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Fabrication and Enhancement of Aluminum-Based Microchannel Devices

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FABRICATION AND ENHANCEMENT OF ALUMINUM-BASED MICROCHANNEL DEVICES

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
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in

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by

Paul J. Hymel
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I started my research thinking that it was mostly a personal matter to design and execute experiments, obtain results, and draw conclusions. I realize now that I couldn’t have been more incorrect—research, as with just about any other field, is just as dependent upon forming relationships, mentoring, and dependence upon others. Thus, there are several people I need to thank for their help along my journey.

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Abstract
Microscale molding replication and transient liquid phase (TLP) bonding were used to fabricate Al-based microchannel heat exchangers (MHEs) and micro gas chromatograph (mGC) columns. Metal-based microchannel heat exchangers often experience corrosion as a result of their operating conditions. To address this problem, an internal anodization method was developed in Al microtubes by pulsing the flow of electrolyte through a microtube when the current dropped below a set value. The anodic aluminum oxide (AAO) films were characterized by scanning electron microscopy (SEM), focused ion beam (FIB) cross sections, and X-ray energy dispersive spectroscopy (EDS) to determine their growth rate and morphology. The AAO was sealed by immersing in near-boiling water, and then subjected to a linear sweep voltammetry corrosion test in NaCl, which showed an order of magnitude decrease in the corrosion current between un-anodized and anodized/sealed microtubes. The anodization process was extended to MHEs, and subsequent corrosion testing showed superior resistance to ion diffusion within the AAO film. Al-based mGC columns were fabricated and tested for carrier gas flow rate and single-compound efficiency, then they were subsequently anodized using the same process as the MHEs at 30V or 50V for 3 hours or 8 hours. They were re-tested for single compound efficiency then used to separate an n-C\textsubscript{4} through n-C\textsubscript{9} hydrocarbon standard. Comparison with a commercial column of the same length showed that the mGC columns had a lower resolution because of lower retention times for all compounds. Additionally, the n-C\textsubscript{8} and n-C\textsubscript{9} peaks had significant tailing. On the other hand, the mGC columns had higher efficiency than the commercial column for n-C\textsubscript{5}, n-C\textsubscript{6}, and n-C\textsubscript{7}. Characterization via SEM and EDS showed that inconsistent AAO morphology was one likely cause of the lower resolution and tailing. A series of recommendations for manufacturing improvements were provided, including changes to the anodization process and surface treatment of the AAO to lower the distribution of active site energies.
1. **Introduction**

Microfabrication is an interdisciplinary field combining fundamental sciences, such as physics and chemistry, and engineering and applied sciences, such as electrical engineering, mechanical engineering, and materials science and engineering (MS&E). Microfabrication is concerned with miniaturizing electrical and mechanical devices. The earliest developments in the field were rooted in silicon-based very-large-scale-integration R&D [1]. As a by-product of the extensive work to develop methods for miniaturizing integrated circuits, Si is now used as a basis for many micron-scale sensors and actuators, including accelerometers [2], navigational gyroscopes [3], pressure sensors [4], and valves [5]. Although techniques derived from the original Si technology can produce structures with aspect ratios greater than 10 and resolution on the micron scale, high cost is a major limitation [6]. Metal-based microsystems can offer different properties from Si, such as increased mechanical robustness [7] and electrical or thermal conductivity [8].

Both additive and subtractive manufacturing processes are used in metal-based microsystem fabrication. Chemical and electrochemical etching are two of the most common subtractive processes, in which a metal substrate is covered with a polymer or oxide that shields certain surface areas from reacting with the etchant [9]. Micro electrical discharge machining (μEDM) is another subtractive technique that uses high electric potential applied between an electrode and substrate immersed in a liquid dielectric to create electrical discharge arcs that vaporize a pattern into the substrate, as defined by the electrode shape. Additive methods for metal-based microsystems include electrodeposition and physical vapor deposition. Electrodeposition utilizes the reverse reaction of electrochemical etching to deposit metals; instead of metal atoms from the base metal being oxidized and going into solution, ions from the solution are reduced and incorporate onto the base metal [6]. Physical vapor deposition (PVD) is another additive technique usually used to make much thinner metal films than plating processes. In general, PVD utilizes ejection of atoms from one material to deposit them on another substrate. One particular method of PVD is sputtering, which utilizes ions from a plasma to bombard a target, causing atom ejection [10].

Many of these techniques are serial in nature, and they can take days to produce metal layers thick enough for high aspect ratio microstructures, which is often the end product of microfabrication processes. An alternative to these methods is based on the well-known LIGA (Lithographie, Galvanoformung, Abformung) technique, which is German for X-ray lithography, electrodeposition, and molding [11]. For metals, compression molding with an insert that is pressed into the substrate is a more suitable technique than injection molding because of their high melting temperatures compared to polymers [8]. Although traditional time-consuming or expensive microfabrication methods may be required to make the mold insert, it can be used for many successive mold replications, which can take minutes instead of days to complete with the use of proper equipment.

Microscale molding replication in metals has been studied extensively by Dr. Meng’s research group at Louisiana State University. They first investigated the use of LIGA-fabricated Ni mold inserts consisting of an array of cylindrical microposts with aspect ratios of 5:1 to mold Pb and Zn [12]. The molding process was carried out at ~300°C to lower the flow stress of the molded metals. Surface modification of the mold insert with a Ti-containing hydrocarbon (Ti-C:H) thin film was necessary for the Zn specimen because it forms intermetallic compounds with Ni, which contributed to high de-molding forces [12]. They later repeated the experiment to mold Al at ~450°C and verified that the Ti-C:H thin film coating was necessary to prevent high
de-molding forces [13]. One disadvantage of using electroplated Ni mold inserts was their nanocrystalline structure, which underwent grain growth at the temperatures used for molding and resulted in a loss of strength [14]. Therefore, tantalum inserts were fabricated by μEDM, coated with Ti-C:H, and used to mold parallel microchannel arrays in Al and Cu with aspect ratios of ~1.4:1 at ~400°C [15]. The μEDM was used in sinking mode, and the cathode was a 500μm-thick Mo sheet, which made parallel cuts in the Ta at a pitch of ~750μm [15]. Later, Inconel X750 was used as the mold insert material because of its superior retention of mechanical properties at the high molding temperatures [16].

In many applications, an open microstructure must be covered to make an enclosed flow path. For Si-based Microsystems, one common method is anodic bonding with borosilicate glass [17]. Metal-based Microsystems can also be enclosed using anodic bonding, but the mechanical and thermal properties of the glass often counteract the advantages gained by using a metal system in the first place [7]. Therefore, it is desirable to bond the microstructure base metal to a cover of the same material. Conventional macroscale joining techniques such as fusion welding require bulk melting, which is difficult to control in microscale devices. One promising technique for joining metal to metal is the transient liquid phase (TLP) bonding technique [18]. TLP bonding utilizes a melting-point-depressant (MPD) in between two substrates to be bonded. Intermediate MPD layers have consisted of a single metal [19] or two metals [20]. If a single metal is chosen, it must have a eutectic point with the substrate metal. If two metals are used, then they must have a eutectic point with each other but not necessarily with the substrate metal; however, the eutectic temperature must be lower than the bulk melting point of the substrate metal [21]. When the two substrates and intermediate layer are heated as a sandwich structure, solid-state diffusion creates areas in the intermediate layer that have the eutectic composition. When the temperature of the structure reaches the eutectic temperature, the zones with the eutectic composition melt, and the liquid layer grows as more metal adjacent to the liquid diffuses into it. The liquid reaches a composition where solidification takes place at the given temperature, usually due to exhaustion of the MPD layer metal. Mei, et al. studied the use of the Al-Ge binary system to bond Al high aspect ratio microstructures [20, 22, 23]. They used a co-sputtered Al-Ge thin film with thickness ~2μm on each Al substrate as the MPD, which created an estimated final liquid layer thickness of ~50μm [23]. Control of the final liquid layer thickness is important, especially as the height of microstructures decreases.

Metal-based Microsystems are well-suited for microfluidic-type systems, especially when mechanical robustness and fast heat transfer is required. In 1981, Tuckerman and Pease pointed out that the convection coefficient in water-cooled heat sinks under laminar flow had an inverse relationship with the water channel width, so microscale channels were advantageous [24]. High aspect ratio microchannel heat exchangers (MHEs), which had even better heat transfer performance because of their increased wall contact area to channel cross section area ratio, were fabricated by several groups, but most efforts concentrated on Si-based devices [25-27]. Some commercial Cu-based MHEs are made using chemical etching, laser machining, or micromilling [28]. Microscale molding replication has an advantage over these processes because of its rapid and cost-effective replication potential. Mei, et al. first applied the micro molding and Al-Ge TLP bonding to Al-based MHEs [23]. Later, Mei and Lu applied the micro molding and Al-Cu TLP bonding to Cu-based MHEs [29-32]. Their heat transfer testing results showed that for Reynolds number <1500, the Cu- and Al-based MHEs had similar Nusselt numbers that exceeded those obtained by Lee et al. [33] in Cu-based microchannels, which was thought to be a result of higher surface roughness [30]. Although MHE fabrication by micro molding has been
well-studied, and MHE devices have been tested, metal MHEs face the problem of corrosion under certain operating conditions [34].

Another well-studied application in the Si-based microfluidics field is micro gas chromatography (mGC) column fabrication. Gas chromatography (GC) is an analytical chemistry technique used to separate gaseous mixtures into constituents and determine the concentrations of each. In addition to the column, GC systems also contain an injector, which inserts a narrow pulse of analytes into the column, and a detector, which senses the compounds as they elute from the column in distinct segments. The inside walls of the column are coated by a thin liquid or solid layer that interacts with the gas mixture, causing the components to move through the column at different effective velocities. Two advantages of mGCs are analysis times as much as 60 times shorter [35] and portability [36]. The first mGC column was produced by Terry, et al. in 1979, and included an injector and detector all mounted on a 5cm diameter Si wafer. The other most notable Si-based column was made by Reidy, et al. at the University of Michigan [35]. As of 2007, it had the highest efficiency of any mGC column to date [37]. Metal-based mGC columns offer two advantages over Si-based devices: faster heating rates for temperature programming and increased mechanical robustness. In 2007, Bhushan et al. fabricated a Ni-based mGC column using the LIGA method without the Abformung step by using two-sided electroplating to achieve an enclosed channel [38, 39]. In 2012, Iwaya, et al. developed a stainless-steel based mGC column using wet etching and incorporated it into a portable chromatography instrument [36]. Metal micro molding replication coupled with TLP bonding offers a high-throughput alternative to these fabrication processes.

In the first part of this thesis, micro molding and TLP bonding are used to fabricate Al-based MHEs. This fabrication process is then extended by anodizing the internal surfaces of the microchannels and sealing the resulting alumina layer to protect from corrosion. This method was tested using an electrochemical corrosion test comparing the sealed alumina layer’s effective electrical resistance to the resistance of an untreated MHE. In the second part of this thesis, micro molding and TLP bonding are used to fabricate Al-based mGC columns. An anodization method similar to the one used for MHEs is used to deposit a layer of alumina on the internal surfaces of the mGC channel for use as the stationary phase. The mGC columns are used to separate an n-C₄ through n-C₉ hydrocarbon standard and their performance is compared to a commercial column under similar operating conditions. Based on the results, a number of future fabrication steps are recommended to enhance the performance of the mGC column.
2. Internal Passivation of Aluminum-Based Microchannel Heat Exchangers

2.1 Introduction

High-performance heat transfer technologies are of significant current interest for cooling of advanced microelectronics [40] and avionics [41, 42]. Lack of sufficient cooling capacity often limits the performance of electronic devices. Cooling of power electronics and photonic devices is similarly important. As one example, thermal management is critical for power electronics in hybrid electric vehicles and electric vehicles. Key power electronic devices, such as converters, inverters, and motor controllers, generate heat fluxes up to 400W/cm$^2$ [43]. Crucial to safe and reliable device operation is the use of cooling systems capable of dissipating KWs of heat within the limited volume, weight, and cost specifications demanded by applications. As another example, high power diode lasers [44] are used in a wide range of industrial applications [45, 46]. They generate coherent light output in a narrow wavelength band, and can be used as efficient pump sources for solid-state lasers or as direct light sources for surface treatment, welding, ablation, etc. Contemporary laser diode bars are capable of producing hundreds of watts of CW output power. With typical electrical-to-optical efficiencies of 50-75%, generated waste heat fluxes can reach ~1kW/cm$^2$. Efficient removal of such waste heat is critical to proper device function.

Tuckerman and Pease showed in 1981 that significant increases in liquid-solid convective heat transfer rates can be achieved by decreasing cooling channel dimensions to the micro scale [24]. While the majority of work on microchannel heat exchangers (MHEs) since then focused on Si-based devices [25-27], heat transfer devices based on metals such as Cu and Al have higher bulk thermal conductivities than Si [8]. Lu et al. fabricated Cu-based, single-layered MHEs using micro electro discharge machining (μEDM), which yielded a heat flux removal capacity of 240W/cm$^2$ at Reynolds number (Re) of ~1200 [31]. Double-layered Cu MHEs in both in-line and counter flow configurations were also fabricated with μEDM, which decreased the pressure drop for liquid flow by over 50% as compared to single-layered MHEs [32]. Metal-based MHEs combine high heat transfer performance and low area/volume footprint, as well as high mechanical robustness [31, 32].

Cooling by liquid flow through metal-based microchannel arrays are used for waste heat removal in high power devices, such as laser diode packages. Commercially available microchannel coolers are made from multiple layers of Cu sheet metals, patterned through photolithographic etching, micromilling, or laser micromachining, and assembled through diffusional bonding at temperatures ~800°C [28, 47]. While Cu microchannel coolers provide excellent thermal performance, water used as the cooling liquid corrodes Cu [48, 49]. When Cu microchannel coolers are used to provide cooling to laser diode packages, electrical current passes through the Cu microchannel cooler to the cooling water, leading to electrochemical corrosion [34]. To minimize such deleterious effects, deionized water is typically used as the cooling liquid, necessitating stringent requirements on the entire cooling system [34]. Additional erosion-corrosion may occur within Cu microchannel coolers at locations with high-velocity water impingement [34]. To alleviate corrosion, electrochemical corrosion, and erosion-corrosion problems, internal surfaces of metal-based microchannel coolers need to be passivated. Technologies which are able to achieve satisfactory internal surface passivation for metal-based microchannel coolers will significantly improve cooling system reliability and lifetime. Low-cost manufacturing and surface treatment processes are of particular interest.
With respect to surface passivation, Al and Cu exhibit significantly different behaviors because of the strong thermodynamic driving force for aluminum oxide formation. We have previously demonstrated fabrication protocols for Al-based microchannel devices [30, 50]. Since formation of aluminum oxide through electrochemical anodization is well known [51], electrochemical growth of a passive aluminum oxide layer in Al-based MHEs provides a potential solution to corrosion prevention in metal-based MHEs. Anodization of the internal surfaces of Al tubes has been used in previous studies to generate self-ordered anodic aluminum oxide (AAO) nanopores for microreactor applications [52, 53]. Those methods focused on creating a high pore-density structure to maximize reactor area. In contrast, surface passivation requires an even-thickness, low pore-density structure. In this work, we report design and demonstration of a surface passivation process for the interior surfaces of Al-based MHEs using electrochemical anodization. The process was first verified in Al microtubes because of their simpler geometry, allowing for a more thorough characterization of AAO morphology and more quantitative testing of electrochemical corrosion. The anodization process was then extended to Al-based MHE devices, whose complex geometry provides an additional challenge to both surface passivation and verification of corrosion resistance.

2.2 Experimental Procedure

2.2A Anodization of Al Microtubes

All chemicals used for anodization treatments were reagent grade, and all solutions were prepared with deionized water. Cylindrical tubes made of the aluminum alloy 3003 (~1.5at.% Mn, ~0.7at.% Fe, ~0.8at.% Mg, balance Al), with ~900μm ID and ~1500μm OD, were obtained from McMaster Carr (Elmhurst, IL). A typical cross-sectional image of the as-received tubes is shown in Figure 1.

As-received microtubes were cut into 4cm-long sections. Prior to the anodization treatment, the tube sections were chemically polished by submerging in 1M NaOH for 30s. A 2-electrode configuration electrochemical system, with capability of electrolyte circulation, was constructed using a Flojet 12V diaphragm pump powered by a DC power supply (Sorensen XFR 20-60, Ametek, San Diego, CA), poly-vinyl-chloride pipes and rubber tubing for the electrolyte circulation system, a poly-propylene container serving as the electrolyte reservoir, and a programmable DC power supply (6575A, Agilent, Santa Clara, CA) for applying bias between the microtube and a Pt foil counter electrode. The rubber tubing fit tightly over each end of the microtubes, creating an enclosed electrolyte flow path through the microtube interior. A schematic of the electrochemical system configuration is shown in Figure 2.

In order not to anodize the tube external surfaces, the outer surfaces of the NaOH-polished microtube were coated with epoxy (S-206, ITW Devcon, Danvers, MA), which covered ~1cm from each end of the tube. Through the rubber tubing attachment, the microtube was then placed into the electrolyte circulation system. The electrolyte used was a 0.3M oxalic acid (H₂C₂O₄) solution placed in an ice bath (~0°C). A 25mm×25mm Pt foil counter electrode (99.9% metals basis, Alfa Aesar, Ward Hill, MA) was placed in the electrolyte reservoir. The Agilent 6575A power supply was used to increase the potential from 0 to a specified final voltage (30, 40, or 50V) at a rate of 4 V/min. A data acquisition/IO unit (34970A, Agilent, Santa Clara, CA) was used to measure the voltage and current in the electrochemical cell at a sampling rate of 1Hz.
Figure 1: A cross-sectional SE image of an as-received Al3003 tube used for initial testing of the electrochemical passivation process.

Figure 2: A schematic of the microtube anodization system.
Anodization was carried out under conditions of either a constant electrolyte flow or a pulsed electrolyte flow. The internal volume of the microtube is small and that the microtube is placed outside the electrolyte reservoir, making it likely that electrolyte depletion occurs as the anodization reaction proceeds (see Section 2.3A below). With these considerations, the pulsed electrolyte flow condition was adopted as a means to obviate possible mass transport problems. For pulsed electrolyte flow anodization, the Agilent 34970A unit was used to turn the diaphragm pump on when the current in the electrochemical cell dropped to a designated threshold value, forcing flow of fresh electrolyte into the interior of the microtube. After fresh electrolyte is forced to flow through the entire tube interior, the pump was cut off and anodization proceeded again with a stationary electrolyte present within the tube. Figure 3 shows a typical dataset of current vs. time during anodization of one microtube, which shows the manifestation of repeated anodization/electrolyte replenishment cycles, as fresh electrolyte is repeatedly pumped into the microtube.

![Current vs. time plot](image)

Figure 3: A typical current vs. time plot for microtube anodization, showing the repeated current drops due to electrolyte depletion and the sharp current increases due to fresh electrolyte supply by turning the pump on for ~5s.

The anodization process was carried out for 3h, 4h, and 6h, after which the tube was removed from the electrolyte flow circuit, rinsed with deionized water, dried in air, and the epoxy was removed. A 1cm section of the treated tube was cut off for cross sectional observation, and the remaining 3cm section was cut in half down its length using μEDM. One half-section was used to characterize the AAO morphology, and the other half-section was used for subsequent corrosion current tests.
2.2B Corrosion Testing of Anodized Al Microtubes

The tube half-sections designated for corrosion testing was first placed in deionized water heated to 95–98°C for 30 min. This oxide sealing process causes the AAO to form AlO(OH), which diminishes the size of nano-pores in the AAO [54]. A standard 3-electrode configuration was utilized for the corrosion test, and the electrolyte was a 1M NaCl solution. The reference electrode was a saturated calomel electrode (SCE) (13-620-259, Fischer Scientific, Pittsburgh, PA) and the counter electrode was the same platinum foil used in the anodization process. The 3 cm tube half-section served as the working electrode. It was coated with an electrically insulating epoxy from Devcon except for two sections: a 0.5 cm section on one end left bare for connection to a potentiostat (7060, Amel, Milano, Italy), and a 0.5 cm section with the anodized and sealed tube interior exposed to the corrosion testing electrolyte. The three electrodes were placed in a beaker at room temperature with the NaCl electrolyte, and a linear sweep voltammetry method was employed for corrosion testing in the potential range of -1.25V to 1.75V vs. SCE with a voltage sweep rate of 1 mV/s.

2.2C Fabrication of Al MHEs

Al MHEs were fabricated following a procedure similar to that reported in a previous paper [30]. Al 1100 coupons with a thickness of ~6.35 mm were cut into 42 mm × 42 mm squares. A mold insert was fabricated from a ~22 mm × ~22 mm × ~3 mm Inconel X750 plate using μEDM. An array of parallel μEDM cuts was made on the top surface of the Inconel plate, using ~0.5 mm thick Mo sheets as electrodes in the sinking mode. The finished Inconel mold insert consisted of an array of 26 parallel rectangular protrusions off the top surface. The protrusions had heights of ~500 μm, widths of ~200 μm, and lengths of ~20 mm. As-cut Inconel plates were electrochemically surface etched in a perchloric acid/acetic acid solution (1:1 HClO₄/CH₃COOH) solutions galvanostatically at 0.75 A with anodic bias against a graphite counter electrode until the voltage reached 7.5 V (typically ~3 min). After electropolishing, the Inconel plate was dried, loaded into a vacuum deposition chamber, and evacuated to a base pressure of <1×10⁻⁶ Torr. An elemental Cr thin film interlayer, ~300 nm in thickness, was sputter deposited onto the Inconel plate. Immediately following the Cr interlayer deposition, an amorphous silicon nitride (a-Si:N) coating was deposited by sputtering elemental Si targets in an Ar/N₂ mixture. The a-Si:N thickness was ~1 μm.

Microchannel arrays in Al coupons were formed through compression molding with the a-Si:N coated Inconel insert [13]. The compression molding system consisted of a hydraulically-acutated single-axis testing system (MTS858, MTS Systems, Eden Prairie, MN) retrofitted with a vacuum chamber around the grip section. A bellows adapter facilitated a sealed connection for the force actuator into the vacuum chamber. Two stages containing cartridge heaters were attached to the upper force actuator and base of the vacuum chamber. The mold insert was fastened to the upper stage, and the Al coupons were attached to the lower stage. The chamber was evacuated to typical pressures of ~1×10⁻⁵ Torr, and the heaters were turned on. Thermocouples near the specimen mounting surface of each heater stage were used to monitor temperatures. The molding temperature was held at 267±8°C, and the molding process was carried out in the force-controlled mode. When the molding temperature was reached, the force was increased from 0 to ~18 kN at a rate of 1.83 kN/min. Once the targeted molding force was reached, the force was held constant for 30 s, and then the insert was retracted from the Al coupon. Typical de-molding forces were 3-6 kN. Following this molding procedure, open and
parallel arrays of microchannels were fabricated onto the surfaces of Al coupons, with widths of ~200µm, lengths of ~20mm, and varying depths in accordance to the maximum molding force.

To convert open microchannel arrays into enclosed microchannel devices, cover plates with 3.175mm (0.125in) NPT inlet and outlet connections, together with liquid inlet and outlet plena, were fabricated from 42mm × 42mm × 12.7mm Al6061 coupons using conventional machining techniques. Faying surfaces of the molded Al coupon containing the open microchannel array and the cover plate containing the inlet/outlet plena were polished to a mirror finish with 1µm polycrystalline diamond suspension. An optical image of the open microchannel structure, plenum coupon, and an assembled MHE is shown in Figure 4.

![Figure 4](image_url)

Figure 4: (left to right) A compression-molded open microchannel structure on one Al coupon, a plenum coupon, and an assembled MHE. The numbers on the ruler denote millimeters.

Transient liquid phase (TLP) bonding was used to join the microchannel coupon and the plenum coupon together. To achieve interfacial melting at a temperature substantially lower than the bulk melting temperature, TLP bonding requires the presence of a melting point depressant intermediate bonding layer placed in between the faying surfaces to be joined [18]. In this work, a near-eutectic Al-Cu thin film was used as the intermediate bonding layer. The mechanically polished cover plate was cleaned in acetone and methanol, etched in Keller’s Reagent (2.5 Vol.% HNO₃, 1.5 Vol.% HCl, 1 Vol.% HF, 95 Vol.% H₂O) [55], and placed in an inductive coupled plasma (ICP) assisted sputter deposition tool. The base pressure of the deposition tool was ~1×10⁻⁶Torr. The deposition tool housed two balanced magnetron sputter sources, one fitted with an elemental Al target (99.9%+) and the other with an elemental Cu target (99.9%+). Prior to sputter deposition, the cover plate surface was etched in an Ar (99.999%+) ICP, with a -50V bias applied. Balanced magnetron sputter co-deposition in Ar followed the ICP surface-etch
immediately in the dc current-controlled mode. The Al and Cu target currents were adjusted such that the overall composition of the resulting thin film is close to the eutectic composition of Al$_{83}$Cu$_{17}$ [56]. The deposition time was adjusted such that the thickness of the Al-Cu thin film was ~1.25µm.

Prior to TLP bonding, the molded Al coupon containing the open microchannel array was etched with Keller’s Reagent. Immediately after etching, the molded coupon and the cover plate with the near-eutectic Al-Cu thin film deposited on top were placed face-to-face in the molding chamber, with the mold insert removed. The chamber was evacuated, and the heaters were turned on. When the temperature reached ~500°C, the upper stage was lowered to contact the specimen assembly, and the compression force was increased so that applied pressure was ~1.1MPa. When the temperature reached ~580°C, the heaters were turned off, and the bonding pressure was held until the temperature dropped below 500°C. At that point, the pressure was removed, and the specimen was allowed to cool naturally to room temperature.

To examine the quality of MHE assembly, one specimen was cut in half perpendicular to the channel direction with a sectioning saw, followed by mechanical polishing of the channel cross section to a mirror finish using colloidal silica on a vibratory polisher (GIGA-0900, Pace Technologies, Tucson, AZ). An image of a portion of the polished channel cross section is shown in Figure 5. This particular microchannel array has nearly square channel cross sections. Figure 5 shows no evidence of bond line separation or void formation near the bonding interface region, indicating that TLP bonding of Al coupons with near-eutectic Al-Cu intermediate layers yields MHE devices with sufficient quality, and that the devices should function as intended.

Figure 5: A cross-sectional SEM image of a portion of one MHE, showing typical integrity of structures and high bonding quality.
2.2D  Anodization of Al-Based MHEs

Bonded Al MHEs were placed in a circulation system and etched in 1M NaOH solution for 1.5min at a flow rate of ~50 ml/min. Then, they were rinsed with deionized water for 1.5min at a flow rate of ~50ml/min and dried with compressed air at 50psi for 1min. The MHEs were then connected to the anodization electrolyte (0.3M oxalic acid) circulation system. The MHEs were placed in an ice bath, and physical continuity of the electrolyte was verified. The same Pt counter electrode used in the microtube anodization experiments was inserted into the electrolyte reservoir. The working electrode was attached to the outer surface of the MHE via an electrical eyelet and screw, and the potential was increased from 0 to 70V using a programmable DC power supply (PWS4721, Tektronix, Beaverton, OR). A multi-function data acquisition unit (DAQ) (OMB-DAQ-2416-4AO, Omega, Stamford, CT) was used to turn on the electrolyte pump to replenish ions within the MHE channels when the anodization current reached a designated low threshold value. The DAQ was also used to record cell current and voltage at a rate of 1Hz. The anodization process was performed for 8h and 10h to determine the time required for adequate passivation. Once the anodization process was completed, MHEs were removed from the electrolyte circulation system and flushed with DI water for 1.5min at a flow rate of ~50ml/min and dried with compressed air for 1min. They were then placed in a beaker containing 95\(^\circ\)—98\(^\circ\)C DI water for 30min for sealing. After sealing, the MHEs were dried with compressed air for 1min.

2.2E  Corrosion Testing of Al-Based MHEs

It was not possible to perform a corrosion test analogous to the one used for Al microtubes because of the inability to remove Cl\(_2\) and O\(_2\) bubbles formed in the channel due to the electrolysis of NaCl [57] and water [58], respectively, which tend to insulate the inner channel surface from the electrolyte. Therefore, a qualitative test of the sealed AAO electrical resistance was performed. A manifold consisting of one inlet and three outlet flow paths, all of equal lengths, was utilized to connect one un-anodized MHE and two anodized MHEs (one anodized for 8h and the other for 10h) to the anodization circuit simultaneously. Schematics of the MHEs connected to the manifold are shown in Figure 6. The anodization procedure was repeated with this test configuration with a constant electrolyte flow rate of ~50mL/min per MHE, except the MHEs were in ambient air and the voltage was only ramped up to 30V. The currents passing through all three MHEs were recorded simultaneously, which was facilitated by measuring the voltage across a 1\(\Omega\) resistor between each MHE and the positive terminal of the power supply.

2.2F  Materials Characterization

A focused ion beam (FIB) instrument (Quanta3D FEG, FEI, Hillsboro, OR), combining a Schottky field-emission electron source and a high-current Ga\(^+\) ion source, was used for characterization of as-received and anodized materials. Excited by primary electrons or Ga\(^+\) ions, secondary electron (SE) or ion-induced secondary electron (ISE) images of specimens can be formed. The focused Ga\(^+\) ion beam was also used to form site-selective cross-sections into specimen surfaces. An ion beam catalyzed Pt deposition system from an organometallic Pt gas source was also attached to the FIB, enabling site-selective Pt deposition for specimen surface protection prior to Ga\(^+\) ion cutting. An X-ray energy dispersive spectroscopy (EDS) system (EDAX, Mahwah, NJ) was attached to the FIB, enabling elemental analysis of specimens.
Circular cross sections of anodized Al tubes were mechanically polished to ~1\(\mu\)m surface roughness with polycrystalline diamond suspension, and mounted in epoxy for end-on evaluation of the AAO layer uniformity. The 3cm-long tube half-sections were first observed in plan-view to determine the AAO surface morphology. The presence of AAO was verified with EDS. Further examination of the AAO morphology and thickness was accomplished through FIB cross-sectional cuts made into the surface at random locations, with cut dimensions of 10-15\(\mu\)m in width and ~10\(\mu\)m in depth. To determine the AAO thickness, 7 separate measurements of the distance between the top of the AAO layer and the AAO-Al interface were made perpendicular to the surface. To investigate the AAO layer in anodized Al MHEs, the MHEs were cut perpendicular to the length of the microchannels, and the cut surface was polished to a mirror finish. The FIB instrument was then used to make a cross-sectional cut into the channel sidewall. The presence of AAO was again verified with EDS, and the AAO thickness was measured from the cross-sectional images.

### 2.3 Results and Discussion

#### 2.3A Characterization of Anodized Al Microtubes

A typical cross-sectional SE image of a portion of an anodized microtube is shown in Figure 7. The AAO layer exhibits a white contrast in the image, and has a thickness of ~1\(\mu\)m. It has a reasonably uniform thickness despite the high roughness of the tube’s inner surface. This image also indicates that the AAO is fairly robust because no portion appears to be chipped off or disconnected from the Al substrate as a result of the mechanical polishing process.

A plan-view SE image indicative of the typical as-anodized AAO surface morphology is shown in Figure 8(a). From the image, it appears that the AAO has a high porosity and sponge-like structure. However, the AAO layer appears to change beneath its top surface, as evidenced in a typical FIB cross-section in Figure 8(b), which shows clearly the presence of a nanopore structure inside the AAO. The nanopores are not all aligned along a single direction because of the presence of Al substrate surface roughness leading to microscale surface curvature.
Figure 7: A typical SE image of the microtube cross section showing the conformal AAO layer.

Figure 8: a) An SE image showing the typical surface morphology of as-anodized AAO in microtubes. b) A typical FIB cross section of the AAO in microtubes, showing the presence of a nanoporous structure.

Rather, the nanopore structure is observed to grow approximately perpendicular to the local Al surface. The dark area between the Al substrate and AAO is thought to be a thin and dense layer of barrier-type oxide, as reported in the literature [51]. Another FIB cross section is shown in Figure 9, which illustrates the tendency of the AAO to enclose cracks present in the original Al
substrate. This occurs because the electrolyte penetrates into the cracks and interacts with the Al surface there in a similar way. This observation reveals the potential of anodization-based surface passivation, because it implies that AAO will form even around deep cracks in the original Al substrate surface.

![AAO FIB Cross Section](image)

Figure 9: A FIB cross section showing the tendency of the AAO to enclose cracks present in the original Al substrate.

FIB cross sections made in different anodically treated specimens were used to estimate the AAO thickness, as exemplified in Figure 10. Results of AAO thickness measurements from specimens anodized at different times and voltages are shown in Figures Figure 11(a) and Figure 11(b). In agreement with the literature pertaining to anodization of flat Al foils in oxalic acid, at a constant anodization potential of 50V, the presently measured AAO thickness shown in Figure 11(a) appears to increase approximately linearly with anodization time [59]. Previous anodization experiments carried out on flat foils in oxalic acid at room temperature showed an exponential increase of oxide thickness with increasing anodization voltage [60].

In the present range of anodization voltage tested, at a constant anodization time of 4h, data shown in Figure 11(b) indicates an increase of AAO thickness with voltage, and is not inconsistent with an exponential relationship. From the literature, the barrier layer thickness near the AAO/substrate interface should increase with increasing anodization voltage [51]. The present measurements were made to determine the entire oxide layer thickness, and the barrier layer thickness was well within the measurement uncertainty. Therefore, no conclusions could be drawn about the effect of voltage on the barrier layer thickness in the present experiments.

For most aluminum anodizations, the current typically decreases during anodization because the AAO thickness increases, making it more difficult to pass current, then, the anodization current increases as pores form [61-63].
Figure 10: One example of a typical FIB cross section used to measure the AAO thickness. The average AAO thickness of this specimen was determined to be $5.8 \pm 1.5 \mu$m.

![Figure 10](image)

Figure 11: a) Measured AAO thickness vs. anodization time at 50V, showing an approximately linear relationship. b) Measured AAO thickness vs. anodization voltage at a constant time of 4h, which shows a weak dependence on voltage in the voltage range tested.

![Figure 11](image)

However, in the diffusion limited microtube geometry, pore growth is limited, so there is no point at which the current increases during an anodization conducted under constant electrolyte flow conditions. Under pulsed electrolyte flow, the current drops as the anodization proceeds, followed by a current increase when fresh electrolyte is pumped into the tube. From the SE
images, the surface layer of the AAO is sponge-like, and below it, the pores extend in a branchlike structure, indicating a denser, more compact oxide near the base of the AAO film and a more porous AAO at the surface. Oxalic acid plays an important role in AAO pore growth, since the AAO dissolution reaction that forms the pores is acid catalyzed, and the counterion incorporates into the AAO [61-63]. The current drops as transport of the active electrolyte species responsible for pore growth occurs at a lower rate than consumption of the species at the tube surface during anodization. Then the current is restored to its initial value when fresh electrolyte is pumped into the tube, restoring the initial conditions.

Examining the AAO formed under different electrolyte flow conditions, anodization under continuous electrolyte flow resulted in non-uniform AAO with the thickness being 60% greater at the microtube inlet than outlet, whereas anodization under pulsed electrolyte flow resulted in a more uniform AAO with the thicknesses at the microtube inlet and outlet being approximately equal. This asymmetry can thus be attributed to the electrolyte flow. Although the AAO thickness is influenced by a number of factors, it is ultimately controlled by pore depth. With all other variables held constant, introducing a constant electrolyte flow causes a concentration gradient of active electrolyte species along the length of the microtube, with the concentration being greater at the microtube inlet than the outlet, leading to the difference in the AAO thickness observed. Thus, pulsed electrolyte flow was adopted for the present study.

2.3B Corrosion Testing of Anodized Al Microtubes

Unanodized Al half-tubes and anodized Al half-tubes, after sealing in near-boiling distilled water for 30min, were subjected to an electrochemical corrosion test to measure and compare their corrosion currents. Figure 12 illustrates typical potentiodynamic polarization curves of the bare and oxidized/sealed Al half-tubes in near-neutral pH NaCl solutions. The two curves correspond to the log of current density for two specimens over the potential range of -1.25V to +1.75 V. It is evident that the plots contain two parts; namely, a cathodic region and an anodic region. The cathodic region represents an oxygen reduction reaction occurring on the cathode [64],

\[ \text{O}_2 + \text{H}_2\text{O} + 2\epsilon^- \rightarrow 2\text{OH}^- \]  

while the anodic region describes the dominant oxidation reaction of Al metal on the tube [64]:

\[ 2\text{Al} + 6\text{OH}^- \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 6\epsilon^- \]  

In the NaCl solution, pitting corrosion is likely to occur in the anodic region in the presence of aggressive chloride species [64]:

\[ \text{Al(OH)}_3 + \text{Cl}^- \rightarrow \text{Al(OH)}_2\text{Cl} + \text{OH}^- \]  

\[ \text{Al(OH)}_2\text{Cl} + \text{Cl}^- \rightarrow \text{Al(OH)Cl}_2 + \text{OH}^- \]  

\[ \text{Al(OH)Cl}_2 + \text{Cl}^- \rightarrow \text{AlCl}_3 + \text{OH}^- \]  

According to the data shown in Figure 12, the anodic corrosion current of the oxidized tubing was reduced by one order of magnitude from that of the un-anodized Al tube as the potential increased, suggesting that the oxidation rate of metal on the former was significantly slower than
that on the latter. This is ascribed to the fact that the sealed alumina layer covering the surface of Al tube hinders the inward movement of ions from the solution to corrode Al metal substrate.

![Figure 12: Tube corrosion test results showing a factor of 10 decrease in corrosion current for a tube anodized for 4h at 50V as compared to an un-anodized (UA) tube.](image)

The polarization curves for the un-anodized tubes agree well with similar experiments performed by Lee, et al on flat sheets [65] in both magnitude and shape. The anodized and sealed tube results agree with the results of Lee, et al in shape, but the reduction of corrosion current is much less pronounced in the present experiments. This may be due to the fact that the present oxide layer is much thinner, and that the present oxide sealing was carried out in boiling water, as compared to in NiF$_2$ [65]. Based on the enhanced anticorrosion performance of anodized Al tube, we conclude that our proposed method to anodize inner surface of Al microtubes and seal the as-grown porous AAO film in boiling water is a feasible and effective way to improve the corrosion resistance of Al micro devices with complicated tubing or channel structures.

2.3C Corrosion Testing of Al MHEs

There were several issues associated with conducting an electrochemical corrosion test for Al MHEs in an analogous manner to how anodized Al microtubes were tested. The complex geometry of the MHEs, once fabricated and internally passivated, would make it very difficult to be cut in half and immersed in a beaker-type electrochemical cell, as was done with the microtubes. Flow-through corrosion tests using a three-electrode setup were also attempted with microtubes using an apparatus similar to the microtube anodization system, except the counter and reference electrodes were inserted into the connecting electrolyte tubing immediately downstream of the microtube. Below a critical tube inner diameter, there was no noticeable corrosion current even for un-anodized specimens using this test procedure. Since gasification was always observed at the working electrode during the standard beaker corrosion tests, one
possibility was that Cl₂ and O₂ bubbles formed on the internal surfaces of the tubular working electrode in the lower and upper ranges of the potential sweep, respectively, which effectively insulated the metal surface from the electrolyte [57, 58].

Corrosion tests have been developed for automotive radiators, which have similar flow-path geometry and characteristic dimensions. One such procedure is to simulate the effects of an engine coolant by pumping it through the radiator at an appropriate temperature, with solution conductivity and pH measurements made in situ and pitting characteristics and ion concentrations in the coolant examined after the designated testing time frame [66]. Another method, often used in conjunction with non-electrochemical corrosion measurements, is potentiodynamic polarization testing of coupons of the radiator material immersed in a beaker of the corrosive liquid [67]. These tests are designed to show the susceptibility of the radiator metal to corrosion in its operating environment. In the current case, a test procedure is required to determine whether the AAO formed on the internal surfaces of the anodized MHEs, like AAO on flat Al coupons, offers adequate protection against corrosion of the MHE under relevant operating conditions [34, 59]. Therefore, in analogy to corrosion testing of automotive radiators, an alternative test was employed for the Al MHEs, which qualitatively compares the resistance of anodized and sealed MHEs versus un-anodized MHEs in a corrosive electrolyte in the presence of a potential difference.

Since the anodization reaction was used as a corrosion test, both anodized and sealed as well as un-anodized specimens tended to grow AAO layers during the test. However, the anodized and sealed MHEs were expected to have a dense and passive layer of AAO already formed, which inhibits the further oxidation of Al metal by providing a diffusion barrier for O²⁻ ions [61]. The un-anodized specimen, without the AAO layer, had no such protection, so its effective current should be higher. It is important to note that the values of current in this corrosion test are not important; rather, a difference in current between the un-anodized and passivated MHEs is what should be observed.

The results of one typical corrosion test conducted in this manner are shown in Figure 13. The un-anodized specimen clearly has a larger current than the anodized and sealed specimens, and the current difference between the specimens grows with increasing voltage. It is interesting to note that there is very little difference between the performance of the 8h and 10h anodized and sealed specimens. From this test, it appears that an optimal anodization time exists, beyond which the benefit in terms of additional corrosion protection diminishes.

2.3D Characterization of Al MHEs

An image of the top surface of sealed AAO in an MHE channel is shown in Figure 14. This structure is the same as the one observed in anodized and sealed microtubes, and it agrees with experiments performed on flat Al sheets [68]. A FIB cross section into one microchannel sidewall is shown in Figure 15. The AAO is conformal to the Al surface with a uniform thickness of ~1μm, after an anodization condition of 10h at 50V. This growth rate of ~0.1μm/hr is about 80% lower than the growth rate observed in Al microtubes. Since the AAO growth rate is affected by several factors, it is not clear why such a large difference was observed.
Figure 13: Corrosion test results for one set of anodized Al MHEs tested against an unanodized Al MHE.

Figure 14: Surface morphology of AAO sealed in near-boiling water for 30 mins.
2.4 Summary

We have employed a pulsed-electrolyte-flow method for anodization of the internal surfaces of Al microtubes and Al-based MHEs. This method produces a uniform surface morphology and anodic aluminum oxide thickness, which are desirable characteristics in a passivation layer. Characterization performed on the anodized Al microtubes showed a nearly linear dependence of oxide thickness on anodization time and a weak dependence on anodization voltage. Sealing in near-boiling water yielded a microstructural change that closed the nanopores within the AAO and completed the passivation process. Linear sweep voltammetry corrosion testing of the microtubes showed an order of magnitude reduction in corrosion current when compared to un-anodized tubes. Al MHEs were anodized and sealed using the same method used for the microtubes. They were corrosion tested by placing anodized and un-anodized specimens in parallel loops of the anodization system and simultaneously measuring the current flowing to each MHE. Although qualitative in nature, those results showed that the anodized MHEs consistently had lower current than the un-anodized MHE. The present results show that internal surface passivation of aluminum microchannel devices can be achieved through anodic oxide formation. This method can be applied to other aluminum based micro-devices where internal surface passivation is desired.
3. Fabrication and Testing of Al-based Micro Gas Chromatographs

3.1 Introduction

Gas chromatography (GC) is an important analytical chemistry method for separating and quantifying mixtures of permanent gases, volatile compounds, and semi-volatile compounds. This method involves inserting a pulse of analyte gas mixture into a long, circular column with diameter in the micron-mm range. The mixture is carried through the column by an inert carrier gas such as hydrogen, and the column is internally coated with a stationary phase that retains each analyte gas differently. The gases exit the column separated into distinct peaks from the least retained compound to the most retained compound [69]. Conventional GC columns today are usually 10-50m long open tubular columns (OTC) made of fused silica with typical internal diameters as low as 100μm [70]. They are coiled in a circle ~10cm in diameter, and any heating required for separation is performed in an oven, which restricts portability. This conventional GC column technology is considered to be mature [71], but the drive for testing speed as well as device portability and robustness has spawned the newer area of microfabricated GCs (mGCs).

The first attempt to produce a microfabricated, chip-based mGC was by Terry et al. in 1979 [72]. They anisotropically etched a 1.5m-long, 200μm × 30μm channel in a 5cm silicon wafer, then anodically bonded on a Pyrex cover plate and integrated an injection valve and thermal conductivity detector onto the wafer [72]. After dynamic coating with stationary phase, the maximum number of plates achieved was 2300 for n-heptane [72]. Although the performance was much lower than OTCs at that time, their work led to many more investigations of mGC design and fabrication. Another notable achievement in Si-based mGCs was the high efficiency achieved by Reidy, et al in 2006 using a static-coated column [35]. The stand-alone 3m-long columns, made by deep reactive ion etching (DRIE), had ~4000 theoretical plates per meter and a peak capacity over 100 in ~500s, which is nearly double the efficiency they had previously obtained by dynamic coating [73].

Silicon-based mGC columns have disadvantages such as lower mechanical robustness and lower bulk thermal conductivity when compared to metals [8]. While much less work has been done in this area, at least two groups have successfully fabricated metal-based mGC columns. In 2007, Bhushan, et al. used the LIGA process to fabricate 0.5- and 2m-long, 50μm × 600μm columns with integral split injection in Ni [38]. The 2m column produced up to 17,500 theoretical plates for methane, and the 0.5m column fully separated a mixture of n-hexane, n-octane, n-decane, and n-dodecane in ~1.5s after static coating with OV-1 [39]. More recently, Iwaya et al. have fabricated a mGC column stable up to 550°C from stainless steel by etching a channel into facing surfaces of two plates, diffusion-bonding the plates together, and brazing connection ports [36]. They verified the channel alignment with acoustic microscopy, and after dynamic coating, the HETP was found to be ~0.05cm for octane, which is similar to those reported by Lambertus, et al. on chips fabricated using DRIE in Si [36, 73].

The above experiments were all carried out with a liquid-polymer stationary phase such as poly(dimethylsiloxane) (PDMS), which is a common non-polar coating [74]. This is referred to as gas-liquid chromatography (GLC), and it is practical for separating compounds with boiling points above room temperature. To separate permanent gases and volatile organic compounds (VOCs), the liquid stationary phase is often replaced by a porous solid coating such as graphitized carbon black, alumina, silica, and some porous polymers in a porous layer open tubular (PLOT) column. This method is known as gas-solid chromatography (GSC) [75]. The adsorptive nature of GSC makes its mass transfer to and from the stationary phase sites much faster than diffusion in GLC [76]. Additionally, the surface chemistry of solid stationary phases
can be tuned to control the selectivity for different compounds [77]. Little work has been done in the field of mGC PLOT column fabrication. Stadermann, et al. used DRIE to fabricate a 50cm long Si-based mGC column and grew a ~1μm thick layer of single-wall carbon nanotubes (SWNTs) on the bottom etch surface [78]. They deposited a thin-film resistive heater on the chip to yield temperature increase rates of 60°C/s, and the device separated n-hexane, n-octane, n-nonane, and n-decane with a resolution slightly less than 1.0 in ~1s [78]. After improving their SWNT growth recipe to make a uniform layer and using resist as a bonding agent for the cover plate, they separated n-hexane, n-octane, n-nonane, n-decane, and n-undecane with improved resolution in ~2.2s [79].

The γ phase of alumina (γ-Al₂O₃) is a common stationary phase in GSC, owing its activity to surface hydroxyl groups and Lewis acid and base sites [80]. Typically, conventional PLOT columns with alumina stationary phase are made from fused silica or stainless steel, and the stationary phase is deposited onto the internal surface by passing a solution through the column [70, 77, 81]. While these columns have high efficiency in separating C₁-C₄ hydrocarbons, they have the typical disadvantages of long analysis time, low portability, and lack of robustness. A unique problem for these columns is the tendency for the alumina to de-bond from the inner capillary wall under fluctuations of head pressure greater than ~1.5 psi/s [82].

Aluminum possesses a high thermal conductivity even among metals [8], and the anodization of aluminum to form nanoporous Al₂O₃ is a well-understood process [51, 59, 61]. Additionally, internal anodization of small-diameter tubes has been reported by two groups [52, 53]. The mechanical properties of Al make it an excellent candidate for micro-scale molding replication, a process which we have studied extensively [13, 16, 83-85]. We have also studied eutectic or transient liquid phase (TLP) bonding in the Al-Ge and Cu-Al binary phase systems, which is used to bond an Al cover onto the open molded microchannel structure [20, 23, 31]. We have previously successfully anodized the internal surface of microchannel heat exchangers for the purpose of corrosion protection [P.J. Hymel et al., in preparation]. Here, we introduce a possible extension of our current techniques to the fabrication of an Al-based mGC column with an anodic aluminum oxide (AAO) solid stationary phase. Such a column provides opportunities for high-throughput column chip manufacturing, fast temperature programming capability, miniaturization, and robustness of the column and the stationary phase.

3.2 Experimental Procedure

3.2A Microscale Molding Replication of Open mGC Column Patterns

A mold insert was fabricated from a ~27mm × ~27mm × ~3.5mm Inconel X750 plate using micro milling. The insert had a serpentine pattern with 57 parallel protrusions separated by ~350μm and connected by 180° turns at each end. The protrusions had a height of ~400μm, width of ~80μm, and length of ~19mm each, which yielded a total length of ~1.2m. The insert was electrochemically polished (ECP) in a solution of 50 vol.% acetic acid and 50 vol.% perchloric acid for ~5min to remove burrs and surface roughness from the machining process. A constant current of 0.75A was used, and the insert was etched until the voltage reached 7.5V, which took 5min. Following ECP, the insert was dried, inserted into a vacuum deposition chamber, and evacuated to a base pressure of <1×10⁻⁶Torr. An elemental Cr thin film interlayer, ~300nm in thickness, was sputter deposited on the Inconel plate. Immediately following the Cr deposition, the Inconel plate was conformally coated with a thin amorphous silicon nitride (a-SiN) coating by sputtering elemental Si targets in an Ar/N₂ mixture. The a-Si: N thickness was ~1μm.
Al 1100 coupons with a thickness of ~6.35 mm were cut into 50mm × 58mm rectangles and homogenized at ~400° C overnight in an oven. The microchannel pattern was formed through compression molding with the Inconel insert [30]. The compression molding system consisted of a single-axis hydraulic tensile test apparatus (MTS858, MTS Systems, Eden Prairie, MN) modified by enclosing the grip section with a vacuum chamber. The force actuator was enclosed by a bellows adapter, which facilitated a sealed connection into the chamber. A stage with cartridge heaters was attached to the bottom of the vacuum chamber, and a type-K thermocouple was secured in a hole drilled ~1mm away from the top surface of the stage. A similar heater stage with another type-K thermocouple was attached to the force actuator. The mold insert was attached to the top heater stage. The chamber was evacuated to a pressure of ~1 × 10⁻⁵ Torr, and the heaters were turned on. When the heater stage temperatures reached 267±8°C, the molding was initiated. The force was ramped from 0 to ~20kN at a rate of ~1.8kN/min. Once the target force was reached, a constant-force hold was executed for 30 seconds, and then the insert was removed from the Al coupon. Typical de-molding forces were ~3.5-6 kN. The final result of the molding process was an open channel structure in the Al coupon with typical width ~80μm, depth varying between ~160-240μm depending on final molding force and temperature, and a total length of ~1.2m. Figure 16 shows the mold insert and corresponding as-molded structure for the column inlet/outlet. Figure 17 shows typical measurements of the mold insert and as-molded open microchannel. Note that the mold insert protrusion cross section is actually somewhat trapezoidal, which explains the difference between the width at the top of the protrusion and the measured channel width of the molded structure. This observation was verified by cross sections of the fully-assembled mGC column device.

To facilitate insertion of ~0.793mm OD polyether ether ketone (PEEK) tubes (TPK.502, Valco Instruments, Houston, TX) for connection between the GC column and test equipment, holes were cut in both the open microchannel pattern and its mating cover coupon using micro electro discharge machining (μEDM) in the sinking mode. The compression-molded coupon was cut from its original dimensions to ~42mm × ~40mm, and the cover coupon was fabricated to match it. A ~0.793mm OD stainless steel tube (T5N5D, Valco Instruments, Houston, TX) was used as the electrode. It was placed in a vice with its axis horizontal, and lowered vertically to
make half-circle-shaped cross section cuts in each of the coupons. The depths of cut below the surface of the cover and molded coupons were ~430\( \mu \text{m} \) and ~630\( \mu \text{m} \), respectively, to account for the fact that the centerline of the mGC column channel was ~100\( \mu \text{m} \) below the surface of the molded coupon. Figure 18 shows the mold insert and a molded mGC column channel coupon after cutting the tube holes.

Figure 17: SE images of a) the mold insert showing approximate dimensions, b) as-molded open microchannel structure showing successful replication of the mold insert pattern.

Figure 18: Optical image of a micro milled 1.2m-long Inconel mold insert and the corresponding open molded mGC column channel structure. Numbers on the ruler are in mm.
3.2B Fabrication of Enclosed mGC Column Structures by Transient Liquid Phase Bonding

Transonic liquid phase (TLP) bonding was used to join the open mGC column channel coupon and its cover coupon together. This bonding technique utilizes a melting-point-depressant (MPD) intermediate layer between the two faying surfaces to ensure that the interface melts at a lower temperature than the bulk materials being joined [18]. In this case, a near-eutectic composition Al-Cu thin film with thickness ~1µm was used as the MPD. Both coupons were mechanically ground and polished to a mirror finish in 1µm polycrystalline diamond suspension, cleaned in acetone and methanol, and etched with Keller’s Reagent (2.5 Vol.% HNO₃, 1.5 Vol.% HCl, 1 Vol.% HF, 95 Vol.% H₂O) [55]. The open microchannel coupon was not etched until ~5min before bonding. Immediately after etching, the cover coupon was placed in an inductive coupled plasma (ICP) assisted sputter deposition system, and evacuated to a base pressure of ~1x10⁻⁶ Torr. The deposition system housed two balanced magnetron sputter sources, one fitted with an elemental Al target (99.9%+) and the other with an elemental Cu target (99.9%+). Prior to sputter deposition, the cover plate surface was etched in an Ar (99.999%+) ICP, with a -50V bias applied. Balanced magnetron sputter co-deposition in Ar followed the ICP surface-etch immediately in the dc current-controlled mode. The Al and Cu target currents were adjusted such that the overall composition of the resulting thin film was close to the eutectic composition of Al₈₃Cu₁₇ [56]. The deposition time was adjusted such that the thickness of the Al-Cu thin film was ~1µm. After removing from the deposition system, the cover coupon was placed on top of the open microchannel coupon, two ~0.793mm OD stainless steel tubes were placed in the µEDM holes to keep the coupons aligned, and the assembly was placed in the bonding system. The typical time between removal of the cover coupon from the deposition system and evacuation of the bonding system was ~10mins. The apparatus used for bonding was the same one used for molding; however, the mold insert was removed so that the two flat heater stage surfaces contacted the mGC column assembly. The cartridge heaters were turned on until the thermocouples reached ~500°C, and the top actuator was ramped down to a bonding pressure of ~0.9MPa at a rate of ~0.3MPa/min. Once the final pressure as reached, a constant-force hold was executed until the temperatures reached ~580°C, which is well above the Al-Cu eutectic temperature of ~545°C. At that point, the heaters were turned off, and the temperature was allowed to drop below 500°C before removing the bonding pressure. The bonded mGC columns were allowed to cool in air. After reaching room temperature, the stainless steel alignment tubes were removed, and ~0.793mm PEEK tubes with lengths ~5cm were bonded into the holes using epoxy (Loctite Hysol 9460, Henkel, Dusseldorf, Germany). To eliminate as much dead volume in the connection as possible, epoxy was spread onto the tube from 8mm up to ~0.5mm from the end to be inserted. Upon insertion into the bonding hole, the epoxy filled in most of the gap between the tube OD and hole ID. The epoxy was cured in a drying oven at 80°C for 5 hours before further testing was completed.

3.2C Flow Testing

Each mGC column was first tested for flow continuity and leaks using deionized water at 90psi. The test system contained 90µm and 10µm filters in series to prevent particulates from entering the column and blocking the flow. Upon completion of the initial test, each mGC column was tested for hydrogen flow. As shown schematically in Figure 19, the test apparatus consisted of a pressure regulator with gauge, zero-dead volume connections to the mGC column PEEK tubes, and a hydrogen flow meter (ProFlow 6000, Restek, Bellafonte, PA). After checking for hydrogen leaks with a gas leak detector (21-050, Gow-Mac, Bethlehem, PA), the
pressure was varied from 10 to 50 psi in steps of 10 psi, and the flow rate was allowed to equilibrate before recording each flow rate measurement.

Figure 19: A schematic of the hydrogen flow testing setup.

3.2D Methane Peak Testing

The mGC columns were tested with methane gas pulses to determine baseline efficiency information. The test platform was a modified microFAST GC (Analytical Specialists, Baton Rouge, LA) with a flame ionization detector (FID) and Valco 10-port diaphragm valve with a ~2μl sample loop, into which methane was directly injected using a syringe. Figure 20 shows the sample loop configurations during methane sampling and injection. At injection, the H₂ carrier gas loop was re-directed to empty the methane sample loop at the set carrier gas pressure. Injection times were 4s, and the carrier gas pressure was varied from 10 to 50 psi in steps of 10 psi corresponding to carrier gas velocities between ~300cm/s and ~1200cm/s. The chromatogram data were used to find the HETP of each chip at each carrier gas velocity. Width at half-height values were determined using a programming scheme to find the time coordinate that minimized the difference between its corresponding detector output value and one half of the peak height. Methane peak testing was also conducted after each anodization to quantify any differences in baseline performance as a result of anodization.

3.2E Internal Anodization

After initial methane peak tests, the mGC column channels were internally anodized to create an AAO adsorbent phase. Figure 21 shows a schematic of the anodization system. The electrolyte was 0.3M oxalic acid, and it was stored in a sample cylinder (304L-HDF4-500-T, Swagelok, Solon, OH). Industrial-grade nitrogen gas (Air Liquide) was used to supply pressure at 80 psi to the sample cylinder to drive the flow of electrolyte through 3.175mm OD PEEK tubing (TPK.102, Valco Instruments, Houston, TX) to the mGC column. Two inline filters, 75μm and 10μm (CFE series, Valco Instruments, Houston, TX), were placed in connections to prevent particulates from entering the mGC column channel. The mGC column was the working electrode, and it was connected to the positive terminal of a DC programmable power supply (6575A, Agilent, Santa Clara, CA). The outlet of the mGC column was connected to a ~350mm long, 1.588mm OD peek tube (Upchurch Scientific, Oak Harbor, WA), which terminated in a beaker of electrolyte. A 25.4mm × 25.4mm Pt counter electrode (99.9% metals basis, Alfa
Aesar, Ward Hill, MA) was placed in the electrolyte. This configuration confined the electrode separation to ~350 mm, and the diameter of the electrolyte path was ~0.793mm.

Figure 20: A schematic of the microFAST GC test platform.

Figure 21: A schematic of the mGC column internal anodization system.
The anodization was executed in potentiostatic mode at 30V and 50V. The mGC column working electrode was cooled to ~5°C in an ice bath, and the potential was ramped up from 0 to the anodization voltage at 4V/min. The anodization voltage and current were recorded by an Agilent (34972A) data logger and plotted in real time on a computer. After initially purging the electrolyte flow path of any air bubbles, the electrolyte flow was turned off by a control system consisting of a solenoid valve and relay. Upon closing the solenoid valve, a pressure relief valve was opened to return the electrolyte flow system to atmospheric pressure. As a result of ion depletion near the oxide-electrolyte surface [61], the anodization current dropped from its maximum value throughout the anodization process. The control system was used to automatically open the solenoid valve when the current dropped below a set value, which allowed the electrolyte to flow for ~15s and increase the current to its original value. Once the valve closed again, the pressure relief valve was opened to vent the compressed nitrogen. The current was also observed to drop when a gas bubble exited the mGC column, which effectively opened the electrolyte flow circuit between the two electrodes. This caused the solenoid valve to open and push the bubble toward the electrolyte beaker, which usually took several minutes because of the low flow rate.

After the anodization time elapsed, the mGC column was removed from the system and flushed with de-ionized water from the flow testing system for at least 5 minutes. Two of the mGC columns were re-anodized for an additional 5h after initial hydrocarbon separation tests were completed.

3.2F Hydrocarbon Standard Separation

It is well-known that water readily adsorbs onto alumina surfaces [86]. Most PLOT column GC manufacturers recommend flowing carrier gas through the column at 200°C for 15-30mins to desorb most of the water [87]. Since the glass transition temperature of PEEK is ~140°C [88], mGC columns were heated to 105±5°C for 1hr at 40psi H₂ flow, then allowed to cool in ambient air with the carrier gas still flowing. This process was completed before every series of separation experiments for each mGC column. The columns were removed from the carrier gas flow briefly to insert into the microFAST GC test platform, and then the carrier gas was turned on to the microFAST GC. A standard mixture of 100 ppm of butane (C₄H₁₀), pentane (C₅H₁₂), hexane (C₆H₁₄), heptane (C₇H₁₆), octane (C₈H₁₈), and nonane (C₉H₂₀) was thermally desorbed from a Tenax GR sorbent trap and injected into the column. The injector and detector (FID) temperatures were set at 150°C. Since the carrier gas pressure was used for injection, the typical pressure was 14-20psi, and typical injection times varied from ~600-1300ms. Several sample runs were made to determine a good operating pressure and injection time (usually ~20psi and ~950ms) for each mGC column at isothermal and isobaric operating conditions. Then, pressure programming under various conditions was employed to decrease the elution time of the heavier compounds. Separations were completed for each mGC column after 3h of anodization at ~18±3°C, then two mGC columns were re-anodized for an additional 5h and re-tested at 18±3°C. All columns were tested again at 10±3°C to determine the effect of lowering temperature on the separation quality.

To obtain a standard for comparison, a 25m commercial capillary PLOT column (CP7519 Al₂O₃/KCl, Agilent, Santa Clara, CA) was cut to a length of 1.2m and tested in the microFAST GC system. The column was treated with the same water removal process as the mGC columns. The data sheet included with the column included a sample chromatogram obtained isothermally at 130°C with a carrier gas pressure of ~7psi [82]. Separations were
performed for the same C₄-C₉ mixture on the Agilent column at 25°C and 130°C at carrier gas pressures of 8psi, 15psi, and 22psi with injection times of ~1400ms, ~950ms, and ~550ms, respectively. The injector and FID temperatures were both set to 150°C.

3.2G Materials Characterization

A focused ion beam (FIB) instrument (Quanta3D FEG, FEI, Hillsboro, OR), combining a Schottky field-emission electron source and a high-current Ga⁺ ion source, was used for characterization of eutectic bonding, channel cross sections, and AAO morphology and thickness. Primary electrons were used to produce secondary electron (SE) images, and primary Ga⁺ ions were used to produce ion-induced secondary electron (ISE) images. The focused Ga⁺ ion beam was also used to make site-selective cross sections in the specimen surfaces, particularly of the bond line and AAO layer.

One mGC column was cut in half with a sectioning saw perpendicular to the channel axes. After mounting in epoxy (EpoKwick, Buehler, Dusseldorf, Germany), the cut face was mechanically ground with SiC paper, polished with ~1μm polycrystalline diamond suspension, and vibratory polished with colloidal silica (GIGA-0900, Pace Technologies, Tucson, AZ). The other side of the mGC column was also prepared for observation by grinding off the Al cover coupon to reveal the open microchannel structure.

Dimensions for 55 channels were measured from the channel cross section specimen using an optical microscope (VanGuard 1242MM, VEE GEE Scientific, Kirkland, WA) and AMScope computer software suite (United Scope, Irvine, CA). The bond line was also examined in plan view and with a FIB cross section. To reveal the bond line in plan view, an area of the Al surface was etched with the ion beam at a current of 30nA for ~30s. The FIB cross section was made in this same area to examine the thickness and quality of the bond line.

3.2H Transient Heating Testing

Temperature programming is an integral part of analytical GC practice mainly because the analysis time can be decreased with very little loss of resolution [89]. For fast GC, temperature programming rates must be much higher than conventional oven GCs, which are typically up to 50°C/min [90]. One mGC column was fly-cut from a total thickness of ~12.7mm to ~6.35mm by taking off equal amounts of material on each side. This final thickness represents the thickness required by the new low-dead-volume connection design to be implemented in the future. Two thermocouple holes ~4mm deep and ~1.6mm in diameter were drilled on the bond line halfway across the 42mm sides of the mGC column. Two heater blocks were fabricated from Al blocks with footprint 42mm × 40mm and thickness ~16mm by drilling four evenly-space 6.35mm diameter through-holes on the 40mm × 16mm face. Four 150-W cartridge heaters were installed in the holes for each block, and the mGC column was secured between the two blocks using a thin layer of thermal grease (TX-4, Tuniq). The heaters in each block were wired to a potentiometer in parallel so that the total power from each block was 600W. The potentiometers were plugged into the house 120V electrical supply. Type-K thermocouples (Omega, Stamford, CT) connected to a DAQ (OMB-DAQ-2416, Omega, Stamford, CT) and LABVIEW (National Instruments, Austin, TX) program were used to record the temperature at a sample rate of 30Hz and averaging time of 2Hz. The bottom heater block was placed on the surface of a hot plate, and the top block was left open to the ambient air. When the heaters were turned on, the temperature was recorded until the thermocouples reached 200°C, the maximum recommended temperature for alumina columns.
3.3 Results and Discussion

3.3A Transient Liquid Phase Bonding

An ISE image of the channel cross sections is shown in Figure 22. The bond line region is denoted by the dashed line, and there appears to be complete fusion of the two surfaces. After a brief Ga\(^+\) ion etch on the specimen surface, the bond line was revealed, as shown in Figure 23.

![Figure 22: An ISE image of mGC column channel cross sections. The dashed line shows the approximate location of the bond line.](image)

![Figure 23: A plan-view SE image of an Al-Cu TLP bond line.](image)
The thickness is on the order of 100nm, meaning that most of the Cu from the ~1μm Al-Cu film has diffused into the Al matrix. Although different in appearance from the two substrates, closer examination showed that the line was completely filled in, and no mechanical separation existed between the faying surfaces. The difference in appearance between the bond line and substrates may be attributed to differences in their etch rates. Figure 24 shows a SE image of the FIB cross section made in the surface to show the bond line ~10μm underneath the top surface. Again, complete bonding is revealed in the cross section, but there exist small voids typical of TLP bonding [91]. The contrast and etch rate variation between the bond line and substrate suggest that a different composition exists in the ~100nm bond line. Chen, et al. studied the microstructural evolution in TLP bonding of Cu plates with an Al intermediate layer using in-situ X-ray diffraction; similar experiments will be conducted in the future to characterize the present TLP bond system [19]. Based on the characterization described above, we conclude that the TLP bonding process was successfully executed.

Figure 24: An SE image of the bond line in FIB cross section.

3.3B Flow Testing
Approximate measurements of the cross section dimension for the mGC column anodized for 8h at 50V were used to calculate the theoretical flow rate of hydrogen through it. Since the channels had a trapezoidal shape, the hydraulic diameter was found from the four times the ratio of area to perimeter [92]. The compressible Hagen-Pouiseuille equation [92] was used to find an estimate for the outlet velocity:

\[
u_o = \frac{(dh)^2 p_o(y^2 - 1)}{16\eta L} \quad \text{Eq. (1)}
\]
Since the flow is compressible, the outlet velocity can be multiplied by the correction factor, $f_2$, developed by James and Martin [93]:

$$f_2 = \frac{3 \gamma^2 - 1}{2 \gamma^3 - 1} \quad \text{Eq. (2)}$$

where $\gamma$ is the ratio of absolute inlet to outlet pressures. In Eq. (1), $d_h$ is the hydraulic diameter, $p_o$ is the absolute pressure at the column outlet, $\eta$ is the carrier gas viscosity, and $L$ is the column length. Each mGC column was flow tested with hydrogen to obtain a qualitative estimate of the channel cross section dimensions and to determine the existence of any leaks or blockages. The flow rates obtained were for the column outlet; therefore, they were also multiplied by $f_2$ to obtain the average flow rate. Figure 25 is a plot of the average flow rate at different pressures as measured directly and calculated from the cross section dimensions. Most variations in the two data sets can be attributed to the typical ~50μm difference in channel depth at different sections of the column before bonding. This issue can be addressed by modifying the existing molding system to promote better alignment and by using an automatic polisher for the bond preparation step.

![figure 25](image-url)

Figure 25: Plot of flow rate data vs. pressure and comparison to theory for given channel dimensions.

3.3C Methane Peak Testing

Figure 26 shows three methane peaks obtained from an un-anodized mGC column at a carrier gas average velocity of ~520cm/s. The retention time and peak shape are both very repeatable, and the difference in peak height resulted from slightly different amounts of methane.
being loaded into the sample loop for each run. The theoretical retention time for a compound is given by [89]:

\[ t_r = (1 + k')t_m. \]  \hspace{1cm} \text{Eq. (3)}

In Eq. (3), \( k' \) is the capacity ratio related to the gas-solid adsorption coefficients, \( K_A \) and \( K_c \) [87], by

\[ \frac{1}{k'} = \frac{\beta}{K_A} (1 + K_c \bar{P}), \]  \hspace{1cm} \text{Eq. (4)}

where \( \beta \) is the volume ratio of mobile phase to stationary phase and \( \bar{P} \) is the average carrier gas pressure along the column [77]. In Eq. (3), \( t_m \) is the retention time for an unretained compound given by

\[ t_m = \frac{L}{u}. \]  \hspace{1cm} \text{Eq. (5)}

Assuming \( k' = 0 \), i.e., that methane is not retained by Al, the retention time should be \(~0.3 \text{s}\), but it was measured to be nearly \( 2 \text{s} \). Figure 27 illustrates this pattern at over a range of carrier velocities tested with a methane peak. Similar results were obtained for an Agilent CP7519 Al\(_2\)O\(_3\)/KCl PLOT column cut to \( 1.2 \text{m} \), although the values of the retention time were lower because the column diameter was \( 320 \mu\text{m} \). Aluminum naturally forms Al\(_2\)O\(_3\) in air [94], and experiments have measured retention of methane by Al\(_2\)O\(_3\) [95, 96]. Therefore, we can conclude...
that methane injection testing is not the most appropriate unretained compound test for baseline GSC system performance on Al columns because it is retained by the natural Al surface oxide.

![Figure 27: Plot of unretained retention time (RT) vs. carrier gas velocity for un-anodized and anodized mGC column (50V) and against calculated values based on flow rate measurements.](image)

The ideal unretained peak shape is Gaussian, but the peaks in the figure exhibit an asymmetric tail, which negatively impacts the efficiency of a column. Efficiency is quantified by the number of theoretical plates, \( N \), a concept borrowed from distillation theory [69]. One plate is a distance along the column in which an analyte reaches equilibrium with the stationary phase. For the best efficiency, it is ideal to maximize the number of plates. The number of theoretical plates for a specific compound in a given column can be determined empirically from a chromatogram by [89]

\[
N = 5.54 \left( \frac{t_r}{w_h} \right)^2, \quad \text{Eq. (6)}
\]

where \( w_h \) is the width of the peak at half-height. Often, it is convenient to compare the intrinsic efficiencies of columns with different lengths using the height equivalent to a theoretical plate, \( H \). \( H \) is the quotient of the column length and the number of plates and should therefore be minimized for best performance. A theoretical estimate for the \( H \) for circular columns can be found by using the Giddings equation [76]:

34
In Eq. (7), $D_g$ is the gas-phase diffusion coefficient; $r$ is the column radius; $f_1$ is the Giddings-Golay compressibility coefficient [97] given by

$$f_1 = \frac{9(y^4-1)(y^2-1)}{8y^3-1}; \quad \text{Eq. (8)}$$

$a_k$ is the accommodation coefficient given by the fraction of molecules that adsorb to the surface upon impact, $u_m$ is the average velocity of analytes in the carrier gas, $V_g$ is the volume of gas phase in the column, $S$ is the surface area of adsorbent, $f_n$ is the adsorbent heterogeneity factor, and ECE stands for extra-column effects. Two main problems arise with the use of Eq. (7) for prediction of column performance: its error for rectangular columns and the inability to accurately measure parameters such as the surface area of adsorbent, especially in AAO. However, Eq. (7) does assist analysis by providing relationships for how certain parameters such as the column cross-section dimension, surface area, etc. affect the efficiency.

Figure 28: Plot of unretained HETP vs. carrier gas velocity for un-anodized mGC column and mGC columns anodized at 50V.

The tailing observed in Figure 26 can be attributed mainly to two causes: connection dead volume and adsorbent inhomogeneity. Connection dead volumes are mainly attributed to the bonded PEEK tube connections, and manifest themselves in the ECE term of Eq. (7). Despite efforts to minimize dead volume, there is likely a difference in the tube hole depth for each of the
mating coupons, which prevents the PEEK tube face from properly seating in the bottom of the hole. There is also a short length, <1mm, of tube near the mating face that was not covered with epoxy to ensure that the connection would not become plugged. New connections machined from the bonded Al coupons are in progress, which should diminish the dead volume problem. Alumina adsorbents are well-known for possessing several different active surface sites [86, 87, 98, 99]. Since the surface contains multiple types of sites with different binding energies, this causes methane molecules to experience a variation in dwell time depending on which type of surface site they adsorb to, creating a lagging effect in the elution curve and loss in chromatographic resolution.

Figure 28 shows a plot of $H$ vs carrier gas velocity for a column in the unanodized state and after 3h and 8h of anodization at 50V. The $H$ is lowest after 3h of anodization and highest after 8h of anodization. These results need to be repeated before conclusions can be drawn.

3.3D Anodic Oxide Observation

The presence of oxide in the microchannel was verified using X-ray energy dispersive spectroscopy (EDS). There were two different oxide morphologies observed from plan-view and tilted plan-view SE images of the AAO surface, as seen in Figure 29. In Figure 29 (a), the oxide surface is very porous and has a dendritic appearance. In contrast, the oxide surface in Figure 29 (b) has a dense, smooth appearance. Note the white particles on the surface are contamination from silica particles used in the polishing process. The two different structures appeared to be distributed throughout the channel length, although the denser oxide was more prevalent. It is not clear at this time why such a drastic morphological variation occurred. A previous examination of the same pulsed-electrolyte-flow anodization method yielded uniform oxide coverage and morphology in ~2cm-long parallel microchannel arrays [P.J. Hymel et al, in preparation]. The two main differences in the current experimental method are the length of the microchannel and the open-loop fluid circuit between the mGC column and Pt counter electrode. Mitigation of gas bubbles forming and exiting the column should be investigated, since a bubble nucleating in the middle of the column opens the electrolyte circuit for half of the channel length.

![Figure 29: SE images of the alumina surface in two different locations in the mGC column channel showing a large difference in morphology.](image-url)
3.3E Hydrocarbon Standard Separation

The chromatogram in Figure 30 was achieved for the mGC column anodized for 3h at 50V at an injection time of 900ms and injection pressure of 18psi, which was ramped up to 30psi at 1psi/s after a hold time of 4s. The total analysis time is ~25s for separation of n-C$_4$ to n-C$_9$ hydrocarbons. Several issues were observed: 1) n-C$_4$ and n-C$_5$ are not separated; 2) n-C$_5$ and n-C$_6$ are nearly co-eluting; and 3) there is significant peak asymmetry starting with n-C$_8$. Similar chromatograms to the ones presented were obtained for the mGC columns anodized at 30V, and it was not clear that one anodization condition was better than the other. Therefore, only the chromatograms obtained at 50V will be presented.

![Chromatogram of a C4–C9 mixture separated at 18°C by an mGC column after 3h anodization at 50V.](image)

Figure 30: Chromatogram of a C4–C9 mixture separated at 18°C by an mGC column after 3h anodization at 50V.

Figure 31 shows a chromatogram for the same mGC column after being re-anodized for an additional 5h at 50V. The conditions were temperature of ~18°C, injection time of 1s, and an injection pressure of 20psi ramped up to 60psi at 1psi/s after a hold time of 10s. The total analysis time is ~40s due to increased oxide thickness. Examining Eq. (4), an increase in the oxide thickness increases the volume of stationary phase in the column, which increases the capacity ratio. From Eq. (3), this leads to a general increase in retention time and resolution. The relationship between capacity ratio and resolution is as follows:

$$R = \frac{\alpha - 1}{\alpha} \frac{\sqrt{N}}{k\tau} \frac{4}{1 + k\tau}$$  \hspace{1cm} \text{Eq. (9)}
In Eq. (9), \( \alpha \), the separation ratio, is the ratio of capacity ratios of the second compound to the first compound for a series of two eluting compounds; \( N \) is the number of theoretical plates in the column, and \( R \) is the resolution. A resolution of 1.0 means that the tangents of two adjacent peaks intersect at the baseline, and a resolution of 1.5 fully separates the two peaks. Visual inspection shows that the resolution increased for the n-C\(_4\)/C\(_5\), n-C\(_6\), n-C\(_7\), and n-C\(_8\) separations when compared to the chromatogram after 3h of anodization. On the other hand, the peak widths for each compound except for the n-C\(_4\)/C\(_5\) peak increased, which negatively affects chromatographic resolution because \( N \) decreased. In Figure 31, the peak tailing is worse for n-C\(_7\) and higher alkanes. This is most likely related to the variation in active site energies discussed for methane peak tests, but the additional AAO from the second anodization exacerbated the problem in two ways. First, considering the SEM images in Figure 29, the two different morphologies observed likely contained different prevailing active site types. If an analyte was in a higher-energy-site area of the column adjacent to a low-energy-site area of the column, the analyte molecules adsorbed to the higher energy sites would lag far behind those that bound to the lower energy sites. The second reason why the additional AAO increased peak width was because it increased the thickness of the stationary phase, which generally served to increase the active surface area due to AAO’s porous structure [51].

Figure 32 shows a chromatogram obtained from the same column after the additional 5h anodization. The temperature was changed to 10°C, the injection pressure was 20psi, the injection time was 950ms, and the pressure was increased to 30psi at 1psi/s after a 12s hold. There is clearly better separation for every group of compounds. The improvement is due to the
fact that the adsorption coefficient, $K_A$, increases with decreasing temperature [69], and consequently, so does the capacity ratio and resolution.

Figure 32: Chromatogram of a C4-C9 mixture separated at 10°C by an mGC column after 8h oxidation at 50V.

The chromatograms obtained for the hydrocarbon standard mixture in the Agilent column at 25°C and all carrier gas pressures showed that only three compounds eluted in the 10min analysis time allowed by the microFAST GC. The time required for the third compound, n-C$_6$, to elute decreased with increasing pressure, as is predicted by Eq. (3), since the increase in pressure increased carrier gas velocity and ultimately decreased $t_m$. Figure 33 shows the chromatogram obtained at a carrier gas pressure of 22psi, injection time of 550ms, and column temperature of 130°C. The time axis was cut to ~350s because nothing eluted past n-C$_8$ in the allowable analysis time. The most obvious difference between the chromatograms obtained by the mGC column and the Agilent column is the absence of broad peak tailing in the Agilent chromatogram. This results from two main things: strict control of the oxide particle size, phase, and oxide thickness; and deactivation of the oxide with KCl to decrease the surface site energy variation [87]. It should be noted that the Agilent column was recommended for separation of methane through n-C$_4$ [70], so separating n-C$_4$ through n-C$_9$ is not an optimal test. However, the trap in the microFAST GC platform was not designed to retain very light compounds, so the mixture starting with n-C$_4$ was the closest to Agilent’s recommendation.
Figure 33: Chromatogram of a C4-C9 mixture separated by the Agilent PLOT Al₂O₃/KCl column at 130°C.

Table 1: Comparison of measured HETP for mGC column and Agilent PLOT column.

<table>
<thead>
<tr>
<th>Compound</th>
<th>tᵣ (s)</th>
<th>w₁/₂ (s)</th>
<th>HETP</th>
<th>tᵣ (s)</th>
<th>w₁/₂ (s)</th>
<th>HETP</th>
</tr>
</thead>
<tbody>
<tr>
<td>butane</td>
<td>2.04</td>
<td>0.168</td>
<td>0.147</td>
<td>2.04</td>
<td>0.168</td>
<td>0.147</td>
</tr>
<tr>
<td>pentane</td>
<td>2.16</td>
<td>0.205</td>
<td>0.195</td>
<td>4.11</td>
<td>0.528</td>
<td>0.357</td>
</tr>
<tr>
<td>hexane</td>
<td>2.59</td>
<td>0.253</td>
<td>0.207</td>
<td>13.79</td>
<td>2.66</td>
<td>0.805</td>
</tr>
<tr>
<td>heptane</td>
<td>4.51</td>
<td>0.94</td>
<td>0.940</td>
<td>50.32</td>
<td>11.46</td>
<td>1.122</td>
</tr>
</tbody>
</table>

Table 1 is a comparison of the n-C₄ through n-C₇ peaks from the mGC and Agilent column chromatograms. A comparison of the first 8s of analysis from Figure 32 and Figure 33 (the mGC column anodized for 8h at 50V, 10°C and the Agilent column at 130°C) is shown in Figure 34. Examining the short period of time in Figure 34 and the H values in Table 1 brings to light several observations. First, the retention time for each compound in the mGC column is shorter than that in the Agilent column even with the drastic difference in operating temperatures. The n-C₄/C₅ peak from the mGC column has the same retention time as the n-C₄ peak from the
Agilent column, but the n-C₅ peak from the Agilent column elutes about 1s later than the n-C₆ peak from the mGC column. Comparing the $H$ values of n-C₅, n-C₆, and n-C₇ between the two columns shows that the mGC column actually had higher efficiency than the Agilent column for all three compounds despite the fact that the n-C₅ peak width used for the mGC column included co-eluted n-C₄. For the n-C₇ peak, the mGC column $H$ is closest to the Agilent column $H$ because the peak is asymmetric. That significant tailing increases the peak width and drastically increases the $H$, which negatively affects resolution. Although the mGC column has better efficiency than the Agilent column, from visual inspection, the Agilent column clearly has better peak resolution. From Eq. (9), the resolution only increases as the square root of the efficiency.

![Figure 34: Comparison of first 8s of analysis for mGC column at 10°C anodized for 8h at 50V and the Agilent PLOT Al₂O₃/KCl column at 130°C.](image)

On the other hand, the capacity index term, $k'/(1 + k')$, is important for low capacity ratios, such as those seen by n-C₄ and n-C₅ [77]. The most significant term in Eq. (9) is the selectivity index, $(\alpha - 1)/\alpha$, because for $\alpha$ slightly greater than 1 (barely separable compounds), the term increases roughly as $\alpha - 1$ [77]. This means that the resolution can roughly double just by increasing $\alpha$ from 1.01 to 1.02. Therefore, although the mGC column efficiency can certainly be improved, it is more important to take steps in the design and fabrication process that will increase the capacity ratio for light compounds and increase selectivity.

3.3F Transient Heater Testing

A typical plot of the mGC column bond line temperature increase is shown in Figure 35. The black squares are the average of the two thermocouple temperatures. The linear fit shows an
approximate temperature increase of ~7°C/s. Although this is likely to be fast enough for a fast GC application, it would be impossible to apply 1200W of power in portable GC applications. Temperature ramp rates of up to 1000°/min (~17°C/s) have been reported by Reidy [90], and ramp rates of 33°C/s were reported by Reid, et al. [79] using integrated resistive heating with a fraction of the power consumption.

![Graph of temperature at the center of the mGC column vs. time during transient heating with a total input power of 1200W.](image)

\[ y = 7.0129x + 2.4711 \]

**Figure 35**: Graph of temperature at the center of the mGC column vs. time during transient heating with a total input power of 1200W.

### 3.4 Suggested Future Work

#### 3.4A Low Dead Volume Connections

The current mGC columns used PEEK tubing bonded with epoxy to interface with the injector and detector of the testing platforms, which introduced the dead volume issues stated earlier. The original connection design made use of the strong metallurgical bond between the two Al coupons by machining out all the material except for a cylindrical section centered around the exit channel, as shown in Figure 36. Methane peak tests of these mGC columns had significant tailing, which is often caused by large dead volumes. Further examination of the connection between the microchannel dimensions in the Al machined tube and the internal diameter of the injector and detector fittings explained the issue. Although the hydraulic diameters of the rectangular mGC column channel and circular mating fittings matched, the 500μm width of the mGC column channel was nearly twice the circular fitting diameter. This was significant dead volume/cause of flow eddies, but because the mGC column channel width was determined by the mold insert dimensions, nothing could be changed until a modified mold insert was fabricated. Thus, circular tubing was used as a temporary solution. Polymer tubing was required because a non-Al metal could not be in contact with the mGC column during the
anodization process. PEEK was selected because it has a higher glass transition temperature than some other polymer options [88], but it is not as robust to mechanical deformation or high temperature as metal tubing is. When a new mold insert is designed, the inlet and outlet widths should not expand beyond ~200-250μm, depending on the size of fittings used to connect with the injector and detector. Flow simulations should be performed to determine the correct angle of expansion of the inlet and outlet to minimize flow eddies, which tend to mix already-separated compounds.

![Image](image.png)

Figure 36: Proposed mGC column design with tube connections machined out of the TLP-bonded Al coupons.

3.4B AAO Structure and Uniformity Optimization

Berezkin lists several suggestions for optimizing the efficiency of a GSC column, including surface homogeneity, consistent pore size and density, and good adhesion between the adsorption layer and inner column surface [87]. Using AAO for the stationary phase solves several problems presented by conventional coating with microparticle suspensions, such as control of particle size and adhesion to the inner column surface. On the other hand, the structure and thickness must be carefully controlled via the anodization conditions. The AAO layer produced in the current work was not satisfactory in terms of morphology, especially because of the two distinct surface structures observed. Anodization of Al is known to produce a well-ordered nanoporous structure when conditions are controlled, especially by using two-step anodization [51, 59, 61]. That morphology is much more desirable for use as an adsorbent because of its high surface area and high ordering.

3.4C Deactivation with Potassium Chloride

As previously stated, the Agilent column experienced much more symmetric peaks because its adsorbent layer was deactivated with KCl. Virgin alumina possesses several different surface sites with a range of binding energies, which has the effect of retaining molecules of the same compound for different times and broadening peaks. Inorganic salts, such as KCl, are often used to coat the alumina surface to decrease the number of active sites and cover the most active
sites, as shown in Figure 37 [87]. It is difficult to find exact descriptions of the methods used to deposit KCl in the literature, but one method described is to wash the column twice with 2% potassium chloride solution and repeatedly dry and heat [77]. This method obviously leaves many variables un-explained, but it can serve as a guideline for future attempts.

![Figure 37: Illustration of the surface sites on a) virgin alumina b) treatment with 1% KCl and c) treatment with 10% KCl.](image)

3.4D Transient Heater Testing

Three improvements can be made to increase the heating rate and efficiency of the mGC columns. The first is to eliminate the thermal resistance associated with the interfaces between the two heater blocks and the mGC column by making the heaters or heater containment integrated into the column. The temperatures of the heater blocks was observed to be as much as 100°C higher than the mGC column during the transient, which shows a large loss in efficiency across the contact surfaces, despite the application of thermal grease. Similarly, there is a thermal resistance in the small air gap between the cartridge heaters and their hole internal surfaces. Tighter machining tolerances and application of thermal paste could mitigate this problem somewhat. The second method to improve the heating performance is to decrease the thermal mass of the heaters and heater containment. This is an optimization problem; analysis must be done to maximize the power per unit thermal mass of the heater/heater containment structure. The third method to improve heating performance is to properly insulate the entire mGC-heater assembly. All three modes of heat transfer, especially radiation, increase with increasing temperature gradients with the surroundings [100]. Fully insulating the assembly would reduce those gradients, although in practice, a working mGC column could not be tightly bound by insulation because it must be cooled quickly by forced convection. This was attempted in the current test, but at the temperatures reached by the heater blocks, the insulation melted.

3.5 Summary

Microscale molding replication and TLP bonding of Al 1100 were used to fabricate Al-based mGC columns with epoxy-bonded tube connections. The interior surfaces of the mGC columns were anodized to form AAO, which was used as an adsorbent for GSC separations of an n-C₄ through n-C₉ hydrocarbon standard mixture in the microFAST GC platform. The chromatographic resolution of the chips increased with anodization time because of the thicker oxide layer which increased the surface area of interaction. Resolution also increased when separations were performed at 10°C because the analytes spent more time in the stationary phase.
on average. However, both of these conditions exacerbated the problem of peak tailing, which is caused by large active site binding energy variation. The efficiency of the mGC column was at least 20% greater than that of an Agilent Al₂O₃/KCl column with the same length for n-C₅, n-C₆, and n-C₇, but the Agilent column had much higher resolution. Scanning electron micrographs of the mGC column oxide surface showed that there were two different surface morphologies present, which likely contributed to the peak tailing and lower capacity ratios, leading to lower resolution. Transient heat transfer testing was performed to determine the possible temperature increase rate of an mGC column chip. At a power input of ~0.36 W/cm², the temperature increase rate was ~7°C/s. An input power of 1200 W was used to produce this result, which is not practical in a portable-type GC instrument, so optimization of the heating process will be investigated.
4. Conclusions

An internal Al anodization technique based on pulsed electrolyte flow was developed in Al microtubes. The AAO exhibited the typical nanoporous structure, and the AAO growth rate as a function of anodizing time and voltage was determined. After sealing the AAO in near-boiling water, anodized/sealed tubes showed a tenfold decrease in corrosion current compared to un-anodized tubes in a linear sweep voltammetry corrosion test. The same anodization and sealing procedure was applied to MHEs, and a lower AAO growth rate was observed. A corrosion test to compare the relative AAO resistance to ion transport was devised. Using this test, anodized/sealed MHEs had a higher resistance to ion transport than un-anodized MHEs.

Aluminum-based mGC columns were fabricated using the microscale molding replication process coupled with TLP bonding. The mGC column flow rates agreed well with calculated values based on the measured dimensions of the microchannels. Methane pulse tests were performed, which showed that as-bonded mGC columns retain methane and that there is a distribution of active sites on the native Al$_2$O$_3$ layer. The columns were anodized for 3h or 8h at 30V or 50V at ~5° then used to separate an n-C$_4$ through n-C$_9$ hydrocarbon standard mixture. There was little difference in the performance of mGC columns anodized at 30V and 50V, but columns anodized for 8h showed better chromatographic resolution than those anodized for 3h. Additionally, the mGC columns were compared to a commercial open tubular column cut to the same length, and the mGC columns showed much lower retention times and significant peak tailing, although their efficiency was higher. Two different morphologies observed in SEM images of the AAO surface probably contributed to both the short retention time and peak tailing. Based on the results, several recommendations were made for future work on Al-based mGC columns, including controlling the AAO morphology and coating the surface with KCl to decrease the distribution of active site binding energies.
References


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Appendix: Electrical Schematics for Anodization Systems

mGC Column Anodization System
The Agilent 6575A power supply was used to provide the bias for anodization between the mGC column and CE. A computer program linked to the Omegabus was used to set a ramp rate and final voltage as an analog input to the power supply to control the anodization voltage. The Agilent 34902A multiplexer was used to measure temperature, anodization voltage, and anodization current. A MATLAB program was written to dynamically plot the data and if the current dropped below a set value, it sent a signal to the Agilent 34907A to send an analog output signal to the Omega solid state relay to turn it on. The Omega relay was used as an automatic switch for the control circuit to a mechanical SPDT relay, which was used to actuate the solenoid valve and circulate the electrolyte for 15s.
MHE Anodization System

This system was designed to execute the NaOH cleaning, anodization, and sealing processes. Therefore, there is a separate pump for NaOH, room temperature DI water, oxalic acid, and hot DI water. The pumps are all run from the same power supply and controlled by a relay and combination of switches. As a safety precaution, there are level sensors in the oxalic acid tank and hot water tank, which set off level alarms in the LabView program and stop all processes if the tank levels fall too low. There are also heaters with a temperature control system that allow the oxalic acid and hot water temperatures to be set. The 72V, 1.2A programmable power supply is configured to provide the anodization voltage. The power supply’s output voltage is controlled by a program in LabView on a laptop computer. The applied voltage, anodization current, and temperature are measured throughout the anodization process using the OMB-DAQ-2416. All of these measured values are displayed in real time graphs on the computer for the user to monitor. When the current drops below a set value, the LabView program sends a signal to SSR1 that gives power to the pump to circulate the electrolyte, and then turns off when the current rises above the set value.
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