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Manufacturing Processes for Ceramic and Metal Microcomponents

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1. INTRODUCTION

The development of microfabrication techniques through the past years has led to a diversity of miniaturized mechanical and electromechanical components and systems. These microelectro-mechanical systems (MEMS) can vary from relatively simple structures to highly sophisticated systems. Typical applications of MEMS include accelerometers for automobile airbags, pressure and biomedical sensors, ink jet printers, drug delivery systems, blood analyzers, micromirrors for high-definition optical displays, wireless electronics, and microheat exchangers for cooling of electronic circuits [1, 2]. This has been supported by the increase in the global market of MEMS devices. The global market for MEMS devices and production equipment was worth $11.7 billion in 2014. This market is expected to hit $12.8 billion in 2015 and $21.9 billion by 2020 [3].

Probably the first allusion to the idea of MEMS was made by the physicist Dr Richard Feynman in his famous talk titled, "There's plenty of room at the bottom" on 29th December 1959 [4]. Following this, Petersen [5] suggested the use of silicon as the material for micromechanical structures, which is considered the foundation for the current MEMS technology. During the 1990s, the development of MEMS nourished significantly as a result of the innovations created during the integrated circuit (IC) revolution of the 1960s–1980s concerning processes, equipment, and materials. From this, MEMS technology has been applied

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dominantly in sensors, actuators and other mechanical components [6–10].

MEMS technology is known to be an interdisciplinary field that relies upon solid integration of design, materials and manufacturing expertise from different areas including IC fabrication technology, mechanical engineering, materials science, electrical engineering, chemistry and chemical engineering, as well as fluid engineering, optics, instrumentation and packaging. The material properties of the MEMS components have a great influence on the device performance. The selection of the suitable material to manufacture microdevices depends strongly on the application. Process temperature and pressure range, corrosivity of the applied fluids, thermal conductivity, specific heat capacity, as well as electrical and other properties defined by the application are crucial to choose the most appropriate material [11].

Silicon-based materials have been used for MEMS devices for decades because of their advantages in terms of its good mechanical properties, low density, high strength and micromachining versatility [12–16]. However, silicon is not suitable for high temperature applications due to its poor temperature resistance. For instance, the silicon technology is not normally used in chemical process engineering [11]. Also, silicon is known to be sensitive to small dust particles that may prevent bonding with other materials [17] and consequently special fabrication conditions such as a clean room [18, 19] are inevitably required. Due to the demands for different applications, other materials such as polymers and ceramics have been included with the MEMS technology [20, 21] in response to the development of microfabrication techniques.

Other challenges in the MEMS industry are how the manufacturing techniques will affect the device performance and how to improve the fabrication method in order to accommodate more intricate design requirements and geometries [21, 22]. Also, the throughput of the application affects the choice of the fabrication technique. Some fabrication techniques are suitable for producing one or a few devices, while others are applicable to mass production [11]. The micromanufacturing techniques have developed greatly to meet the demands of the MEMS technology. Generally, these techniques should enable high precision and reliable batch manufacturing. Several techniques may be employed together in realizing a complete MEMS system. Many of these microfabrication techniques are based upon the traditional silicon-based microlithographic techniques [13, 22–24] such as polysilicon surface micromachining and silicon bulk micromachining. Surface micromachining usually involves a series of deposition and etching of thin structural and sacrificial films, while bulk micromachining refers to creating mechanical features by selectively etching inside a substrate [25, 26].

Although metals do not exhibit similar advantages as silicon concerning mechanical properties, they are widely used in MEMS fabrication. Commonly used metals include gold, nickel, aluminium, stainless steel, copper, chromium, titanium, tungsten, platinum, and silver [1, 11, 27–30], where aluminium is the most widely used [31]. High precision metallic components such as stainless steel and its composites can find wide applications from luxury watches and precision gauges to biomedical devices and instruments. Micromechanical components of micro-engines, micro-gas sensors, and acoustic sensors are among the examples of microcomponents made of metals and metal alloys [32–39]. The microfabrication methods used for metallic MEMS components generally have their origins in the conventional precision machining methods or silicon-based micromachining. The methods are improved to suit the machined metal properties and the desired surface finish of the microcomponent. Soft lithography, laser micromachining, microelectrical discharge machining, micrometal injection molding, focus ion beam (FIB) and three-dimensional printing are examples of microfabrication techniques that are suitable for metals [11, 39, 40].

Owing to their outstanding mechanical, physical and chemical properties, ceramics are widely used in microfabrication industry. Compared to metals, ceramics have higher strength, lower density, lower thermal expansion coefficient and very high melting temperature. These properties imply suitability of ceramic microcomponents to high load and temperature environment and dimensional stability during operation [11]. Despite their extraordinary properties, their toughness is lower than metals and their flexural strength is affected by the surface roughness properties. Also, the brittle and hard nature of ceramics introduces difficulties in the fabrication process [41–44]. Therefore, much research work has been conducted on new machining and joining techniques for ceramic. The advances in ceramics and ceramic composites fabrication techniques provide the possibility to create a vast range of new ceramic systems having tailored and functional properties [45]. Components of micro-engines, micro-turbines, and micro-fuel cells, piezoelectric energy harvesters, microelectrochemical sensors and microneedles are a few examples of ceramic applications in the MEMS industry [45–53].

Microfabrication methods of ceramic metal microcomponents can be classified into four groups [45]: additive manufacturing methods (AM) or rapid prototyping (RP) and patterning processes, subtractive processes, property modification processes. Stereolithography, laser microsintering (LMS), laminated object manufacturing (LOM), ink jet printing (IJP) and three-dimensional printing are examples of the additive manufacturing techniques form methods which involve the production of 3-D parts directly from the 3-D CAD data. Coextrusion, microceramic injection molding, and soft lithography are examples of patterning methods from which the microinjection molding is considered the most established method for mass production microcomponents [54–57], and soft lithography is the most promising technique because it enables fabrication of high precision complex-shaped ceramic microcomponents at low cost [56–62].

In this chapter, focus is given to the micromanufacturing methods with emphasis on metallic and ceramic microcomponents. The rest of this chapter consists of three sections. Section 2 gives a comprehensive literature review on the microfabrication methods used for ceramic and metal microcomponents showing the advantages and disadvantages of each technique. The methods are evaluated according to their characteristics and resultant microcomponents properties. Section 3 reviews the properties of different ceramic, metallic materials and their composites that are used in microfabrication. In addition, it also includes different examples of ceramic and metallic microcomponents. In Section 4, a conclusion is drawn and the applications and limitations of each fabrication technique are also discussed.

2. MICROFABRICATION TECHNIQUES

Microfabrication techniques of metal and ceramic components can be broadly classified into four categories;

(1) additive processes,
(2) patterning processes,
(3) subtractive processes,
(4) property modification processes, as shown in Figure 1.

Additive manufacturing techniques include stereolithography (SLA), fused deposition modeling (FDM), laser microsintering (LMS), laminated object manufacturing (LOM), and jet printing (JP). On the other hand, patterning processes include microinjection molding (μIM), electrophoretic deposition and electroforming (EPD, EF), coextrusion (Co), and soft lithography (SL). Thirdly, subtractive processes include etching, microelectrical discharge machining (μEDM), and laser micromachining (LMM). Finally, property modification processes include thermal oxidation, chemical vapor deposition (CVD) and physical vapor deposition (PVD).

2.1. Additives Techniques

Additives techniques (AM), also called rapid prototyping techniques, are a set of manufacturing processes that are capable of producing complex three-dimensional parts directly from a computer model. Parts are constructed by adding layers of materials on point, line or planar surfaces. Additive manufacturing is a direct writing technique that does not require molds. A moving device such as laser, light or ink jet performs the shaping of the designed pattern [63–65]. Objects in these types of techniques are created incrementally or layer by layer.

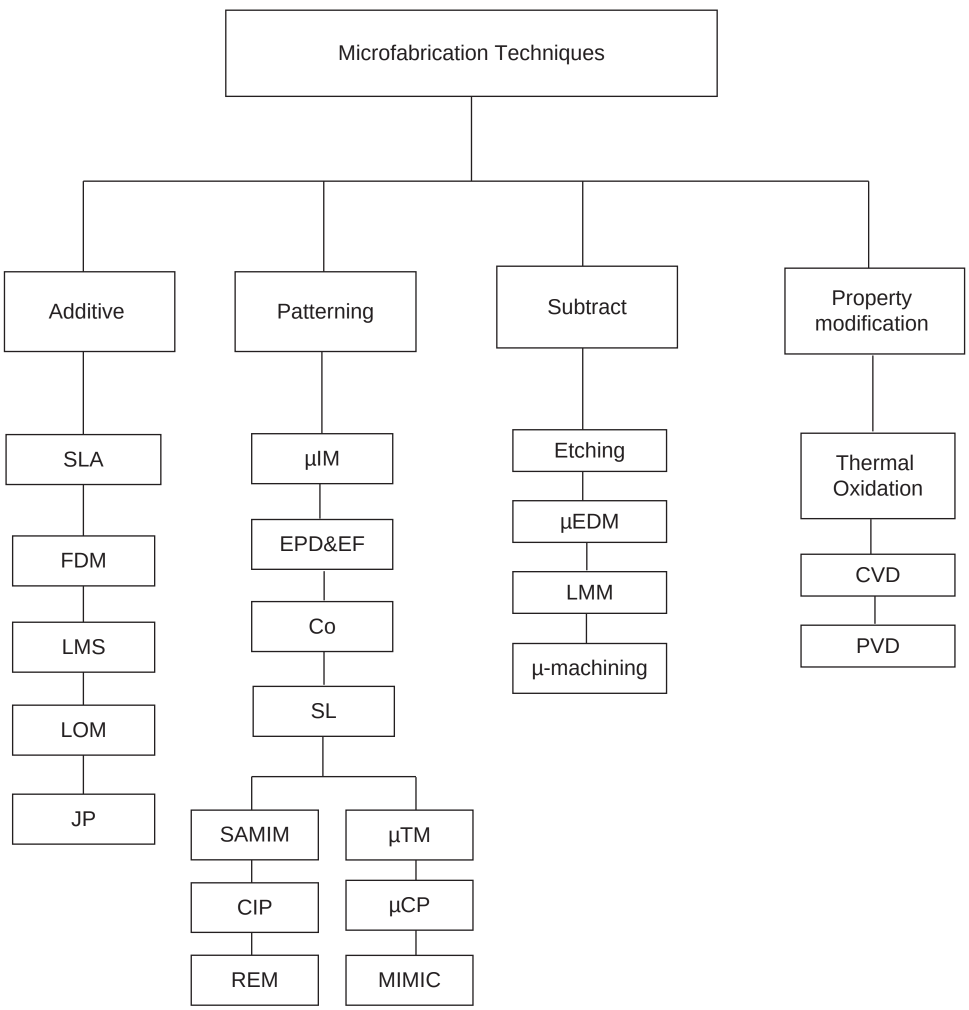

Figure 1. Micromanufacturing techniques, stereolithography (SLA), fused deposition modeling (FDM), laser microsintering (LMS), laminated object manufacturing (LOM), jet printing (JP), microinjection molding (μIM), electrophoretic deposition and electroforming (EPD, EF), coextrusion (Co), soft lithography (SL), microcontact printing (μCP), replica molding (REM), microtransfer molding (μTM), micromolding in capillaries (MIMIC), solvent-assisted micromolding (SAMIM), cold isostatic pressing (CIP), microelectrical discharge machining (μEDM), laser micromachining (LMM), thermal oxidation, chemical vapor deposition (CVD) and physical vapor deposition (PVD).

2.1.1. Stereolithography (SLA)

Using stereolithography (SLA), complex shaped three-dimensional microcomponents can be manufactured by building up many sequential layers defined by a CAD design. A 3D CAD model is divided into a series of 2D layers with uniform thickness. Forming of these layers is achieved using a space scanning mirror and a UV beam that is absorbed by a photo sensitive polymer consisting of monomer and photo initiators leading to the polymerization; i.e., conversion of the liquid monomer to the solid polymer. As a result, a polymer layer is formed according to each 2D file. After one layer is solidified, a new layer of liquid resin follows until it forms the complicated 3D micro component layer by layer, as shown in Figure 2 [66–68].

For ceramic microcomponent fabrication, micro-stereolithography can be applied by using a ceramic mixture composed of ceramic powder embedded in a photo initiator polymer matrix. Upon UV polymerization, the ceramic particles are bonded by the polymer and the ceramic green body is thus formed. The next step is the debinding process of the green parts to burn out the polymer content. Finally, the molded parts are placed in a sintering furnace to obtain the final structure. The resulting ceramic parts could be either working components or molds for later casting processes.

Indirect ceramic SLA was developed to enable the fabrication of fine and dense structures. In this process, a casting mold (permanent or lost) is fabricated using SLA into which ceramic or metal slurry is poured and cured. Afterward, the green parts are obtained from the SLA mold either by demolding (permanent mold) or by thermal decomposition (lost mold). Finally, the green parts are sintered to obtain the final microcomponents [69].

One major problem that limits the use of SLA is the poor mechanical properties and the rough surface finish of the fabricated components. Poor mechanical properties can be attributed to poor adhesion between layers and to the low density of the ceramic microcomponents [66–69]. On the other hand, surface roughness is mainly depending on the thickness of the formed 2D layers, the designed draft angle and the light penetration depth. To improve the surface finish quality, layer thickness and draft angle should be kept as low as possible. In addition, light penetration depth should be controlled in order to achieve accurate polymerization depth [70, 71]. Rough surface may also be attributed to the stair stepping caused by the build-up layers. Recent efforts have been performed to reduce SLA stair stepping including vector-by-vector micro-stereolithography, integral micro-stereolithography and slant beam rotation. These improvements can decrease the resolution to 5 μm and the surface finish to about 1.1 μm. According to [72–74], SLA can be improved by debinding the ceramic/resin objects with a slow heating rate of 0.1 to 1 °C/min and holding temperature at 600 °C, followed by sintering the green components at 1600 °C.

Fused Deposition Modeling (FDM). In fused deposition modeling (FDM), a thermoplastic ceramic polymer in the form of a filament is forced through a small temperature-controlled extruder onto a platform. The filament is moved between two driving wheels and acts as a piston to drive the extrudate. Liquefier is heated to melt the filament material. The nozzle can be moved in both horizontal and vertical directions by a numerically controlled mechanism. The nozzle follows a tool-path controlled by a computer-aided manufacturing (CAM) software package. After finishing each layer, the base platform is lowered to deposit the next layer until the three-dimensional part is completely fabricated from bottom up, one layer at a time. The technique is shown schematically in Figure 3 [63–65].

The FDM technique is affected by several parameters including material, geometry properties, machine and operation specifications, from which the material properties must be optimized first by preparing a new material feedstock. In addition, the rest of the variables should be optimized to determine the internal and external quality of FDM parts. A variety of ceramic materials has been used in FDM, including silica, alumina, silicon nitride and lead zirconium titanate (PZT).

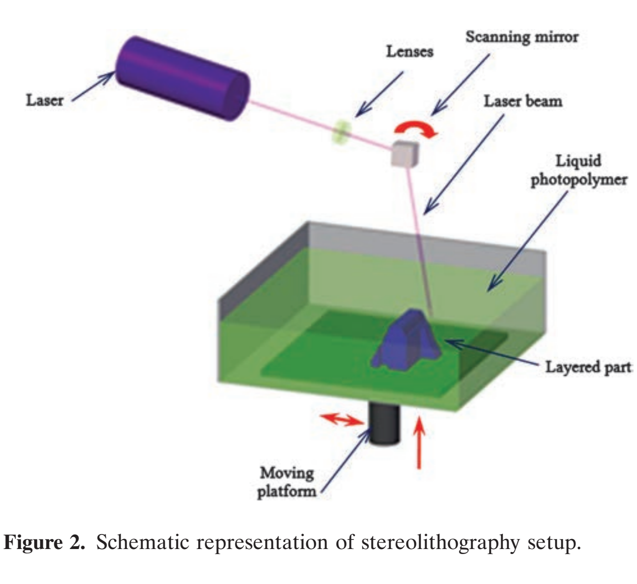

Figure 2. Schematic representation of stereolithography setup.

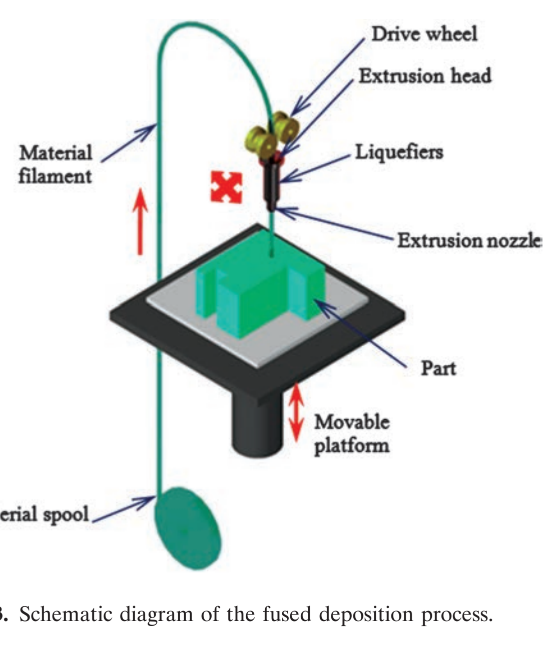

Figure 3. Schematic diagram of the fused deposition process.

The formation of internal and surface defects is a major drawback of the FDM process. This can be attributed to possible poor bonding between the contiguous layers or defective filling. As for surface defects, several developments have been carried out to prevent their formation such as green, partial sintering, and final machining. Internal defects include voids, flaws, pores, delaminations and cracks in the green ceramic parts. Such defects are undesirable for structural and functional applications. The causes of the defect formation can be easily traced and prevented through optimization of the process variables and achievement of satisfactory process techniques to address the complications. Hence, it is likely to fabricate better quality green ceramic parts. In addition, elimination of the surface and internal defects can improve the sintered density from 95% to 98% [75–78].

Laser Microsintering (LMS). Laser microsintering (LMS) is a direct fabrication technique based on laser selective sintering. It uses a high-power laser to fuse ceramic powder into three-dimensional microcomponents. A laser beam selectively scans over a thin powder bed and sinters the powder particles. Afterwards, another layer of the powder is applied for subsequent forming of a second cross section, according to a CAD design. The process is repeated until forming the full part. In contrast to stereolithography and fused deposition modeling, no special support structures are needed for the formed part, since;he non-formed parts of the powder bed provide enough support for the forming process. Once the microcomponents are formed, the shaped part can be lifted from the powder bed, as shown in Figure 4.

For ceramic materials, it is difficult to obtain a complete shape compared to metals and polymers due to thermal shock and transparency of ceramic oxides. Special requirements are essential for ceramic forming; the powder size should be in sub micrometer range to reach the required resolution, and the absorption coefficient should be near infrared laser wavelength to be sufficient to transfer the energy into the material.

The powder is usually mixed with a lower melting point second phase binder, either by particle coating or as a mixture of ceramic powder and binder particles. The organic binders are burned out in the firing process, while inorganic binders in some cases can act as a second phase. Using the LMS technique, alumina microcomponents with a resolution up to 50 μm were fabricated. In addition, the average density of the measured alumina specimens was 98.5% of the theoretical density using CO_2-laser irradiation. The laser scanning velocity varied between 95 and 400 mm/s [79–82].

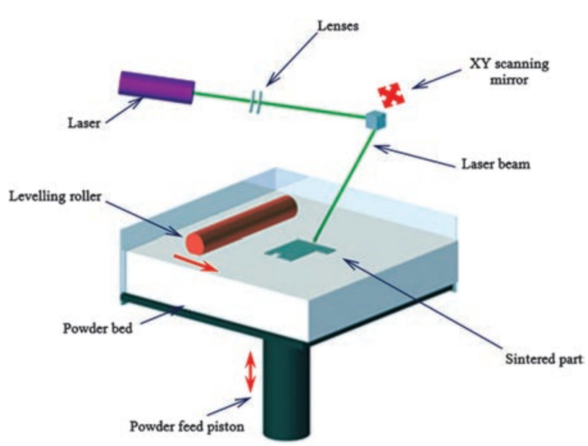

Figure 4. Schematic diagram of selective laser melting process.

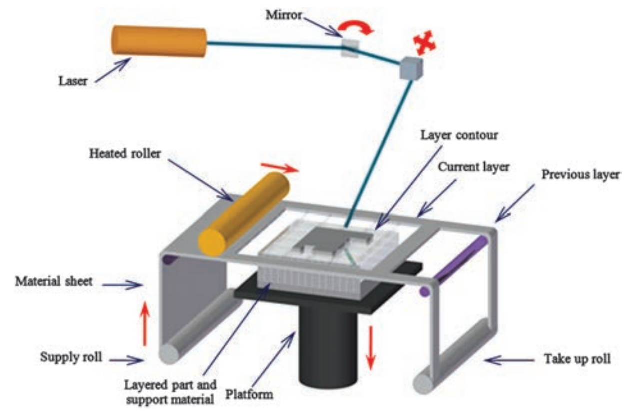

Figure 5. Schematic diagram of laminated object manufacturing process.

Laminated Object Manufacturing (LOM). Laminated object manufacturing (LOM) was first developed in 1991 by Helisys of Torrance. Parts are built up by bonding layers of contoured thin adhesive-coated ceramic laminates. As schematically shown in Figure 5, the outline of the first layer is cut by means of laser beam, according to the CAD design. Next, the platform goes up slightly and the heated roller applies pressure to bond another layer on top of the previous deposited layer. The laser cutting and bonding are repeated until the part is completely constructed. The remaining extra material supports the cut part during construction [64–83].

As explained in the fabrication technique, LOM is partly considered a subtractive process when compared to other solid free-forming processes, because the contours of the parts are tracked while the rest of the roll is discarded. It is also considered the fastest method among the AM methods for ceramic parts fabrication [64–83]. LOM has been used to fabricate ceramic parts using thin ceramic sheets (100 μm). Since each layer is pre-formed (tapes), microstructural defect formation inside each layer is minimized. However, it is difficult to prevent forming of flaws in the interfaces of successive layers. This technique is remarkably useful for forming multilayers of functionally graded materials or multilayered composites, as different material tapes can be added onto designed supply rolls [83–88].

Jet Printing (JP). Jet 3D printing (JP) using powder bed system and binder jet was originally developed by Massachusetts Institute of Technology (MIT) in 1990. The process is similar to selective laser sintering, but an ink jet head prints a polymer-based binder according to the current cross section of the part to bind powder, rather than a laser to sinter the material, as shown in Figure 6. Therefore, it is considered a simple and low-cost process. The deposited binder bonds the printed areas together, while the

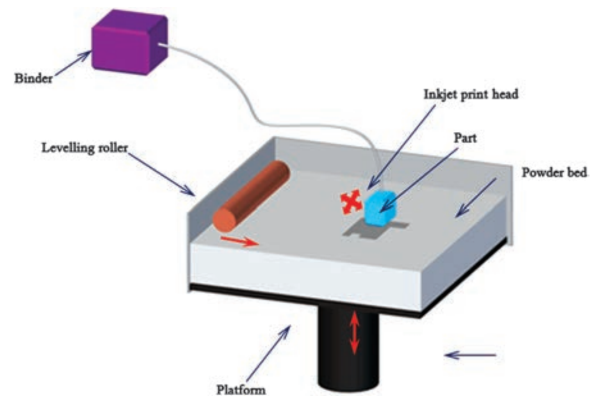

Figure 6. Schematic diagram of powder bed jet system.

imprinted areas work as a support to the printed areas during the forming process. Afterward, the part is lifted from the powder bed and the debinding and sintering process follows. Fine, dispersed and homogenous ceramic powder is recommended to improve the quality of the microcomponents in terms of density and surface finish. To account for this requirement, a slurry-based ceramic mixture has been developed. A layer of the slurry is sprayed over the platform. After drying, the ink jet head selectively prints a layer in the desired areas to pattern the structure. The slurry process prevents internal microstructural inhomogeneities and flaws formation. In addition, it improves green density and shrinkage significantly [89–92].

Another type of ink jet printing (JP) uses a slurry jet to print the required model, where ceramic mixture in a slurry state is as a binder. Here, the ceramic powder is prepared in suspension to form a colloidal mixture and deposited through the jet head instead of the binder systems. After drying, the patterned areas solidify to form microcomponents. After completing the layer build-up a milling head smooths the surface. The particle collector receives the particles coming out from the smoothing process. Then, the platform is lowered by an elevator to enable the addition of a new layer. This process is repeated until the full part is built, as shown in Figure 7. Rheological properties of the ceramic mixture and viscoelastic properties play the key roles for making optimized ceramic ink. Ink jet printing produces good accuracy with acceptable surface finish.

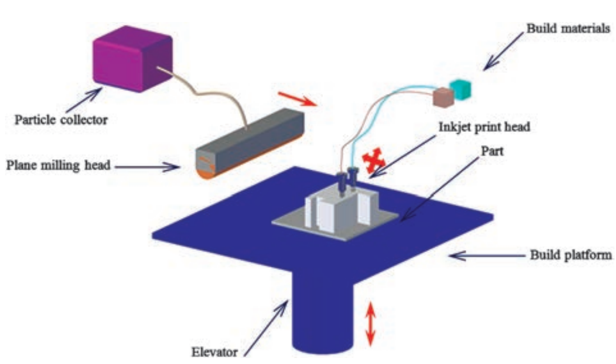

Figure 7. Schematic diagram of ink jet printing process.

However, it is regarded as a slow fabrication process, with fragile products.

According to the printer used, there are two groups of ink jet printing systems. The first one is continuous ink jet printing and the second one is drop-on-demand ink jet printing. Ceramic suspension with a 40% vol. solid loading can be obtained using ink jet printing [93, 94]. Al_2O_3 suspension can be prepared using *n*-alkane at low temperatures of 50–60 °C. Freestanding ceramic parts such as a rotation wheel with green wall thickness of 100 μm can be successfully obtained by using the drop-on-demand technique. After sintering, the final linear shrinkage reaches 18% with a final sintered relative density of 80% [95, 96].

2.2. Patterning

Patterning methods represent the conventional forming techniques based upon molding. Those well-established techniques are normally used for fabricating microcomponents in the milli/micro-meter size. In this section, patterning techniques for microfabrication of ceramic and metal microcomponents are reviewed.

Microinjection Molding (μIM). Microinjection molding is a popular forming technique for ceramic and metal microfabrication. The technique is much similar to plastic injection molding. It can be used to fabricate a wide variety of sizes, complexity and materials. The microinjection molding process starts with melting polymer or wax and mixing it with ceramic or metal powder to form a composite slurry to fill molds under heat and pressure, as shown in Figure 8. The molds are then left to cool and solidify so that the green parts can be demolded. Demolding can be problematic in case of small features and high aspect ratio microcomponents as a result of the increased surface area. Usually, a photoresist made by UV or X-ray lithography is utilized as a lost mold to overcome the demolding problems. After forming a part, the mold is removed by plasma etching to avoid the microcomponents damage caused by the traditional melting or dissolving methods. Low melting temperature materials can be used as binders in a low-pressure injection molding technique (LPIM). This method allows for the use of low temperature of 60–100 °C and pressures at 0.2 MPa, which offers the opportunity to use soft molds instead of photoresist molds. Slow thermal debinding processes at a rate of 0.1 °C/min and sintered at 1500 °C for 1 hour were used to sinter zirconia micro parts. After sintering, microcomponents exhibited 98% theoretical density and 12% linear shrinkage [97–100].

Some common applications include micro-gears and the watch making industry, automotive industry, medical and surgical instruments, micro-engines and rotators, and micro switches and connectors. The first metallic microcomponents fabricated by micro μIM were reported in [101, 102]. The feedstock is a mixture of powder and binder to be injected into a μIM machine. However, one key is to select an appropriate powder shape and size along with appropriate binder type to meet the requirement of feedstock properties. Spherical and irregular powder shapes are commonly used in μIM. The irregular powder shape produces high green strength between the particles and their neighbors by

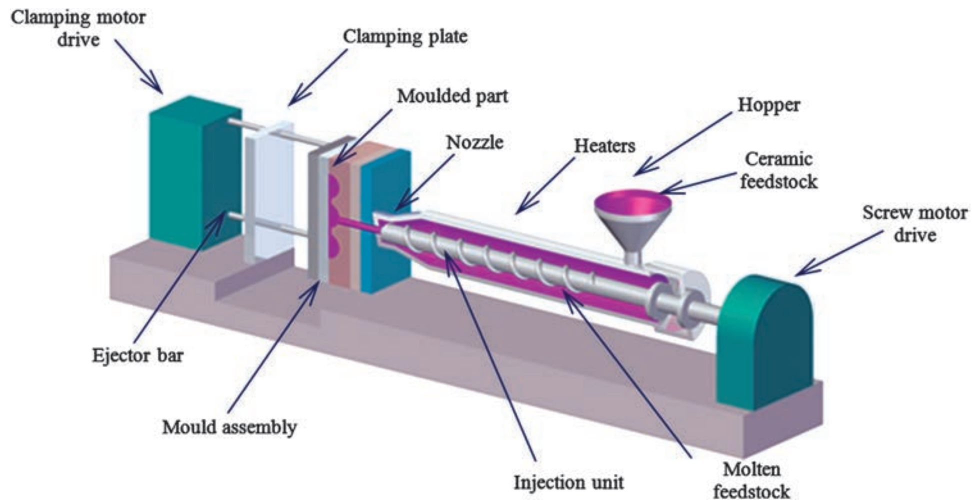

Figure 8. Schematic diagram of injection molding setup.

plastic deformation under the applied pressure and it produces good powder integrity in the green part [103, 104]. On the other hand, the spherical powder shape is also used in the μIM process to produce a good density packing of green parts [105, 106]. Selection of the powder size mainly depends on the minimum feature size of the part to be fabricated. To micrometallic components with isotropic behavior, the minimum grain size should be smaller than that of the minimum feature of the microcomponent. Consequently, the powder size should be at least smaller than the minimum feature to be fabricated [107–109]. The binder's main function is to hold the powder into a designed shape and maintain it until the debinding and sintering process. However, the binder should have good flow behavior during forming feedstock, and rapid viscosity after creating the green parts. The binder should also produce a good interaction with the powder and be removed completely before the sintering process [105, 110, 111].

The most common conventional types of binder are wax, thermoplastic and thermosetting [111, 112]. Some binders are removed before the sintering process by heating the green parts below the sintering temperature. Other binders can be dissolved using special solvents. Gel casting is another type of binder system to create complex shapes from ceramic and metallic powders. Instead of producing a feedstock as in the conventional binder system, gel casting produces a gel/powder slurry to fill the desired shape. The hard green parts are formed by chemical polymerization of the gel/powder slurry after adding catalyst and initiator. Like most conventional binders, gel casting binder can be removed thermally before the sintering temperature. Many details can be found in [113–120]. Because some materials are subjected to oxidation during the debinding and sintering processes, the processes are performed under inert gaseous atmosphere or vacuum [121–123]. The μIM method has the advantage of creating flexible shapes and designs in a wide range of materials and applications in mass production. However, the surface finish and shrinkage after sintering is the main issue to be considered. It also produces some defects in the compacted powder due to inhomogeneous density distribution resulting from the friction between the powder and the die wall [124, 125].

Electrophoretic Deposition and Electroforming. Electrophoretic deposition (EPD) comprises a broad range of processes including electrocoating, cathodic electrodeposition, and electrophoretic coating, or electrophoretic painting. In these processes, electric current is applied to well-dispersed colloidal particles in a liquid medium. As a result, the suspended particles deposit on the electrode surface, as illustrated in Figure 9. All colloidal particles used to form stable suspensions and can carry a charge may be used in electrophoretic deposition including polymers, pigments, dyes, ceramics and metals [126–130], followed by demolding and sintering in order to intensify the powder compact. Micro molds that are coated or plated with a conductive layer have been used to shape ceramic microcomponents using EPD. To produce parts with high mechanical properties and low surface roughness, well-dispersed suspensions should be employed. One of the disadvantages of this technique is the resultant low sintered density. Also, the

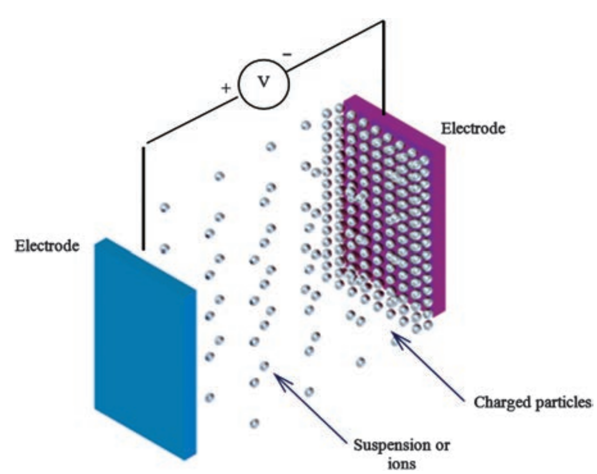

Figure 9. Schematic diagram of electrophoretic deposition and electroforming principal.

necessity to burn out the mold is a drawback, since it may damage the microcomponents due to high organic content in the mold.

Electroforming (EF) is a process originated from the popular electroplating process. The process was first used in 1837 by Jacobi through the electrodeposition process of copper onto a plate. Similar to electrophoretic deposition, it uses electrically charged suspension flowing between an anode and a cathode submerged in a fluid. However, in contrast to dielectric electrolytes used in electrophoretic deposition, the fluids in electroforming are conductive. Also, the electroforming is built from the ions of the metal being deposited and transformed into atoms as soon as discharged at the electrode. On the other hand, in the electrophoretic process, the coating is shaped by a build-up of large particles which can be ceramic, polymeric or metallic. In electroforming, 3D metal micro parts can be manufactured by filling a mold with electrode posited material, which is removed at a later stage, Figure 9. The electroforming process has the capability to replicate high aspect ratio structures with high resolution. It has been a popular process because it is productive, cheap and easy to work with. Much research has been carried out to optimize the process parameters of this technique.

Electroforming is widely utilized for producing microcomponents of metallic materials [131] and it can be employed to precisely fabricate microcomponents with height less than 0.5 mm. When a microcomponent thicker than 0.5 mm is desired, processing time of over 100 hours is usually required, and thus restricts its further application [132].

Coextrusion. Extrusion is a very powerful process to form parts with fixed cross section such as cylinders, plates and honeycombs. Material is forced through a die of the desired cross-section as demonstrated in Figure 10. Extrusion can be used to fabricate a wide range of materials, but is considered advantageous for working brittle materials such as ceramics. In ceramic extrusion, the process is the same as in plastic and metals extrusion except it uses plasticizers and binders to provide enough plasticity when forcing the feedstock through the die. The micro extrusion processing is based on conventional extrusion processing but the size is in micrometer scale. Two different materials are involved in the coextrusion process. One is a primary material while the other is a support material. For simple shapes process, forming is carried out by using round or square dies. Size reduction is performed while the pattern in which the various compounds are assembled is maintained. Complex parts have been performed by using coextrusion with carbon black as the support material in the extrusion and the sacrificial material in the sintering step. Feature size of 10 μm was successfully achieved using coextrusion. Alumina objects were supported by burying in powder during sintering. The binder was removed with the following heating schedule in air: 5 °C/min to 100 °C; 1 °C/min to 250 °C; hold 1 h; heat 1 °C/min to 500 °C; hold 1 h. Sintering was done by heating at 5 °C/min to 1600 °C [133]. The coextrusion process does not require expensive micromachining tools. In addition, it can be used to achieve very fine micro-features with high aspect ratios. However, the extruded parts require post machining such as cutting and grinding. This is can be complicated for such fine microcomponents [134, 135].

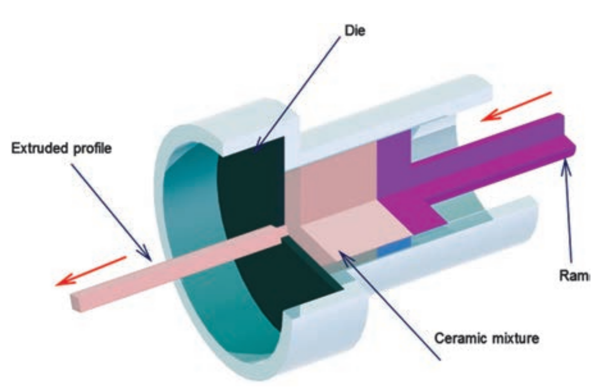

Figure 10. Schematic diagram of coextrusion process.

Soft Lithography (SL). Soft lithography is a group of non-photolithographic techniques for fabrication of micro and nanostructures based on replica molding, self-assembly and non-photosensitive materials. A soft mold is used as a stamp with patterned relief microstructures on its surface to generate components with micro and nano features. The elastomeric stamp or mold with patterned relief structures is the key element in soft lithography. Several materials have been used for the elastomeric stamps, from which poly dimethylsiloxane (PDMS) elastomers (or silicone rubbers) are used in most applications. Some groups have used polyurethanes, cross-linked Novolac resins and polyimides. Soft lithography is an increasingly popular technique for its low-cost template replication feature for a wide variety of applications. There are five sub techniques of soft lithography, which are microcontact printing (μCP), replica molding (REM), microtransfer molding (μTM), micromolding in capillaries (MIMIC), and solvent-assisted micromolding (SAMIM) [136–139]. Soft lithography is similar to micro μIM technique in most of the sequential stages. The common stages of SM technique are: creating a soft mold insert, preparing slurries (a mixture of powder and binder), filling the soft mold, drying and demolding (create green part), debinding and sintering to obtain the final micro parts. The main difference between soft lithography and μIM techniques is the mold insert type. In soft lithography the mold insert is a soft mold, which is commonly fabricated of silicone rubber (polydimethylsiloxane PDMS), while in micro μIM, the mold insert is commonly fabricated of rigid materials. The creation of the soft mold insert commonly depends on the soft lithography process. The master mold of the required microcomponents is fabricated using the photolithography process, and then the negative replica of the soft mold is created using PDMS [140–150]. In the soft lithography technique, the soft mold is filled with feedstock slurry under atmospheric pressure and room temperature. The binder characteristic should have low viscosity at room temperature while filling the soft mold.

Microcontact Printing (μCP). Microcontact printing (μCP) is a soft lithography technique that uses a PDMS soft mold to form patterns in submicron lateral dimensions. Ceramic or metallic suspension of ink is transferred to the top surface of a substrate by direct contact, as shown in

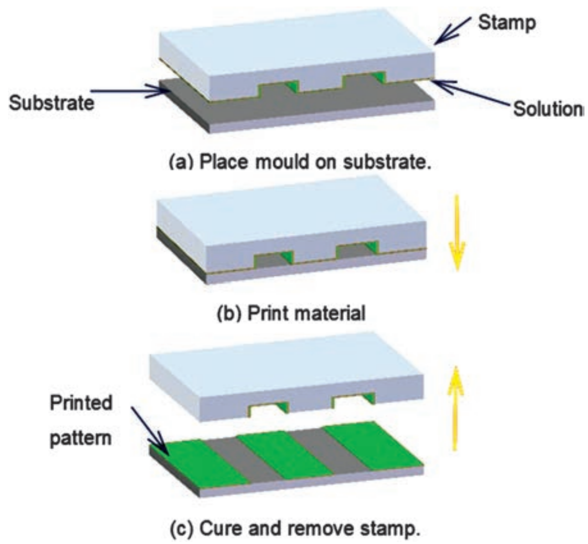

Figure 11. Schematic illustration of the general process of microcontact printing.

Figure 11. The process resembles using a common stamp to transfer ink from an ink pad to a piece of paper. It is considered a flexible technique because it is possible to use a planar surface with a planar stamp, a planar surface with a rolling stamp and a rolling surface with a planar stamp. The technique is an attractive process because it is simple, inexpensive and very efficient [151–153].

Replica Molding (REM). Replica molding is considered an efficient technique for pattern replication from a rigid or elastomeric mold into another material by liquid solidifying when in contact with the mold, as shown in Figure 12. Elastomeric molds offer the possibility to control the shape and size of micro features of the molds by mechanical deformation. Various kinds of ceramic suspensions and curable prepolymers have been patterned using replica molding. The capability and versatility of this procedure has been demonstrated for nanomanufacturing [154]. First, molds are fabricated using high-resolution nanolithographic processes. The nanostructures would then be duplicated into multiple copies by replica molding with organic polymers. This process has also been successfully used for the fabrication of topologically complex, optically functional surfaces that would be difficult to fabricate with other techniques [155].

Microtransfer Molding (μTM). Microtransfer molding (μTM) uses a patterned PDMS master mold. A drop of ceramic suspension or liquid prepolymer such as polyurethane is used to fill the recessed regions of the master mould. The excess suspension is cleared away by cleaning with a flat razor blade or by blowing off with a nitrogen gun. The filled mold is then placed on a substrate and the entire assembly is irradiated or heated. After the curing process, i.e., solidification, the soft mold is peeled away gently to leave a replica pattern on the top surface of the substrate, as illustrated in Figure 13. Microtransfer molding can fabricate microstructures of a wide variety of materials apart from organic polymers such as sol-gels, glassy carbon, and ceramics. In addition, both interconnected and freestanding microstructures are possible to produce. The most significant advantage of μTM over other microlithographic methods is its simplicity and suitability to manufacture micro patterns on non-planar surfaces,

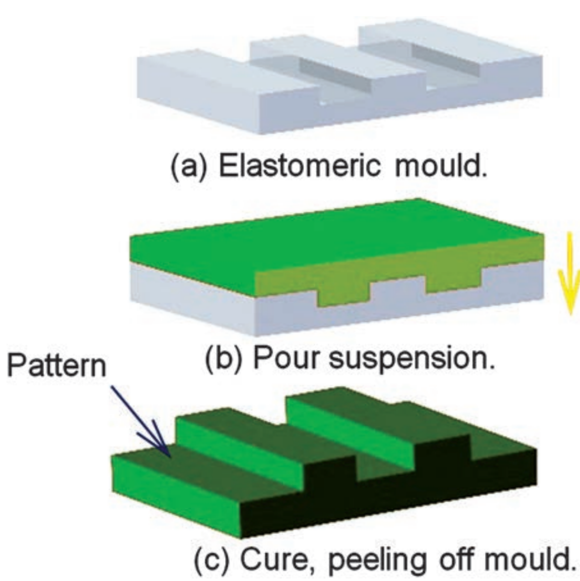

Figure 12. Schematic illustration of replica molding process.

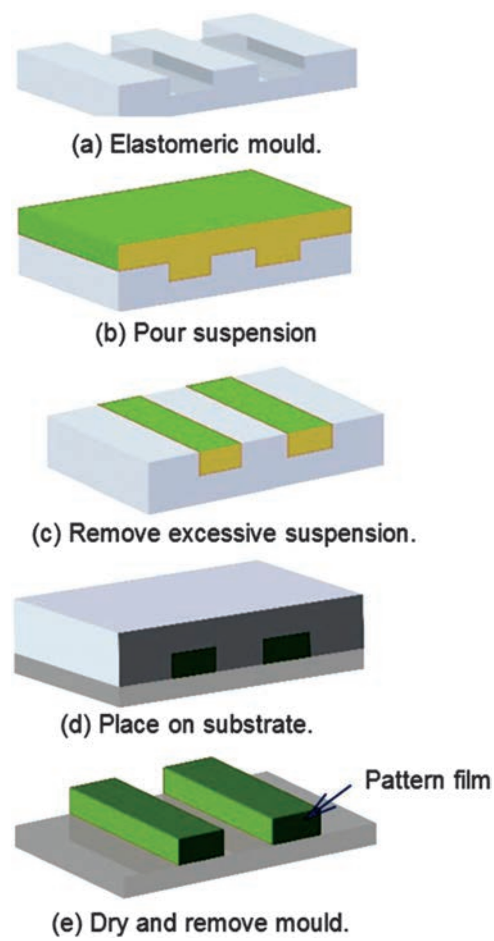

Figure 13. Schematic illustration of microtransfer molding process.

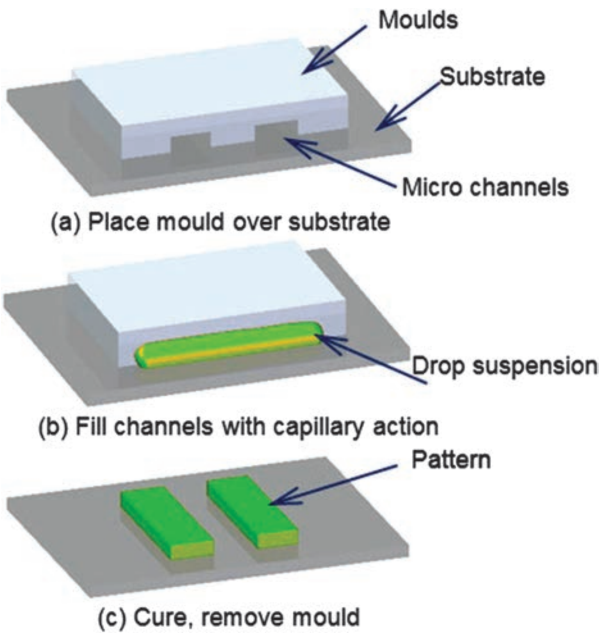

Figure 14. Schematic illustration of micromolding in capillaries process.

a property that is crucial for building three-dimensional microstructures [156–158].

Micromolding in Capillaries (MIMIC). Micromolding in capillaries is similar to microtransfer molding but the PDMS mold has a microchannel structure. The PDMS mold is placed face down on top of a substrate and creates conformal contact to that surface. When a low-viscosity ceramic suspension or prepolymer is dropped at the opening of the network channels, the suspension freely fills the microchannels by capillary forces. The assembly is then left to cure into a solid. Afterward, the PDMS mold is peeled off and a residual solid micro pattern remains on the surface of the substrate, as shown in Figure 14. MIMIC represents another non-photolithographic technique that forms microstructures on planar and curved surfaces. MIMIC is well-suited to pattern a wide range of materials such as UV-curable prepolymers, suspensions or solutions of functional or structural polymers, precursor polymers, glassy carbon and sol–gel materials. MIMIC technique is considered remarkable for its simplicity and its accuracy in transferring the patterns from the soft mold to the ceramic structures that it forms [159–161].

Solvent-Assisted Micromolding (SAMIM). Solvent-assisted micromolding (SAMIM) is a process used to fabricate microcomponents on the surfaces of polymeric substrates. It can also be used to modify the surface structures of polymers. This process combines the methodology of both replica molding and embossing, as shown in Figure 15. In this technique, a substrate is coated with preceramic polymer and a PDMS soft mold is covered with a wetting solvent. Next, the PDMS mold is placed on the surface of the coated substrate. The solvent dissolves the polymer in contact forming the resulting pattern on the surface of the soft mold. Afterward, the solvent is evaporated

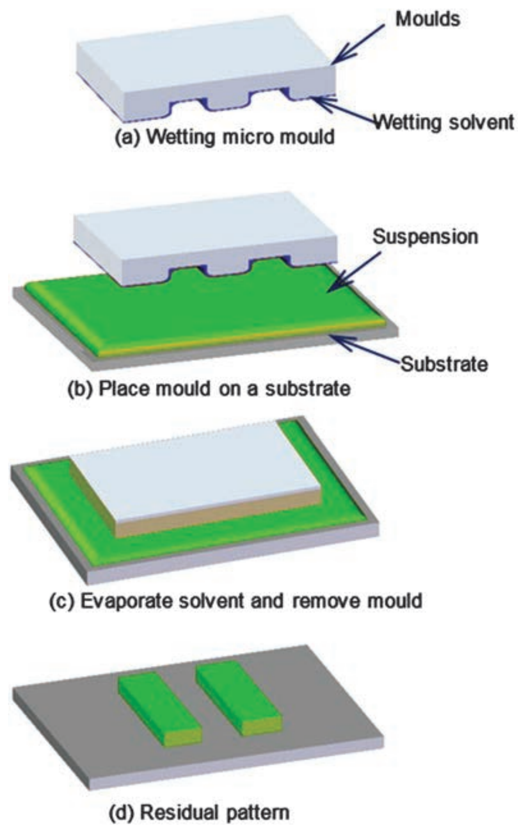

Figure 15. Schematic illustration of solvent-assisted micromolding process.

and the polymer solidifies to form the desired patterns attached to that on the surface of the mold [162, 163].

Cold Isostatic Pressing (CIP). A cold isostatic pressing method (CIP) is mainly dependant on powder metallurgy processes. In the CIP method, the feedstock (a mixture of binder/powder) is pressed under hydrostatic pressure to improve the homogeneity and retention of the green components [164–168]. The most common types of cold isostatic pressing techniques are wet and dry bags. In wet bag, the rubber mold is filled with feedstock (a mixture of powder and binder) and then dropped inside the pressure vessel filled by water. After applying the target pressure, the mold is removed each cycle and refilled. The green parts obtained are then debound and sintered. In this type, the complex shapes can be fabricated. In the dry bag type, the mold itself is an integral part of the pressing vessel, and it is commonly used when small and simple shapes are required [169–175]. The cold isostatic pressing technique was developed to fabricate large scale parts and it is limited to microscale one. However, the development of creating micro engine parts of stainless steel powder has been successful using silicone rubber (polydimethylsiloxane mold) [176, 177] release. Figure 16 shows the detailed fabrication of micro engine gear by cold isostatic pressing techniques.

2.3. Subtract Processes

Subtractive micromanufacturing processes use etching or removal of a part of the substrate to manufacture

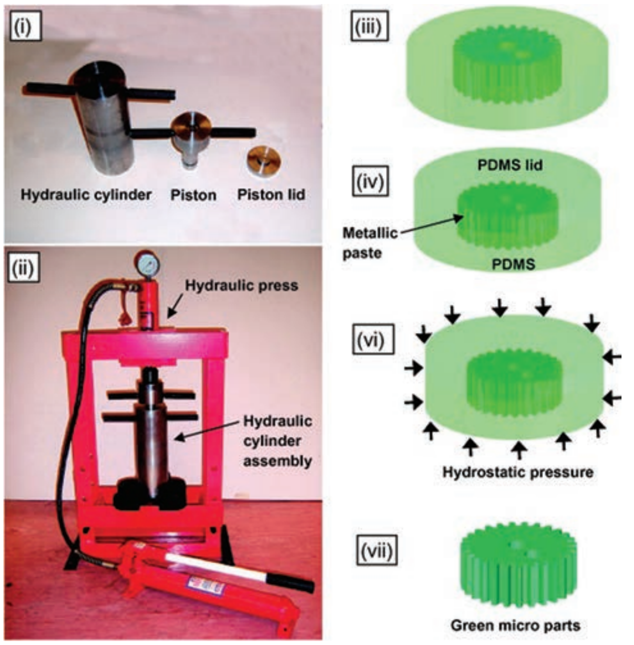

Figure 16. Schematic diagram of the cold isostatic pressing technique. Reprinted with permission from [176], M. Imbaby, et al., Fabrication of 316-L stainless steel microcomponents using encapsulating soft mold and isopressing technique. *Microelectronic Engineering* 87, 1623 (2010). © 2010, Elsevier.

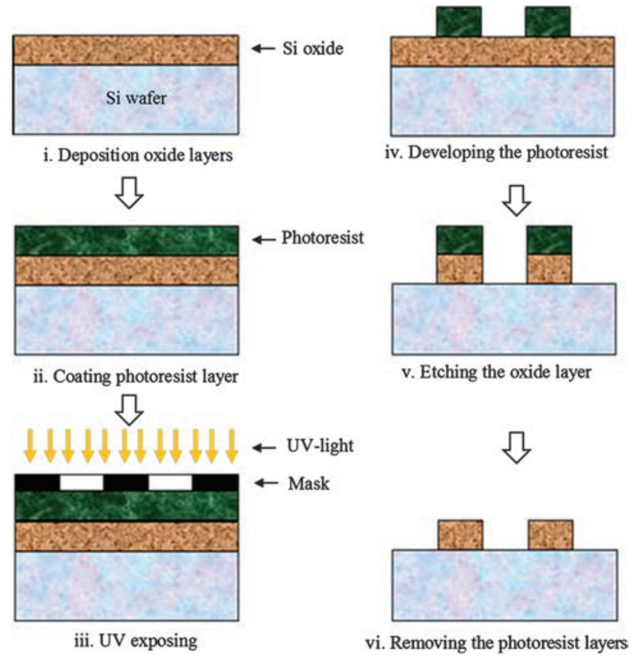

Figure 17. Schematic diagram showing the etching micromachining process.

micropatterns. This group of processes includes etching, microelectrical discharge machining, laser micromachining, and micromachining.

Etching. The etching process can be classified into two main types: wet and dry etching. In the wet etching process the silicon oxide or metallic layer on the top of the surface of silicon wafer is removed by immersing the wafer into etching solvent. The solvent attacks the micro features to be removed and then dissolves [178]. On the other hand, the dry etching process is a purely physical process; i.e., the micro feature to be removed is milled using a focus ion beam or using reactive ion etching [179, 180]. This technique is commonly used in the application of a microelectro device system. It has a limitation of creating freestanding micro metallic components. However, it has the advantages of creating number of identical features at one wafer with high accuracy. Figure 17 shows a SEM micro sieve pore fabricated by the wet etching process [70].

Microelectrical Discharge Machining (μEDM). Electrical discharge machining is used to create a wide range of simple and complex shapes on a conductive work piece, typically a metal piece. The process includes EDM machine, work piece to be formed and electrode (machine tool), Figure 18. The EDM machine creates an electrical discharge between the work piece and electrode to erode the materials of the work piece. To create a micro feature in a work piece, micro EDM is emerged. There are three categories of micro EDM machines: micro-wired EDM, hole-boring, and shaped-working electrode [181]. In hole-boring and shaped-working electrode the electrode is deteriorated during the process, and hence it is replaced during the process until all of the micro features are created. However, the micrometallic features have been successfully created with different sizes [181, 182]. In microwire EDM, the electrode is a microwire drawn continuously during the process. It can produce high accuracy 3D micro features on a metallic work piece [183, 184]. Although micro EDM is an effective technique of creating micro parts in a metallic work piece, it has the disadvantage of creating micro features in nonconductive materials. In addition, the electrode wear is another issue during the eroding process. Micro gears had been created on a tungsten carbide super-hard alloy (WC-Co) using the micro EDM technique [185]. Three electrodes were

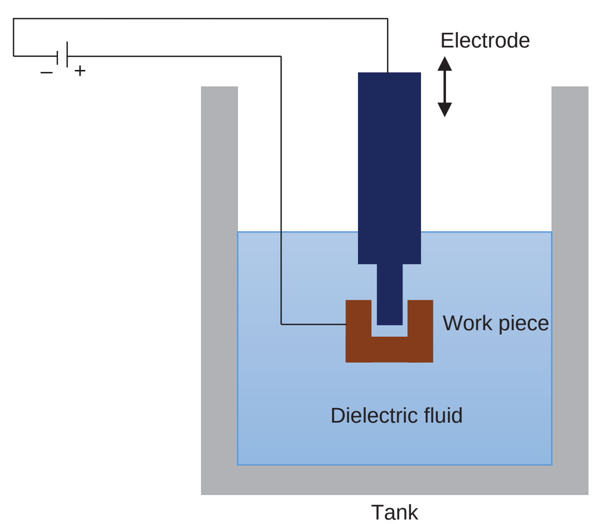

Figure 18. Schematic diagram showing microelectrical discharge machining.

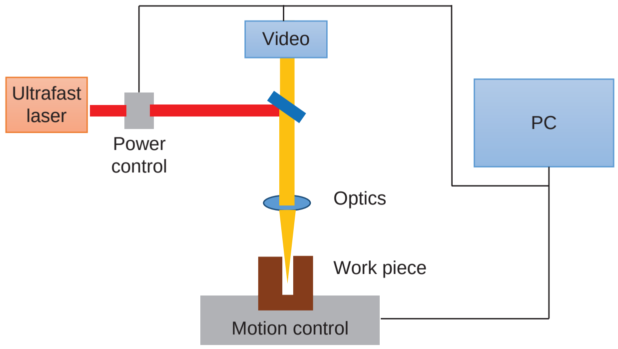

Figure 19. Schematic diagram showing the microelectrical discharge machining.

changed during the process to create the micro gear feature. Another issue of using the micro EDM technique is a heat-affected zone at the location of eroding the materials [186].

Laser Micromachining (LMM). Laser micromachining is a technique used for creating micro features by laser beam, Figure 19. When a laser beam with high power intensity and narrow divergence strikes the target material, it removes fine particles from the surface. However, the laser is operated in a pulsed mode instead of a continuous one in which the particles are removed each pulse. To create a micro feature on a metallic material such as a silicon wafer the desired shape is controlled by chromium in a quartz mask placed on top of the wafer. The material is removed wherever a laser beam goes through the quartz part on the mask and strikes the target material. The advantage of using LMM is the wide range of different materials that can be created (such as plastic, ceramics, glass, then metal), while it is limited to conductive materials in the micro EDM technique [187, 188]. Like micro EDM, the LMM produces some problems in the created micro features. When a laser beam strikes the material surface, a heat-affected zone is created, which affects the properties of the material [189–191].

Micromachining and Micromilling. Over a century, the conventional cutting tool machines such as drills, mills and lathes have been used for machining various macro parts with different sizes and shapes. Recently, a modern computer numerically controlled machine (CNC) is developed to create 3D complex shapes of a wide range of materials not only in macro scale but also in micro scale of a feature smaller than 10 micrometer [192, 193]. The design of the 3D complex shapes is done by CAD software and then attached to the CNC machine to form the required shape.

Another method of creating micro structures on a metallic work piece is a focus ion beam (FIB). Focus ion beam is a micro/nano milling technique used for milling various micro/nano structures based on ion removal from the surface of work piece. When the ion beam with certain intensity strikes the target surface, a small amount of material in the form of ions or atoms is removed from the surface. It covers a wide range of applications such as transmission electron microscopes (TEM), oblique submicron cut, micro-cantilever beam and different silicon micromilling [194–198]. The disadvantage of this technique is the material removal rate in the form of atoms or ions, and hence it is a very slow process.

2.4. Property Modification Processes

2.4.1. Thermal Oxidation

Thermal oxidation involves the generation of a thin layer of oxide (usually silicon dioxide) on the surface of a wafer and is usually used for semiconductor applications. The thermal oxidation of silicon is usually carried out in a water vapor or oxygen atmosphere over the temperature range 700–1250 °C. The formed silicon dioxide layer is amorphous and stable. The first diffusive transport of oxygen through the growing amorphous SiO_2 layer is performed followed by the reaction with Si at the interface. Wet oxygen is used for the formation of thicker protective layers. This type has been widely studied in the past years [199, 200].

2.4.2. Chemical Vapor Deposition (CVD)

Both chemical vapor deposition (CVD) and physical vapor deposition (PVD) are widely used for thin films preparation [3, 23, 201]. CVD involves a chemical reaction between the constituents of a vapor phase diluted with an inert carrier gas at a hot surface (typically higher than 300 °C) producing a deposited solid thin film, as shown in Figure 20. CVD is usually used when the oxide layer must be grown over materials other than silicon, such as aluminum or silicon nitride. It can be used also to produce silicon dioxide thin films, but the density of a CVD silicon dioxide film and its bonding to the substrate are generally poorer than that achieved by thermal. Chemical vapor deposition of SiO_2 is accomplished by a reaction between a silicon compound such as silane (SiH_4) with oxygen onto a heated substrate. The reaction is carried out at around 425 °C and can be summarized by:

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2 \quad (1)$$

Therefore, CVD is only used either when the substrate surface is not silicon or when the high temperature used in thermal oxidation cannot be tolerated.

The reactants are adsorbed on the heated substrate surface inside the CVD reaction chamber. Atoms undergo a series of processes resulting in film formation. CVD uses

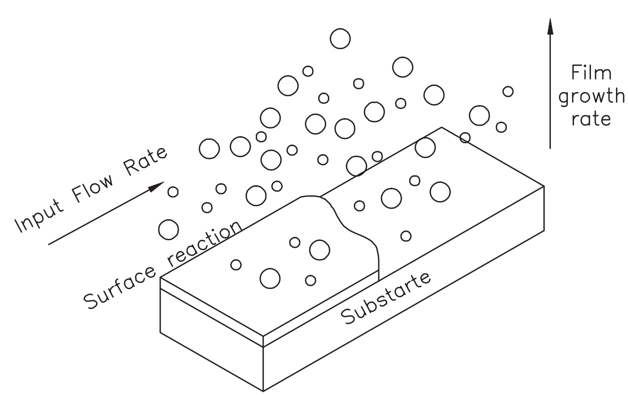

Figure 20. Chemical vapor deposition process.

the same building technique in surface micromachining. There are several techniques used in CVD such as plasma-enhanced CVD (PECVD), high-density plasma CVD (HDPCVD), atmospheric pressure CVD (APCVD), low-pressure CVD (LPCVD), very low-pressure CVD (VLPCVD), electron cyclotron resonance CVD (ECR-CVD), metalorganic CVD (MOCVD), and atomic layer deposition (ALD). Regardless of the deposition method, the reaction takes place as soon as a molecule has reached the surface. The molecular phenomena at the surface to be considered include sticking coefficient, surface adsorption, surface diffusion, surface reaction, desorption, and film or crystal growth. Gaseous byproducts are desorbed and removed from the reaction chamber. Two types of reactions may occur; heterogeneous reactions, where the solid material is formed on or close to the heated substrate, and homogeneous reactions that occur in the gas phase. Homogeneous reactions lead to poor adhesion, low density, and high defect films. Accordingly, heterogeneous reactions are preferred. The gas phase or surface process determines the rate of deposition and is the slowest CVD step. The compounds deposited are determined by the sample surface chemistry, its temperature, and thermodynamics.

In CVD, amorphous, polycrystalline, epitaxial, and uniaxially oriented polycrystalline layers can be deposited with a high degree of purity, control, and economy. Therefore, The CVD technique is considered very versatile, and may work over a wide range of temperatures and pressures. CVD is extensively used in the semiconductor industry. Miniaturized transistors have been produced using very thin film deposition of silicon. More recently, CVD copper and low dielectric insulators ($\varepsilon < 3$) are considered important CVD applications. Some modern applications of CVD include coated carbide tools, solar cells, depositing refractory metals on jet engine turbine blades, and other applications where resistance to wear, corrosion, erosion, and thermal shock are important.

2.4.3. Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD) can be applied to almost all combinations of coating substances and substrate materials. PVD reactors may use raw source material in solid, liquid or vapor states with different configurations. It can be used to apply a wide variety of metals, alloys, ceramics and other inorganic compounds, and even polymers; see Figure 21. In practice, the technique is widely used for metals deposition. Possible substrates include semiconductors, metals, glass, and plastics. The vaporized material inside the PVD reactors encounters few intermolecular collisions while traveling to the substrate. This is attributed to the low pressures used in PVD. As a result, modeling of deposition rates is relatively easy [23].

The procedure of the PVD technique is summarized in the following steps:

(1) the synthesis of the coating vapor from the source material,
(2) transport of the vapor to the substrate, and
(3) condensation of vapors onto the surface of the substrate.

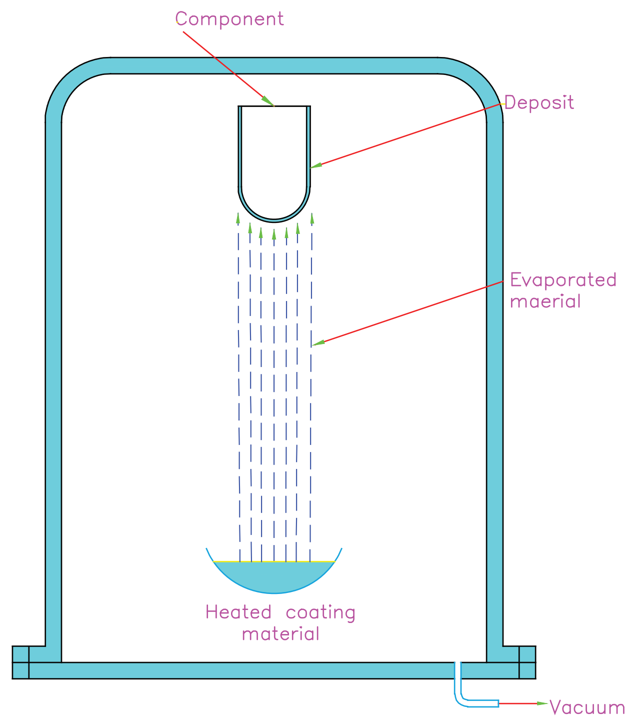

Figure 21. Schematic of physical vapor deposition.

Evacuation of the PVD chamber precedes these steps because the procedure is carried out in vacuum. The substrates are placed upside down to avoid contamination. The PVD techniques are classified into five principal types:

(1) thermal evaporation,
(2) sputtering,
(3) ion plating and cluster deposition,
(4) laser sputter deposition or laser ablation deposition, and
(5) aerosol deposition.

Sputtering gives better conformal coating than evaporation. Ion plating and cluster deposition rely on evaporation and plasma ionization. Aerosol deposition involves the impact of solid particles at high speed on a substrate. This promising new process is considered significantly different from all other PVD processes.

(PVD is applied in the fabrication of electronic devices, microelectromechanical systems (MEMS), and nanoelectromechanical systems (NEMS), principally for depositing metal to form electrical connections. Moreover, applications include thin decorative coatings on plastic and metal parts such as trophies, toys, pens and pencils, watchcases, and interior trims in automobiles. In this case, the coatings are thin films of aluminum (around 150 nm) coated with clear lacquer to give a high-gloss silver or chrome appearance. Also, PVD is used to apply antireflection coatings of magnesium fluoride ($MgFl_2$) onto optical lenses. Ion plating is widely used to coat titanium nitride (TiN) onto cutting tools and plastic injection molds for wear resistance. Pulsed laser deposition (PLD) is particularly useful when dealing with complex compounds, as in the case of the deposition of high-temperature superconductor films (HTSC); for example, $YBa_2Cu_3O_7$–x. Another example application of PLD is the deposition of the biocompatible calcium-phosphate-based ceramic, calcium hydroxyapatite, or $Ca_{10}(PO_4)6(OH)_2$. Aerosol impact deposition is advantageous in making ceramic films at low temperature on nearly all types of substrates.)

Comparing PVD and CVD, it can be noted that CVD operates at elevated temperatures while PVD operates at room temperature. This yields a better quality of the CVD crystalline films and a possibility to control grain size. It is also possible to deposit refractory materials at temperatures below their melting or sintering temperatures using CVD. Another difference is that CVD does not require vacuum equipment, which is an advantage. Moreover, CVD results in good bonding of coating to substrate surface. However, there are several disadvantages associated with CVD including the use of corrosive and/or toxic chemicals that require a closed chamber, special pumping and disposal equipment. Also, many gases used in CVD systems are toxic, corrosive, flammable and explosive. Moreover, certain reaction ingredients are considered expensive. Owing to the complexity and strong coupling phenomena involved in CVD, occurring at multiple length and time scales, simulation modeling of the entire CVD process is considered challenging in comparison with PVD process modeling.

3. CERAMICS, METALS AND THEIR COMPOSITE MICRO PARTS

3.1. Ceramics

Ceramic materials are classified as one of the main families of engineering materials. The origin of the word ceramics is the Greek keramos, meaning potter's clay, or wares made from fired clay. Ceramic materials are generally inorganic compounds between non-metallic and metallic or nonmetallic elements. Oxides, nitrides, borides, silicides and carbides are the most common forms of ceramics. Ceramic materials include the materials composed of clay minerals, cement and glass, and this explains why ceramic materials is the most available materials in nature. Ceramic materials are generally insulative to both heat and electricity. They are typically more resistant to high temperatures and harsh environments than polymers and metals. Ceramic materials are generally brittle and show very limited ductility, which may cause problems in manufacturing and processing of ceramic products.

Ceramics are classified into three groups: traditional ceramics, engineering ceramics and glasses. Traditional ceramics include silicates used for clay products, bricks, cements and stones. Engineering ceramics developed recently and they are based on oxides and carbides. Their mechanical and physical properties are very high compared with traditional ceramics. Glass ceramics is based on silica, and its structure is an amorphous structure.

Ceramic compounds are formed from ionic and covalent bonds and this explains the major properties of ceramics. The ionic and covalent bonds are the strongest atomic bonds and present high lattice resistance to the motion of dislocations, and this results in hard and stiff materials with low ductility. This also results in high melting temperatures, although some ceramics decompose rather than melt at elevated temperatures. In the ionic and covalent bonds the valence electrons are held together and there are no free electrons as in metallic bonds. This results in low thermal and electrical conductivity [202–204].

Compared to metals, ceramics have higher strength, lower density, a lower thermal expansion coefficient and very high melting temperature. Ceramics have a high melting temperature accompanied with a low thermal expansion coefficient and dimensional stability at high temperature, which make ceramics one of the optimum materials for high operating temperature applications such as engines and micro engines. The drawback of monolithic ceramics is that most ceramics have low toughness and fracture toughness compared with that of metals. For this reason, the flexural strength of ceramic materials is dependent on the surface roughness [205].

Alumina (Al_2O_3) is categorized as engineering ceramics or technical ceramics. It is very common because it is cheap and easy to process. The availability of alumina in highly purified grades motivates its use an application in material research [206]. Alumina often exists in the form hydrous alumina oxide phases or combined with other minerals. The most thermally stable phase form of aluminium oxides is α-Al_2O_3. The general physical and mechanical properties of 99.5% pure sintered α-Al_2O_3 with a grain size of 5 μm is presented in Table 1. Increasing the purity of Alumina increases its maximum operating temperature; pure alumina can operate up to 1700 °C, and its melting point is 2050 °C. Alumina has moderately high thermal conductivity, low thermal expansion and high strength. For these properties alumina has a good thermal shock resistance and is commonly used in the manufacturing of high temperature furnace products, such as spark plugs, crucibles, tubes and thermocouple cases.

The hardness and the abrasion of alumina are very high, which explains the excessive use of alumina in many mechanical elements such as piston pumps and deep drawing tools. Alumina is found in different grades ranging from 80–99.9% alumina—the rest is porosity, glass impurities or added components. Furthermore, alumina shows very good dielectric properties, making it popular in electronic components [207–209].

Alumina is also one of the main materials used in microfabrication. The manufacturing of alumina microcomponents has been done by many researchers. The manufacturing process of alumina microcomponents was first

Table 1. Selected properties of sintered α-Al_2O_3.

Properties	Unit
Density (g/cc)	3.97–3.99
Shear modulus (GPa)	161–164
Elastic modulus (GPa)	380–405
Flexural strength (MPa)	150–450
Hardness Vickers (GPa)	15–19
Fracture toughness ($MPa \cdot m^{1/2}$)	3.5–6
Tensile strength (MPa)	267
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	30–40

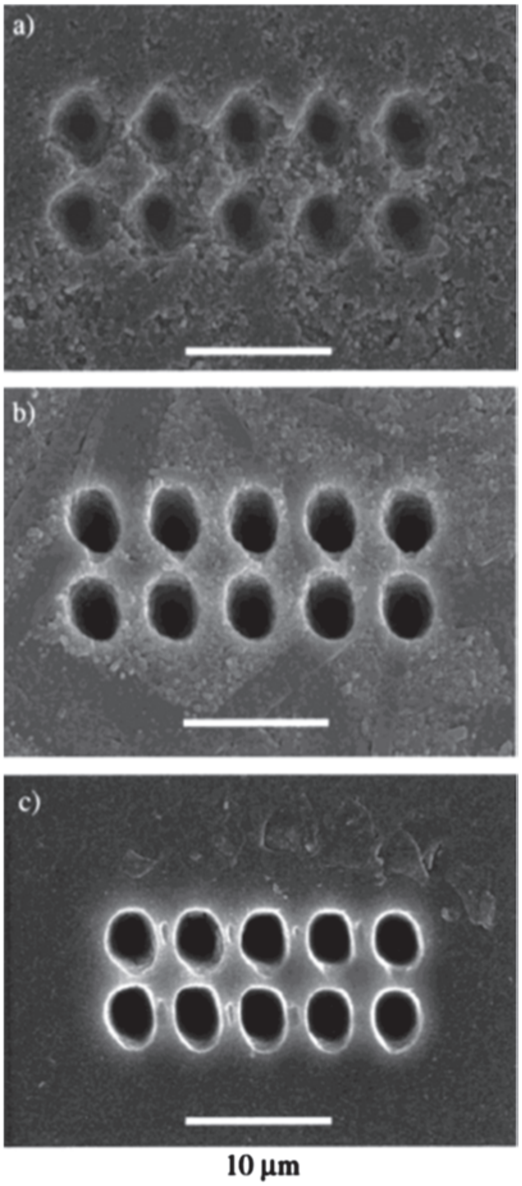

Figure 22. Ceramic cavities fabricated with an average diameter of (a) 0.5 μm, (b) 0.2 μm, (c) 45 nm. Reprinted with permission from [211], U. P. Schonholzer, et al., Microfabrication of ceramics by filling of photoresist molds. *Advanced Materials*, (2000). © 2000, John Wiley and Sons.

introduced by Schonholzer et al. [210, 211]. Figure 22 shows a formed structure using a photoresist mold. Samples fabricated in this research reached the full density and shrinkage of 15%. The effect of particle size on the ceramic components feature resolution is investigated only in cavities.

Hassanin et al. [212] studied also the influence of powder size on the colloidal ceramic suspension, and ceramic microcomponents properties using three powder sizes. They studied the stability of the prepared ceramic suspensions as a function of dispersant amount. They also studied the dried and fired sample properties in terms of shrinkage, surface morphology and hardness properties. They found that the axial shrinkage of the micro parts increased with decreasing of the particle size. In addition, the part resolution, shape retention and surface roughness depend on the starting material. As the particle size decrease, the micro parts resolution and the surface roughness improve; see Figure 23.

Jin et al. developed alumina microcomponents using soft lithography and using PDMA soft mold [213]. A high concentration alumina suspension of 84% wt was used in filling the molds. A microcomponent with aspect ratio of 10 was produced and 17% linear shrinkage was recognized. Moreover, Zhu et al. also produced alumina microcomponents using PDMA elastomeric molds [214]. They investigated the rheological properties (zeta potential and viscosity) of aqueous alumina suspensions at variable pH values and dispersant concentration. The result of this investigation enabled the optimization of the alumina suspension parameters at 70% wt alumina suspension and shrinkage. Zhang et al. fabricated alumina micro three-dimensional freestanding mechanical parts using both solid mold embossing and soft mold centrifugal casting [215, 216]. A high concentration alumina suspension of 84% wt to fill the mold was used. The substrate in which the pattern was molded was fabricated from alumina and coated with a photo resist sacrificial layer. The sacrificial layer was dissolved in acetone after the formation of the green structure. Sintering the green component showed a low shrinkage percentage of 15%.

Zirconia (zirconium dioxide) is one of the polymorphic materials since it has a different structure at different temperatures, namely monoclinic, tetragonal and cubic. From room temperature and up to 1170 °C zirconia exists in monoclinic structure, from 1170 to 2370 °C zirconia structure changes to tetragonal and from 2370 °C to 2716 °C (melting point) zirconia takes the cubic structure [217, 218]. The transformation from monoclinic to tetragonal during heating up is accompanied by a 5% decrease in volume, and vice versa by cooling. These changes may result in crack formation, and this explains why pure zirconia is not suitable for crack-free applications where temperature changes.

Several oxides can be added to zirconia in order to stabilize its structure transformation. These oxides allow the generation of multiphase materials, which slow down or eliminate the crystal structure transformation. This improves its strength, enables its use in severe applications and motivates the use of stabilized zirconia as a structural material [219]. The most popular additives to zirconia are Y_2O_3, CaO and MgO.

The addition of yttria to pure zirconia formed a yttria-stabilized zirconia (YSZ) with improved mechanical and electromechanical properties. Doping zirconia with yttria Y_2O_3) replaces Zr4+ with Y3+, adds oxygen vacancies and increases the ionic conductivity [220]. For this reason, yttria-stabilized zirconia has been established as one of the most commonly used electrolyte materials for solid oxide fuel cell applications. YSZ has high corrosion resistance and low thermal conductivities which motivates the use of it in micro engines fabrication [221–223]. Some selected properties of sintered 8YSZ are presented in Table 2. These properties enable the engine to operate at higher temperatures, and enable complete fuel combustion and increased combustion efficiency.

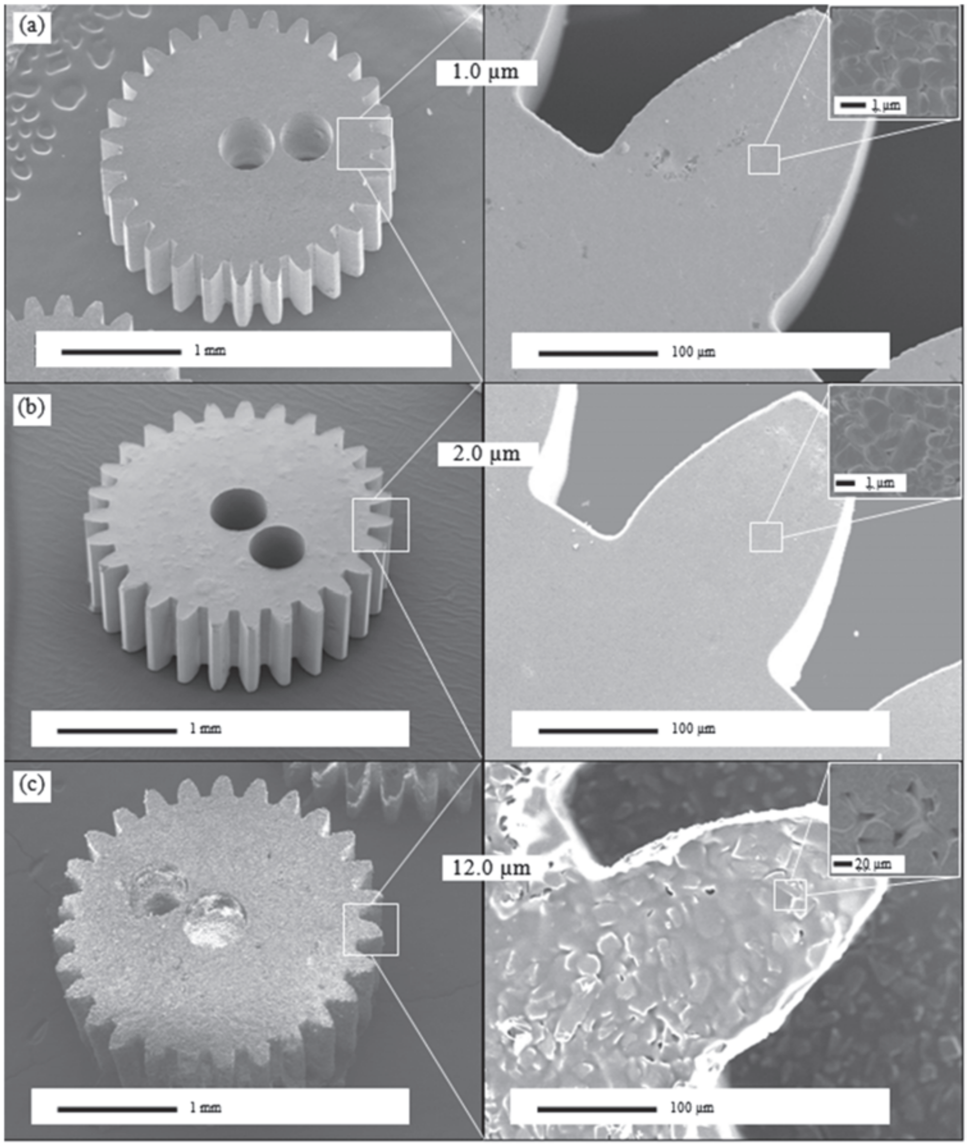

Figure 23. SEM images of ceramic micro parts using powder size of (a) 1.0 μm, (b) 2.0 μm, (c) 12.0 μm. Reprinted with permission from [212], H. Hassanin and K. Jiang, Effects of particle size on soft lithography process, the green and sintered micro alumina parts. *International Journal of Applied Ceramic Technology* 10, 1014 (2013). © 2013, John Wiley and Sons.

Piotter et al. investigated microinjection molding for fabrication of zirconia micro parts [53]. Muller and co-workers also used the microinjection molding process for fabrication of three-point bending test samples [224, 225]. They found that the effect of grain size on the strength is negligible.

Table 2. Selected properties of sintered 8YSZ [221–223].

Properties	Units
Density (g/cc)	5.953
Elastic modulus (GPa)	200
Flexural strength (MPa)	250–416
Hardness vickers (GPa)	13.8
Fracture toughness ($MPa \cdot m^{1/2}$)	1.6
Tensile strength (MPa)	276
Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)	2

Hassanin et al. [226] used a modified slip casting manufacturing technique to produce net shape zirconia micro parts. They used an optimized slip casting process as a low-cost and mass production route to obtain a smooth surface and near net shape microcomponents. The molds were prepared through the use of UV lithography and soft molding. They used a porous layer at the bottom of the mold to infiltrate the water of the applied suspension; see Figure 24.

Good shape retention and high-resolution micro features have been obtained using the modified manufacturing technique. They also studied the effect of particle size on the properties of the manufactured zirconia ceramics. They optimized the ceramic suspension and found that zirconia powder with powder mean diameter of 400 nm produced the most desired micro gears. The sintered micro parts found using this powder were about 99%, 21%, 520 MPa, 15 GPa,

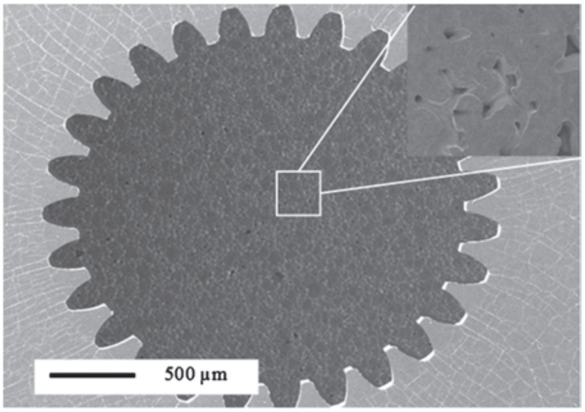

Figure 24. SEM image of PDMS through mold placed on a porous substrate. Reprinted with permission from [226], H. Hassanin and K. Jiang, Fabrication and characterization of stabilized zirconia micro parts via slip casting and soft molding. *Scripta Materialia* 69, 433 (2013). © 2013, Elsevier.

52.2 nm for the density, shrinkage, flexural strength, micro hardness and roughness, respectively; see Table 3.

Yu et al. used the microinjection molding process in the fabrication of tensile bars and 3 mm micro gears [227]. They investigated the effect of change in volumetric ratio between powder and polymeric binder (solid loading) on the sintered product density, weight loss and Vickers hardness. They also investigated the optimum process that leads to minimization of the agglomeration of the powder.

Other ceramic materials have been used in various MEMS applications. Borosilicate ceramic thin film has been used for micro gas sensor applications. The coefficient of thermal expansion of borosilicate ceramic is similar to low-temperature co-fired ceramics (LTCC), which means that the MEMS device can be manufactured using a glass cantilever fixed on a silicon or ceramic substrate [228]. SiOC ceramic microcomponents have been manufactured by the stereolithography process. They can be manufactured with a feature size of $\approx$200 μm in UV-polymerized solution, which were transformed, after firing, to SiOC microcomponents [229]. LTCC was also used as an important material for micro sensors [230], while PZT ceramics have been used for MEMS) piezoelectric gyroscope [231].

3.2. Metals

Metals are the family of materials that include metallic elements and their alloys. Metallic elements are characterized by having one, two or three free electrons at their outer valence. The outer free electrons are non-localized electrons; i.e., they are not connected to a particular atom but connected to the entire metal. These free electrons form a sea of electrons or electron cloud that are attracted to the positive ionic core forming the metallic bond. The metallic bond in metals is one of the primary bonds but it is generally less strong than ionic and covalent bonds. The different types of metals may have a range of variable properties, but metals in general are good thermal and electrical conductors, and a polished metal surface has a lustrous appearance which can be simply explained by the movement of outer free electrons in metals. In addition, metals are strong, malleable (can be pressed or hammered permanently without breaking or cracking), ductile, and many common metals are relatively cheap, therefore many metals are mainly used as a structural material in extensive applications.

Table 3. Summary of the sintered properties [226].

Particle size	400 nm	650 nm	1 μm	1.9 μm
Sintered density	98.6%	98.5%	98%	95.1
Linear shrinkage (%)	21	20.9	18.9	18.1
Vickers hardness (GPa)	14.7	14.65	14.5	14.0
Flexural strength (MPa)	497	508	315	210
Surface roughness (nm)	214.58	54.38	70.122	84.13

Source: Reprinted with permission from [212], H. Hassanin and K. Jiang, Fabrication and characterization of stabilized zirconia micro parts via slip casting and soft molding. *Scripta Materialia* 69, 433 2013. © 2013, Elsevier.

Many metals are important in their pure state such as copper, aluminium, silver and gold, but the rapid technology progress in all aspects introduces challenges and requirements for improved material properties. In metals this can be done by alloying. Alloy by definition is a metal composed of two or more elements with a minimum of one metallic element. These alloys can be either an elemental solid solution or intermediate phases. Alloying of metal enables enhancing the strength, hardness, ductility, corrosion resistance, fracture toughness and many other properties, compared with pure metals.

Metal products can be classified in terms of the manufacturing process as cast metal, wrought metals and powder metals. Cast metals are metals in which the initial form is casting. Wrought metals, in which the metal has been worked after casting, include rolling, drawing or any otherwise forming. This processing normally affects the mechanical properties of the products. Powder metals are metals in which the initial form of the metal is a powder, and manufacturing is done using powder metallurgy techniques. In the scale of nanomaterials, metals are used in many applications such as hard etch mask, thin film conducting interconnectors and structural elements in micro sensors and micro actuators. Metallic thin film can be formed using different deposition methods such as evaporation, sputtering, CVD and electroplating.

Nickel is a hard, ductile, malleable and ferromagnetic material. It also has a good thermal and electrical conductivity. In addition, it has the ability to resist most atmospheric acids. These excellent properties make it a favorable material in many MEMS applications. Nickel microchannel, microwell, micromixer, and micro gear have been successfully fabricated using centrifugal-assisted micromolding. A nickel alloy slurry with a solid loading of 85 wt% and 5 wt% PVP as the surfactant was prepared for the manufacturing process. The micro hardness was found to be improved with the increasing of sintering temperature. The maximum Vickers micro hardness and Young's modulus achieved were 167.8 HV and 175.4 GPa at a sintering temperature of 1070° [232].

Stainless steel is the one of the most commonly used materials in the MEMS industry. It has been used in the manufacture of many of the micro parts such as support bone fracture, dental devices, stents, plates, and screws.

This is because stainless steel has excellent biocompatibility and superior mechanical properties such as high mechanical strength, good ductility and excellent corrosion resistance due to the high chromium content, which increases the resistance to crevice and pitting, and allows a strong adhesion, corrosion resistance and self-healing by developing a coating oxide of Cr_2O_3 [30, 233].

Platinum is a ductile precious material that demonstrates good corrosion resistance at high temperatures. Platinum is mostly used as a catalyst material for its extraordinary chemical properties. A catalytic gas sensing system using micro heated platinum aerogel has been developed with a low power consumption [234]. Other metal materials have been successfully used in the MEMS industry such as copper, aluminium, gold and silver [235–238].

3.3. Composites

Composite materials are defined as the composition of two or more materials or physically distinct phases. The properties of this composition is different from the properties of its constituents. In composite materials, there are two types of constituents which are the matrix and reinforcement. The reinforcement material is surrounded by the matrix material, which maintains the reinforcement materials' relative position.

The most interesting in composite materials that it enables the combination of all families of materials. Using the composite material, the advantages of different materials can be combined into a new material. It also enables tailoring of a new material for specific applications. Using composite materials results in strong and stiff materials with stiffness-to-weight ratios greater than steel and aluminium, which is very desirable in many applications. The progress in the powder metallurgy fabrication process motivates the forming of ceramic metal composite materials. There are many difficulties in the joining techniques between ceramics and metals [239, 240].

In the scale of microfabrication, some applications require material properties more resistant to severe environments. Although several monolithic ceramics have many MEMS applications, there are some applications requiring material properties more resistant to severe environments. Using composite ceramics enables the creation of many new composite materials with specific properties to match challenging applications. In the case of ceramic matrix composite, the matrix is ceramic material and the embedded phase may be metallic ceramic or polymer. This embedded phase may be a particulate fiber or textile.

Composite materials have been widely used in many MEMS applications [53, 219, 221–225, 227, 241]. There are two common types of ceramic composites which have many applications in microfabrication components. The first is ceramic matrix microcomponents and the second is functionally graded ceramic composites. Electrophoretic deposition (EPD) is one of the common methods used for the fabrication of microcomponents from ceramic composite materials. Zaman et al. manufactured a boehmite/multi-wall carbon nanotube (MWCNT) composite micro gears. The matrix material is stoichiometric boehmite powder and the reinforcement material is carbon nanotubes. Aluminium acetate powders $(2Al(OH)(C_2H_3O_2)_2)$

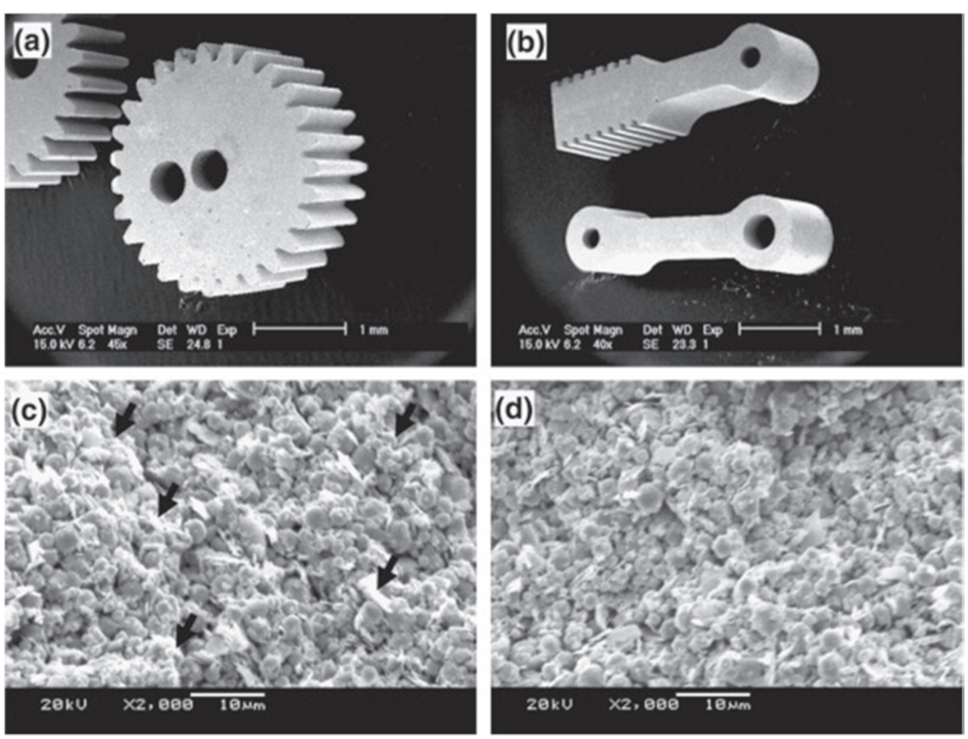

Figure 25. Composite micro parts: (a) micro gears; (b) micro pistons. Fractured surface of 10% alumina composite: (c) dispersed powders together; (d) powders dispersed separately. Reprinted with permission from [40] M. F. Imbaby and K. Jiang, Fabrication of free standing 316-L stainless steel–Al_2O_3 composite micro machine parts by soft molding. *Acta Materialia* 57, 4751 (2009). © 2009, Elsevier.

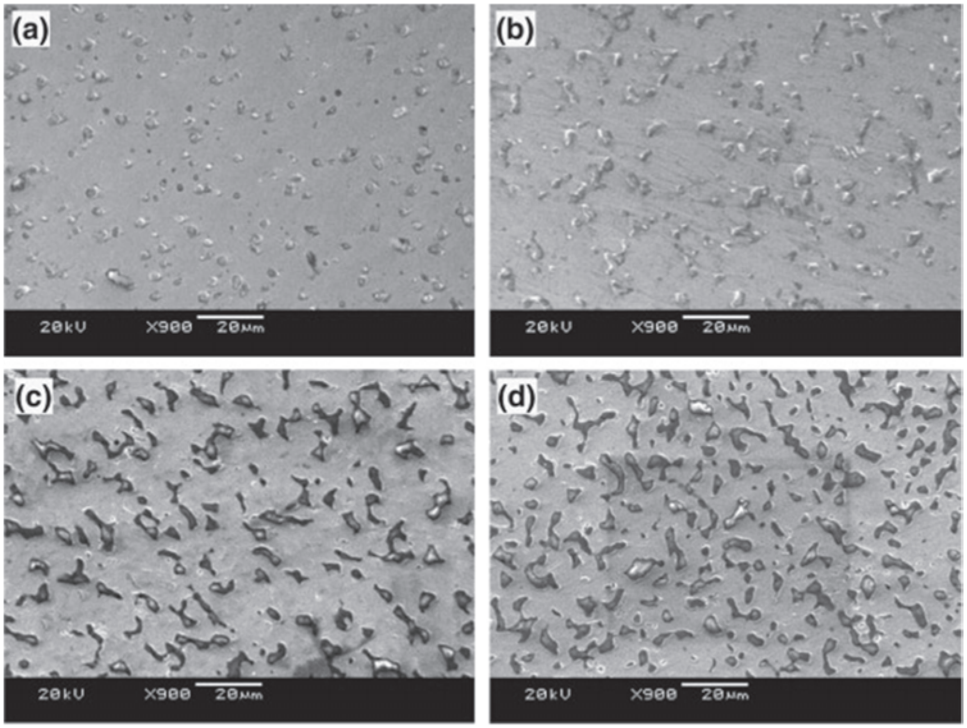

Figure 26. Composite stainless steel alumina micro parts using alumina content of (a) 2.5%; (b) 5%; (c) 7.5%; (d) 10%. Reprinted with permission from [40], M. F. Imbaby and K. Jiang, Fabrication of free standing 316-L stainless steel–Al_2O_3 composite micro machine parts by soft molding. *Acta Materialia* 57, 4751 (2009). © 2009, Elsevier.

and MWCNT are used through the hydrothermal process for preparation of boehmite/multi-wall carbon nanotube (MWCNT) composite powders. A kinetically stable suspension of MWCNT–boehmite composite powders were obtained. Small components such as micro gears were successfully fabricated using EPD technique in short time [242].

Zirconia-toughened alumina composites were investigated by Gadow et al. They used the injection molding process in formation of the microcomponents. They introduced a pressureless method for sintering. The smallest sample dimension fabricated was $0.65 \times 5.7 \times 2.8$ mm. After sintering, the samples reached approximately the theoretical density and with very fine grains by modifying the feedstock mixture ratio. The sintering temperature was 1500 °C. The sintered grain size was in the range of 0.4 to 1.4 μm, which improved the mechanical properties. However, the fabricated samples were small components in irregular shapes [243]. Silica titania composites were used for fabrication of micro gears using sol–gel casting technique [244]. Surface condensation was used to disperse and incorporate nanoscale oxide particles into the gel network. The addition of titania nanoparticles to the sols greatly reduced the volume shrinkage of gels and improved the mechanical strength of the microcomponents. Chan et al. investigated the permeability of the molds and surface properties for sol–gel casting [244]. They claimed that the produced ceramic composite micro gears have dense sidewalls because of the high quality PMMA mold. Meanwhile, the bottom surface was porous due to the impermeable bottom surface of the mold and restricted shrinkage.

Imbaby et al. fabricated stainless steel–alumina composite microcomponents using soft molding and dispersion processes. They found that optimization of the surfactant amount enhanced the density of the green parts. The work showed that the technique of mixing powders has a significant influence on the dispersion quality of the prepared slurry. The dispersion of two powders separately before the mixing process showed to improve the slurry homogeneity. The introduced approach had the ability to be applied in many composite materials for the manufacturing of net shape composite microcomponents; see Figures 25 and 26 [40, 240].

3.4. Functionally Graded Material

Functionally graded material (FGM) may be characterized by the variation in composition and structure gradually over volume, resulting in corresponding changes in the properties of the material. The materials can be designed for specific function and applications. Various approaches based on the bulk (particulate processing), preform processing, layer processing and melt processing are used to fabricate the functionally graded materials. Functionally graded composite materials (FGM) are classified as composite materials where both the composition and the structure of each material in the composite gradually vary over the volume, resulting in variable properties through the material with the dimensions [245–247]. The changes in properties may be one, two or three-dimensional.

Takagi et al. investigated the properties of the PZT/Pt composites with the aim of fabricating a PZT/Pt FGM

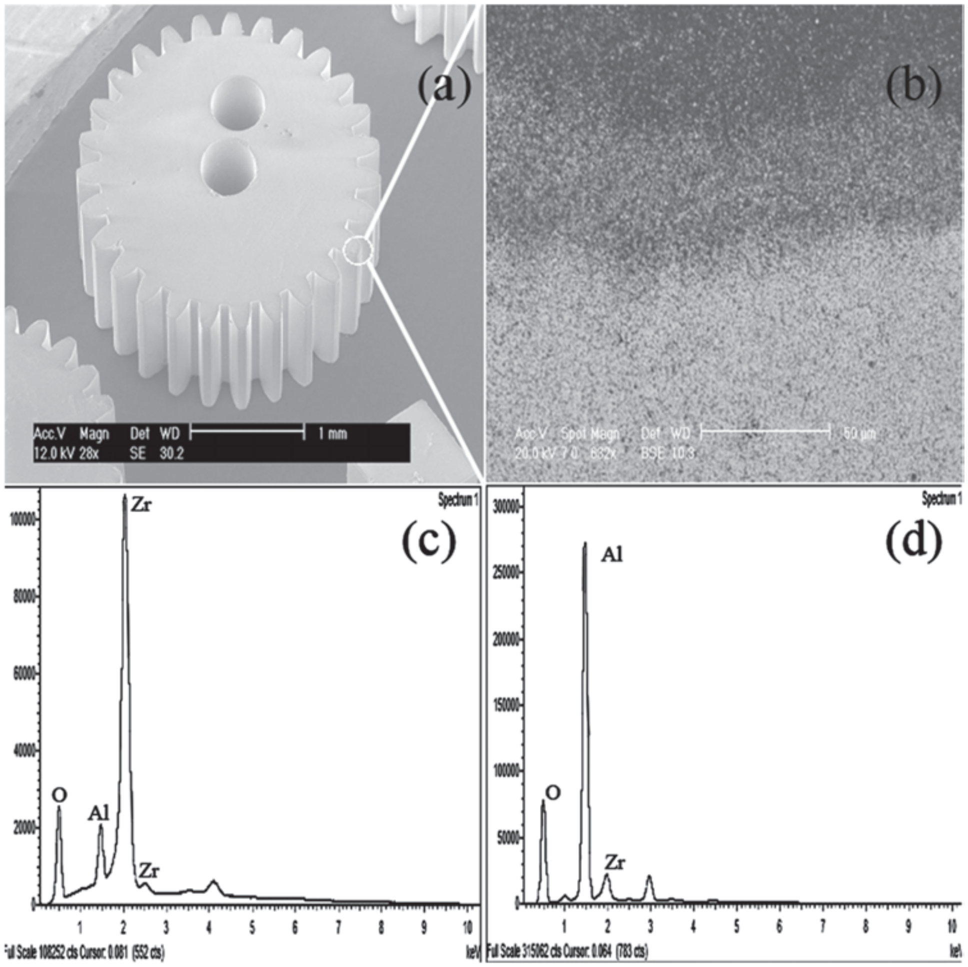

Figure 27. SEM of a FGM micro gear, (b) BSE of the interface, (c) EDS of the dark area, (D) EDS of bright area. Reprinted with permission from [46] H. Hassanin and K. Jiang, Functionally graded microceramic components. *Microelectronic Engineering* 87, 1610 (2010). © 2010, Elsevier.

bimorph with gradient microstructure for improved mechanical reliability [248]. Addition of Pt particles into the PZT matrix resulted in improving the mechanical properties of composite parts, especially the fracture toughness. Although they did not fabricate the final bimorph, but concluded that a bending-type actuator with graded microstructure from PZT to PZT/Pt composites can be manufactured by powder processing. Imgrund et al. investigated the fabrication of a combination of magnetic and non-magnetic bimetals made of 316L/17-4PH and 316L/Fe parts in millimeters scale [249, 250]. Microinjection molding technique was used for the fabrication of the microcomponents. Fine powders of 3–7 μm mixed with a wax polymer binder system were used to prepare the feedstock. Additionally, the isothermal and non-isothermal sintering properties of the moulded parts under hydrogen atmosphere were evaluated.

An alumina-zirconia FGM microcomponent has been also fabricated for its outstanding functional properties [251]. The manufacturing process began with preparing the micromolds using a modified soft lithography. Next, highly stable ceramic suspensions of each of the proposed layers were prepared using colloidal processing. The thickness of each ceramic layer was obtained by controlling the green properties of the layer. Freestanding ceramic functionally graded material micro parts were successfully manufactured, as shown in Figure 27 [46].

FGM microceramic components have been fabricated using the infiltration of not-porous zirconia micro parts. The desired porosity has been controlled by altering the colloidal powder process and the sintering temperature. The presence of silicon and carbon elements in the zirconia matrix has been shown close to the surface of the microcomponents. The approach offered a precise tool to tailor the graded materials microstructure [252].

4. CONCLUSION

The advent in micro/nano electromechanical systems (MEMS/NEMS) has been the main thrust for the development of high-performance miniaturized systems that can function as mechanical and/or electrical components. In this chapter we reviewed the main techniques for producing metal and ceramic microcomponents, including additive manufacturing methods (AM) or rapid prototyping (RP), patterning processes, subtractive processes and property modification processes. The specifications, pros and cons of each technique are also highlighted in this chapter. Additive manufacturing techniques presented in the literature include stereolithography, laser microsintering, three-dimensional printing, fused deposition modeling, laminated object manufacturing and ink jet printing. On the other hand, patterning fabrication techniques reviewed here include, injection molding, electrophoretic deposition, coextrusion and soft lithography. Subtractive techniques include etching, micro-electrical discharge machining, laser micromachining, micromachining and micromilling. Finally, property modification processes include thermal oxidation, chemical vapor deposition (CVD) and physical vapor deposition (PVD).

Among the additive manufacturing techniques, soft lithography is a reliable technology that offers a cheap and mass production strategy, with the ability to fabricate large areas for microfabrication for a wide range of materials. This set of processes represents a non-photo-lithographic technique for making micro parts and micro devices, either free-standing or on a substrate. When compared to the reported techniques, soft lithographical micro parts had high resolution, good surface finish and high-density components.

Additive manufacturing (AM) has been identified as one of the most auspicious and promising microfabrication techniques of net-shape metallic and ceramic microcomponents. AM allows the design freedom of micro parts without the need of machine tools. This permits the FEA, CFD and CAD programmers to enable excellent products. AM makes it possible to create items with internal details that fit with micro parts requirements. Moreover, AM voids post process and any additional assembly steps. AM poses reduced materials and energy, and minimizes the use of chemicals needed for etching or cleaning. Besides, AM does not require a clean room or use of expensive equipment. Nonetheless, AM products are associated with poor surface finish, placing it under considerable investigation by manufacturing scientists.

GLOSSARY

Additive Manufacturing (AM) also called 3D printing refers to a wide range of manufacturing processes used to build a three-dimensional part. In AM, layers of material are built according to a CAD file to create a part. Recently, the meaning of AM has grown to include a wide range of processes such as fused deposition modeling, selective laser melting, selective laser sintering, electron beam melting, direct laser manufacturing and others.

Computer-aided design is the utilization of computers to support the making, alteration, study, or analysis of a certain design, which help to improve the design quality and the productivity of the design chain. The output is typically in the form of computer files for manufacturing such as additive manufacturing, other machining processes, or print.

Chemical vapor deposition (CVD) involves a chemical reaction between the constituents of a vapor phase diluted with an inert carrier gas at a hot surface (typically higher than 300 °C) producing a deposited solid thin film.

Electro-forming (EF) is a patterning process to fabricate metal components by accurate accumulation of metals on the surface of an electrode. In this method, metal components can be built atom by atom, which offers high aspect ratios and high resolution.

Electrophoretic deposition (EPD) is a form of patterning fabrication in which particles of a colloidal suspension travel by the effect of an electric current and accumulateon the surface of an electrode. Electrophoretic deposition can process polymers, ceramics and metals.

Fused deposition modeling (FDM) is one of the additive manufacturing techniques, which is typically used for both prototyping and manufacturing applications. It works by building parts in layers; a plastic or metal wire is uncoiled and provides material to build a component.

Functionally graded materials (FGM) is a type of composite material which is characterized by varying the structure and composition of a part gradually over volume or length, causing changes in the behavior and performance of the material.

Focus Ion Beam (FIB) is a process used specifically in the MEMES industry for specific deposition and milling of materials. It works in a similar way as a scanning electron microscope. However, an FIB process uses a high resolution focused beam of ions, rather than an electron beam.

Jet printing (JP) is an additive manufacturing process used for building objects designed by a computer or a CAD file. An inkjet head travels across a platform or a powder bed, spraying a binder. A layer of material in a powder form is coating the surface and the process is repeated until the build is done.

Laser microsintering (LMS) is an additive manufacturing process used for building metal or ceramic parts designed by a computer or a CAD file. It is a modification of selective laser sintering or melting aiming to enhance the resolution of selective laser sintering, down to 10 μm.

Laminated Object Manufacturing (LOM) is a patterning process in which layers of plastic, metal or ceramic layer are bonded layer by layer and cut to specific shape. Parts built with this process can be machined or drilled after printing.

Microinjection molding (μIM) is a microfabrication patterning technique for producing microcomponents by injecting feedstock into a micromould. Microinjection molding has the capability to use a wide variety of materials, including plastic, metals and ceramics. The feedstock for the object is moved into a heated reservoir, blended, and injected into a mold pattern, where it allows cooling and gets sufficient strength for demolding.

Microcontact printing (μCP) is a type of soft-lithography (SL) that utilizes the micro features on a polydimethylsiloxane (PDMS) mold to form a shape of self-assembled layers of ink on the top of a substrate. It has a wide range of applications including cell biology, surface modification, and electronics.

Microtransfer molding (μTM) is a patterning process where a mold made from an elastomer material is filled with a suspension made from ceramic or polymer material and placed on a substrate. Next, the suspension is cured or dried and the stamp is demoulded. This technique can generate micro and nano features and also is able to produce multi-layer components.

Micromolding in capillaries (MIMIC) is a simple patterning process to manufacture three-dimensional micro parts of different materials. This process is based on the filling of tiny passages (capillaries) developed between two conformal surfaces with a fluid. The fluid may be a polymer or suspension to be patterned.

Physical vapor deposition (PVD) The procedure of the PVD technique involves the synthesis of the coating vapor from the source material, transport of the vapor to the substrate and condensation of vapors onto the surface of the substrate.

Replica molding (REM) is a simple patterning process for building different materials using a micro mould. This mold is made by casting an elastomer from the master mould. The mold is then filled with a suspension, which is dried or cured and demoulded.

Solvent-assisted micromolding (SAMIM) is a patterning process for building different materials. The principle of this method combines both replica molding and embossing. SAMIM works by wetting of the elastomer mold with a solvent. The solvent fills the cavities on the mold surface to minimize the contact part of the liquid/vapor interface.

Scanning electron microscope (SEM) is one type of electron microscope that delivers micrographs by scanning a part with a focused electron beam. The electrons hit the sample atoms, constructing different signals that can be received and identified, and that include information of the sample's topography characteristics.

Stereolithography (SLA) is a type of additive manufacturing processes, which is used for creating prototypes and making parts layer-by-layer using photo-polymerization of a photosensitive liquid.

Thermal oxidation involves the generation of a thin layer of oxide usually used for semiconductor applications. The thermal oxidation of silicon is usually carried out in a water vapor or oxygen atmosphere over the temperature range 700–1250 °C.

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