Laminated Ceramic Microfluidic Components for Microreactor Applications

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Abstract

Laminated ceramic components are being developed at Pacific Northwest National Laboratory (PNNL) for use in microfluidic chemical processing and energy management systems, including microreactors and biological reactors. Thin layers of green ceramic tape are patterned with microfluidic flow features using one of a number of cutting processes. The patterned layers are then stacked and laminated with other layers of green tape, ceramic plate, or other materials using a series of processing steps. The resulting monolithic, leak-tight microfluidic ceramic components are capable of tolerating high temperature or chemically corrosive environments. As with other laminated metal and plastic microcomponents developed at PNNL, channel aspect ratios can be very high, providing large surface area channels. This geometry is conducive to the inclusion of catalysts and other surface modifications. Fabrication issues associated with the green ceramic tape in this type of application are discussed, and examples of test components produced using these processes are presented.

Introduction

At PNNL, we have been actively involved in the development of micro-reactor components for a variety of applications including manportable heating and cooling, automotive, and remote processes (Drost et al. 1997; Ameel et al. 1996). Many of these applications use high-temperature chemical processes (e.g., combustion) that make it necessary to use thermally and chemically resistant materials such as high temperature metals in the construction of these components. Thermal management requirements for these devices have been important considerations in their design and construction. Chemical processes typically rely in thermal transport into or away from reactants to sustain endothermic processes or to remove waste heat generated by endothermic processes. Ideally, heat generated in one part of the reaction process can be used in another. Thermal management in microreactors can be challenging because of the small dimensions involved and the materials typically used for their construction.

We have found that lamination and diffusion bonding methods are extremely useful for producing solid metal components having internal microchannel arrays that are used to promote heat transfer between fluids (Matson et al. 1998, 1999; Tonkovich et al. 1998). These unique components are fabricated using patterned metal shims, which are stacked to produce the desired internal microchannel structures. The stacked devices are then diffusion bonded at elevated temperatures and pressures to yield monolithic leak-tight solid metal components that can then be further machined, welded, or otherwise processed to form the final configuration. The microchannel arrays produced by this method have high surface areas and small gaps between channel walls, promoting heat transfer to or from the fluids flowing through them. Many of these types of laminated microchannel components have been produced using stainless steel, although for lower temperature applications, copper and aluminum laminated devices have also been demonstrated.

As applications for microchannel reactors broaden, materials challenges have become more pronounced. Higher temperature capability and increased oxidation resistance requirements have pushed the development of microchannel ceramic components having similar microchannel structures to those produced from metals. Ceramic microchannel devices are also considered to be excellent candidates for catalyst supports in microreactor devices. In this paper, we report preliminary efforts to develop processes suitable for fabricating laminated ceramic microchannel chemical reactors and other high-temperature microchannel components using commercially available green ceramic tape.

Laminated Microchannel Devices

The lamination process allows fabrication of monolithic devices having complex internal structures suitable for microfluidic applications. The process requires the use of thin patterned shims that, when assembled in the appropriate arrangement, produce a series of thin gaps or voids which can act as flow channels or fluid headers. Metal shims can be patterned using a number of possible processes, although we have found that photochemical etching typically provides adequate feature resolution and produces shims having good surface characteristics. For devices incorporating microchannel arrays, the shims containing the flow channel cutouts are alternated with shims that don't have the cutout areas. The shims without cutouts then act as fins between the channels. Channel widths are determined by the thickness of the material used to produce the channel shims. Channel heights and lengths are determined by the cutout area of the shim, and the channel aspect ratio (height/width) can be made as large as the material of the shim permits. Headers at the ends of the microchannels are formed by openings common to all the shims and that are aligned when the shims are assembled prior to bonding.

Figure 1 shows an assembly diagram for a simple microchannel array device produced by lamination. Although the device shown in the figure contains only a pair of microchannel arrays, much more complex devices can be produced using this method. For example, devices accommodating multiple fluids and/or containing several fluid flow levels and functionalities can be produced by appropriate shim design and assembly (Matson et al. 1998, 1999). This type of patterned shim assembly method allows the fabrication of fluidic devices with internal structures not attainable by any other method.

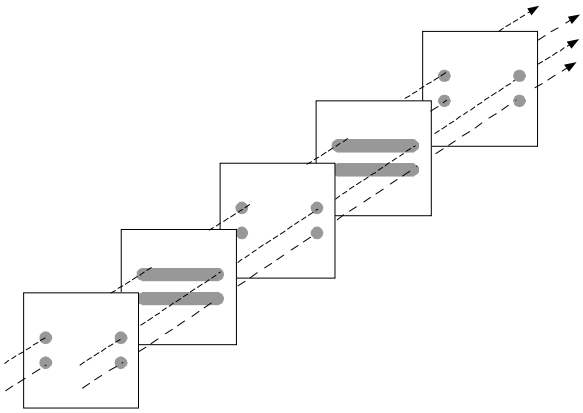

Figure 1. Assembly Diagram for a Simple Laminated Microchannel Device

All-metal laminated microfluidic components are bonded into monolithic units using a diffusion bonding process. If adjacent shims are in intimate contact at elevated temperatures for a sufficient amount of time, the metallic components in the shims can interdiffuse, essentially welding the parts together. Diffusion bonding of a stack of metal shims is typically done in a vacuum furnace to avoid surface oxidation during the bonding process. Pressure must also be applied to the stack during bonding to ensure that each shim remains in intimate contact with the shims on either side. Insufficient pressure or surface irregularities resulting in poor contact can result in unbonded sections and resulting leaks. Post-bonding processes for metallic laminated devices may include additional machining to reduce overall mass, add sealing grooves, enlarge access ports for weld and fitting connections, or improve device aesthetics. Tubes can also be welded into place on the laminated devices to accommodate fluid connections.

While the procedures used to produce metal laminated devices are reasonably well established, using ceramic materials to produce similar structures presents additional challenges. To pattern the ceramic shims that are to be bonded, we start with a green (unfired) ceramic tape (Ferro type A6-C-10). This material, which is available in standard thicknesses from 125 to 250 microns, contains an organic binder that makes it very flexible in its unfired state. The green tape is also easily cut. Our earliest ceramic test pieces were produced using shims that had been hand-cut with a hobby knife. Higher quality patterned green ceramic tape shims were later produced using computer aided drawing (CAD)-driven laser machining methods. For production-scale applications, a stamping process could be adapted for producing large quantities of the green state shims. Examples of simple laser-patterned green ceramic tape shims are shown in Figure 2.

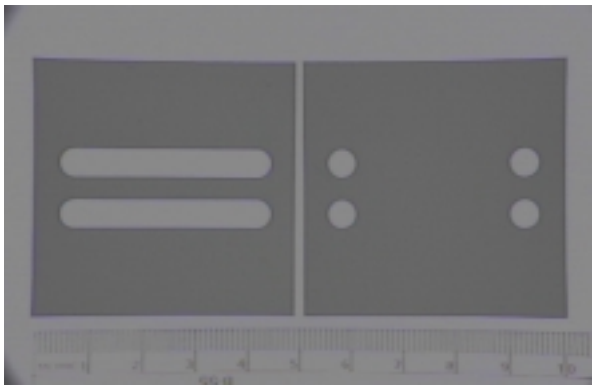

Figure 2. Green Ceramic Tape Shims Produced by Laser Patterning

After patterning, the green tape shims are individually thermally preconditioned at 50°C for 20 to 30 minutes. This preconditioning bake begins to remove some of the binder and moisture from the tape and stiffens the shims somewhat for easier handling. An alternative approach to the preconditioning bake is a 12- to 24-hour exposure in a dry nitrogen atmosphere. The shims are then stacked into their final laminated configuration for heat-treatment and bonding. Because oxidation is not an issue for the ceramic materials, the heat-treating can be performed in air rather than in a vacuum or inert atmosphere furnace, as required for metallic laminates.

The laminated stack is bonded into a monolithic ceramic part by heating the stack under compression at moderate temperature. We typically accomplish this phase of the process by uniaxially pressing the stack in a hydraulic press with heated platens at 13.8 MPa and 70°C for 10 minutes. Alternatively, a hot isostatic press could be used.

Additional heat treatments are required to complete the bonding process and to cure the ceramic part. These are typically accomplished in a box furnace with no load placed on the laminated part. In the first phase of this high-temperature treatment, the temperature of the part is ramped slowly (~1°C/min) to 400°C, where it is subjected to a soak for a time related to its overall thickness. During this phase of the treatment, the remaining binder in the ceramic tape is baked out. For parts up to ~1 cm thick, this can typically be accomplished with a two-hour soak; longer times are required for thicker parts. Inadequate soak times at 400°C have been found to produce warped or otherwise distorted laminated ceramic parts. On completion of the 400°C soak, the parts are ramped up to 875°C at 5°C/min and held at temperature for 30 minutes before being allowed to cool slowly to room temperature. If desired, ceramic tubes can be added to inlet and outlet ports of the ceramic stack using high-temperature epoxy.

A complication in using green ceramic tape to produce laminated monolithic devices is the significant dimensional change that occurs between the initial stack of green shims and the completed part. These changes occur because of binder loss and ceramic densification during heat-treatment. Typically, the ceramic part is subject to shrinkage of up to 12.5% in the x and y directions and as much as 15% in thickness. These dimensional changes must be accounted for in the design of the laminated part and the initial dimensions of the green tape shims. The shrinkage factor also precludes or severely complicates the possibility of co-laminating shims produced with green ceramic tape with other pre-fired ceramics or other materials that do not exhibit similar shrinkage characteristics.

An additional potential complication with using the green ceramic tape is related to the flexibility of the starting material. The tape can sag where it is unsupported, such as over channel shims if the shims are stacked horizontally. This effect can be mitigated by ensuring that 1) the device design does not include wider unsupported gaps than are necessary, 2) there is adequate pre-stack heat treatment, and 3) the choice of stack orientation is correct during initial stages of the stacked component heat treatment.

Sacrificial layer materials that can be placed in the cavities to support the structure during bonding are also being evaluated. Carbon-based pastes that are thermally removed during the high-temperature firing phase appear most promising at this time. However, because it is difficult to obtain an even distribution of paste in the channels during assembly, we are not optimistic about the prospects for this approach.

Results

Simple ceramic microchannel devices have been produced from patterned green ceramic tape shims using the lamination/thermal bonding process. An example of one of our first efforts at producing this type of device is shown in Figure 3. Outside dimensions of the device without added header tubes were approximately 4.5 x 4.5 x 1.0 cm. This component was fabricated from 250-micron-thick green tape. To increase the channel width to beyond the thickness of the green tape, two channel shims were included between each pair of fin shims. Five fin shims were assembled on either end of the laminated stack to provide extra thickness of material into which to attach connection tubes. Overall, the laminated device contained a total of 40 patterned green tape shims. Warpage of the component shown in Figure 3 resulted because the 400°C soak time used to produce this particular device was inadequate, as explained above. Despite the obvious distortion of the part, the device was leak tested with compressed air at 0.35 MPa and showed no leaks to the outside from the interior microchannels. Details of the internal microchannel structure, as seen through a header port prior to adding connection tubes, are shown in Figure 4.

Figure 5 is a second laminated ceramic microchannel device with outer dimensions similar to the one in Figure 3. The internal flowpath for this device consists of a single multilevel serpentine microchannel, requiring only a single inlet and outlet port. The lamination and bonding conditions for this second device are optimized to allow the fabrication of a largely undistorted monolithic structure.

Figure 3. Thermally Bonded Ceramic Microchannel Device prior to Fine Tuning Lamination Process

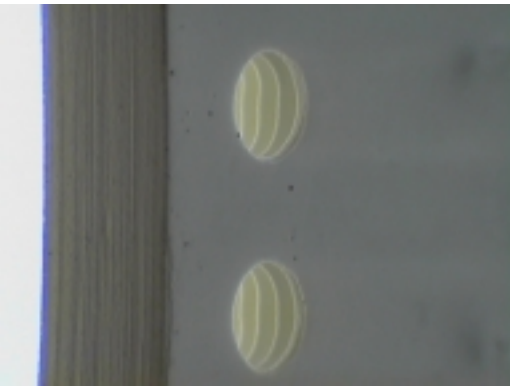

Figure 4. View Through Header Ports of a Laminated Ceramic Component Showing Microchannel Details

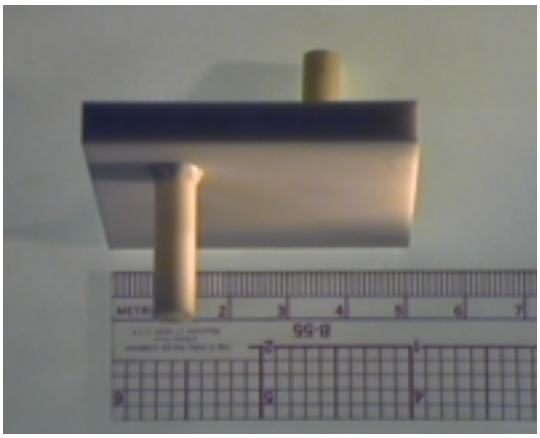

Figure 5. Ceramic Serpentine Microchannel Device Produced after Optimizing Lamination Process

Summary

The lamination/bonding process was used to produce monolithic ceramic microchannel devices similar to those produced previously using metals. Commercially available green ceramic tape was patterned to form the individual shims making up the laminates. Shim patterning was done by hand or using a laser machining process. Bonding was performed without vacuum or inert atmospheres using a conventional press with heated platens and a box furnace. Although the green tape bonded to form solid, leaktight microchannel devices, material and structural issues such as shrinkage and sagging of the green tape prior to final heat treatment are not yet fully resolved.

PNNL continues to evaluate lamination and bonding processes for fabricating ceramic microchannel devices because of ongoing needs for novel microchemical processing applications. Future efforts will include testing and evaluating ceramic microchannel devices as heat exchangers and catalyst supports for high-temperature reactors.

Acknowledgment

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