Chapter 17
The Use of Multiple Materials in Additive Manufacturing

17.1 Introduction

Almost since the very beginning, experimenters have tried to use more than one material in Additive Manufacturing machines. In fact, multiple materials are a fundamental benefit to how some AM technologies work. The Laminated Object Manufacturing (LOM) process, for example, was one of the earliest AM technologies developed and required that sheet material (paper) be combined with a resin to bond the sheets together to form a composite object of paper and resin.

Many vendors and researchers have added further materials to the single-material AM technologies in order to enhance the basic process, either to optimize the process or to improve the properties of the final part in some way. This chapter will explore the different AM processes with respect to how multiple materials have been included in them. It will go on to discuss the different ways in which materials can be combined as an attempt to classify the various types of multiple material structures. Key research milestones will be presented with an aim to understand the benefits of multiple materials in AM for product development and how this technology may develop in the future.

17.2 Multiple Material Approaches

Multiple materials can be introduced to an AM process according to a variety of different strategies, for example:

– Two or more discrete materials can be placed next to each other. The interface between the materials can be such that they are either simply in contact with each other or where they are bonded together in some way. Two discrete materials are often used when generating supports, such as in the FDM process, where supports may be of a different material to the part and can, therefore, be easily removed once the build has been completed.

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– A material can be processed in such a way that there is porosity in some segments or throughout the whole of the resulting part. It is quite common for powder based systems to display such porosity. This porosity can allow the use of a liquefied secondary material for infiltration. In some processes, the porosity may be varied in different regions (for example, by varying the laser power in the SLS Powder Bed Fusion process) so that the ratio of parent material to infiltrant can also be varied throughout the part. Furthermore, infiltration may occur during the AM process at the layer level rather than merely as a post-AM process. The binders used in the 3D Printing processes are an example of this approach. 3D Printed parts often require an additional post-build infiltration to further strengthen the part, adding a third material component into the structure.
– Feed material can be presented to the AM process as a blend of two or more different materials. In some cases, it may be possible to vary the ratio of each material to permit the fabrication of functionally graded components. In other cases, the entire batch of feedstock material will have the same blend; e.g., SLA resins can have ceramic or other particles mixed in with them to produce a composite, as can some SLS powders.

The reasons for applying multiple material strategies are many-fold, revolving around the purpose of the additional materials used. These purposes can include:

– *Improving the mechanical properties of the resulting parts*: Additional materials may increase the hardness, heat deflection properties or tensile behavior for example.
– *Providing additional functionality in the resulting part*: Parts may have different colors, varying electrical conductivity, or variable mechanical properties (as opposed to globally improving the mechanical properties). In such cases, additional materials with differing properties would be placed in strategic locations around the parts.
– *Improving the performance of the AM process*: In these cases, additional material may be used to help in part fabrication, such as a barrier material that separates two regions that, after removal of the secondary material, enables relative motion between the regions.

In some cases, the above-mentioned purposes can be achieved merely by presenting new materials or build strategies (e.g., software modifications) to the system. In other instances, the AM process machinery (e.g., the material delivery system) must be modified to include the new material.

17.3 Discrete Multiple Material Processes

The most common use of discrete multiple materials is where there is a need to support and/or separate part material from the surrounding environment. For example, the FDM process and the printing technology from Solidscape both use

Fig. 17.1 A skull model made in two materials using FDM. Note the tumor is of a different colored material to the healthy bone (image courtesy of Stratasys)

a secondary material deposition device to create a support material that can be easily removed from the part material after the layered manufacturing stages have been completed. With Solidscape, the secondary material is also used to encapsulate the part, which helps provide a better external surface finish. In both cases, it is much simpler to use a secondary deposition head rather than feed more than one material through the same head.

The FDM process has been demonstrated as capable of providing discrete multiple material parts. In these cases, the secondary nozzle has been used to not only build supports (as in the normal case), but also to fabricate distinct features for parts. This, of course, is generally limited to two materials since currently there are no FDM machines with more than two nozzles. The most obvious application for this approach is to use different colored materials to identify features within a single component, like the bone tumor identified among the healthy bone in Fig. 17.1. However, the second material need not be just a different color from the primary one; other material property variations may also be considered. An adaptation of this approach is in the use of the WaterWorks, water soluble support material. In this case the secondary material, as well as being used for supports, can be placed as a temporary barrier that may be used to construct parts with overlapping or interlocking features, like nested balls or links in a chain. Results similar to this can be obtained using powder systems like 3D Printing (3DP) or Selective Laser Sintering (SLS); where the untreated powder acts as the barrier or support for the fabricated part and which must then be removed following the AM process. Stereolithography can also be made to show a discrete multiple-material effect with the use of resins like Stereocol that change color when overexposed to curing radiation from the SLA machine laser.

Objet technologies [1] provide a mechanism where droplets of photocurable resin can be mixed with differing ratios of curing agent to result in polymers with different Shore ratings called 'Digital Materials'. This process permits the creation of regions within a layer with different properties. Furthermore, the Connex process developed for some Objet machines includes two different feed routes for the photopolymer resin, most commonly used to provide two different color materials.

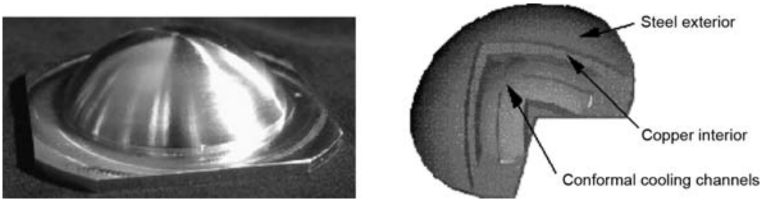

Fig. 17.2 A part made using SDM that shows internal regions of different materials (image courtesy of CMU)

The approach described earlier using FDM to create bi-color models can, therefore, be carried out using this process in a simpler manner and with the further benefit of changing each material property in different regions as well.

Three research and development projects of note that extend this principle are the Shape Deposition Manufacturing process developed at Stanford and Carnegie Mellon, the Reprap project at Bath University, and the work of Lipson and his team at Cornell University.

Shaped Deposition Manufacturing, an example of which can be seen in Fig. 17.2, involves a potentially complex series of operations that can include both additive and subtractive fabrication [2]. In this example, a welding process can be used to add the metal regions. Machining is then used to add precision to the part before further addition of a different material or geometric segment. To create the internal conformal cooling channels, a sacrificial material with a lower melting point to the copper or steel can be used. As can be seen from this figure, the additive processes do not have to be layer-based and in fact involve the decomposition of the product's geometry so that volumetric regions of the part can be constructed in sequence. Segmentation of each region must initially be based on a single material (i.e., one region must have the same material) which can be further subdivided in terms of the geometry of the part (e.g., the transition region from an overcutting region to an undercutting one, which may be difficult to achieve in a single processing stage if subtractive manufacturing is used). This decomposition permits the build-up of parts with numerous separate materials, some of which can be sacrificial materials that can be used to support overhanging structures or to encapsulate objects during the build stage so that they can be separated later. While SDM can become very complex, it can be realized in a simplified manner using just one additive process accompanied by a machining center. However, it is probably this complexity issue that has prevented more work being carried out on this process; but it still remains one of the few AM processes that uses a non-layer based build strategy. Furthermore, some of the ideas generated in this system have influenced later research.

The Reprap project [3] and the work at Cornell, primarily based around the Fab@home technology [4] have somewhat similar goals in that they both aim to be able to produce machinery using AM with both electrical and mechanical elements. Both works revolve around extrusion-based processing, taking advantage of the wide variety of material compositions that can be extruded in a viscous liquid form.

Gels or molten materials can be extruded that either have specified material properties themselves, or can be used to transport other materials with such properties (such as Direct Write inks) within the mixture or in particle form. Multiple material components have been constructed using these processes, including some simple electromechanical devices and even some rudimentary batteries. While these are some way from the ultimate Reprap goal of being able to create a machine that can construct all the components of the machine itself, the results are nonetheless impressive.

17.4 Porous Multiple Material Processes

Of course, if color variations are the primary consideration for an AM-based application, then color 3D Printing, like that provided by the ZCorp machines, may be a better option than the previously described FDM approach. The reason this would be preferable is due to the use of three and four color inkjet printing technology to add color while simultaneously binding the powder particles together. It should be noted, however, that the strength of resulting parts may not match up to some functional applications, even if followed by a post-build infiltration stage. If part strength and color are requirements, then the system demonstrated in prototype form at the University of Hong Kong that combines the Selective Laser Sintering process with color printing technology may eventually be an option [5]. Research there indicated that it is possible to control the level of porosity by adjusting the laser power (as shown in Fig. 17.3a). While this of course also varies the mechanical properties of the resulting components, it means there are varying amounts of space available for application of infiltrants (like the conductive ink shown in Fig. 17.3b). One piece of research indicated that conductive inks could be used to fill in the voids [6]. Highly porous regions would allow ink to penetrate deeper into the part, thus providing a mechanism for creating integral, 3D conductive channeling. A similar approach to controlled porosity can be practiced using

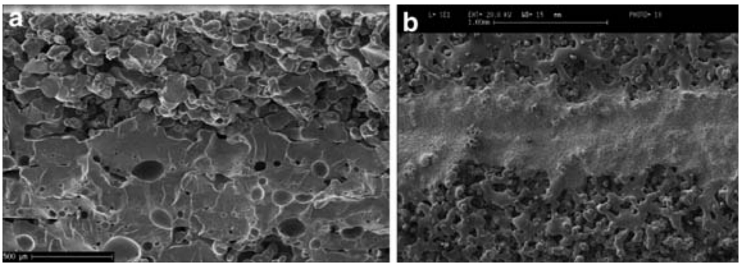

Fig. 17.3 (**a**) An SLS part made using different laser power settings in different regions, showing a porous top surface covering a more dense lower segment. (**b**) An SLS part viewed from above where the porous surface has been printed with a conductive ink

FDM. The inherent scaffold capabilities of FDM enable controlled porosity to be designed into a structure. Infiltration of that porosity by a secondary material will result in variable composite properties that are related to the ratio of FDM to infiltrant material in any particular region.

Using 3DP to deposit inks with varying properties into porous media can result in many opportunities. The number of materials relates to the number of separate channels available for printing. Of course, all the materials except the base material must be deposited in the form of a liquid. Liquids can be curable, like resins, and they may include nano-particles. Binders can change the mechanical properties of the parts, like tensile strength, hardness, or elastomeric behavior. Alternatively, they can change the electrical or thermal conductivity. Additional studies by Gibson and his team identified that carbon-based inks printed into SLS powders can change the thermal properties during sintering, causing more heat to flow in the carbonized region. If carbon ink is printed around the perimeter of a layer, this may help in providing smoother and higher density surfaces by preventing heat flow out of the part to the surrounding powder.

The two processes under development by Khoshnevis and his team at the University of Southern California [7], Selective Inhibition Sintering (SIS) and Contour Crafting (CC) are worth discussing here. As discussed in Chap. 5, SIS involves the printing of an inhibitor onto a powder bed. Each layer is typically sintered using a flash heater. Powder particles sinter where no inhibitor was placed to form the part. Parts made using SIS can be much stronger than 3DP parts and can even be post-sintered to produce very hard ceramic components.

Contour crafting is a form of thick layer FDM. The understanding is that FDM suffers primarily from being slow and from poor surface finish. Contour Crafting uses a trowel mechanism that smoothes the surface of the layers according to local contour information from the CAD file. This enables thick layers to be built without serious stair-stepping penalties. While this may not be a particular advantage for small components, it does work very well for large components. In fact, Khoshnevis is focusing on the construction of full-scale buildings using this approach. This naturally requires the fabrication of multiple material structures to be successful, including the incorporation of steel reinforcement for concrete walls, plus plastic conduits to permit the convenient incorporation of electrical wiring, water and sewage pipes, etc. This may also be considered in many ways similar to the Reprap and Cornell projects. It is included in this section, however, because it can also illustrate the use of varying forms of porosity to facilitate construction of complex multiple material components. By leaving voids in components, it is possible to conceive very complex structures that are essentially still built using AM technology. This implies the construction of objects that cannot (or at least would be extremely difficult to) be built any other way.

The use of variable porosity is probably best illustrated by applications in bone tissue engineering. In such applications, both micro and macro porosity is generally considered to be a requirement. Micro porosity allows cells to adhere to the scaffold and thus add to the structural integrity of the scaffold as these cells proliferate into multiple cell structures. Macro porosity permits the cells to enter into the scaffold and further circulation of nutrients and expression of waste products to promote healthy cell growth. Currently, most research into bone tissue engineering uses regular, uniform cellular structures for the scaffold. The likelihood however is that at least some forms of cell growth should be promoted in a directional manner so that fibrous tissue can be grown. Furthermore, some scaffolds may be constructed to house different types of cells. For example, an articulating jointed bone, like the ball-joint shaped femur that moves inside a hip socket, would not only require bone cells but also cartilage at the joint surface. It is known that different cells prefer different scaffold structures and materials. Such a scaffold must therefore have a highly heterogeneous structure. Currently, no approach for creating scaffolds that encourage cell proliferation has resulted in a sufficiently strong mechanical structure suitable for load-bearing bone, although there has been some advancement for non-load bearing applications. Future development of such processes to suit a larger range of applications may require the use of complex geometries and composites so that good material properties can be obtained throughout the cell growth and scaffold degradation process.

17.5 Blended Multiple Material Processes

Probably the most widely used multiple material AM-based applications involve the use of blended materials. The most common and widely used of these were developed for the Selective Laser Sintering (SLS) process for indirect processing of metals and ceramics, as described in Chap. 5. Blends of polymer binders and metal or ceramic powders leads to the creation of a green part which is subsequently furnace processed to create the final, usable composite component. These composites can be tailored to optimize hardness, thermal conductivity, wear resistance, or reduction in shrinkage, dependant on the materials chosen and specified application.

The use of powders is very compatible with AM, as can be seen by the success of the 3DP and SLS processes and their variants. Most powders are deposited in a uniform manner from a feed chamber. The use of blended powders does not require any significant change in the process equipment, although the settings are likely to change due to the differing thermal transfer properties. However, if the requirement is to vary the powder composition, significant modifications would need to be made to the process. Beam deposition processes, such as the LENS process, deliver the powder into the melt zone at the same time as the energy is delivered [1]. These processes typically provide a mechanism for delivering more than one powder into this zone through the use of multiple powder feeders. The most common method for multiple materials in beam deposition processes are for different mixtures of compatible powders to be delivered at different z-heights from different powder feeders. However, if the powder feed delay is known accurately, material can be changed on-the-fly within a single layer. However, accurately knowing and controlling the feed rate and delay for multiple feeders at the same time is difficult, and thus this is rarely practiced. Instead, for the case of a part where a single composite mixture of powders is desired, it is much easier to pre-mix the powders before putting them in a single powder feeder than to put the components in separate powder feeders and try to optimize the flow of each such that the desired mixture is achieved in the melt pool.

Many applications for composites require fibers to add strength in the fiber direction. This may be particularly useful in applications where toughness and impact resistance is required, the fibers providing strength and energy absorption. One major disadvantage when using powders is that there is typically no directionality to the composite (unless creating a directionally-solidified structure using beam deposition). Fibers cannot be easily introduced into powder systems of any useful length or aspect ratio. It is perhaps possible to make use of carbon nanofibres to significantly increase the mechanical properties, but this is very expensive and the fiber distribution (and therefore the strength distribution) may not be regular and fiber orientations are typically random.

The original LOM process used paper, which is a naturally fibrous material. Because of this fibrous material and the use of a polymer resin to hold layers together, the strength of LOM parts in the build plane is considerably higher than the layer separation strength. However, it is very rare that this property can be of real use because the part geometry very rarely conforms to a simple planar structure. Shell structures, however, are quite common; parts that are made in this way may benefit from processes that can include fibers that conform to the shell architecture. The Curved-LOM technology developed at The University of Dayton [8] deposited sheet material over mandrels of the desired geometry so that the sheets conformed to the shell geometry. As well as paper, the sheet material can also be carbon or ceramic fiber-reinforced composite green tapes. Since these fibers can be very strong, cutting the sheets can be difficult and a high-power laser cutting system was developed to achieve this. Placing the curved composite on a non-planar mandrel also requires very complex manipulation technology, thus making this prohibitively expensive to realize commercially (Fig. 17.4).

A more cost-effective albeit limited variation of the Curved-LOM process could be Curved-FDM [9]. Introducing short fibers into the conventional, layer-based, FDM process would result in the same geometry restricted benefits. By applying the

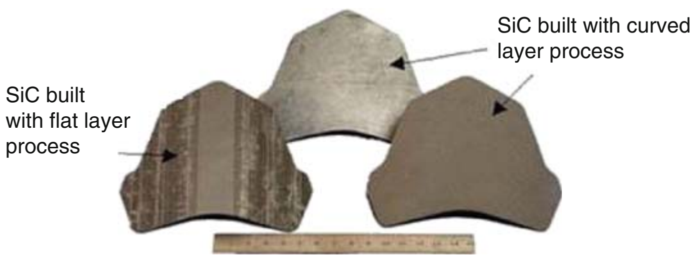

Fig. 17.4 A conventional, planar layer built constant thickness part next to a Curved LOM, showing the potential benefits of smoother surface with more uniform mechanical properties

fibers (aligned according to the melt flow) through the nozzle, conformal to the part surface, there is a better chance of the fiber adding strength to the part. The problems of course lie in the fill ratio, size and aspect ratio of the fibers and whether these can still result in a reasonable increase in part strength to make it viable. Furthermore, a binding agent, like Silane, should be used to chemically bond the fiber to the polymer matrix material and thus improve the overall strength of the part. The cost of a multi-axis FDM process would require very little change to the basic hardware and, therefore, be significantly less than a multi-axis LOM process, although the software pre-processing of the STL file is non-trivial.

17.6 Embedded Component AM

In some ways, embedding secondary components during AM could be considered as a special form of discrete material AM. This approach has been discussed indirectly earlier in this section related to contour crafting. The approach here is to temporarily suspend the base AM process in order to insert components into the system before continuing. Beam deposition systems and extrusion-based processes, for instance can be easily paused to enable component insertion, as material is fed from above and the component being built is not surrounded by powder in a constraining container. However, any inserted component must be able to withstand the temperatures of additional molten material being added thereafter.

It is also feasible to include metal components in a photopolymer processes. SLA is particularly well suited to this. A void can be fabricated in a part that will house the insert. The process is suspended and the insert placed inside the part at an appropriate time. The part must of course be fully below the build surface of the resin bath; otherwise, it would interfere with the recoating blade. The process can then be continued in order to seal off the component, thus partially or even fully encapsulating it with surrounding resin. While this process is indeed possible and has been used in the past, one can imagine that it can be somewhat messy and awkward. Furthermore, stopping and starting the process in this way could lead to registration errors and possible damage to the part. Nevertheless, this methodology has been practised successfully by Sandia National Laboratories and the University of Texas at El Paso, as can be seen from Fig. 11.7 in the Design for AM chapter.

The Ultrasonic Consolidation process developed by Solidica [10] is a low-temperature metal AM technology that allows relatively easy embedding of electronic components. This is achieved since the ultrasonic welding approach used does not generate excessive heat that may damage the embedded component. UC is discussed in detail in Chap. 8. Stopping the process between layers allows an opportunity to embed components; the ultrasonic process permitting the next layer to plastically form around small embedded part as can be seen in Fig. 17.5a. This process also makes it relatively easy to combine more than one material together. Depending upon the material combination, these materials may be either mechanically bonded or metallurgically bonded. In Fig. 17.5b, copper and

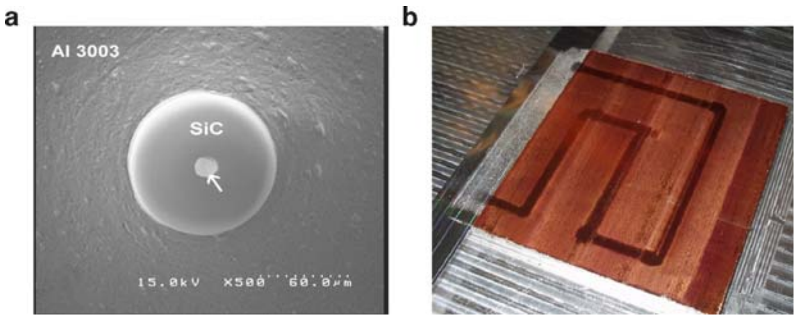

Fig. 17.5 Multiple material structures resulting from the Ultrasonic Consolidation process. (**a**) Shows a SiC fiber embedded inside Al. (**b**) Shows a Cu layer being embedded in Al with internal cooling channels visible through the Cu layer. © Emerald Group Publishing Limited, "Use of Ultrasonic Consolidation for Fabrication of Multi-Material Structures," G.D. Janaki Ram, Chris Robinson, Yanzhe Yang and Brent Stucker, Rapid Prototyping Journal, 13 (4), pp. 226–235, 2007

aluminum have been combined together. This figure illustrates a block of aluminum with integrated cooling channels that was subsequently covered with a copper layer to aid in heat dissipation. The cooling channels are visible through the copper, as regions above unsupported channels are smooth after UC. Subsequent aluminum deposition over the copper has just begun, as can be seen from the single aluminum foil strip on the left-hand-side, covering a portion of the copper layer.

17.7 Commercial Applications Using Multiple Materials

WindForm is a company that produces a range of materials by the same name for use in SLS machines. These materials are polyamides mixed with different additive powders to provide greater strength, stiffness, heat deflection, etc. Their powders include aerospace grade aluminum, glass, and carbon-based particles. Exact details of these additives are undisclosed but the results are very impressive. The functional properties of these parts are focused on applications in the automotive industry, with emphasis on low volume production for performance vehicles. However, what works for performance vehicles will surely work for a large number of other applications. Figure 17.6 shows a brake duct produced for a Formula 1 car that is capable of withstanding actual racing conditions. As can be seen, the quality is of a high level for such a complex part made in the space of a few hours. Some manual and machine finishing is still required for the mating features of the component, but this still results in a very complex part that can be applied, tested, and modified in a short turnaround cycle.

3D Systems and EOS also offer composite materials for their SLS machines. In addition, there is a composite material specially developed by 3D Systems for the SL process. Called Bluestone, this material contains nano-sized ceramic particles

Fig. 17.6 A component made using Windform material (image courtesy of WindForm)

Fig. 17.7 A component made using Bluestone material. Note in particular the opacity of this SLA material, which in reality is a light blue color (image courtesy of 3D Systems)

that provide a means of improving stiffness, rigidity and heat deflection. Nano-particles are used so that they can be evenly dispersed throughout the resin in its liquid state without having to constantly agitate or mix it. The improvements in the performance of Bluestone make parts from this material suitable for electrical housing, higher temperature and wind tunnel applications (a typical part can be seen in Fig. 17.7). These blended composites illustrate the potential for further improving materials performance beyond standard SLS and SL materials. Further developments can be expected as knowledge is gained on the use of these materials and different applications are explored.

17.8 Future Directions

Most of the features discussed in this chapter are being examined as research projects. There is still much that can be done to commercially incorporate multiple materials into AM. This section discusses some of the challenges that need to be faced should multiple material AM become more widespread. The design and analysis issues mentioned in the following section are discussed in greater detail in Chap. 11.

17.8.1 Design Tools

Currently, most CAD systems work on the basis that the part material is homogeneous, although perhaps separate components may be given different attributes. Furthermore, we have seen that the majority of AM systems take STL files as standard input. Since STL is a surface approximation only, there is no knowledge of the material content. Where the desired components have variable structure, there are only a handful of research-based software tools that could be used to describe the material content within the model. For the purposes of structural design, this is not a problem with conventional CAD, but there is difficulty when translating this to machine instructions for manufacture (CAM). We need to know what the material components are from region to region if we desire to use a multiple material system to create our models.

17.8.2 Analysis

A more fundamental problem is how to effectively create a functional model based on multiple materials. This is not just a matter of geometric and aesthetic design, but also functional design based on the mechanical, thermal, electrical, and other requirements of the product. Often the boundary conditions of a part will be known, but the design features to connect boundaries together may not and a specific design must be tested and analyzed using software for a particular material choice. Most approaches are likely to iterate and converge to a solution based on FEA tools. The speed of processing, however, is likely to be a problem as designers are likely to want this information in real-time to allow them to create their designs and iterate them according to the information generated within the analytical system.

17.8.3 Multi-axis Systems

Perhaps not all AM systems are likely to be able to benefit from the addition of extra axes of motion. However, processes like LENS, FDM, and LOM have all been shown to benefit from the additional complexity of motion. Even processes like SLS could benefit from the addition of multiple powder feed mechanisms or by creating a hybrid SLS/3DP-like technology, as discussed in Chap. 5. In fact, many multiple material systems are likely to be hybrid rather than using a single category of material or process.

17.8.4 Materials Development

In addition to creation of a wider range of blended composites, other forms of multiple material systems will possibly come into use. This indeed could be the most interesting development as electrically or thermally conductive, semiconductor, liquid crystal, carbon nanotubes, functional ceramics, etc., come into use. In addition to the further development of embedded technologies, sensors and can even be created from their fundamental material components within the part itself using direct write.

17.8.5 Applications

Parts resulting from these developments of AM technology would have increasing levels of functionality, opening up new application areas. Probably the primary driver in this is the medical application field. The possibility of creating multiple cellular structures using printing technology could eventually lead to artificial creation of replacement organs. The challenges are immense, but the possible benefits are also huge and the knowledge gained along the way may also spill into other areas.

The aerospace industry, for example, is already focusing much effort into composite technology. This is primarily a search for new materials based around conventional manufacturing approaches. AM, with its ability to construct complex geometries, may however prove beneficial in construction of certain components that are more constrained by shape than by performance.

Direct Digital Manufacturing is currently a major goal of many AM vendors and applications researchers. A problem that has always faced manufacturers looking at DDM is that AM produces parts that are generally inferior in performance compared with similar parts made using conventional manufacturing technologies. DDM benefits are mainly in terms of geometry, speed and cost. Using multiple materials with the possibility of functional gradients provides a means to create parts that are not directly competitive but in fact provide additional functionality to components.

17.9 Conclusions

The use of multiple materials can be viewed as a way of overlapping conventional manufacturing with AM. AM currently suffers in comparison to conventional manufacturing when comparing part quality and part performance. Part quality is being dealt with in other areas relating to machine control and application of newer, high precision technologies. Part performance can however be enhanced application of multiple material systems. The use of composites can target functional regions within a part; applying the most appropriate materials in the most appropriate areas. The advantage of AM is that this can be done in a single process and applied to a monolithic structure. It has always been said that AM is a process where you get complexity for free. Perhaps, by making AM technology a little more complex, we can start to build parts that we have yet to even dream of.

17.10 Exercises

1. The Curved LOM and curved FDM techniques are only capable of making a limited range of geometries. Why is this so? With the aid of diagrams, describe what would be the factors that limit the geometric freedom exhibited by these systems.
2. Read about the Objet Connex technology and the concept of Digital Materials. How many different variations are possible within a single part made from a basic combination of two photopolymers?
3. Is it possible to modify the STL file format to include descriptions that may give it multiple material capability? What are the benefits and drawbacks of doing so?
4. What is the benefit of four color inkjet printing compared to three color?
5. Make a list of all the different material categories that can be delivered using AM technology.

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