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Review Article

Manufacturing of Metallic Microreactor for High Pressure and High Temperature Application-Review

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Abstract

Microreactors are devices with reduced characteristic dimensions for performing chemical reactions. Their dimensions are much lower than conventional reactors classically in the sub-millimeter range. Microreactors occupy less space and enable much more controlled processes than conventional macro-scale reactors. Due to their small characteristic length, the flow inside microreactors is typically laminar, which makes the hydrodynamic characteristics well defined and controllable. Hence Reactions such as direct fluorinations, with a high exothermic nature, explosion risks and hazardous/toxic chemicals can be performed in microreactors.. The objective of this work is to manufacture metallic microreactor for high pressure and high temperature application for the production of hydrogen iodide (HI). Proposed work is to manufacture microreactor by using spray etching process which will reduce the overall cost of the microreactor. This microreactor will be extremely useful in pharmaceutical companies and organic chemistry.

Keywords: *Microreactors, pharmaceutical companies etc.*

Introduction

A microreactor is a device in which chemical reactions take place in a confinement with typical lateral dimensions below 1 mm; the most typical form of such confinement are microchannels. The microreactor is usually a continuous flow reactor (contrast with/to a batch reactor). Microreactors are normally operated continuously. This allows the subsequent processing of unstable intermediates and avoids typical batch workup delays (Haswell, 2000)(Jensen, 2001).

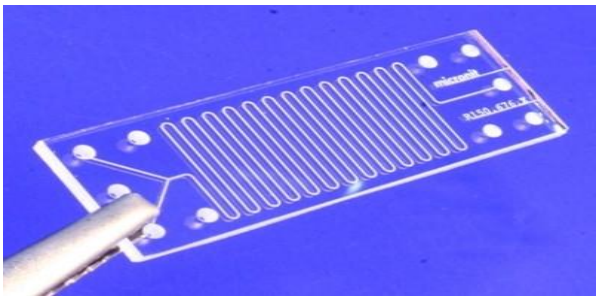

Figure 1 Microreactor

Especially low temperature chemistry with reaction times in the millisecond to second range are no longer stored for hours until dosing of reagents is finished and the next reaction step may be performed. This rapid work avoids decay of precious intermediates and often allows better selectivities.

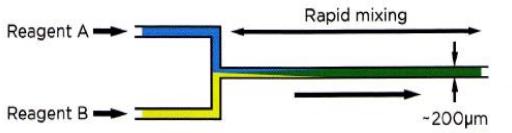

Figure 2 Diffusion mixing in microreactors

Continuous operation and mixing causes a very different concentration profile when compared with a batch process. In a batch, reagent A is filled in and reagent B is slowly added. Thus, B encounters initially a high excess of A. In a microreactor, A and B are mixed nearly instantly and B won't be exposed to a large excess of A. Pressurisation of materials within microreactors (and associated components) is generally easier than with traditional batch reactors. This allows reactions to be increased in rate by raising the temperature beyond the boiling point of the solvent. Pressurisation may also allow dissolution of reactant gasses within the flow stream(Benke, 2014).

Materials Used

Silicon: It has excellent mechanical strength and temperature characteristics, and it has good chemical

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compatibility characteristics. Oxidation of silicon leads to the formation of a glass layer on the surface so that an oxidized silicon microreactor becomes functionally equivalent to a glass reactor. For cases where silicon or glass lacks the necessary chemical resistance such as for fluorination reactions, it is possible to deposit protective coatings(Pattekar, 2004).

*Glass***:** Microreactors provides Optical transparency for analytics or applications in Photochemistry, Chemical stability to handle aggressive chemicals, Good heat resistivity for applications at higher temperature (Junkers, 2004).

Manufacturing techniques for microreactors

Photolithography and wet etching

The simplest generic procedure is illustrated in Fig. 1 and shows a schematic representation of the procedures involved. The substrate is first coated in a layer vapour deposited metal eg. Chromium,a few hundred a thick on top of which a photoresist layer is spincoated. The required channel configuration is prepared in mask form.By exposing the photoresist to an UV light source with the mask covering the chip, it is possible to transfer the desired pattern to the chip.The exposed photoresist is then removed and the bare metal layer etched away. The desired channel pattern is now mark out on the surface on the chip in terms of expose substrate surface, the rest chip remains protected (McCreedy, 2000).

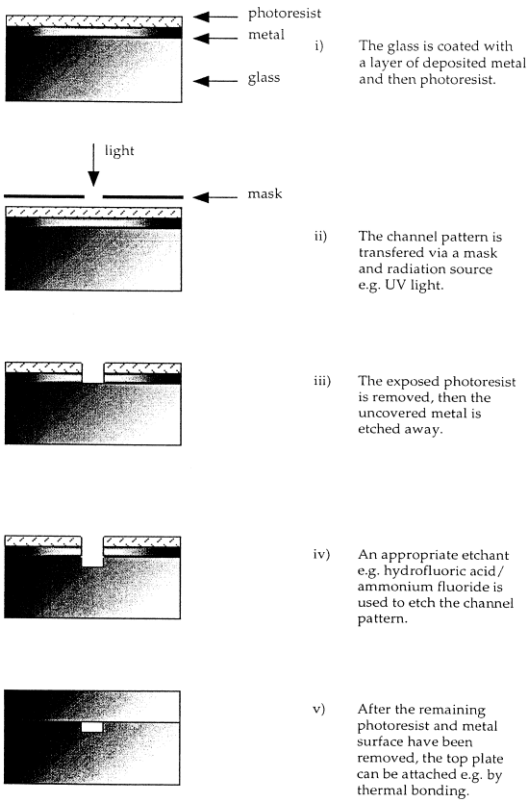

Figure 3 Microchannels by using photolithiography

Etching

Dry and wet etching techniques based on silicon and other semiconductor technologies are well known. For many metals, etching is a relatively cheap and well-established technique to obtain freeform structures with dimensions in the submillimeter range. A photosensitive polymer mask material is applied on the metal to be etched. The mask is exposed to light via a primary mask with structural layers. Here, different technologies are applicable and their details can be found in the literature on semiconductor processing. The polymer is then developed. This means that the non-exposed parts are polymerized in such away that they cannot be diluted by a solvent that is used to remove the rest of the polymer covering the parts to be etched.Thus, a mask is formed, and the metal is etched through the openings of this mask(McCreedy, 2000)(Brandner, 2008).

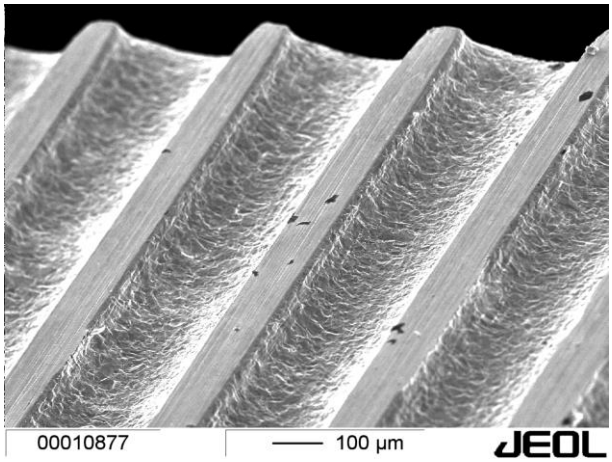

Figure 4 Wet chemically etched microchannels

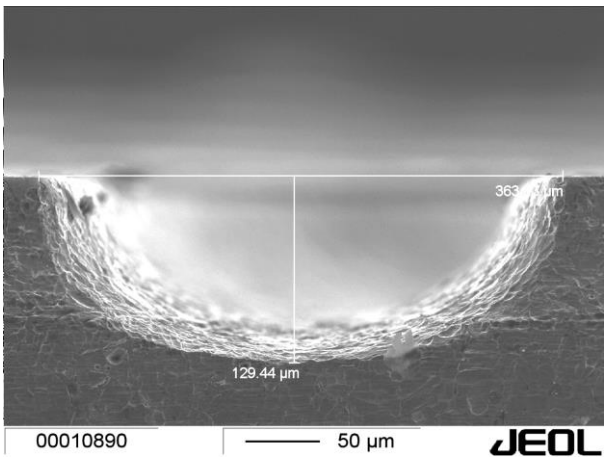

Figure 5 Semielliptic shape of the channels

Machining

Not all materials can be etched in an easy and cheap way. Especially, noble metals or tantalum are stable against most of these corrosive structuring methods. Hence, precision machining may be used to generate

microstructures from these metals as well as from standard metal alloys such as stainless steel or hastelloy. Depending on the material, precision machining can be performed by spark erosion (wire spark erosion and countersunk spark erosion), mechanical precision machining. In this case, mechanical precision machining means milling, drilling, slotting and planning.

The use of mechanical precision machining and the tools suitable for this type depend on the stability of the alloy. For brass and copper, natural diamond microtools are suitable and widely used, while for stainless steel and nickel based alloys, hard metal tools are needed (Brandner, 2008).

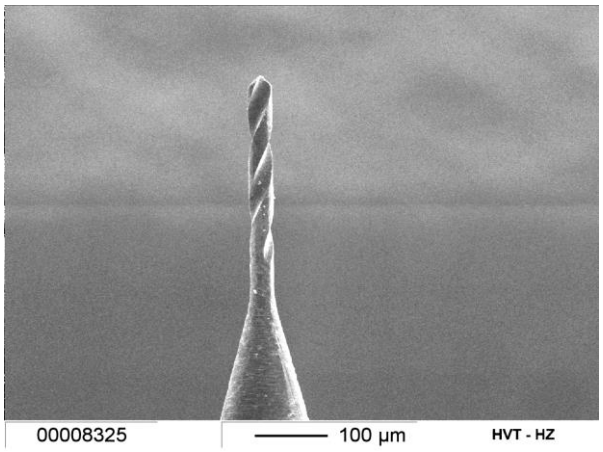

Figure 6 Microdrill made from hard metal

Selective Laser Machining

A special method to manufacture metallic microstructures is SLM. It is one of the rare generative methods for metals and is normally taken into the list of rapid prototyping technologies.

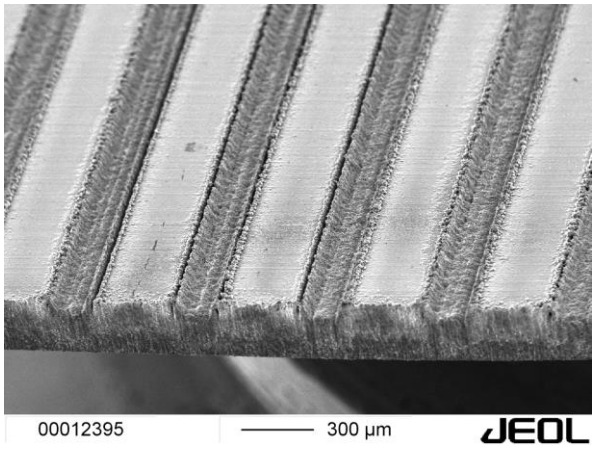

Figure 7 Surface quality of microchannels

The technique is completely different than the abrasive techniques described so far. On a base platform made of the desired metal material, a thin layer of a metal powder is distributed. A focused laser beam is ducted along the structure lines given by a 3D CAD model, which is controlled by a computer. With the laser exposure, the metal powder is melted, forming a welding bead. The first layer of welding beads forming a copy of the 3D CAD structure is generated. After this, the platform is lowered by a certain value, new powder is distributed and the process is repeated. Thus, microstructures are generated layer by layer. In principle, any metal powder can be used for SLM as long as the melting temperature can be reached with the help of the laser. For metal alloys, some problems might occur with dealloying by melting (Brandner, 2008).

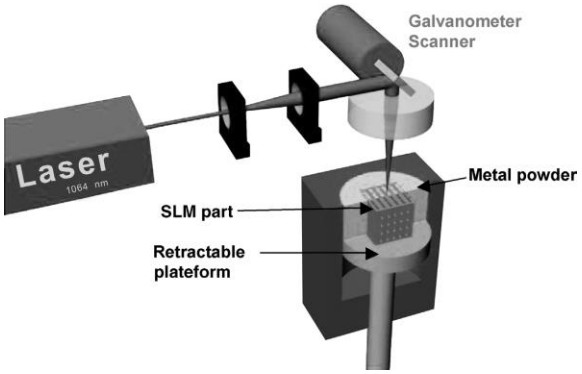

Figure 8 Schematic sketch of the SLM technology for metals

Microreactor Design

The microchannel network design used in actual fabrication to satisfy these constraints is shown in Fig.9. The shaded region shown in the figure are the regions where the mask allows light to pass through during the exposure stage. The design consist of seven microchannels, each of width 1000 µm. The catalyst particle filter is shown in figure. Since a positive photoresist is used in processing as anetch mask of subsequent etching (DRIE) of the patterned silicon substrate, the shaded region in Fig.9.are regions where the photoresist is exposed and the substrate is subsequently etched to form the channel network and the filter. SEM images of microchnnels and the filter are shown in Fig.10 .Location of inlet and outlet holes drilled in the capping pyrex water for the microfluidic interfacing are marked in Fig.9.

The inlet and outlet stategicallu positioned in the network so that the net length traveled by the reacting gas mixture across any alternate parallel path is the same. The when the microchannel network is packed with the catalyst particles and the gas flow is started during operation ,the gas will see an approximately equal resistance to flow across any flow path ,leading to uniform flow distribution across the entire chip area. The objective behind this design is to ensure equal residence times across parallel paths and ensure equal conversion and utilization of catalyst across the entire reactor chip (Pattekar, 2004).

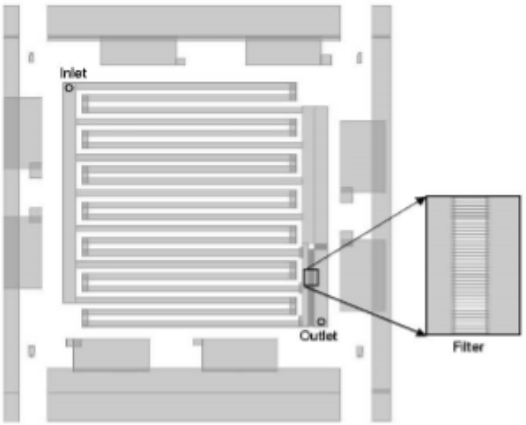

Figure 9 Mask layout for channel network and filter

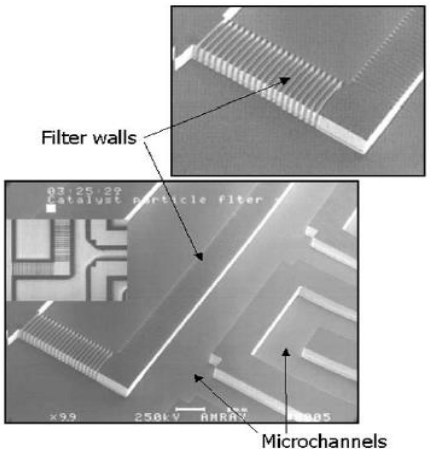

Figure10 Image of microchanel and catalytic filter

Methanol Reforming Process

It is the process in which methanol (CH3OH) and water vapour (H2O) produce hydrogen(H2).This process is typically carried out in the presence of metal oxide catalysts at temperature ranging from 468K to 523K. The chemical reaction take place during the reforming process is outline as follows.

$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$
$CH_3OH \leftrightarrow CO + 2H_2$
$CO + H_2O \leftrightarrow CO_2 + H_2$

The hydrogen from product gases is separated by selective membrane method. Typical residence times for sufficient conversion of methanol to hydrogen are known to be order of 500 to 700 milisecond. The performing reaction is endothermic so some amount of heat is supplied to carry out the reaction. The values of heat load per mol of converted reactants are +48.96,+90.13 and -41.17 KJ/ mol for reactions respectively, with +ve sign is endothermic reaction and –ve sign is exothermic reaction. By using proper amount of water and methanol we can minimize the formation of CO. Generally value of methanol (CH3OH) and water vapour is 1:1 mol(Benke, 2014). During the steady state operation at 200°C for the reaction run shown,2.5ml of 1:1.5 molar CH_3OH: H_2O was passed through the microreactor at a flow rate of 5 cc/h of the liquid mixture. The liquid mixture inside the syringe pump prior to feeding into the microreactor was maintained at the room temperature of 20°C, resulting in the feed liquid specific gravity of 0.9067 g/cc. This translates into a methanol feed rate of 2.46g/h and a total methanol feed of 1.23 g. on the exit side,all methanol and water was condensed and collected as liquid before the gas were mixed with 1.5 SLPM of argon and sent to the mass spectrometer for analysis. The net amount of liquid thus collected was 0.7 ml, with a measured specific gravity of 0.9643 g/cc at 20 °C

Species	Flow Rate (gram-mole/hr)
Inlet CH_3OH	0.076875
Inlet H_2O	0.1153
Exit CH_3OH	0.00908125
Exit H_2O	0.05884
Exit H_2	0.1764
Exit CO_2	0.05114
Exit CO	0.01951

Applications

Pharmaceutical researching

To develop a new generation of drugs, pharmaceutical companies need to be able to synthesise chemicals with enhanced speed. The use of microreactors can facilitate substantial progress in slective drug testing. Indeed the miniaturisation of chemical reactors offers many advantages of relevance to the pharmaceutical industry.

Synthesis of organic and the hazardous compounds continuous technology enable the generation and immediate use of unstable or hazardous intermediates as well as the combination of many reactions in series to achieve multistep synthesis. Microchannel reactor was used, for example, for the fast synthesis of acetic acid esters, including methyl acetate, ethyl acetate, *n*-propyl acetate and *n*-butyl acetate, etc.

In Refineries and the Energy Industry

Microreactors can be used in the refinery and energy sectors too. The primary research efforts in the energy field are focused on fuel processing as a (potential) hydrogen source, mostly for distributed consumption through fuel cells. Catalyst development, along with reactor design and testing for the reforming and removal of carbon monoxide through water-gas shift, preferential oxidation, selective methanation and membrane separation are therefore under investigation.

Miniaturised Analytical Systems in the biomedical field

One of the main aims of this kind of research is to develop a miniaturised total analytical system (μ-TAS).

Optimally, such devices would automatically perform sampling, sample preparation, separation, detection and data processing in a fully-integrated manner.

Summary

To conclude, microreactor chemistry is emerging and involves a promise to become a novel method on which to build a new chemical processing technology. With this device, comparable process conditions can be realized in the laboratory allowing to optimize many parameters and conditions quickly and in the production plant, with high flow rates and controllable safety requirements.Microreactors can be used in number of different areas where miniature scale chemical processing is desirable such as portable chemical analysis units, units for on-demand manufacture of minute amounts of hazardous chemicals which can be produced from less toxic reagents and applications where it is desirable to store chemical in the form of unreacted component due to its ease and portability of storage.

This study can be used as a general framework for design, modelling and development of microscale chemical reactors and provide a good basis for proper utilization of diverse concept from the fields of chemical engineering.

References

Haswell S.J., Skelton V. (2000), Chemical and biochemical microreactors, (Department of Chemistry, Faculty of Science and Environment, University of Hull, Vol 19 No 6

Jensen K.F. (2001), Microreaction engineering * is small Better?, (Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge,USA, Chemical Engineering Science 56 293-303.)

Pattekar A.V., Kothare M.V.(2004), A microreactor for Hydrogen production in micro fuel cell applications,, Journal of micromechanical systems, Vol 13 No 1

McCreedy T. (2000), Fabrication techniques and materials commonly used for the production of microreactors and micro total analytical systems, , Department of Chemistry, University of Hull, trends in analytical chemistry, Vol 19 No 6

Brandner J.J. (2008), Fabrication of Microreactors Made from Metals and Ceramics, Microreactors in Organic Synthesis and Catalysis, ISBN: 978-3-527-31869-8

Junkers M. (2004), Microreactor Technology, Sigma Aldritch chem files, Vol 9

Benke M., Nemethne J. (2014), Microreactors: a new concept for chemical synthesis and technological feasibility, Materials Science and Engineering, Volume 39 No 2

Y. Wang, J. Holladay (2005), Silicon Based Microreactors in Microreactor Technology and Process Intensification, American Chemical Society Publication, Washington DC