2
Metallic, Steel, Ceramic and Plastic Microreactors

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2.1
Introduction

The material used to manufacture microreactors is heavily dependent on the desired application. Here, the application temperature range, the corrosivity of the fluids used, need for catalyst integration or to avoid catalytic blind activities, the absolute pressure, thermal conductivity, specific heat capacity, electrical properties and some other parameters have a large influence to the choice of material. The design of the microstructures itself also has to be considered; some specific designs are only achievable with, e.g., metals because a certain manufacturing technique is required. Moreover, depending on the number of devices needed, some manufacturing techniques are suitable, but others are not. In this chapter, the fabrication of microstructure components and devices out of metals, steels, ceramics and polymers will be described, together with bonding, sealing and packaging of devices. Manufacturing processes for metal microstructure components, ceramic microstructures and microstructures made of certain polymers are described, setting the focus to some established technologies. The technologies are not described in detail; detailed information can be found elsewhere [1–5]. For each material there is a very short bonding section, in which the most common bonding and sealing techniques are briefly described [4, 6].

Two different constitutional manufacturing technologies can be performed with all materials considered here: erosive and generative manufacturing. All technologies such as embossing or molding are considered to be included in generative techniques, whereas processes such as punching can be (but are not necessarily) abrasive and are definitely non-generative processes – they just form out the material to a certain way, standing in between the manufacturing processes. Nevertheless, they will be described together with punching in Section 2.2.4.

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2.2 Manufacturing Techniques for Metals

Metals and metal alloys are mostly used for conventional devices in process engineering, thus it is the same in microprocess technology. The material range is set from noble metals such as gold, silver, platinum, rhodium and palladium via stainless steel to copper, aluminum and Ni based alloys [1, 4–6]. Most manufacturing technologies for metallic microstructures have their roots either in silicon device production or conventional precision machining. The processes well known from those techniques have been tried out for microstructure dimensions, adapted and improved to reach the desired precision and surface quality. Rarely was it possible to use the same manufacturing process for macroscale and microscale devices to obtain sufficient results. In most cases, more or less strong changes within the design of the device, the methodology of the process and the manufacturing process itself were necessary to provide the accuracy and quality needed for microstructure devices suitable for process or reaction engineering. Almost all techniques used for microstructures in metal are abrasive, so techniques such as punching are considered to be non-abrasive, but also non-generative. As mentioned above, they belong to the metal forming technologies and some remarks about them are included in this section.

2.2.1 Etching

Etching techniques are well known from silicon technology. For many metals, etching is a cheap and well-established technology to obtain free form structures with dimensions in the sub-millimeter range. The technology is well described in the literature [1–5, 7]. A photosensitive polymer mask material is applied to the metal to be etched, and the mask is exposed to light via a structure primary mask. Then the polymer is developed and the parts to be etched are removed and etched. When etching techniques are used, two main points have to be considered. First, the aspect ratio (the ratio of structure width to structure depth) can only be <0.5 at the optimum for wet chemical etching. Due to isotropic wet chemical etching, the minimum width of a structure is twice the depth, plus the width of the mask openings. This is not the case for dry etching technologies such as reactive ion etching (RIE), where aspect ratios larger than 0.5 can be reached. However, these techniques are used only rarely to machine metal microstructures. More details of the principal processes can be found in [1].

Second, wet chemical etching always results in semi-elliptical or semi-circular structures with fairly high surface roughness (in the range of several microns), again due to the isotropic etching. In Figure 2.1, a stainless-steel microchannel structure manufactured by wet chemical etching is shown. The sinusoidal microchannels are used for heat exchangers. They are about 150 μm wide and 70 μm deep. Figure 2.2 shows a detail of the face area of such a microchannel. The semi-circular structure is clearly seen. Details on the etching processes and etchants can be found elsewhere [1, 4, 7, 8].

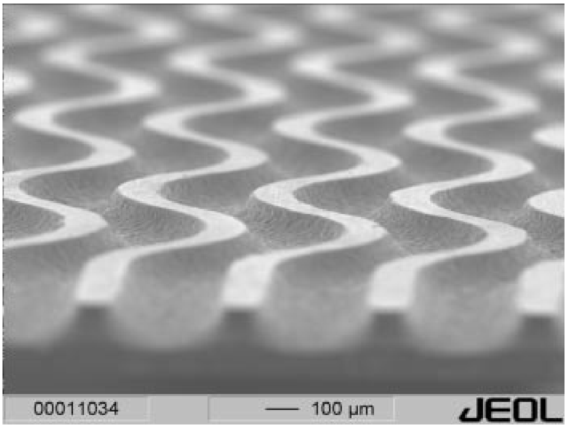

Figure 2.1 Sinusoidal microchannels etched in stainless steel. The channels are about 150 µm wide and 60 µm deep.

Another application of etching is the so-called lamination process [9, 10]. Here, thin metal plates are chemically etched to form patterns. The thin strips are then stacked in a specific arrangement to form the desired microstructure and bonded. This technology is well adapted for mass production and very cost effective. A detailed description can be found in [11]. This shim or sheet technology has become very popular for its easy application and many possibilities for more or less free design. In addition to chemical etching, spark erosion techniques (see below) and even punching have been tried for manufacturing single lamination sheets. Details on this and other manufacturing processes can be found in [12, 13]. Figures on laminated microreactors are given in [12].

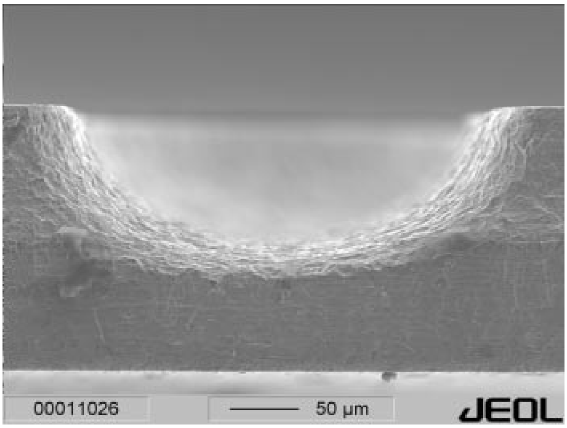

Figure 2.2 Detailed view of the face area of an etched microchannel in stainless steel. The semi-elliptical shape can be clearly seen.

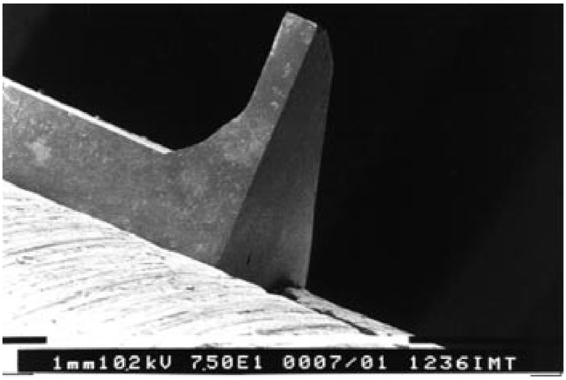

Figure 2.3 Natural diamond tool for precision micromachining.

2.2.2 Machining

Not all materials can be etched; especially noble metals are stable against this corrosive structuring method. Hence precision machining may be used to generate microstructures from noble metals and also standard metal alloys such as stainless steel. Depending on the material, precision machining can be performed by spark erosion (wire spark erosion, countersunk spark erosion), laser machining or mechanical precision machining. In this case, mechanical precision machining means milling, drilling, slotting and planing, comparable to the techniques well known in conventional dimension machining. Whereas spark erosion and laser machining are suitable for any metal, the use of mechanical precision machining and the tools suitable for this job depend on the stability of the alloy. For brass and copper, natural diamond microtools are suitable, whereas for stainless steel and nickel-based alloys hard metal tools are needed. In Figure 2.3, a natural diamond cutter is shown, and Figure 2.4 shows a hard metal drill. Figure 2.5 shows photographs of a rhodium

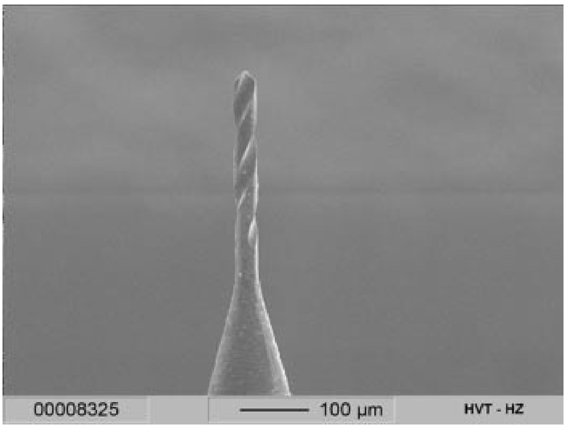

Figure 2.4 Hard metal drill for mechanical precision machining.

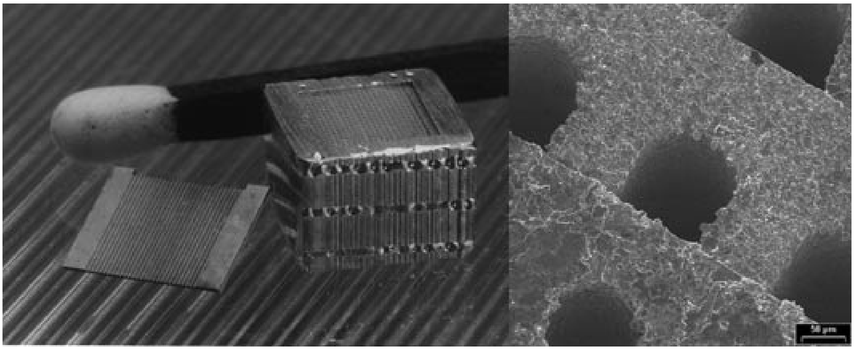

Figure 2.5 Honeycomb catalyst made of microstructured rhodium foils. The single foils (left) have been machined by wire spark erosion and then bonded to form the honeycomb (center, right: SEM).

honeycomb microchannel catalyst system. The channels have been machined by wire spark erosion, as can bee seen in the detailed picture on the right.

The surface quality achieved with these techniques varies widely, depending on the material and on the machining parameters. Spark erosion techniques lead to a rough surface. The surface quality obtained with laser ablation depends heavily on the material to be structured and on the correct parameter settings. Figure 2.6 shows results of laser ablation obtained in stainless steel by using incorrect parameters.

With copper or brass as base material, the best surface quality is obtained with mechanical precision machining, followed by an electropolishing step. By this means, a surface roughness of down to 30 nm can be reached. Figure 2.7 shows the surface of a single OF copper microchannel after the electropolishing step. For all techniques, details can be found in [1, 4, 14–20].

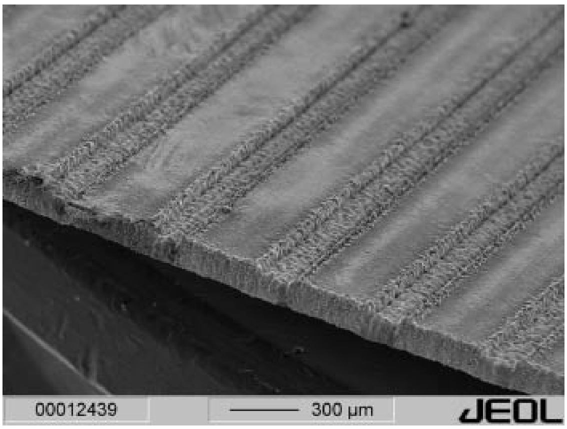

Figure 2.6 Laser ablation in a stainless-steel foil. The machining was performed with incorrect laser parameter settings.

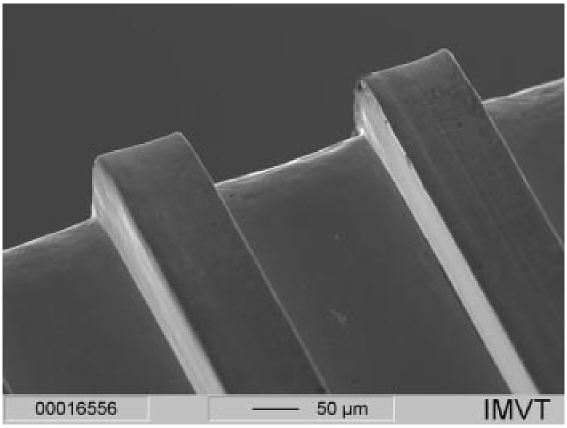

Figure 2.7 Microchannel machined in OF copper. The very high surface quality is obvious.

2.2.3
Generative Method: Selective Laser Melting

A special method to manufacture microstructures is selective laser melting (SLM). This is one of the rare generative methods and is considered to be a rapid prototyping technology. The technique is completely different to the abrasive techniques described so far. A metal powder is distributed on a base platform made of the desired metal material. A focused laser beam is run along structure lines given by a 3D CAD model and controlled by a computer. During the laser exposure, the metal powder is melted, forming a welding bead. After generating a first layer of beads, the platform is lowered by a certain value, new powder is distributed and the process repeated. Thus, microstructures are generated layer by layer. In principle, any metal powder can be used for SLM, provided that the melting temperature can be reached with the laser focus. Details of this relatively new technology can be found in [21–23]. In Figure 2.8,

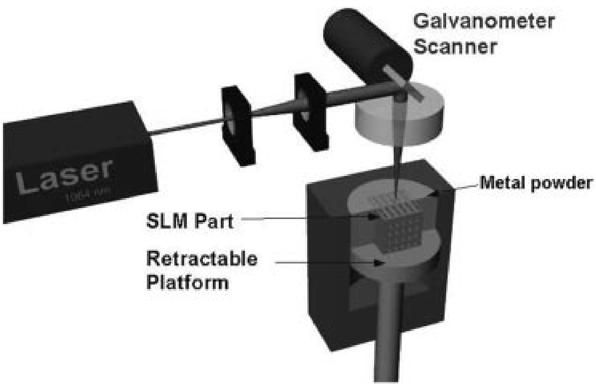

Figure 2.8 Scheme of the SLM process.

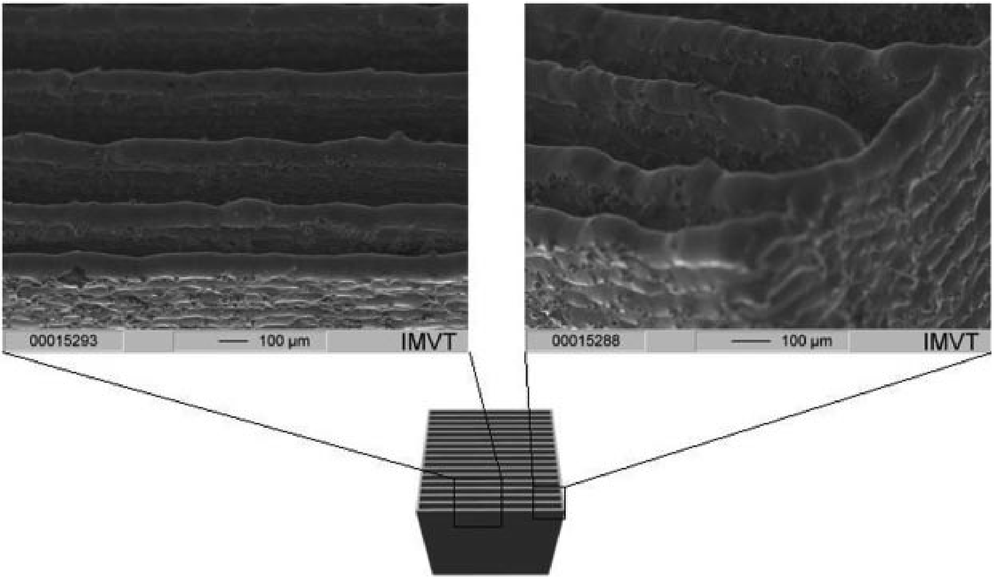

Figure 2.9 CAD model of a microstructured cube (bottom) and SEM images (top) of the inner and outer walls of this cube, manufactured by SLM.

a schematic diagram shows the working principle of this technique, and Figure 2.9 shows a microstructured stainless-steel cube manufactured by SLM.

2.2.4
Metal Forming Techniques

Almost all technologies described so far are suitable for prototyping or small series production only. It simply takes a lot of time to manufacture large numbers of microstructures by laser ablation or wire erosion, by milling or SLM. This is not the case for etching: Here, large numbers of microstructure devices are very easy to generate.

Another possibility for obtaining large numbers of microstructures is embossing. As has been shown [24], even microstructures down to a few tens of micrometers can be easily achieved with embossing technology. In Figure 2.10, a microchannel metal foil is shown. The channels were manufactured by embossing technology.

To create not only channels but also holes and throughputs, punching is a good technique even for microstructures. The key to this technology is a precise negative model, which can be manufactured by, e.g., precision machining or spark erosion techniques. In such a model, structures of different heights can be included to allow the very efficient mass production of microstructured metal sheets with holes, slits and openings combined with more conventional structures such as channels and voids within a single working step. Hence punching and embossing are now attracting increasing attention for cheap and easy series production of device parts.

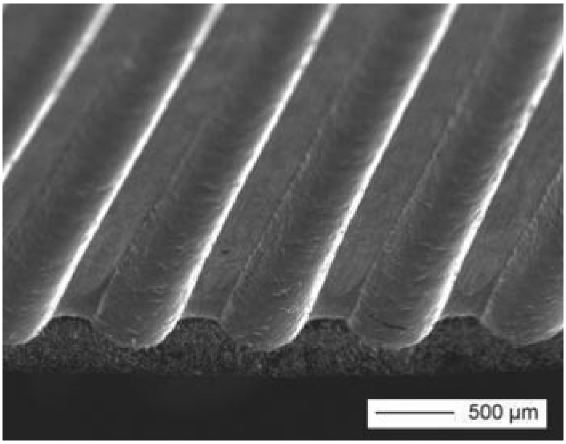

Figure 2.10 Microchannels manufactured in a stainless-steel foil by embossing.

2.2.5
Assembling and Bonding of Metal Microstructures

Although assembling of a number of device parts is not really a problem in the macroscale world, on the microscale this step is more delicate. The main point is the adjustment and alignment accuracy of the parts, in addition to sealing, fixation and bonding technology problems. Depending on the surface quality and the bonding technology applied, aligning errors may reach similar dimensions to the microstructures themselves! An example is shown in Figure 2.11. Here, a number of microstructured foils with wet chemically etched microchannels have been aligned to form fully elliptical channels. Misalignment will lead to non-regular channels and therefore may interfere with the bonding technique. A correct alignment will lead to only small deviations from the desired elliptical shape and the distortion while

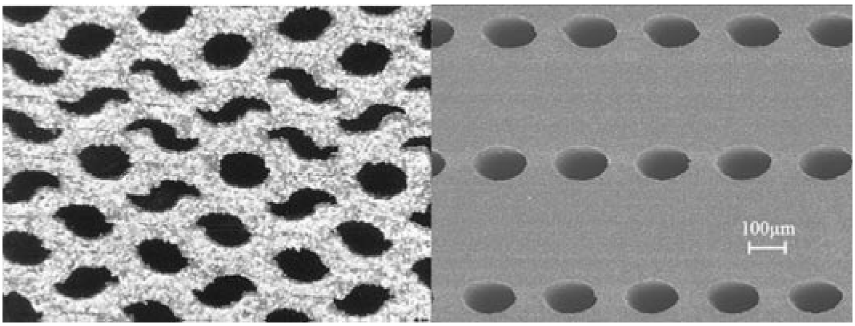

Figure 2.11 Left: incorrect alignment of etched microstructure foils lead to non-elliptical microchannels after diffusion bonding. Right: correct alignment, where the etched foils form fully elliptical microchannels.

bonding will be small. Alignment techniques used to avoid errors can be simple mechanical methods (e.g. use of alignment pins), edge-catches in a specially designed assembling device or optical methods. Most of these methods come from silicon processing technology, where precise alignment of multiple mask layers is needed to guarantee the functionality of the manufactured devices [1, 3].

On the microscale, burr formation generated by mechanical micromachining or laser machining may lead to significant problems with the assembly of device parts and also with the bonding. Therefore, special attention has to be paid to burr microstructures or to avoid burr formation.

Bonding of metals can be performed by various techniques. Common for microstructures is welding (laser, e-beam, WYG), brazing, diffusion bonding and either low- or high-temperature soldering. Even gluing and clamping, including different sealing techniques, might be options. Details to the processes can be found in [1, 2, 4, 5, 25–33]. It is obvious that the choice of the bonding technique has to be made depending on the process parameters that the device needs to handle later on. It is not possible to run a device bonded by low-temperature soldering at several hundred degrees, now will a glued device withstand an absolute pressure of several hundred bar.

2.3 Ceramic and Glass Devices

Microstructure devices made from ceramics and glass can be applied for process parameters which cannot be reached with either metals or polymers. Tolerance of high temperatures of up to more than 1000 °C, no catalytic blind activity and some easy ways to integrate catalytically active materials make ceramic a very interesting material. Glass is chemically resistant to almost all chemicals and also provides good resistivity at elevated temperatures. In addition, optical transparency of glass leads to some very interesting possibilities, such as photochemistry or a closer look inside several fluid dynamic and process parameters with on-line analytical methods using optical fibers. Nevertheless, microfabrication of components made from glass and ceramics is limited to some known technologies and, therefore, not very cost efficient.

2.3.1 Ceramic Devices

The conventional way to obtain ceramic microstructures is to prepare a feedstock or a slurry, fluid or plastic molding, injection molding or casting (CIM, HPIM, tape casting), de-molding, de-binding and sintering. Most ceramic materials will shrink during the sintering process, so there has to be a certain tolerance to the dimensions. Solid free-form techniques such as printing, fused deposition and stereolithography are also possible with ceramic slurries. There are certain ceramic materials which can be mechanically machined. Details of this manufacturing

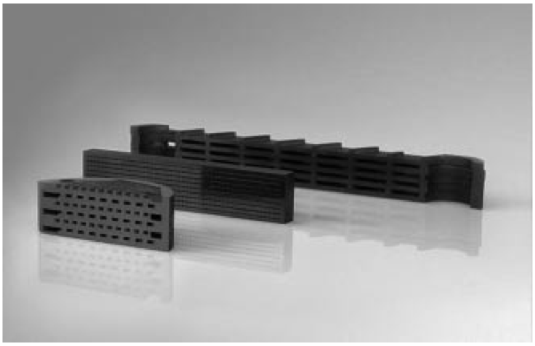

Figure 2.12 Ceramic microstructure devices. Source: ESK, Kempten, Germany; www.esk.com.

processes can be found elsewhere [6, 34–45]. In Figure 2.12, ceramic microstructure devices are shown [46].

In the last year, the application of selective laser melting (SLM) to ceramics has also been tried, and proved to work. The principle of this technique was described above. First preliminary experiments showed promising results [23].

Independently of the manufacturing process, the grain size of the ceramic powder used to generate the precursor or the slurry has to be small enough to reproduce precisely all details of the desired microstructure. Even after sintering, which is normally accompanied by coarsening of the grain size, the grains should be at least one order of magnitude smaller than the smallest dimension of the device. Additives also play an important role in the manufacturing process. Removing additives in a wrong way may lead to distortions and cracks or even to de-binding of microscopic parts of the desired microstructured device. Densification of the material is achieved by sintering, for alumina at a temperature of e.g. about 1600 °C, whereas zirconia needs temperatures of only around 1500 °C.

The most critical point is the correct microstructure design: due to the specific properties of ceramics, it is not suitable simply to transfer the design of metallic or polymer devices to a ceramic. Special needs for sealing, assembling and joining and also for interconnections to metal devices have to be considered. Moreover, guidelines for micrometer design are still lacking and experience obtained with macroscopic devices cannot be transferred directly to the microscale [6].

Another possibility for the application of ceramic materials is the use of coatings and foams inside, e.g., metallic microstructure devices. Here, well-known technologies such as CVD processes, sputtering, electrophoretic deposition, sol–gel methods in combinations with spin coating or dip coating or wash coating methods and the use of anodic oxidation for aluminum-based devices will lead to either dense, protective ceramic coatings or to porous layers used as catalyst supports. In Figure 2.13, an example of a sol–gel layer is given. Figure 2.14 shows a porous layer obtained by anodic oxidation.

Ceramic foams can be inserted into microstructured devices made from metals and polymers to enhance the surface area, act as catalyst supports or even work as heaters. Details of these processes can be found in [34–47].

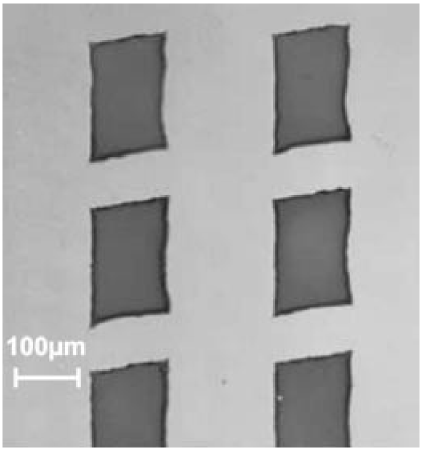

Figure 2.13 Microchannels covered by an alumina layer obtained with the sol–gel technique.

2.3.1.1 **Joining and Sealing**

Joining of ceramic materials should only involve materials with similar properties. Especially the thermal expansion coefficient is a crucial point when either joining ceramic materials to each other or, even worse, joining ceramics to metals. Figure 2.15 shows an example of a ceramic microstructure device connected to metal flanges and fittings.

Ideally, joining of ceramics to each other is done in the green state before firing. While the firing process takes place, the ceramic is bound together tightly to form a single ceramic body from all parts. Another possibility is soldering with, e.g., glass–ceramic sealants. Here, the working temperature of the device is limited by

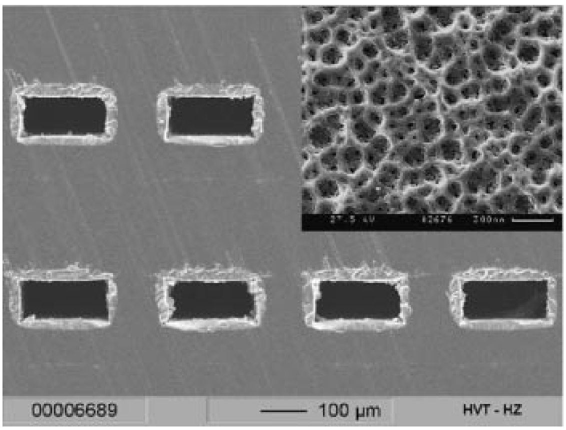

Figure 2.14 Porous alumina layer inside microchannels in an aluminum microstructured device. The porous layer was obtained by anodic oxidation.

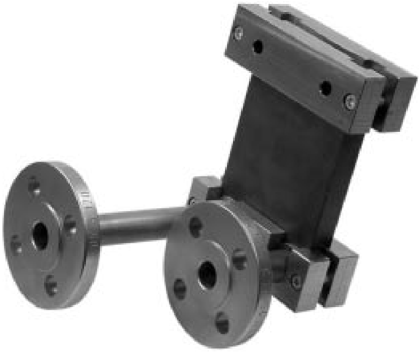

Figure 2.15 Ceramic microstructure device connected to flange fittings. Source: ESK, Kempten, Germany; www.esk.com.

the melting temperature of the sealant. Reversible assembling and sealing with clamping technologies or gluing is also possible. Conventional seals such as polymer O-rings or metal gaskets may be used as in metal technology. The adaptation of ceramic microstructure devices to metallic process equipment should be done as far away from high temperatures as possible. Due to the very different thermal expansion coefficients of the two material classes, problems will most likely occur here. Then the sealing used should be designed to minimize tensile stresses as far as possible. For more details, see [1, 6, 34–47].

2.3.2 Glass Devices

Glass as a material for microstructured devices is especially of interest due to its high chemical resistivity and optical transparency. There are not many techniques available to microstructure glass [6, 48]. The most common are wet chemical (isotropic) etching using hydrofluoric acid and sandblasting. Apart from these two, photosensitive glass is available which is structured either by exposure to UV radiation and a subsequent etching step or by laser patterning. In both cases, a photochemical reaction takes place, changing the structure of the exposed glass areas to be dissolved later in HF. The exposed area is etched faster than the non-exposed area. Whereas for photosensitive glasses such as Foturan an etch mask is needed, laser patterning can be performed by a pulsed UV laser without a mask but controlled by a CAD model – similarly to the stereolithography described earlier [48–50]. An example of a device is shown in Figure 2.16.

Bonding of glass devices is slightly easier than with ceramics. Bonding between glass parts of single devices can be done by diffusion bonding, anodic bonding, soldering or gluing. Connections to non-glass materials such as ceramic, silicon or metal are done by anodic bonding, gluing, sputtering or electroforming. Again, the most critical point is the thermal expansion coefficient, which differs between the materials to be bonded. Hence the same remarks as mentioned above for ceramics are valid [48, 49].

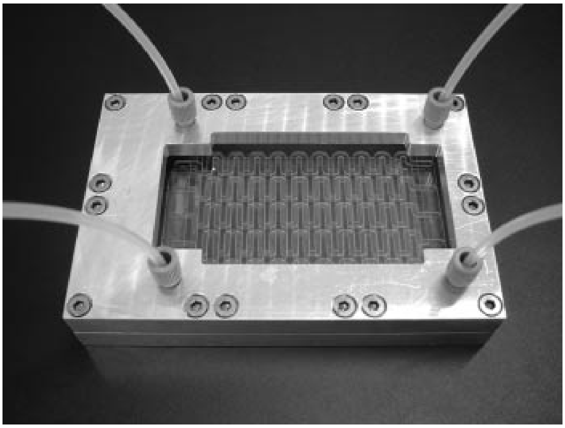

Figure 2.16 Residence time module made of glass. Source: mikroglas GmbH; www.mikroglas.de/index_e.html.

2.4 Polymer Microreactors

Polymer materials are widely used in conventional process engineering. Hence it is an option to think about the possibilities of applying polymers to microstructured devices or to manufacture those devices completely from polymers. It is obvious that the use of polymer devices is much more dependent on the parameters of the process to which the device will be applied than for any other material. High temperatures normally prevent the use of polymers, although there are some high-tech polymeric materials to withstand temperatures up to 400 °C and more. High pressures may also be a reason not to use plastic materials, and also the use of solvents not suitable for the polymeric material. Hence it is much more complicated to apply plastic materials to process engineering than other material classes, especially since it is not trivial to integrate catalytically active sites into a polymer device. Therefore, most applications of polymer microstructured reactors come from biotechnology and medical research and development, where the low temperature and low pressure resistance is not disadvantageous, but the cheap mass production possibilities are advantages for the generation of single-use units. Another major advantage of polymeric materials is often the optical transparency, useful for application in various analytical methods [51–55].

Various manufacturing techniques for polymers are known in conventional macroscale techniques. Again, two possibilities of processing have to be considered, abrasive techniques (machining, laser ablation) and generative techniques (embossing, injection molding, microstereolithography), which will not be separated strictly in this discussion.

Mostly used are injection molding and hot embossing. Both technologies are also common for microscale devices. These two manufacturing techniques are very well established to the mass and series production of devices [1, 6, 51–55]. In Figure 2.17, a so-called biodisk is shown, generated in large numbers by injection molding. The

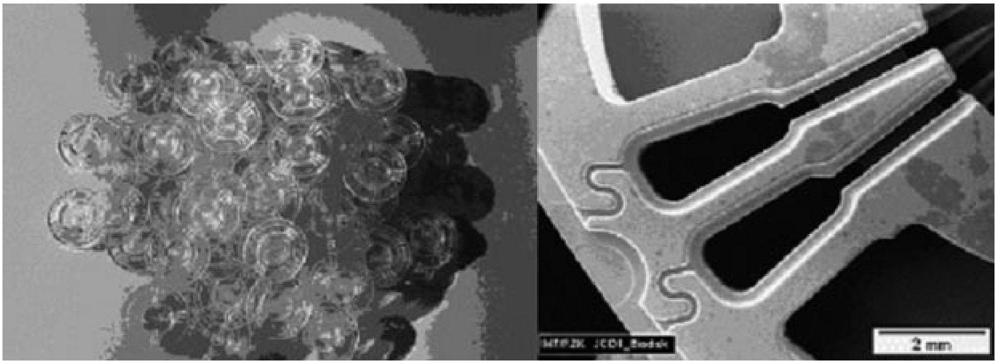

Figure 2.17 Left: Biodisk, injection molded in PMMA. Right: SEM detail of the Biodisk.

material used is poly(methyl methacrylate) (PMMA), and the mold insert was manufactured from brass by precision machining.

In addition to the manufacturing techniques described so far, there are some others that are not so common, especially not for mass production. Among them, the best known is laser machining. Different possibilities exist, mostly excimer or UV–Nd:YAG lasers pulsed at high frequencies [56–58].

Another very interesting technology for the generation of small numbers of prototypes is microstereolithography [59–62]. Like the SLM process described above, it is based on the layer-by-layer generation of microstructures due to exposure of photosensitive monomer plastic to a focused low-power laser with the desired wavelength. The exposure leads to polymerization and, therefore, to polymer microstructure walls. After the generation of one layer, the base platform used to build the device on is lowered by a specific value and flooded with the monomer again. The next layer can then be generated. The laser focusing is controlled by a computer, following the lines of a 3D CAD model. In Figure 2.18, a microstructured device made by microstereolithography is shown. The polymer used here is stable up to a temperature of about 100 °C and is more or less optically transparent.

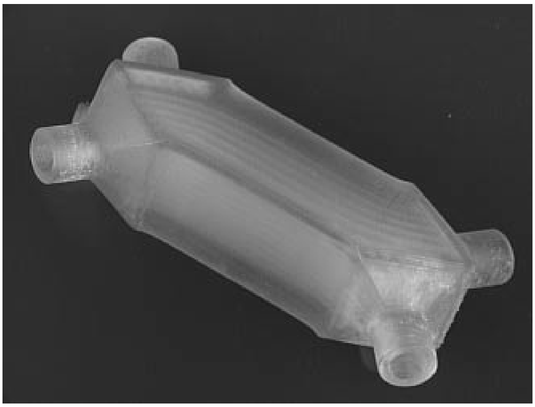

Figure 2.18 Counterflow design microstructured heat exchanger made by microstereolithography.

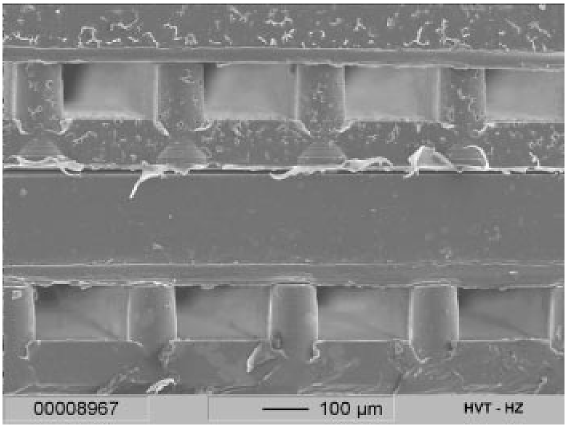

Figure 2.19 Stack of poly(vinylidene fluoride) foils after a welding step. Welding was not performed correctly, hence the stack shows a gap right in the center of the structures.

2.4.1
Bonding of Polymer Materials

Various techniques are possible for bonding polymer materials. There are different opportunities for gluing and welding. Whereas the gluing method depends heavily on the polymer used, welding methods such as ultrasonic welding, laser welding and solution welding can, in principle, be performed with all polymer materials. In Figure 2.19, a stack of poly(vinylidene fluoride) foils is shown after a welding step. Details of the joining and sealing processes can be found in [6, 63–71].

2.5
Conclusion

Manufacturing of microreactors from metals, ceramics and plastic was described briefly. The material for the microreactor is chosen in consistence to the process demands as well as with regard to the number of microreactors to be produced. The most common techniques for different material classes—metals, ceramic and glass as well as polymers - have been described or referenced. Aspects like assembling, bonding and sealing have also been integrated into this chapter. However, it is not exhaustive.

In most cases nowadays only a small number of devices is manufactured. Therefore, techniques like mechanical machining and the corresponding bonding techniques can be used as described here. In future applications mass production of microreactors might be necessary. Then, some of the production processes described in this chapter will not be suitable anymore, while others may be better suited and gain in advertence. This is especially true for assembling, sealing and bonding. Here, future developments will most likely show major impact onto the production of microreactors.

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