform due to the nature of the forming processes. Density variations and stacking sequences lead to anisotropic physical properties that ultimately degrade the performance of the component. Thus, much of the past 15 years of ceramics processing research has been focused on the development of forming processes with excellent shape capabilities and improved reliability.

Our research has concentrated on combining modern ceramics processing with a solid freeform fabrication (SFF) method. The specific technique studied is 3-Dimensional Printing, 3DP™. This process is capable of producing complex-shaped ceramic, metal and polymer components directly from CAD files.[1] The 3DP™ process has been integrated with colloidal ceramic processing to produce parts using submicron powders.[2] There are four fundamental aspects of the process that have been studied in detail. They are formation of the powder bed, the development of the binder system, liquid interaction between the slurry and binder systems and the redispersion of the unprinted powder bed. The physical properties of the printed parts are influenced by one or more of these principles.[3,4,5,6] This paper discusses the physics and implications of forming ceramic components using the slurry-based 3DP™ process. RF components have been successfully fabricated using this process and their dielectric properties are briefly discussed.

Experimental Procedure

The Slurry-Based 3DP™ Process

Part generation began by jetting a well dispersed, 35 vol. % dielectric ceramic (MR2, TDK USA Corp.) slurry through a 127 μm orifice nozzle to form the powder bed, as illustrated in Figure 1a. The slurry was deposited by a single jet rastering over a porous substrate in the x and y directions, the "fast axis" and "slow axis", respectively. The deposited slurry lines are stitched together forming the slurry layer, which solidified via slip casting. This wet layer was dried using a IR heat lamp upon the completion of the rastering process.

The binder, a polyacrylic acid (Acumer 1510, Rohm and Haas, Philadelphia, PA) and glycerol aqueous solution, was printed through an ink-jet nozzle (40 μm orifice) in a rastering procedure similar to the slurry jetting process. Binder droplets were selectively printed using a charge and deflection continuous jet printhead producing a 2-D image. The layer was heated to remove excess water. Sequential slurry and binder deposition processes were repeated to complete the part. Figure 1a illustrates the binder printing procedure.

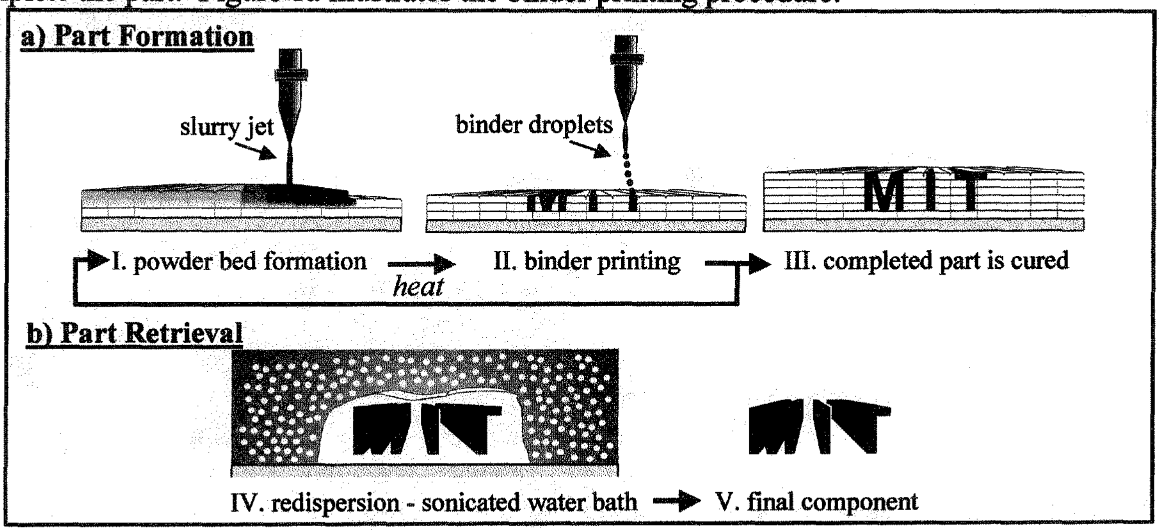


Figure 1: Slurry-Based 3DP™ a) Part Formation Process and b) Part Retrieval.

Imbedded parts were placed in an oven to thermally cross-link the binder. The binder was cured at 150°C for 45 min in an inert environment. The imbedded part and the powder bed matrix were placed into a sonicated water bath, as shown in Figure 1b. The unprinted powder bed spontaneously redispersed and the final components were recovered.

Results and Discussion

Powder Bed Microstructure and Formation Technique

The microstructure of the powder bed depends on the method used for its formation. The current technique used for powder bed formation is based on rastering a single slurry jet across a porous substrate. This process can produce a small population of relatively large pores (~5 to 10 μm). This results from slurry lines slip casting independently, creating valleys between adjacent slurry lines. The next layer of slurry will deposit a line directly over this valley, and a void will be produced if the slurry does not perfectly fill the valley between slurry lines.

Tape casting of powder bed layers was examined in an attempt to eliminate creation of voids. This method proved unsuccessful due to the formation of macro-scale bubbles (~1mm, see Figure 2). These were the result of entrapped air displaced from within the underlying pore structure by infiltrating liquid, which was forced up through the layer of slurry.

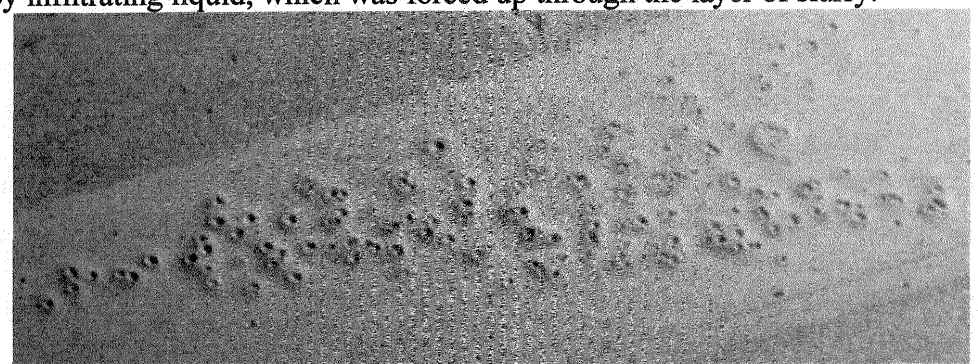


Figure 2: Tape Cast Powder Bed "Bubbling".

A new approach to 3DP™ layer fabrication, termed line merging, is under development to rapidly deposit defect free slurry layers. This method is a compromise between the previous two methods. A jet of slurry is raster-scanned over the surface of the powder bed rapidly enough so that each new line of slurry is deposited before the previous line has slip cast fully ($t_{cast} < 300$ ms), but not fast enough to entrap air and produce bubbles (as in tape casting). Initial trials with Al_2O_3 powder beds have been completed, and the results look promising.

The Binder System

The binder system used in the slurry-based 3DP™ process must meet several requirements. One criterion for selection is based on its solubility characteristics. The binder is initially required to be a solution phase in order to infiltrate the fine pore structure of the 3DP™ powder bed, however the binder solubility requirements change drastically during the process. The imbedded 3DP™ parts are removed from the powder bed by redispersing the surrounding unprinted powder using a liquid medium. This demands that the binder be insoluble such that the printed components retain their geometries. Additional criteria emphasize the binder's intrinsic properties that determine the ink-jet printing performance of the binder as well as its powder bed interaction.

Four different binders have been investigated that include a styrene-acrylic copolymer, a cyanoacrylate, a urethane acrylate oligomer and a polyacrylic acid - glycerol system. The polyacrylic acid (Acumer 1510, Rohm and Hass, Philadelphia, PA) binder system has proven to be very effective with respect to the outlined criteria. A 2.4 vol.% solution ($\eta = 2.3$ cP and $\gamma = 71$ dynes/cm) was used for printing parts containing 1.0 vol.% binder. The binder was crosslinked at 150°C yielding parts having excellent strength and chemical stability in order to survive the part retrieval process.

Differential Slip Casting

Binder-powder bed interaction plays an important role in controlling printing resolution, surface finish, and microstructure of the 3DP™ part. An important aspect of the binder-powder bed interaction is a differential casting effect of the slurry during the powder bed formation. The effect of the binder system on part formation in the slurry based 3DP™ process has been defined by Grau.[6] The casting rates of the slurry were calculated from the model of Aksay and Schilling.[7] The casting process is a colloidal filtration in which the solvent in the slurry is rapidly removed from the thin layer of slurry. The filtration rate is dependent upon the viscosity of the solvent in the slurry, pore fraction and pore size of the powder bed, and contact angle of the liquid on the solid. The rate of colloidal filtration is expected to differ locally for slurry-based 3DP™ powder beds since selected regions are printed with a polymeric binder solution. The regions in the powder bed that are printed with binder will have different pore structures and wetting behavior than regions that do not contain binder.

The casting rate of the slurry may be much lower over the binder-printed region than over the unprinted region when using an aqueous slurry solvent. The slurry casts quickly over the region that was not printed with binder while the slurry remains fluid over the region printed with binder. Slurry then migrates from the binder-printed region towards the surrounding unprinted powder bed. The differential casting kinetics can lead to major structural defects (illustrated schematically in Figure 3): a bump at the interface of the binder-printed region; increased surface roughness on the printed region; a non-uniform (i.e. curved) top surface; and a depression of the top surface below the level of the surrounding bed (adversely affecting height control).

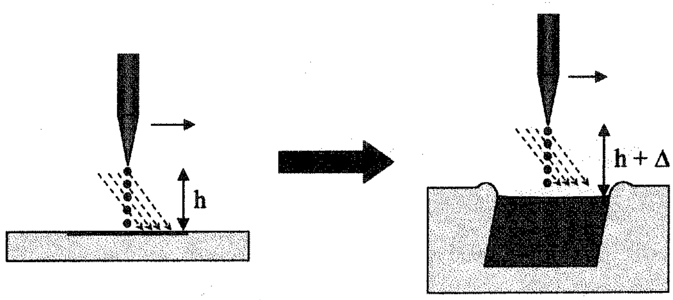
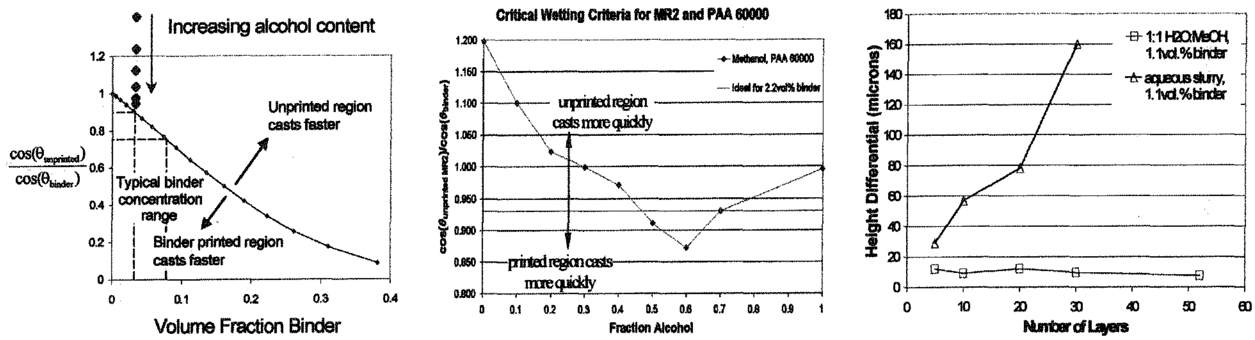


Figure 3: Schematic illustrating defect generation due to differential slip casting.

The effects are minimized by tailoring the wetting behavior of the solvent on the binder-printed region and by minimizing the volume of binder deposited. The curve in Figure 4a shows the ideal ratio of the cosines of the contact angles of the slurry solvent on the binder and on the ceramic powder that will give equal slip casting rates on the two regions. Figure 4b then shows the wetting properties of the binder as a function of alcohol content in the slurry solvent, with the ideal value for a given binder content by the horizontal line. Differential slip casting is minimized by choosing a slurry solvent composition on or near this line.



a) Model of differential slip casting rates

b) Effect of slurry solvent chemistry on wetting behavior

c) Height difference as a function of layers built

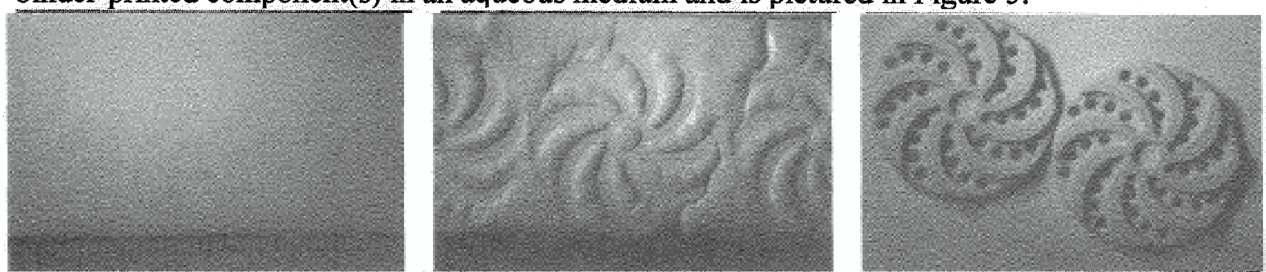
Figure 4: Minimizing differential casting through slurry chemistry modifications.

The effect on the height difference between the part and surrounding powder bed (Δ in Figure 3) is illustrated in Figure 4c for an aqueous slurry and for the optimized slurry chemistry containing alcohol. The optimized chemistry results in a very small height difference that does not increase as further layers are added. This has improved vertical dimensional control to within +/- 10 μm, and allows components of essentially any height to be manufactured.

Part Retrieval

An important characteristic of the slurry-based 3DP™ process is that the printed parts are imbedded within the powder bed matrix. The unprinted powder bed is cohesive due to the slip casting nature of the powder bed fabrication process. Retrieving the imbedded components from this brick-like structure is therefore a critical step.

Part retrieval is achieved by redispersing the unprinted ceramic powder that surrounds the binder-printed component(s) in an aqueous medium and is pictured in Figure 5.



a) powder bed with imbedded components

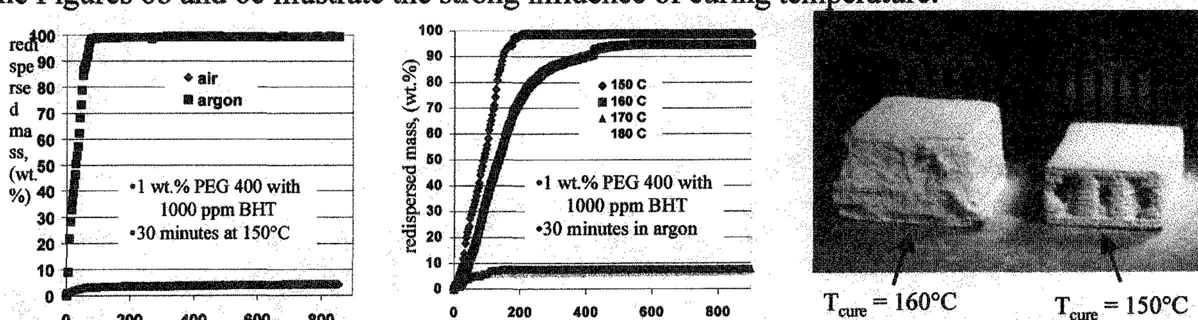
b) powder bed in water bath

c) final components

Figure 5: Slurry-Based 3DP™ Part Retrieval via Redispersion.

Successful redispersion depends upon the strength of the unprinted powder bed. Interaction forces of the ceramic particles control the strength of the powder bed. These interaction forces are controlled through the chemistry of the slurry used to form the powder bed matrix. A "redispersant", low molecular weight polyethylene glycol (PEG 400, Carbowax, Union Carbide, Danbury, CT) is added to the slurry chemistry and remains in the pore structure of powder bed once it has been dried. PEG 400 offers two possible redispersion mechanisms. PEG forms soluble necks between adjacent ceramic particles. These bridges dissolve and break up the network of particles allowing them to re-establish their electrostatic repulsive forces. A second mechanism results from water's "good solvent" characteristics with respect to PEG. The polymer chains swell and extend as they dissolve in the water entering the powder bed during the redispersion process. This acts as an additional force pushing the particles apart. The effect PEG has on the redispersion behavior of unprinted powder beds is dramatic. The redispersed mass was minimal for those samples without PEG (redispersed mass = 3 wt.%) while those containing 1 wt.% PEG (redispersed mass = 99.9 wt.%) dispersed to a fine powder.

A challenging aspect of slurry-based 3DP™ is designing the process such that redispersion is achieved after thermally curing the binder. The difficulty is a result of the degradation PEG in the presence of oxygen which is accelerated at elevated temperatures (>100°C). The degradation mechanism is complex and is caused by the existence of several possible modes by which the free radicals degrade to low molecular weight fragments[8]. Four approaches have been used to minimize the degradation. Two approaches were to minimize the binder curing time and the curing temperature itself, however, the time and temperature are fixed at a minimum of 150°C for 45 minutes to sufficiently cure the binder. The third was to eliminate the presence of oxygen during elevated temperature processing by curing in an inert argon atmosphere. The final method was to add an anti-oxidant, butylated hydroxy toluene (BHT), to the PEG that reduces the concentration of free radials. The later two techniques proved very effective in reducing the degradation and ultimately restoring the redispersibility of the unprinted powder bed. Figure 6a demonstrates the effect of the curing atmosphere on the redispersed mass while Figures 6b and 6c illustrate the strong influence of curing temperature.

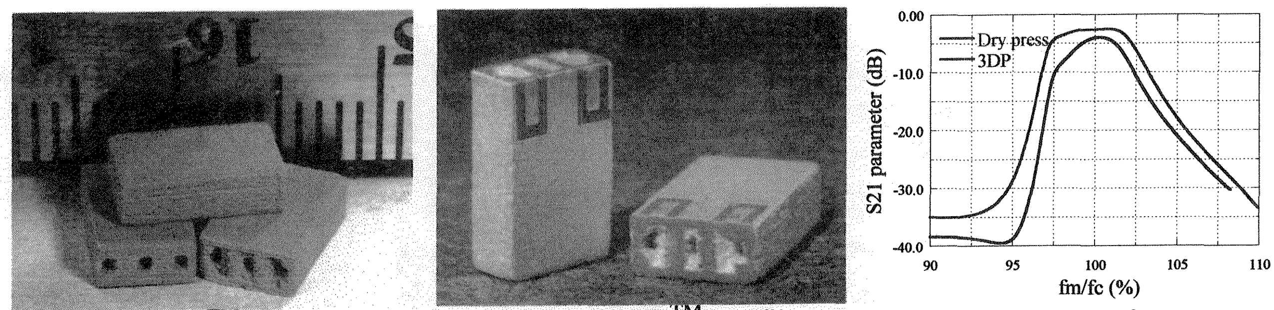


a) atmosphere effects b) temperature effects c) incomplete and complete part retrieval

Figure 6: Curing Conditions and Their Effects on Redispersion.

Radio Filters and Their Properties

A dielectric ceramic slurry (35 vol.%, MR2, TDK USA Corp.) has been integrated into the 3DP™ process and RF components have been directly fabricated with dimensional accuracies as high as ± 20 μm. These components represent the first functioning products manufactured using the slurry-based 3DP™ process. Fired and metallized 3DP™ RF filters are shown in Figures 7a and 7b.

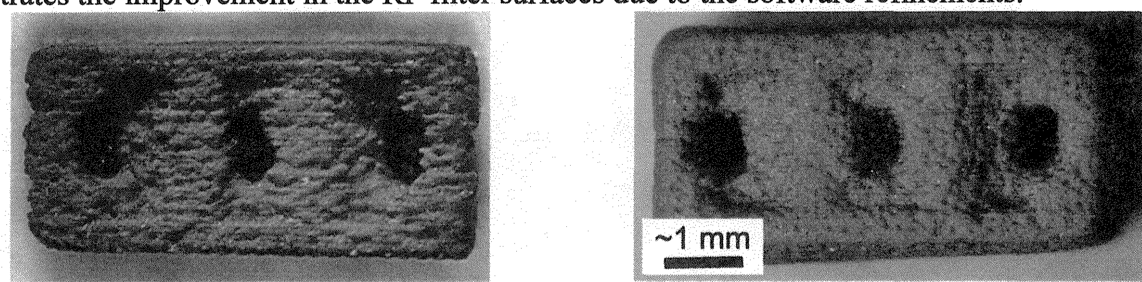


a) fired 3DP™ RF filters b) metallized 3DP™ RF filters c) RF properties

Figure 7: 3DP™ Manufactured RF Filters and Their Dielectric Properties.

The dielectric properties of these preliminary filters were very encouraging. Their properties were compared to those of similar dry-pressed filters as shown in Figure 7c. It is clear that the 3DP™ components functioned as filters having both accurate center frequencies with a respective transmission band, however, the dry-pressed proved to have less insertion loss and a wider transmission band. These differences in performance are in large part a result of the relatively high surface roughness of the 3DP™ filters with respect to the dry-pressed filters.

A significant fraction of this increase in surface roughness was the result of a limit in the resolution of the CAD software used to generate the 3DP file and has been eliminated. Figure 8 illustrates the improvement in the RF filter surfaces due to the software refinements.



a) "initial" surface b) "modified" surface

Figure 8: 3DP™ Software Improvements and the Effect on Surface Finish.

Other modes to achieve better dielectric properties are the basis of current research. One of these measures is the integration of a "Drop on Demand" printing technique which will provide higher accuracy in the placement of binder droplets during the printing process. A second step is focused on controlling the shape and size of the binder primitives that serve as the building block of the printed component. Finally, filters with highly complex geometries are being designed, which emphasizes the advantage of the 3DP™ process. These new geometries will reduce attenuation, and can not be formed using conventional fabrication techniques. Complex geometries have already been formed using the slurry-based process with current dielectric material (MR2) and are pictured in Figure 9. This provides a foundation for a wide range of complex shaped filters.

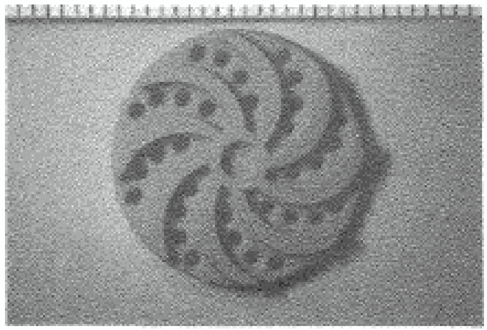


Figure 9: Shape Capability of the Slurry-Based 3DP^{TM} Process. (scale in mm)

Conclusions

The 3DP^{TM} process and colloidal processing techniques have been used to form dielectric ceramic components using a submicron powder. 3DP^{TM} processing parameters and binder-slurry interactions have been optimized to minimize the generation of defects during the fabrication of the component. Imbedded components were successfully retrieved from a cohesive powder bed by adding PEG to the slurry formulation and closely controlling the binder curing conditions. RF filters have been successfully produced that represent the first functioning ceramic produced using this process. Future research is focused on the improvement of the filter properties by improving the surface finish and designing a geometry that will further reduce the attenuation of the filter.

Acknowledgements

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