MICROFABRICATION METHODS FOR MICROCHANNEL REACTORS AND SEPARATIONS SYSTEMS

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ABSTRACT

The fabrication of microchannel chemical solvent separation units and plasma reactors is described. The performance of the solvent separation unit employs kinetic effects due to short contact times encountered in microchannel separations devices which enable differences in the rates of diffusion or reactions with the extractant to facilitate extraction of one chemical species. Laser micromachining, photochemical machining, photolithographic patterning, and diffusion bonding techniques are used to fabricate the unit. The separation unit consists of up to 200 flow and counterflow microchannels separated by micromachined metal membranes, bonded by a lamination technique. Channel width, height and length are 100 μm, 1 cm, and 8 cm respectively, forming an aspect ratio of 100. All sections are fabricated from 304 stainless steel for chemical stability. The separation membrane consists of two sets of micro-pores on opposite sides of the membrane. The pores have diameters ranging from 5 μm to 10 μm, and are etched into the opposite side of the membrane either by laser micromachining and plasma etching. The foils with the different size pores are laminated by diffusion bonding, forming the combination micromembrane. The entire unit consisting of membrane sections, channel sections, and wall sections is laminated and joined by diffusion bonding. The plasma reactor is used to achieve direct catalytic activation of methane, and consists of 500 μm-wide microchannels micromilled in opposing ceramic substrate sections. Aluminum electrodes with a 10 μm-thick aluminum oxide insulator layer are deposited in the bottom of the channels. When placed together with appropriate sealing techniques, the structure forms a set of opposing electrodes in a micro-cavity for generation of a plasma. The gas is flowed through the microchannels during plasma activation.

INTRODUCTION

Chemical reactors and separation devices based on microtechnology designs are attractive for waste treatment or chemical processing applications where comparable full scale equipment may not be feasible due to cost or size limitations, or where processing volume requirements are low. Development of low cost methods for producing microscale chemical processing devices offers the potential for mass production of such units. Consequently, as chemical processing capacity needs change between locations or with time, these variations can be quickly addressed by choice of the number of units in service. Thus, facilities can be easily tailored to individual applications, allowing improved energy efficiency and more effective use of processing capabilities. In addition to providing processing flexibility, microscale chemical systems can effectively utilize unique microscale phenomena, such as enhanced heat and mass transport, to significant advantage [1,2].

Chemical separations is one area of chemical processing in which the use of microfabricated devices offers unique advantages. The low volumes and short wall-to-wall distances inherent to microscale components can be exploited to promote diffusion-limited chemical transport processes. Microchannel flow devices can be specifically designed with high aspect ratio flow channels (i.e., height >> depth) to further promote interactions between flowing fluids and the walls, where chemical interactions, catalysis, or exchange occurs.

Plasma reactors have been demonstrated to be useful for both the synthesis and destruction of chemical species [3]. Plasma reactors offers a unique chemical processing environment where ultraviolet light, ionized gas derived radical species, and photocatalytically active catalysts (such as titania, chromia, and other materials) can produce the desired products with less energy. The development of microscale plasma reactors offers the opportunity to provide the capabilities of these devices for either synthesis or destructive processes at the point-of-need. For example, microplasma reactors have unique potential for indoor air pollution control, and may find applications in small office equipment, automobiles, or in transformers. The reactor developed at PNNL was used to break methane down into ethylene and hydrogen, and convert methane and air to syngas.

The integration of microscale plasma reactors and microscale heat exchangers has the potential to provide improved yields for nonequilibrium chemical processes, efficient synthesis of valuable chemicals, and the decomposition of hazardous compounds. A significant opportunity exists for microplasma reactors to have the capability to synthesize temperature sensitive compounds such as hydrogen peroxide in an energy efficient manner. Performance improvements over full-scale chemical processing plasma devices can result from reduced residence times (enhanced kinetics) and precise and localized temperature control.

We have undertaken the development of a microscale chemical processing devices, including plasma reactors and microchannel solvent separators. Fabrication techniques that have been evaluated for efficient operation and economical assembly of these devices include those that are commonly used in the semiconductor industry as well as novel new processes being developed at the Pacific Northwest National Laboratory (PNNL). Among the fabrication processes are laser micromachining, photochemical machining, photolithographic patterning, and lamination diffusion bonding. We describe progress on the development of fabrication methods for microchemical processing devices.

DEVICE DESIGN AND FABRICATION ISSUES

Operation efficiencies of the microscale chemical processing devices described in this report are intended to benefit from the reduction in scale relative to comparable full-scale units. To achieve the benefits desired, flow channels may require widths as small as 100 μm or less. Fabrication of devices containing such flow channels in robust, chemical-resistant materials requires new fabrication approaches. In addition, it is desirable that such chemical processing devices ultimately be mass produced at low cost. This implies the use of low cost materials and fabrication methods. We believe that the devices described meet the criteria outlined. Other fabrication issues related to the microscale sizes of these units are outlined below.

Microchannel Chemical Contactor

The chemical separations device described in this report is intended to allow redistribution of dissolved species from one solvent into another. The idea is to provide a separation membrane (or a series of membranes) across which immiscible fluids can come in contact, but which would prevent mixing of the fluid streams. In a microchannel concept for such a chemical separation unit, alternating microchannels separated by membranes would contain the two solvents which could be flowing in either the same or in opposite (counterflow) directions. Virtually any number of parallel channels could be incorporated into the device, depending on it's required chemical processing capacity and efficiency.

Microchannels in the chemical separation device must be both narrow and tall (i.e., have a large aspect ratio) to maximize fluid-fluid interactions and, as a result, material transport between the solvents. The membranes that separate adjacent channels must be sufficiently robust to withstand minor pressure differences between the fluids. It must also have a reasonably high porosity to allow fluid contact and efficient transport of species dissolved in the fluids, yet must also have sufficiently small pore size and the proper surface characteristics so as to not allow significant mixing of the fluids themselves. The unit must also be fabricated so that it is both internally and externally leak tight.

The fabrication costs of these units is predicted to be as low as $5 - $10 each [4], which makes economy of scale and batch fabrication attractive.

<u>Microplasma Reactor</u>

As designed, the microplasma reactor consists of two pieces of machinable ceramic containing 150 μm wide by 100 μm deep channels with appropriate inlets and outlets for gases. The channels are 9 cm long and are directly milled in the ceramic housing. High voltage connections required to support plasma generation are made to the channels using sputter-deposited electrodes. The electrodes are aluminum overcoated with an aluminum oxide insulator. A fiber optic probe is inserted through the ceramic into the end of one channel to optically monitor the plasma emission. Major technical challenges for fabrication of the microplasma reactor were to mill 150-μm-wide by 100-μm-deep microchannels in a ceramic, and then to deposit continuous electrodes which were able to sustain high voltages in the bottom of the channels. In addition to fabrication issues, the technical challenges were to generate and sustain a plasma in the micro-size channels, and to determine the products of the reaction in the channels.

<u>COMPONENT FABRICATION METHODS</u>

<u>Laminated Microchannel Device Fabrication</u>

Fabrication of microchannels having narrow widths (≤200 μm) and large aspect ratios (≥10) is difficult to achieve in solid pieces of metal. Slitting saws or electrical discharge machining (EDM) techniques can be used with limited success provided the channels are open on at least one surface. However, both of these machining methods are time consuming where multiple channels are required, making their use very expensive for any but the simplest designs involving microchannels. Other characteristics of these methods may also be detrimental to the characteristics of the devices containing microchannels. For example, the radius of the slitting saws must be accommodated at the ends of channels, channel widths are limited by saw blade thickness, and thin slitting saw blades tend to wander when cutting deep channels in all but the softest metals. EDM machining often leaves irregular surfaces on microchannel walls that can alter the characteristics of fluid flows through the channels.

We have developed a method for producing solid metal microchannel devices using a diffusion bonded laminate approach. With this method, perfectly smooth walled microchannels having virtually any aspect ratio or complex shape can be fabricated with either open edged channels or with the microchannels completely enclosed within a solid block of metal. A diagram showing the assembly of a simple microchannel device using this method is shown in Figure 1. In this example, a series of microchannels having headers at both ends is formed on the interior of a solid block using alternating sheets of machined metal shimstock to produce individual channels and the separating fins. Because only two patterns are required for the shimstock sheets that are stacked to make the microchannel device, the individual layers can be produced in large quantities and very inexpensively using photochemical or electrochemical machining methods. Prior to assembly of the stack of shims, each piece must be thoroughly cleaned to remove organic contaminants and excess oxide coating that could hinder the bonding process. Endcaps containing inlet and outlet ports are added to either end of the stack of machined shims. To consolidate the stack of machined layers and endcaps, the assembly is compressed under pressure in a jig and heated under vacuum to produce a diffusion bond between each of the layers. We have produced monolithic diffusion bonded parts using copper, aluminum, and stainless steel. Typical conditions required to produce gas-tight bonds for these materials are summarized in Table 1.

Table 1. Conditions used to diffusion bond copper and stainless steel laminated microchannel parts.

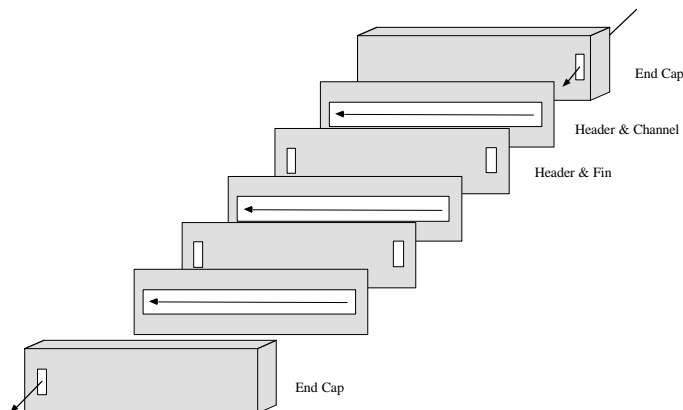| Material	Temperature (°C)	Pressure (psi)
Copper	630	6000
Aluminum	350	10000
Stainless Steel (type 304)	920	4000

Figure 1. Formation of a simple microchannel assembly using the lamination process.

The approach described allows for considerable flexibility in producing microchannel devices. For example, the widths of the channels in the device shown in Figure 1 are determined by the thickness of the shimstock used to produce the individual layers. By simply replacing the "channel" layers with similar parts from a different thickness of material, the channel widths in the finished part can be adjusted. Alternatively, by modifying the inlet and outlet header arrangement and replacing the "fin" layers with micromachined membranes, a simple solvent/solvent extractor can be fabricated (Fig. 2). For instances where a polymeric membrane is desired, the basic assembly of the device is the same as described, but diffusion bonding using high temperatures is not an option. In that case, the channel layers can be sealed against the polymer membrane layers by compression and/or by using an adhesive.

Membrane Fabrication

Fabrication of membrane layers for incorporation into laminated microchannel separators such as described in the previous section poses a challenge. Sufficient porosity must exist in the area between microchannels to allow contact between solvents on either side such that material transport can occur. At the same time, the pore size must be small enough that significant cross contamination between solvents is prevented. We have estimated that pore sizes of about 10 μm are needed to provide the desired transport characteristics.

Demonstration stainless steel membranes suitable for incorporation into diffusion bonded microchannel chemical extractors were produced by photochemical etching process. Hole diameters were on the order of 130 μm. The membranes produced by this method were very clean and well defined with no burrs, and part-to-part reproducibility was excellent. Using this method, thousands of membranes could be manufactured in a single production run. Although pore sizes on the demonstration metal membranes were significantly larger than is desirable for the chemical contactor device, smaller diameter pores can be attained using this method. However, because of the inherent taper to photochemically etched holes, tradeoffs must be made between membrane material thickness, minimum pore size, and total percentage of open area in the membrane. High temperatures used in the diffusion bonding process also limit the ability to apply surface-modifying coatings to the metal membranes.

Polymeric materials offer considerable potential for producing membranes having suitable porosity characteristics for the microchannel contactor separation concept. One approach we have taken to produce polymeric membranes for the microchannel extractor is to laser machine porosity into a solid polymer film. One approach is to directly machine holes into the polymer surface by stepping a pulsed laser from point to point on the polymer surface. Figure 3a shows an example of such a membrane produced by this method using a 248-nm KrF excimer laser direct-write micromachining system (Potomac model LMT 4000). A more efficient approach for producing membranes by the laser machining process is to use a commercial excimer laser having a rectangular beam profile, allowing a mask machining operation. Figure 3b shows an example of a membrane produced by a commercial laser machining operation (Resonetics, Inc., Nashua, NH) using this type of approach.
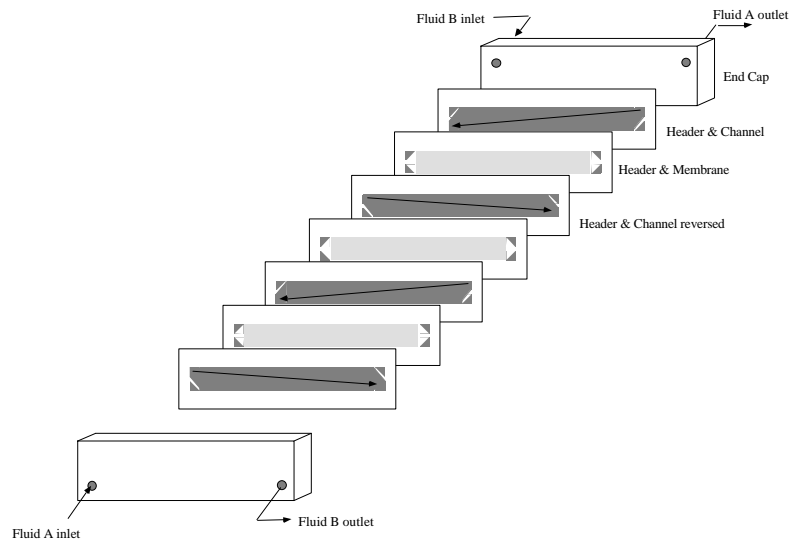
Figure 2. Assembly of a laminated counterflow microchannel chemical separation device using the lamination technique.
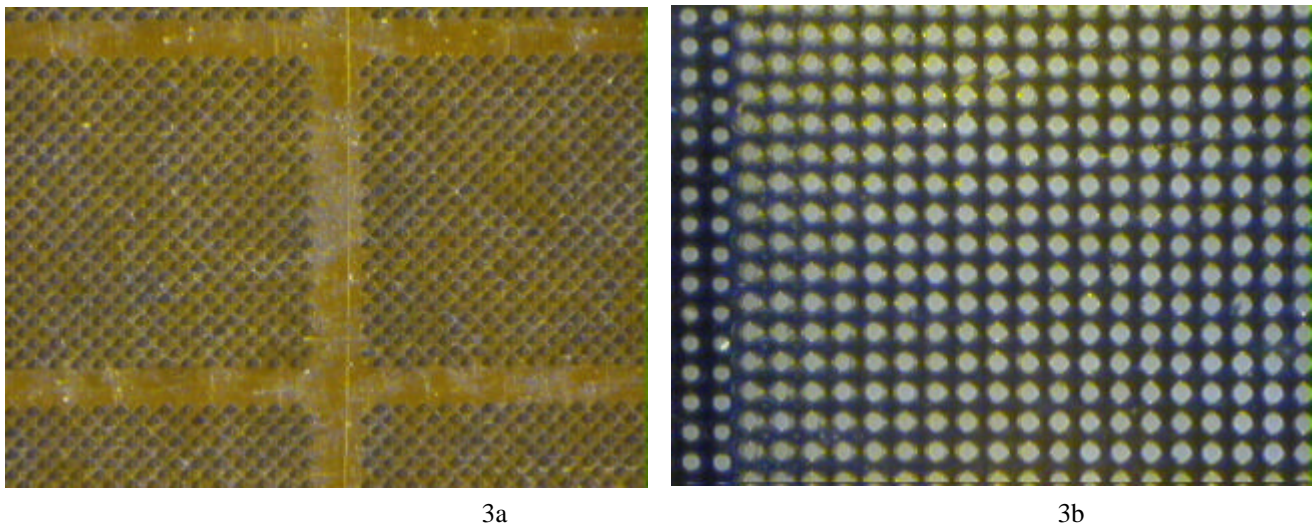

| 3a | 3b |

Figure 3. Comparison polyimide membrane pores fabricated by (3a) direct write and (3b) thru-mask laser micromachining processes.

Initial testing of the polymeric membranes produced by laser machining indicated that the membrane formed by direct drilling holes (Fig 3a) had too low a percentage of open area to attain efficient chemical transport of hexanol between hexane and the aqueous fluid. The mask-machined membrane (Fig. 3b) exhibited breakthrough between the fluids, giving cross contamination. However, by sputter depositing a Teflon coating on both surfaces of the latter membrane, the breakthrough problem was eliminated and solute transfer was attained.

Microplasma Reactor Fabrication

The microplasma reactor was produced using the limits of conventional machining technologies. Mating reaction channels were milled directly into machinable ceramic blocks using an end mill and slitting saw. When assembled, the device formed internal channels with opposing electrodes at the "top" and "bottom" of the channels. Photoresist was then applied to the surface of the block and the walls of the channels so that only the bottom of the channel could be coated. Ten microns of aluminum was deposited into the bottoms of the channels by magnetron sputtering with no

planetary substrate rotation. It was important to keep the angle incidence of the sputtered atoms as near to normal as possible to get complete coverage of the channel bottoms. The photoresist was then removed and 20 μm of aluminum oxide insulator was sputter-deposited over the entire structure, including the bottom and sides of the channels.

After coating deposition, a viton gasket was placed between the two ceramic blocks, and they were bolted together. Inlet and outlet gas fittings were attached to appropriate feedthroughs in the ceramic block. These fittings also functioned as the high voltage connections to the electrodes in the channels.

Initial testing performed to date on the plasma reactor is very encouraging. A stable plasma was ignited in the channels at a voltage to 100V. Plasma current was 17 mA, and the total power sustained by the microchannel reactor was 17 W. Gas chemistry analysis was performed, but is beyond the scope of this paper. Minor arcing was observed in the reactor, as was thought to be due to defects in the Al_2O_3 insulator coating. Future direction for reactor development includes addition of photo-catalytic materials such as TiO_2 to the channels, and integration with microchannel heat exchangers for precise temperature control.

SUMMARY

Microscale chemical components such as the separations unit and the plasma reactor described in this paper have the potential to revolutionize the way chemicals are processed, and to reduce processing costs. Utilizing microscale phenomena will help reduce unwanted byproducts, improve yields resulting from nonequilibrium process, and treat chemical waste. We have described the fabrication processes for these two components. These processes involve new technologies such as laser micromachining and the laminate fabrication process, and microfabrication in ceramics, as well as mature processes such as photochemical micromachining, wet etching, and photolithography. The ultimate goal of this work is low cost fabrication and batch fabrication of microscale chemical systems. This will primarily involve laminate fabrication, which may lower the costs of these components to as little as $5 - $10 each, once this process is refined.

LITERATURE CITED

1. Wegeng, R. S., C. J. Call, and M. K. Drost, "Chemical System Miniaturization", in Proceedings of the 1996 Spring National Meeting of AIChE, New Orleans, LA, February 25-29, 1996.
2. TeGrotenhuis, W. E., R. J. Cameron, M, G Butcher, P. M. Martin, and R. S. Wegeng, "Microchannel Devices for Efficient Contacting of Liquids in Solvent Extraction", to appear in Separation Science and Technology.
3. Drost, M. K. C. J. Call, J. M. Cuta and R. S. Wegeng , 1997, "Microchannel Integrated Evaporator/Combustor Thermal Processes", Journal of Microscale Thermophysics Engineering. Vol 1, No 4, pp 321-333.
4. Drost, M. K., "Microchannel Heat Pump Cost Estimate" PNNL internal communication, September 1997.