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Microsystems for Harsh Environments

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Abstract

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When operating microsystems in harsh environments, many conventionally used techniques are limiting. Further, depending on if the demands arise from the environment or the conditions inside the system, different approaches have to be used. This thesis deals with the challenges encountered when microsystems are used at high pressures and high temperatures.

For microsystems operating at harsh conditions, many parameters will vary extensively with both temperature and pressure, and to maintain control, these variations need to be well understood. Covered within this thesis is the to-date strongest membrane micropump, demonstrated to pump against back-pressures up to 13 MPa, and a gas-tight high pressure valve that manages pressures beyond 20 MPa.

With the ability to manipulate fluids at high pressures in microsystems at elevated temperatures, opportunities are created to use green solvents like supercritical fluids like CO₂. To allow for a reliable and predictable operation in systems using more than one fluid, the behavior of the multiphase flow needs to be controlled. Therefore, the effect of varying temperature and pressure, as well as flow conditions were investigated for multiphase flows of CO₂ and H₂O around and above the critical point of CO₂. Also, the influence of channel surface and geometry was investigated.

Although supercritical CO₂ only requires moderate temperatures, other supercritical fluids or reactions require much higher temperatures. The study how increasing temperature affects a system, a high-temperature testbed inside an electron microscope was created.

One of the challenges for high-temperature systems is the interface towards room temperature components. To circumvent the need of wires, high temperature wireless systems were studied together with a wireless pressure sensing system operating at temperatures up to 1,000 °C for pressures up to 0.3 MPa.

To further extend the capabilities of microsystems and combine high temperatures and high pressures, it is necessary to consider that the requirements differ fundamentally. Therefore, combining high pressures and high temperatures in microsystems results in great challenges, which requires trade-offs and compromises. Here, steel and HTCC based microsystems may prove interesting alternatives for future high performance microsystems.

Keywords: Microsystems, harsh environments, high pressures, high temperatures, supercritical microfluidics

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*"The brick walls are there for a reason.
The brick walls are not there to keep us out.
The brick walls are there to give us a chance
to show how badly we want something."
- Randy Pausch, The Last Lecture*

List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

- I **S. Svensson**, G. Sharma, S. Ogden, K. Hjort, L. Klintberg, High-pressure peristaltic membrane micropump with temperature control, *J. Microelectromech. Syst.*, 19(2010) 1462-1469
- II G. Sharma, **S. Svensson**, S. Ogden, L. Klintberg, K. Hjort, High-pressure stainless steel active membrane microvalves, *J. Micromech. Microeng.*, 21 (2011) 075010
- III S. Ogden, **S. Knaust**, A.P. Dahlin, K. Hjort, R. Bodén, On-chip pump system for high-pressure microfluidic applications, 17th Int Conf on Miniaturized Systems for Chemistry and Life Sciences (MicroTAS 2013, Freiburg, Germany, 27-31 Oct. 2013), 1472-1474
- IV **S. Knaust**, M. Andersson, N. Rogeman, K. Hjort, G. Amberg, L. Klintberg, Influence of flow rate, temperature and pressure on multiphase flows of supercritical carbon dioxide and water using multivariate partial least square regression, Submitted
- V **S. Knaust**, M. Andersson, K. Hjort, L. Klintberg, Influence of surface modifications and channel structure for microflows of supercritical carbon dioxide and water, Submitted
- VI **S. Knaust**, Z. Khaji, P. Sturesson, L. Klintberg, Characterization of dielectric properties of polycrystalline aluminium nitride for high temperature wireless sensor nodes, *J. Phys.: Conf. Ser.* 476 (2013) 012101
- VII P. Sturesson, Z. Khaji, **S. Knaust**, L. Klintberg, G. Thornell, Thermomechanical properties and performance of ceramic resonators for wireless pressure reading in high temperatures, Accepted for publication in *J. Micromech. Microeng.*
- VIII **S. Svensson**, F. Ericson, K. Hjort, L. Klintberg, ESEM as a tool for studying high temperature electronics, IMAPS Int Conf on High Temperature Electronics Networks (HiTEN, Oxford, UK, 18-20 July 2011), 180-187

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Authors contribution

- I. Part of planning, major part of experimental and analysis.
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- III. Part of planning, part of experimental and analysis.
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- V. Part of planning, major part of experimental and half of analysis.
- VI. Part of planning, experimental and evaluation.
- VII. Part of experimental and evaluation.
- VIII. Major part of planning, experimental and analysis.

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1. Introduction

1.1 Introduction

A harsh environment is a wide concept, which could include everything outside the boundaries of our intuitive experience, *e.g.* large operation ranges regarding pressure and temperature, a corrosive environment, or a setting which is demanding for the system in some other way [1]. However, when considering systems for such settings, harsh environments and harsh conditions need to be distinguished.

For harsh environments, the whole system can be considered to be exposed to the demanding setting, *i.e.* the high pressures in deep-water drilling, a spacecraft in orbit, or a wireless sensor node inside a furnace. Here, the high demands are on the whole system, from the structural materials to powering, sensing, actuation, and communications. Considering a system working at harsh conditions, the challenge is local, *i.e.*, the high temperatures generated in high-power transistors, corrosive environments in tubings for chemical plants or high pressures inside an analysis system. For managing harsh conditions, mechanical support fixtures, shields, dissipators or other supporting devices can be used, where sections of the system can be kept at hospitable conditions connected with wiring and tubing. Both of these two distinctions are usually extreme challenges on their own, but affect which tools in the toolbox that can be used to engineer a suitable system for a desired task.

Tools well suited for harsh environments and harsh conditions can be found using microsystem technology (MST). When decreasing dimensions to the microscale, materials that are otherwise not possible to use because of their brittle nature can be used for otherwise unthinkable structures such as flexible membranes, exemplified by the microelectromechanical structures created in thin wafers of single crystalline silicon [2]. Other benefits such as shorter transport lengths, less reagent consumption, and increased control are examples of features utilized within the sub-field of microfluidics [3].

Using MST, many processes are based on batch fabrication. The benefit with batch fabrication is that large quantities of components can be created and modified simultaneously. This reduces both cost and time consumption of process steps in comparison to processes where each component are handled individually. Also, as the amount of material decreases for each device when miniaturized, expensive materials like noble metals or substrates like SiC or sapphire, which are suitable for high temperature operation due to their inert characteristics with relative high melting points, can be used without adding significantly to the cost of the single device.

When handling pressures above 1 MPa in microfluidic systems, the high-pressure region is reached where much of the conventionally used polymer-based techniques starts to reach their limits. In high-pressure microfluidics, the otherwise unavailable environmentally friendly green solvents can be used and the high pressures are often beneficial in many techniques for synthesis, analysis and extraction. To work in these regions, metal or ceramic building materials are preferred. The polymeric materials also fall short reaching temperatures above 300 °C [1]. Under these conditions, even metals, although necessary for many systems starts to be troublesome as they are increasingly reactive with increasing temperature, exemplified by the purple plague intermetallic of AuAl₂. Therefore, for very high temperature systems, restricting the materials to noble and refractory metals and ceramics has been a preferred choice.

For system monitoring, many components have been shown to be able to function at high temperature conditions, including pressure sensors [4], gas sensors [5–7] and flow sensors [8], where the latter has been shown to manage temperatures locally exceeding 1,000 °C. Neudeck *et al.* have shown a wired resonating circuit using a SiC transistor working at 600 °C exceeding 10,000 h of continuous operation [9]. However, many of these systems rely on a wired interface, although wires are not always applicable, *i.e.*, for sensing at high temperatures in rotating structures, such as jet engines [10]. Therefore, wireless communication is an attractive alternative.

Although many passive devices exist for high pressure, the availability of micro-components to manipulate the flow is limited. Hence, for fluid manipulation at high pressure, covered within this work is the to date strongest displacement micropump, Paper I and a gas-tight high-pressure microvalve, Paper II. For the micropump, integrated temperature sensors and different drive cycles were evaluated for high pressure operation to optimize the driving of the micropump. Furthermore, utilizing a peristaltic driving, the pulsating flow of the micropump was minimized in Paper III, by running two pumps in parallel with varying actuator dimensions.

The foundation of the high pressure capability of the micropump was done constructing active high pressure valves, where different membrane materials were evaluated as well as the contact situation between the membrane and the inlet and outlet orifices. This resulted in a valve design capable of sealing at pressures above 20 MPa.

Working over large ranges in pressure and temperature, material properties such as density, viscosity and dielectric constant will vary extensively for certain fluids. For successful operation, this variation needs to be characterized and the implications of these variations need to be understood. Two different approaches were used to investigate the co-flow of fluids, that of CO₂ together with H₂O at temperatures and pressures above the critical point of CO₂. In Paper IV, multivariate data analysis were used to study the effect of varying the pressure and temperature for the co-flow of H₂O and CO₂, and in Paper V,

the pressure and temperature used were kept within a small region to investigate interaction between the fluids and the channel surface.

To circumvent the challenge of material interfaces for high temperature communication with devices, wireless transmission is a useful approach. However, variations in properties affecting the high temperature device need to be known. As the dielectric constant varies with temperature, the resonance frequency will also vary through a change in capacitance. In Paper VI, this change was characterized for temperatures up to 900 °C for AlN-based thick film antennas, and in Paper VII, a capacitive pressure sensor was integrated with the antenna using alumina high temperature co-fired ceramic (HTCC) structures for wireless pressure readings up to 1,000 °C and 0.3 MPa.

Aside from interfacing, for electrical high temperature systems, material movement through diffusion or migration are two of the major challenges. To be able to study such phenomena in a controlled environment at high temperatures with high precision, a testbed was built inside an environmental scanning electron microscope (ESEM) with an heating stage and electrical feedthrough, Paper VIII, where the onset of migration between two Ag electrodes was studied.

Before entering the realm of harsh environments and conditions in chapter 3, important concepts will be briefly introduced in chapter 2, together with materials and techniques used within the scope of this thesis.

1.2 Aim

- To develop active microsystems for harsh conditions, *e.g.*, for supercritical microfluidics.
- To understand the challenges of microsystems for high temperatures or high pressures.
- To increase the control of fluids under conditions with large variations in density and viscosity.

2. Miniaturization

2.1 Decreasing the dimensions

When decreasing the size, the surface to volume ratio increases, which implies that the stored amount of mechanical energy in the system will decrease and thus enables a more safe approach to reach higher pressures. Also, as the surface to volume ratio increases, the surface forces and interfacial forces will be more dominant compared to the bulk forces at macroscopic length scales. Miniaturization is utilized in many commercially available products, *e.g.* sensors with increased sensitivity like the familiar touch controls found in most of today's smartphones.

2.2 Microfluidics

A branch of microsystem technology that has grown into a field of its own is microfluidics, where much of the technology developed for the integrated circuit industry is used to create miniaturized channels and components for fluid manipulation. The downscaling allows for attracting features such as smaller sample volumes, faster reaction times, parallelism and a laminar flow, *i.e.*, the absence of turbulence. Hence, fluids will only mix because of diffusion, and will flow either in parallel or in segmented flows. Although the real boom for microfluidics outside of research remains to come, there are applications encountered by most people in their daily lives such as the ink-jet printers, where picoliter-sized drops are precisely jetted in our printers. Also, small handheld microfluidic systems for blood sugar measurement and pregnancy tests are commercially available with components working in the microfluidic regime. However, larger and more integrated systems are still attractive goals at the horizon [11].

By using the well developed tools for creating mechanical structures in silicon, channels were created for fluidic systems, mostly utilizing silicon and glass. However, being expensive materials with expensive processes associated with the creation of microstructures in these materials, researchers started to look for alternatives. This resulted in that many devices today are instead manufactured in the silicon rubber polydimethylsiloxane (PDMS). The high-pressure capabilities of PDMS are limited, and most high-pressure microfluidic systems have been created in silicon and glass [12–15], although high-pressure systems in steel have also been presented [16].

Dimensionless numbers

The behavior of a fluid is described by the Navier-Stokes equation. To fully solve the equation it is often necessary to utilize a time-consuming computer-based approach because of the complex nature of the equation. However, if certain assumptions can be made, the behavior described by the equation can be translated into dimensionless numbers, which are commonly used as a tool in fluidic dynamics. Three important dimensionless numbers for microfluidic systems are the Reynolds number (Re), the capillary number (Ca) and the Weber number (We) [3].

Re relates the inertial forces to the viscous forces according to

$$Re = \frac{\rho UR}{\eta}, \quad (2.1)$$

where ρ is the fluid density, η is the fluid viscosity, R is a characteristic length and U is the velocity of the fluid. As a rule of thumb, Re around 2,000 is considered a divider between the laminar regime and a turbulent flow, below which the inertia plays an insignificant role for the fluid behavior and microfluidic systems will generally operate in the laminar regime. Within the laminar regime where the viscous forces dominates, fluids will not mix by convection and two flows meeting up in a channel will flow in parallel. Working within this regime is useful as it implies an increased control over the fluids which will behave more predictably with changes compared to the turbulent regime.

For multiphase flows, Ca and We are commonly used as an indicator if the flow is expected to break up into segments or flow in parallel.

The capillary number relates the viscous forces to the interfacial tension, γ , between two fluids as

$$Ca = \frac{\eta U}{\gamma}. \quad (2.2)$$

For Ca below 10^{-5} , the flow is considered to be dominated by the capillary forces, and likewise, for higher values, the viscous forces will be dominating the flow, *e.g.*, friction towards the channel walls. In a similar way, We relates the inertia to the interfacial tension according to

$$We = \frac{\rho RU^2}{\gamma}, \quad (2.3)$$

where a low We indicates that the interfacial tension between the fluids dominates over the fluid momentum. The influence of We can be exemplified by the water tap at the kitchen sink. Close to the nozzle, the flow velocities are usually high, *i.e.* a high We . Here, the inertia of the fluid will cause the H_2O flow to be jetted out of the nozzle in a single stream. However, as the air slows down the fluid, with enough traveling length the fluid velocity will decrease to low enough We , enabling the interfacial tension to minimize the surface energy, which breaks up the flow into drops.

2.3 Materials and manufacturing techniques

Although not used within this work, silicon has been widely used for creating micro-components, ranging from sensors and actuators to structures for fluidics. With a native oxide layer that is easy to create and remove, and that can be used as an insulator, the ability to machine this material is one of the cornerstones enabling the digital revolution. Here follows a short description of the materials and techniques that have been used in the works covered within this thesis to create systems for harsh environments.

Glass

The most commonly used material for high pressure microfluidics is borosilicate glass. Apart from having a linear thermal expansion up to its annealing point around 500 °C, which is reasonably well matched to silicon, it has a major advantage by being transparent. The drawback is that glass is brittle, which can result in spectacular failures in high pressure applications.

Stainless steel

Steel comes in many varieties, although if nothing else is specified, here the common 18-10 grade (SS304) is referred to. Having a good general corrosion resistance in many environments, this material is the preferred choice for many fluidic applications, where the composition can be adopted to match the environment of the intended application. The ductile nature of the material also allows for safe handling of high pressures. However, when used as a membrane in the pump presented in Paper I, the 304 grade was changed to a 301 grade to prevent fatigue.

Parylene

Mostly used as a dielectric and protective layer in electronics, parylene has a high tensile strength around 50 MPa [17], which is comparable to soft metals. By heating parylene above its softening point, *i.e.* 240 °C under high pressure, the material will soften and if two layers are in contact at high pressure, these will merge to a single layer. This technique was used to bond the stainless steel structures for the micropump and microvalve. However, only having an Young's modulus of approximately 3 GPa (Young's modulus of steel is around 210 GPa), this material is unsuitable to use for high pressure applications without mechanical support.

Ceramic microstructures

Thick-film technology refers to printed structures with thicknesses in the order of tens to hundreds of μm , usually manufactured using either stencil or screen printing of metal pastes onto a pre-sintered ceramic substrates like alumina or aluminium nitride (AlN), which is then dried and sintered to remove organic residues and to form coherent metal structures. To create multilayer structures,

glass-based pastes are used for insulation in-between the metal layers. Typical conductor materials are silver or gold alloys and the structures are fired at approximately 800-900 °C. As the pattern is deposited on-top of the ceramic, the substrate only provides structural support and heat dissipation for on-chip heat sources.

As an alternative to thick-film technology, the co-fired ceramics offers embedded structures. Before sintering, layers of tapes consisting of ceramic particles and polymers, and screen printed conductors are laminated using a high pressure. Depending on the composition of the ceramic and conductors, the co-fired ceramic technique is usually divided into low temperature co-fired ceramics (LTCC) and high temperature co-fired ceramics (HTCC), where for LTCC, the ceramic is usually mixed with glass and for conductors silver are used. As glass usually has a softening temperature in the region of 500 °C, these materials are unsuitable for higher temperatures. These structures are therefore sintered at similar temperatures as the thick-film structures, while for HTCC the sintering temperature is usually above 1,500 °C and as conductors either platinum or tungsten are used.

2.4 Compressibility

The approximation of working with incompressible fluids holds true for many microfluidic systems where liquids are used. Working at narrow pressure ranges, even compressible gases could be described using simple approximations, with a slight modification and assuming that the viscosity will not vary significantly [18]. However, for systems with large pressure variations, the density and viscosity may not be considered constant, which is further complicated when phase transitions are present within a system.

For the three fluids¹ used in within this thesis, CO₂, H₂O and paraffin, figure 2.1 shows how the density of the fluids varies with temperature and pressure, respectively. Within the chosen pressure and temperature range in figure 2.1, CO₂ will be both in the gas and liquid state and in the supercritical regime, later described in section 3.1.1. H₂O will be in the liquid state, and paraffin will be in both solid and liquid state.

The compressibility, *i.e.*, the change in volume with varying pressure, of a material is the inverse of the so called bulk modulus (β), defined as

$$\beta = \rho \frac{dP}{d\rho} = -V \frac{dP}{dV}, \quad (2.4)$$

¹Here, paraffin is used both in solid state and liquids state, and is therefore not really what is considered a fluid in its solid state. However, as Malik *et al.* showed in a simulation, the properties in the solid state at elevated temperatures can be described as a fluid with a very high viscosity [19].

where ρ is the density and $dP/d\rho$ is the rate of how much the pressure will vary as a response to a change in density, *i.e.*, its volume. As can be seen in figure 2.1, the three fluids vary in three different ways to changes in pressure and temperature. The density of H₂O is approximately unaffected by both changes in temperature, figure 3.3(a), and pressure, figure 3.3(b), in the range of 30 - 90 °C and 0.1 - 10 MPa. The density of CO₂ on the other hand will vary extensively with both temperature, figure 3.3(c), and pressure, figure 3.4(d), in the range mentioned, covering the gas to liquid phase transition as well as the supercritical region. As the rate of change for the density with pressure is low, the bulk modulus, β , will also be low, *i.e.*, CO₂ has a large compressibility and small changes in pressure results in large changes in volume. Paraffin on the other hand is very insensitive to pressure variations, figure 2.1(e), with only a variation of approximately one percent when increasing the pressure from atmospheric pressure to 20 MPa for the C₂₄H₅₀ [20].

For both paraffin and CO₂, the density varies extensively with temperature. However, for paraffin, most of the variation occurs in a narrow temperature range with a sharp transition. Hence, for increasing temperature, the volume will increase drastically. As the density remains constant with pressure, this expansion will be maintained with the increasing pressure and will generate a large force. Comparing the variation of density with temperature for CO₂, the density decreases drastically with an increased temperature, which at first glance can be thought to also generate large forces. However, as an increased pressures results in the opposite effect, this will negate the potentially high forces as can be seen in figure 3.4(d), as the increase in pressure will decrease the volume. Therefore, to generate large forces using CO₂, more fluid has to be added to the chamber, or alternatively, the volume of the chamber must be decreased.

Also considering the heating and cooling of a compressible fluid, during compression excessive heat will be released, which will increase the temperature, and likewise during expansion, the temperature will decrease, which will cause the temperature to vary locally for systems utilizing these fluids. To minimize this effect, the larger surface to bulk ratio with decreasing sizes will allow for rapid heat transport, which can provide a more thermally stable system that more easily can adapt to changes.

2.5 Relative permittivity

Regarding the electrical properties of a material, these are mainly affected by variations in temperature. When increasing the temperature, not only does the electric and thermal conductivity usually decrease, the insulating properties for non-conducting materials will also vary, which strongly depends on the relative permittivity, ϵ_r , also known as the dielectric constant. The relative

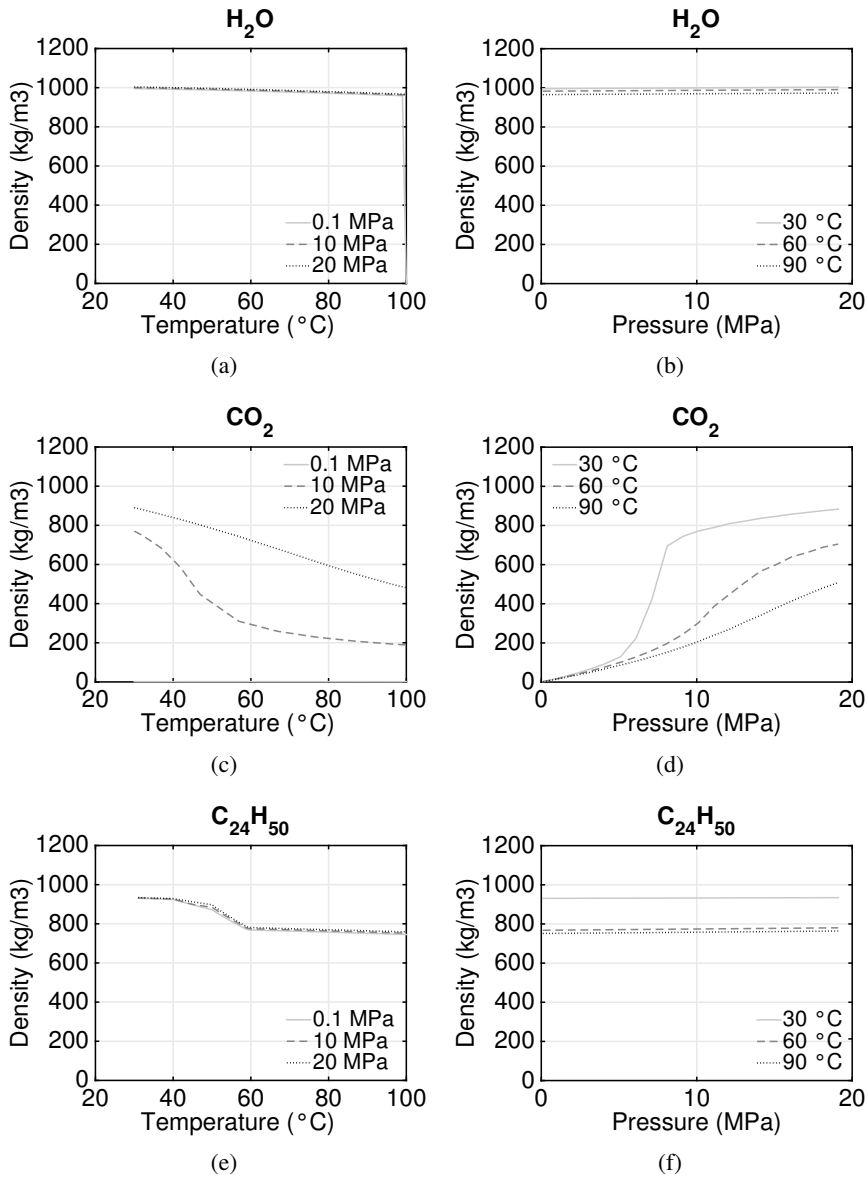


Figure 2.1. The variation of density with temperature (a, c, e) and pressure (b, d, f) for H₂O, CO₂, and paraffin, interpolated from tabulated data [20–23]. Within 20 °C - 100 °C, the density of water is constant and does not vary significantly with pressure either. For the same region, CO₂ varies strongly with both temperature and pressure, partly due to the phase transition between gas and liquid. For the C₂₄H₅₀ paraffin, a large density variation occurs during the solid to liquid phase transition around 45 °C, with no significant variation in density with pressure for a constant temperature.

permittivity describes how a material responds to an electric field by rearranging the electric charges within the material, *i.e.*, polarization [24].

In electronics, the capacitance will tell us how much electrical energy that can be stored and this is directly proportional to ϵ_r . This can be exemplified by the parallel plate capacitor used in Papers VI and VII. The parallel plate capacitor consists of two equally sized metal plates with an area A , separated by a dielectric with the thickness d . The resulting capacitance is defined according to

$$C = \epsilon_0 \epsilon_r \frac{A}{d}, \quad (2.5)$$

where ϵ_0 is the dielectric constant, *i.e.*, the permittivity in vacuum.

As the amount of stored energy within capacitors are inferior compared to batteries, the capacitors are used as small energy buffers and dampeners in circuits. Hence, for resonating structures, it is of critical importance to have a known capacitance, and if not possible at least the variation must be known. The relative permittivity, ϵ_r , varies with the temperature of the material as well as the frequency of the electrical field.

For ceramic materials, the dielectric constant typically has larger variations at lower frequencies. For Al_2O_3 (99.6 wt.%), the shift at 120 Hz between room temperature and 550 °C is an increase of 250%, while at 100 kHz, the increase for the same temperature interval is only 15%, and increasing the frequency to 1 MHz, the shift is down to 10% [25]. This is comparable to the results for AlN in Paper VI, which follows the same pattern with a decreasing shift in relative permittivity with increasing frequency, as can be seen in figure 2.2. However, AlN is more sensitive to changes in temperature and at 1 kHz, the dielectric constant varies exponentially with temperature above approximately 200 °C.

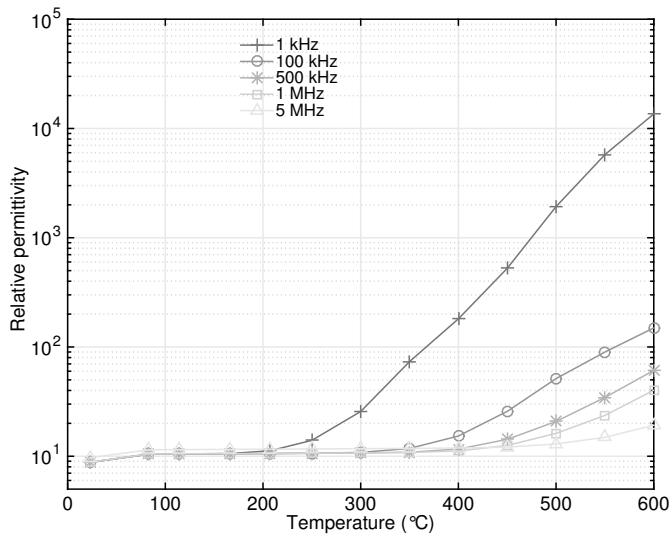


Figure 2.2. The temperature dependency of the relative permittivity for sintered polycrystalline AlN at frequencies between 1 kHz and 5 MHz. At 1 kHz, the relative permittivity is stable up to 200 °C with only small variations, after which, the relative permittivity increases exponentially. For increasing frequency, the stable region is extended to higher temperatures with an increase of only 33% from 20 °C to 500 °C at 5 MHz. [Paper VI]

3. High pressure and high temperature

3.1 Reaching higher in pressure and temperature

Many reactions benefit from higher pressures and temperatures. As stated by the Arrhenius equation, the reaction rate will double at approximately every 10 °C increase near room temperature. Also, increasing the density by increasing the pressure generally increases the reaction rate further. For applications such as microreactors and extraction, increasing the temperature and pressure is often beneficial, and for many syntheses, high pressures or high temperatures are needed [26, 27]. Furthermore, for miniaturized systems, temperature is more easily controlled due to the smaller mass within the system. Another effect from decreasing the dimensions is that the decreasing defect densities result in that even brittle ceramic materials can be used for flexing structures, *i.e.*, the alumina membrane in Paper VII. Also, as the volume decreases, handling high pressures for compressed fluids becomes much safer.

One of the common areas where high pressure micro-components have been used for a long time is within analysis systems, where fluids are pushed through coated narrow columns. This will separate different molecules by the time required for them to pass through the column [28, 29], a technique is known as high performance liquid chromatography (HPLC). To generate the pressures required to push the liquid forward in these systems, strong pumps are required. In Paper I, the strongest-to-date membrane micropump is presented. Using a frequency 0.4 Hz, the pump reliably pumped at a consistent flow rate up to pressures of 13 MPa, as is seen in figure 3.1. The micropump is further discussed in detail in section 3.2.2. Aside from using high pressure pumps for HPLC, these micropumps can also be used for microreactors [15], and to facilitate the higher demand for high pressure generation when moving towards nanofluidics due to the increased low resistance in increasingly narrow channels.

3.1.1 Multiphase microsystems and supercritical fluids

The field of green chemistry is emerging, where the aim is to use more harmless alternatives instead of conventionally used solvents [30]. One solvent used for such purposes is CO₂, which is investigated to replace environmentally harmful conventional solvents [31]. With the increased knowledge, this has led to a growing interest also for the use of supercritical fluids in microfluidics to take advantage of the benefits of miniaturization, *i.e.*, supercritical microfluidics [32].

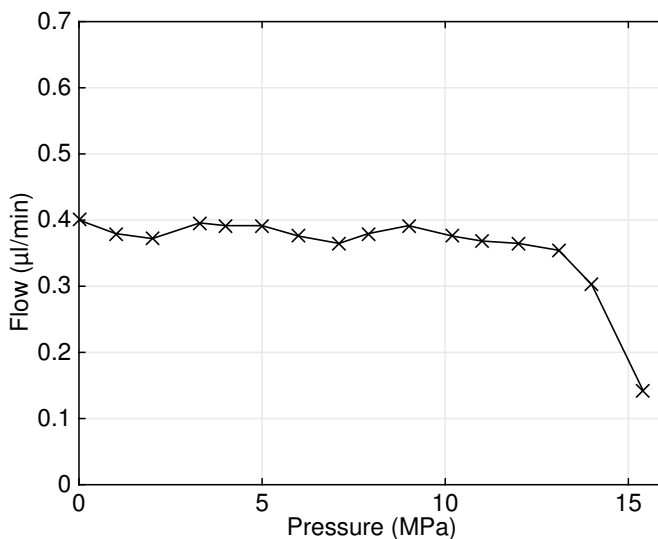


Figure 3.1. The pressure dependence for the flow rate of the high-pressure micropump running at 0.4 Hz. A relatively stable flow rate was achieved up to 13 MPa, after which the flow rate decreased although a positive net flow was still observed at 15 MPa. [Paper I]

For a fluid, the equilibrium between liquid and gas state varies with pressure and temperature along the saturation line, which can be seen in figure 3.2 for CO_2 . By pressurizing and heating the fluid above a critical pressure and temperature, *i.e.*, the critical point, the boundary between the gaseous and liquid state vanishes and the fluid becomes supercritical. While supercritical, the fluid has properties between that of a gas and a liquid, *i.e.*, a viscosity and diffusivity similar to a gas, and a density similar to a liquid. Two of the commonly used green solvents are CO_2 ($T_c=31^\circ\text{C}$, $P_c=7.3$ MPa) and H_2O ($T_c=374^\circ\text{C}$, $P_c=21.8$ MPa). For these two fluids, figure 3.3 shows how the density and viscosity vary in relation to the critical pressure and temperature around the critical point. For both fluids, the relative change in these two entities are similar, and because of the lower critical point of CO_2 , both regarding pressure and temperature, supercritical CO_2 (scCO_2) is suitable as a modeling fluid in microfluidic systems, which could be translated into a system intended for other supercritical fluids from a fluid dynamics perspective. As the critical point of CO_2 is fairly accessible, it is not surprising that the first steps towards miniaturization of analytical microsystems for extraction are mostly focused on supercritical carbon dioxide [12–14]. A more widely used and versatile system have been demonstrated by Marre *et al.*, where a glass/silicon chip have been used for many applications, *e.g.*, a pressure-volume-temperature

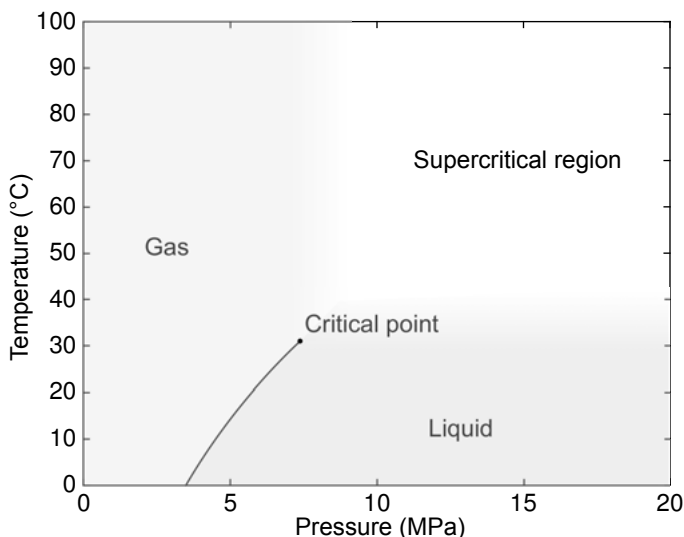


Figure 3.2. The phase diagram of CO₂ around the critical point at 31 °C and 7.4 MPa. Up to the critical point, the saturation line distinguishes the two states of liquid and gas. Extending beyond the critical point, these two states are indistinguishable, and the fluid becomes supercritical.

cell for scCO₂ [33], quantum dot synthesis using supercritical hexane [34], and supercritical water oxidation [15].

One of the future challenges in microfluidics is to provide a stable control of multiphase systems where the two phases have radically different properties when it comes to viscosity and compressibility [35]. One such system is scCO₂ and H₂O. Just recently, the first fluid mechanical study of this multiphase system was performed in glass channels by Ogden *et al.*, where two different flow regimes were identified [36]. By varying the flow rate ratio between the two fluids, the flow behavior was found to change between parallel and segmented flow. In the former, after the two fluids meet, they flow alongside each other down the channel, whereas for the latter regime, the two continuous phases break up into small segments covering the whole channel width. These measurements were conducted for constant temperature and pressure, and thus constant viscosity and density. However, as these two entities will vary extensively around the critical point, the study in Paper IV was conducted, varying both the flow rate, flow rate ratio, pressure and temperature to see how these entities affected the flow behavior inside a 180 μm wide and 40 μm high channel, which was 10 mm long. Because of the many variables covered, multivariate data analysis was used to evaluate the data. Both parallel flow and segmented flow were observed within the ranges investigated for the different parameters, illustrated in figure 3.4(a) and figure 3.4(b), respectively.

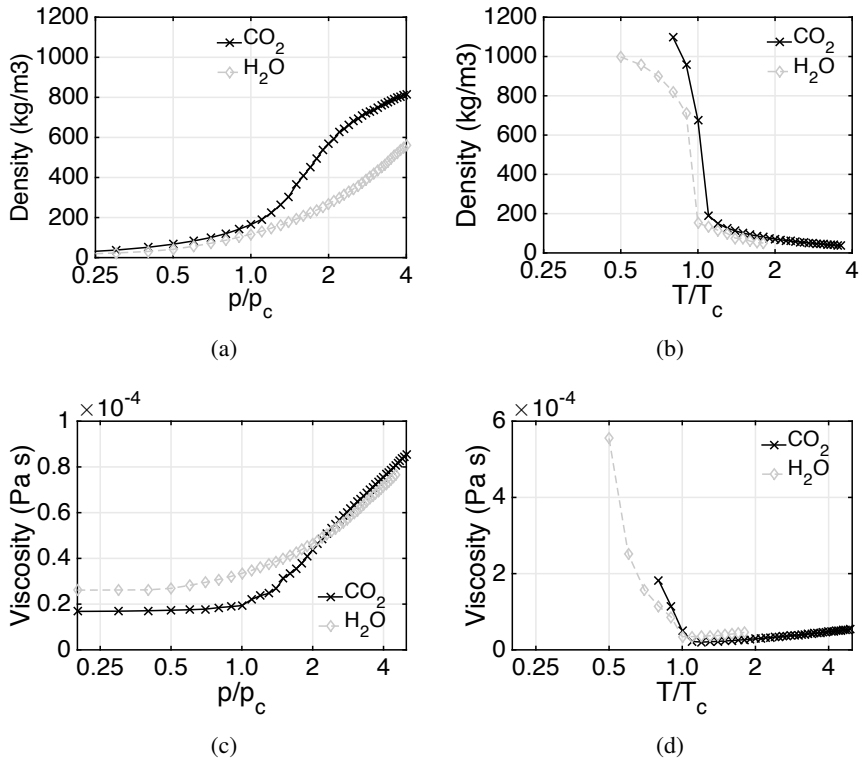


Figure 3.3. The variation of density (a, b) and viscosity (c, d) for CO₂ and H₂O, respectively, normalized to the critical pressure (a, c) and critical temperature (b, d) of respective fluid [21–23]. Increasing the pressure above the critical pressure causes both the density and viscosity to increase, whereas an increasing temperature has the opposite effect on the density and viscosity of the two fluids. For all graphs, the variable held constant was set to 1.1 times the critical value.

For the parallel flow, the CO₂ was pushed to the side down the channel, and the initially equal width of the CO₂ flow compared to the H₂O flow was observed to be approximately one quarter of the H₂O flow down the channel. Here, it was found that the parallel length was affected, not only by the flow rate, but the parallel lengths also became shorter at higher pressures. Interestingly, the temperature did not show any significant influence on the parallel length, which also was observed to be longer than expected if the break-up would be caused only by the better wetting towards the glass surface of H₂O.

The change in density of the fluid, both with varying temperature and pressure of CO₂, give rise to additional challenges for fluidic systems. When the density is different for different parts of the system, assuming a conservation of mass, the flow velocity vary according to the following relation

$$U = \frac{Q_{\text{pump}} \rho_{\text{pump}}}{A \rho_{\text{chip}}}, \quad (3.1)$$

where A is the fluid cross section area in the channel. Hence, as the CO₂ pump needs to be cooled to keep the fluid in the liquid state, and the device needs to be heated to temperatures above the critical point, the flow velocity will be radically different at different locations in the system.

Aside from the influence of the fluids in multiphase flows, the interfacial tension between the fluids, and the surface tension towards the channel wall will affect the behavior inside the channel. To investigate how the wetting affects a multiphase flow for scCO₂ and H₂O, two different silane-based coatings were used to modify the wetting inside a glass channel in Paper V. For a methyl-based surface, the contact angle between the two fluids was found to be close to 90°. This indicates that the surface tension for for both CO₂ and H₂O were similar towards the methyl silane surface. Using a fluor-based silane resulted in contact angles above 120° which indicates that CO₂ have a better wetting towards the fluor-based surface compared to H₂O.

For the methyl silane surface, well defined segments were created directly where the two flows meet which is illustrated in figure 3.4(c). By including a small guide at the center of the channel, only a few μm high, the flow became parallel throughout the channel and the interface between the two fluids were pinned to the guide resulting in equal widths of the two flows. Using the fluor-based silane coating, the flow inside the glass chip became unstable when the surface favored the compressible CO₂.

As the interfacial tension varies with density [37], and that the density for H₂O varies with the CO₂ saturation [38], this also needs to be considered for an increased control of multiphase flow, although not covered with the study in Paper V.

The wetting was also found to be an important factor in the parylene-based pumps and valves, Paper I and Paper II, where the hydrophobic surface could cause trapping of air inside the actuator cavity. Because of the compressibility of air, bubbles will act as a cushion, hence lowering the performance of

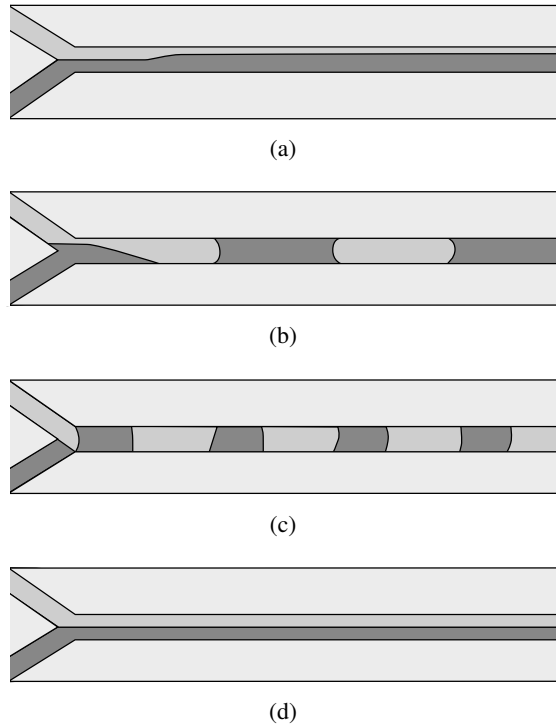


Figure 3.4. An illustration of the multiphase flow of scCO₂ (bright) and H₂O (dark) meeting to the left and flowing rightward under different conditions inside the 180 μm wide, 40 μm high, and 10 mm long glass channel. (a) The observed parallel flow for uncoated glass channels, where the initially equally wide flow of CO₂ to H₂O is pushed towards the side down the channel and thereby increasing the flow velocity. (b) Segmented flow for the uncoated channel where the flow breaks up into segments close to the inlet. (c) Methyl silane coated channel which results in a similar wetting for both fluids, which for a flat channel results in an evenly created segmented flow. (d) Methyl silane coated channel with a guide at the center which pins the fluid interface. This results in a parallel flow with an even width throughout the channel for both fluids. [Paper IV, Paper V]

the actuator. However, by purging the channel with ethanol in an ultrasonic bath, a successful priming was done, which removed all trapped air inside the micropump.

3.1.2 Up to extreme temperatures

Depending on the application, a high temperature has different implications. For the Si integrated circuit technology (IC), manufacturing techniques and materials (polymeric under-fillers, Sn-Pb soldering etc.) limits the possible working temperature of these systems. Usually, the upper limit of a possible working temperature for Si-based systems is considered to be around 125 °C, also being the often cited limit to the high temperature region [39]. There are generally two categories of high temperature systems differentiated by the thermal loading, as the heat can either originate from a high-power component (*e.g.* power electronics) or from a high temperature environment. Here, the latter will be considered, which eliminates the need to consider heat dissipation.

To reach into the high temperature region, both the structures and the active components need to be adapted, going from Si-based systems to systems based on semiconductors with a larger bandgap such as SiC, GaN, or AlN. However, as much of the well developed techniques for assembly are based on polymers, also the supporting techniques for connection/communication, power and adhesion needs to be substituted to high-temperature alternatives.

As MST originates from the IC technology, the natural way is to look for alternatives within this area. Gazing at how this is solved at macroscopic length-scales, this usually encompasses different protective layers which are not possible for microsystems where the excessive space needed for such approaches is seldom available. Also, since heat transfer for small systems is rapid, the whole microsystem will be exposed to the high temperatures.

3.1.3 Thermal expansion

Working with large temperature spans, one of the main challenges is to handle the resulting thermal expansion. This is primarily an issue between two materials with different expansions. Such a configuration will result in stresses at these interfaces, which, in turn, may result in failures. However, although a single material is used, large temperature gradients over the material may still induce large stresses, which may result in failures. The resistance of a material towards these gradients is called the thermal shock resistance [40]. A low thermal expansion of a material will result in lower stresses, and a good heat conduction will allow the material to expand more coherently. Also, a low Young's modulus as well as a high fracture strength will allow the material to deform and handle larger thermal stresses.

For high temperature, the most commonly used material is the ceramic alumina, Paper VII. With a low thermal conductivity of 24 W mK^{-1} [41] at room temperature, the thermal shock resistance of alumina is fairly low which is a limitation for applications with rapid changes in temperature. Polycrystalline AlN is an interesting material, Paper VI, that has a thermal conductivity similar to metals, typically $100\text{-}200 \text{ W mK}^{-1}$ [41]. AlN has mostly been used for power electronics where the heat is generated at the component, rather than heating from the surrounding environment. Aside from having a favorable thermoshock resistance, the thermal expansion of AlN is also well matched to the semiconducting materials of Si, SiC and single crystalline AlN, making the material a suitable substrate for building components [42].

3.2 Flow control at high pressure

3.2.1 Valves and pumps

There are many different technologies to generate force and stroke, such as piezoelectric, electromechanical or electro-osmotic actuation, summarized in reviews by Laser and Santiago [43], Nisar *et al.* [44], and Oh and Ahn [45]. A broad classification of the different micropumps is displacement and dynamic micropumps [43]. The former relies on indirect actuation of components such as piezoelectric, electrostatic, shape-memory alloys, or phase change materials (PCM), which moves a diaphragm that will mechanically affect the fluid. The term dynamic micropumps refers to a direct manipulation of the fluid by a physical phenomenon such as pumps utilizing the centrifugal forces or magneto hydrodynamic pump.

Many of the displacement technologies result in fast actuators that can generate moderate forces, where the strongest displacement micropumps have been achieved using PCM actuation with paraffin as an actuator material, Paper I. However, requiring melting of a material, these actuators have the downside of being slow compared to, *e.g.*, their piezoelectric counterparts. Among the dynamic micropumps, there are micropumps capable of even higher pressures which utilizes the electro-osmotic effect. These pumps have reached pressures up to 50 MPa with the downside of requiring pumping of only ionic liquids [46].

In this thesis, the focus is on paraffin-based PCM actuators. Therefore, no further explanation of the other technologies will be done.

3.2.2 High pressure actuators

Paraffin actuator designs

Paraffin, commonly used for candles, has a variable melting point between $-100 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$, depending on the chain length of the polymer. For an

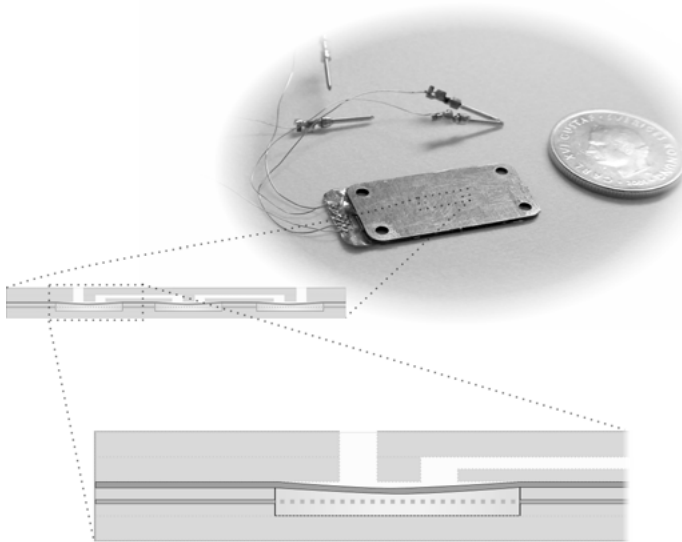


Figure 3.5. The high pressure stainless steel micropump, approximately 1 mm thick beside a 1 SEK coin with a cross-section of the micropump. The micropump consists of three valves connected in series, where each valve consists of a flexible stainless steel membrane enclosing a paraffin filled cavity. Inside each cavity is a heater which is used to melt the paraffin to generate force and stroke, to push the membrane against the inlet orifices, which will close the valve.

increasing length of the paraffin chains, as well as for higher pressures, the melting temperature increases [47].

For paraffin waxes with a melting point around 45 °C, this volume expansion is in the range of 10% to 20% [48], with low variation with pressure. As discussed in the earlier section regarding compressibility, section 2.4, the bulk modulus of paraffin is large, which makes it a suitable material to generate force and stroke for high force actuators. This has been utilized in various actuator designs, covered in a recent review by Ogden *et al.* [49].

The sub-cm³ paraffin-based actuator consists of an enclosed paraffin-filled cavity. The cavity is structured by stacking stainless steel stencils with a copper heater, which is used to melt the paraffin, located in the middle, seen in figure 3.5. During melting, the expansion of paraffin will deflect a thin membrane to generate force and stroke. To be able to measure the temperature of the paraffin, another copper structure, located at the bottom of the cavity, was used as a temperature sensor. Many devices using paraffin has been built for strong actuators [49]. The design used within this thesis has, with small but important modifications, also been used as a latchable valve [50] and as a dispenser [51] capable of working within the high pressure regime.

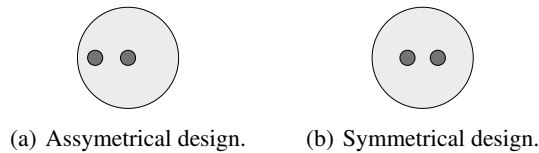


Figure 3.6. The placement of the holes (dark) in relation to the paraffin cavities (bright) for two different designs evaluated in Paper II. (a) The orifice facing the highest pressure is located at the center with the second orifice located towards the rim. (b) Both the inlet and outlet orifice are located at equal distance from the center.

Orifice contact situation

The location of the orifices that are closed and opened when the membrane makes contact was shown to be an important design parameter to create strong actuators, Paper II, where the largest force was possible to be acquired at the center of the actuator cavity. Therefore, by placing the center orifice facing the higher pressure, both at the inlet actuator and the outlet actuator, the strongest pump was expected. Although resulting in the strongest valve with the lowest energy consumption, this design, figure 3.6(a), resulted in a self-sealing behavior when the pressure was above approximately 1.5 MPa, because the paraffin first solidifies around the cavity wall. As the paraffin is still soft close to the melting point, the solidified paraffin is pushed towards the off-center orifice and keeping it closed. Therefore, the pump used a symmetrical design with both orifices close to the center of the cavity at equal distance, figure 3.6(b). Aside from not having the ideal contact situation, this design enabled a bi-directional valve.

For joining of the different metal sheets of the microactuator, thermo-compression of Parylene C was used. Although parylene has a yield strength of approximately 50 MPa, which is comparable to some metals, the Young's modulus is only around 3 GPa, which causes the material to deform already at low pressures [17]. Therefore, to enable the high-pressure capability, a spring loaded fixture was used for both the micropump and microvalve.

Flexible stainless steel membranes

Different membrane materials were evaluated in Paper II, including PDMS, polyimide, SS304 (18-10) and SS301 cold-rolled spring steel. Although PDMS previously has been used for paraffin actuators, PDMS was found permeable to paraffin which made this material unsuitable for the intended application. The polyimide was found to permanently deform under high loads, and also the SS304 was found to suffer from fatigue. Using the spring steel, a long term stable membrane was found.

Peristaltic pumping

One of the simpler designs of a pump is to have a flexing membrane to create motion, and a flow restriction on one side, which will direct the flow [52]. However, this design can not uphold a high system pressure, because a higher pressure down-stream will create a back-flow. If the flow restriction is replaced by valves on each side of the membrane, the valves can direct the flow during the forward-stroke of the membrane and uphold the higher pressure down-stream during the back-stroke of the membrane, hence pushing the liquid forward, which is called a peristaltic pump cycle. For the pump presented in Paper I, all three actuators had the same diameter of the membrane, which results in equal volumes being pushed forward with each stroke for the three actuators. A typical pump cycle for such a design is presented in figure 3.7, where it can be seen that during a full pump cycle the pump generates two forward strokes and one back stroke. Hence, the resulting flow is uneven and pulsating. Also, during half of the cycle there is no net-flow. To study if a more energy efficient driving was possible, a second drive cycle was investigated, Paper I, where the opening and closing of the inlet and outlet valve was done simultaneously. This resulted in higher flow rates, but also a decreased high-pressure capability of the micropump.

Actuation of a miniaturized HPLC system

Paper III attempts to solve the issue of an uneven flow by primarily implementing two improvements. Instead of using three equally sized actuators, the multi-pump system utilizes two small valves at the inlet and outlet, with the primary purpose of preventing a back-flow, and one large actuator in the middle, that was slowly heated to generate a long stroke with a low flow rate. To fill the gap during the refilling of the dispenser where the outlet valve closes, a second pump was driven in parallel with overlapping drive cycles, resulting in a much smoother flow.

For this design, the previously used high pressure ferrules and fittings were changed to glued capillaries which resulted in an unfavorable force distribution on the individual actuators, causing the paraffin expansion to be lost to the expansion of parylene. Hence, this multi-pump design did not manage to pump against high back-pressures.

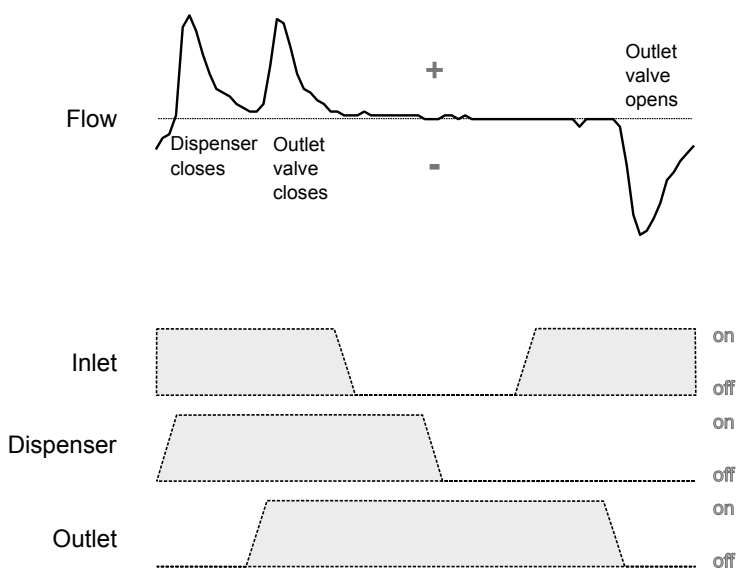


Figure 3.7. The flow rate measured at the outlet of the micropump (top), in correlation to the activation voltage of the three valves (bottom) during a pump cycle. The resulting flow consists of two forward strokes and one back stroke, where each stroke generates the same dispensed volume.

3.2.3 High pressure conclusion

- Using paraffin as an actuator material, the to-date strongest membrane micropump was shown, and the used valve was capable of sealing against pressures above 20 MPa. The peristaltic paraffin micropump managed to pump against pressures up to 13 MPa.
- The importance of orifice placement at the valve seat and membrane material choice was shown important for thermally actuated long term stable high pressure valves and pumps.
- The actuators presented are capable of handling the pressures needed for constructing flow control components for systems working with scCO₂, such as valves, pumps and back-pressure regulators.
- For a stable high pressure multiphase flow including a supercritical fluid, the importance of a stable pressure and a well defined wetting was shown. For a coating with similar contact angles for both phases, the behavior can be controlled by structuring the channel, shown for scCO₂ and H₂O, where the presence of a guide or not changed the behavior from parallel to segmented flow.

3.3 High temperature characterization

3.3.1 Wireless characterization

To interface with devices in harsh environments, wireless communication is an attractive alternative. However, for extreme temperatures, there is a lack in available active components to regulate the communication on-chip. Therefore, the choice was to develop passive resonator components. In Paper VI, the variation of ϵ_r for sintered polycrystalline AlN was studied at temperatures up to 900 °C for different frequencies, as this material is an interesting alternative to use for high temperature circuit-boards. A similar setup was also used in Paper VII to characterize a wireless pressure sensor at temperatures up to 1,000 °C, and pressures up to 0.3 MPa, figure 3.8. As seen in figure 3.8, the sensitivity of the pressure sensor was observed to decrease with increasing temperature. The principle used was that for resonating circuits, when the capacitance, C , varies (discussed in section 2.5), the resonance frequency will shift according to

$$f = \frac{1}{\sqrt{2LC}}, \quad (3.2)$$

where L is the inductance. Using the design of a parallel plate capacitor, the frequency will mainly vary with ϵ_r and the inductance. Further, as the variation in inductance is mainly dependent on the geometry [53], and that variations in geometry will be small for ceramics, as the CTE is low, the resonance frequency will mostly vary according to ϵ_r .

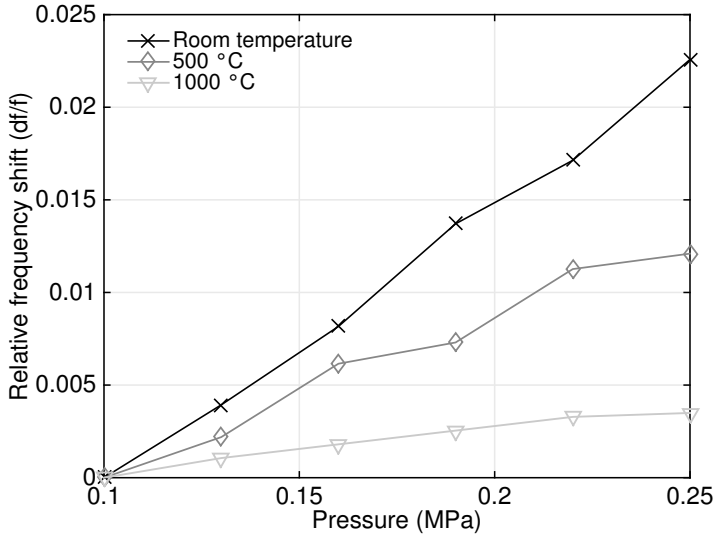


Figure 3.8. The frequency shift of the pressure sensor as a response to varying pressure, measured for three different temperatures of room temperature, 500 °C, and 1000 °C. The sensitivity decreased from approximately 150,000 ppm/MPa, down to 24,000 ppm/MPa at 1000 °C. [Paper VII]

For the pressure sensor, a second capacitance is connected in series to the substrate capacitance, also based on the parallel plate capacitor described by equation 2.5. By having an enclosed air-filled cavity between the two metal plates, a pressure difference between the outside and the reference pressure inside will change the height of the cavity, which will result in a changed capacitance, thus further shifting the resonance frequency of the device.

3.3.2 Electro migration

With a high melting point, being a ductile metal and having the best electrical conductivity of all elements, silver has long been an interesting material for electrical systems. Recently, silver has also been investigated as a high temperature adhesive for attaching components in the form of paste [54] or using diffusion bonding [55] for high temperature circuitry. However, because silver is known to migrate under certain conditions [56,57], a test bed was developed to study the migration in-situ in an environmental scanning electron microscope (ESEM), Paper VIII, to further be able to determine the onset of this process as well as providing live monitoring at high magnification.

Electro migration is the transport of metal through or across a non-metallic medium under an applied electrical field, remaining in its metal state both at the source and at the final destination [58]. This can be further divided into

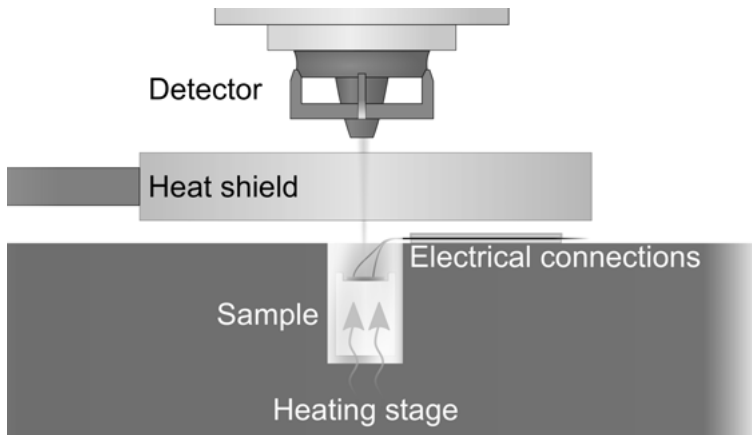
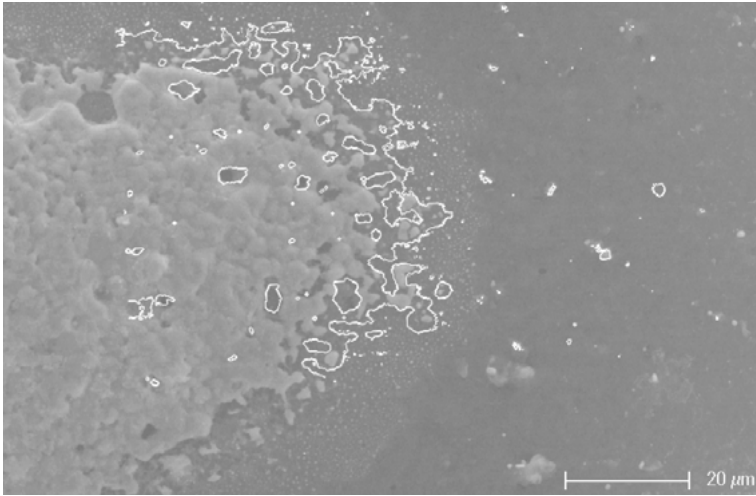


Figure 3.9. A schematic of the high-temperature test bed inside an ESEM. For imaging, the gaseous secondary detector, located at the entrance of the electron column behind a heat shield was used. The sample was mounted in a ceramic crucible in the heating stage and the wires for electrical connection to the sample were placed in between two AlN sheets on top of the heating stage. [Paper VIII]

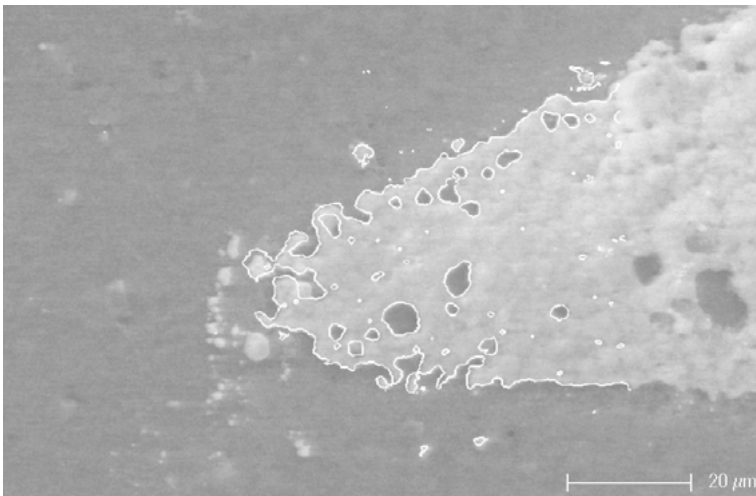
the subcategories of wet and solid-state electro-migration, where the former is due to the creation of local electrolytic cells in films of water present on the surface, whereas the latter is a result of moving electrons that pushes the metal in the direction of the current, usually at high temperatures and current densities [59]. Aside from humidity, the presence of salts has been important factors to consider [56,57]. To be able to study this migration during the process at high magnification, an experimental platform was built inside an environmental SEM (Paper VIII), where a high DC-bias was applied between two silver tips printed on an AlN substrate, figure 3.9. The result after exposure to 700 °C and a current density of 200 V/mm can be seen in figure 3.10, where the initial structures are outlined in white.

3.3.3 High temperature conclusion

- The dielectric properties of polycrystalline AlN were wirelessly characterized up to 900 °C.
- A complete wireless pressure sensing system was developed for temperatures up to 1000 °C. Using Pt as a conductor material, the read range was decreased in comparison to more favorable alternatives such as silver. However, silver migrates at high temperatures, and will melt at the extreme temperatures.
- A method for studying electro-migration in-situ at high magnification was developed for high temperatures.



(a) Anode.



(b) Cathode.

Figure 3.10. Two opposing silver tips after 700 °C and a current density of 200 V/mm in a 3 mbar H₂O atmosphere. The initial structures are outlined in white, and an onset of material transport can be observed at the anode, visible as a bright shadow around the tip. [Paper VIII]

3.4 Summary and remarks

Within this thesis, the designed and evaluated systems have all been setup in such a way that the data processing and reference have been located at room atmosphere and room temperature to reduce the challenge, *i.e.*, the systems have been exposed to harsh conditions. For the wireless transmission, keeping the active sweeping antenna at a constant temperature proved to be a key challenge, as the components used in the antenna are very temperature sensitive, *i.e.*, polymer-based capacitors. Therefore, heating the active antenna only a few °C proved to cause a large drift in resonance frequency. Also, the low read range of the Pt conductors in the pressure sensor resulted in shorter read ranges compared to the silver based conductors in the AlN thick-film structures, although silver suffers from being susceptible to migration and will melt before reaching 1,000 °C.

For systems working in harsh conditions, there are many challenges affecting the system at once. Within the field of microsystem technology, data analysis is a useful tool, although mostly used for calibration purposes using linear regression. However, it is of equal, if not greater, importance for creating reliable processes and to determine the relevance of different variables. With only one response variable, and one variable that can be changed, the commonly used technique of linear regression is useful. However, this concept can also be used for situations where many variables will vary and are co-dependent on each other, *i.e.*, using multivariate data analysis (MVA). In MVA the interactions are assumed to be linear, and instead of fitting a line to the data, an n-dimensional plane can be fitted for the least variance. Based on this idea, two major techniques exist that complement each other in a way that principal component analysis (PCA) evaluates the variation between variables and observations (the measurements) and is useful to find relations within a dataset. Partial least square regression (PLS) relates the variation of the variables to one or many response variables, *i.e.*, a multivariate linear regression. In research, MVA has mainly found its role in pharmaceutical applications [60], but also as a tool of calibration in applications working with large spectra [61–64].

Although MVA can find obscured patterns for systems with many variables that covaries, the statistical tools will not give further knowledge without ensuring that the input data is correct.

As mentioned in an earlier section (2.4), it is of key importance to know both the temperature and pressure to know the density of CO₂, and thereby getting an initial estimation of the flow velocity in different parts of the system, which in turn affects *e.g.*, ratios of different fluids in multiphase systems. Also, for systems utilizing compressible fluids, the pressure and temperature will vary even though one is considered constant due to the thermodynamic relations, where compression and expansion will cause the heat to be released and absorbed, respectively. This will in turn change the flow velocity of the fluid, which may result in another behavior than intended.

For the incompressible paraffin, the density of paraffin has a large variation around the phase transition of solid to liquid. Although the system temperature is relevant in a broader perspective, it is the temperature of the individual actuators that is of most importance. Here, the challenge is to heat enough to ensure that the paraffin is melted, but not allowed to damage the structure. Therefore, in Paper I, copper-based temperature sensors were integrated in each of the pump cavities to be able to individually observe and control each actuator.

As the temperature of a component does not necessarily is the same temperature as the heat source, the system as a whole needs to be considered. In the ESEM setup, a water-cooled fixture ensured stability, and allowed for fast heating and cooling. For the high temperature pressure sensor, heated using a butane flame, the thermal stability was achieved by submerging the component in sand to give enough thermal bulk to even out small variations in temperature, and thereby enabling a reliable temperature measurement.

4. Outlook

The stainless steel technology has some interesting potential to exploit for future work, and it would be desirable to modify the steel-based technology to allow for high-pressure active components intended for CO₂. To enable the use of aggressive fluids operating at higher temperatures, the parylene joints should preferably be changed to soldered or welded joints. Transition liquid phase bonding, or diffusion bonding, is an interesting technique that has been investigated as an alternative to achieve joints capable of handling high temperatures for power electronics. The technique is similar to soldering, where a melt is used to create the initial joint. By using a metal with a low melting point together with a metal with a high melting point, but with a composition chosen so that after the initial melt has joined the two surfaces together, the low melting point metal will diffuse into a bulk consisting of the high melting point metal. Thus, joints can be created at temperatures well below the melting point of the final joint [65]. Currently, the most investigated system is In-based alloys such as In-Ag, because of the attractive properties of these joints for power electronics [55, 66]. However, Ag and In are not ideal in chemically aggressive environments, as they are expected to deteriorate. Ni-Sn is an interesting alternative that have found recent attention [67, 68]. As Ni is a constituent of steel that is often found close to the surface, and the use of Sn for soldering is a well known process, this combination could result in joints capable of both high temperatures, but also mechanically strong joints.

Because steel-based system are opaque, further fluidic studies and early prototyping would preferably be done using glass-based systems, also in the future. Further, to enable windows for optical detection techniques, the glass and steel techniques would preferably be merged, using a solder-based technique. Also, with a reliable interface, other materials and components could be attached to the fluidic system such as pressure and flow sensors that are mostly based on ceramic materials or semiconducting materials such as SiC or AlN. Although suitable for many fluids, *e.g.* scCO₂, both glass and many ceramic materials corrodes in high temperature water environments, and for high temperature water systems, this corrosion is more severe [69]. Considering having a corrosive agent in a microfluidic system at high pressure and high temperature, such as scH₂O, the challenge extends to also include compatible materials for the fluids as both oxygen-based and nitrogen-based ceramic materials will deteriorate under these conditions [70]. However, microsystems utilizing scCO₂ are still in their infancy.

For the current actuator design in the microvalve and micropump, everything is placed in the same layer of the metal stack. Although favorable for

batch production, this has the disadvantage that if one of the three actuators fails, there is no way to replace or fix the device. By using a modular design similar to circuit board technology, individual actuators and features can be tested before mounting to the fluidic system, which allows for a more rapid prototyping. The challenge of having the whole system in one layer manufactured at once became clear for the multipump chip intended for HPLC, which for the follow up designs including 13 actuators spread out on 4 pumps and a valve, of which not seldom only one actuator was defect which ruined the whole device. In combination with diffusion bonding for the individual components, the joints for the fluidic system can initially be done using Sn-based soldering without affecting the individual components. Also, for such a system, individual components could be optimized individually which could ease the initial characterization and optimization to reach a functional state. By employing a modular design, it is also worth considering the opportunities of stacking different components. The current actuator design is below 1 mm in height, but one order of magnitude larger in the horizontal plane. By utilizing also the third dimension in the construction, even more compact systems can be achieved. However, to realize this, the system must be capable of reaching the desired pressures without using a fixture for mechanical support, which could be achievable using soldering.

Paraffin is a good choice as an actuator material for low temperature actuators with melting points up to around 100 °C. For actuators capable of working at temperatures above that temperature, other actuator materials are needed. In a first step to allow for systems capable of operating at temperatures up to approximately 150 °C, the sugar alcohol mannitol is a promising candidate that has a melting point at 168 °C. Using mannitol for a soldered structure, an initial demonstrator has been shown [71], where an expansion of approximately 7% was measured during the phase transition from solid to liquid. However, mannitol has been observed to be incompatible with parylene. Thus, to successfully build a valve using mannitol as an actuator material, improvements in the structuring of the steel and the solder joint is needed for a well defined mannitol volume. Also, for melting, new materials are needed for an electrically insulating high temperature joint that can also support the mechanical load.

By enabling the use of high-temperature valves using the soldered steel technology for flow control, the principle of the valves could be used in combination with the glass capillaries used in Paper IV and Paper V for an active back-pressure regulator. As the stroke of the actuator is short using steel membranes, several valves connected in parallel could improve the flexibility to gradually shut the flow.

For high temperature operation, most active components, such as transistors, are still manufactured on modified Si technology, where the low bandgap prevents operation beyond approximately 200 °C. During recent years, many transistors have started to be developed in SiC and GaN, where the Royal In-

stitute of technology (KTH), Stockholm is developing the needed building blocks of high temperature logic components, primarily intended to be used for control logic for power transistors. By utilizing these components for wireless sensor nodes, more powerful sensors can be used where the current main limitation is the utilization of passive devices, based on metals with a high resistivity which limits the feasible read ranges. To power systems at high temperature, there are two options. Either the energy is stored on-board or transmitted/harvested from the surroundings. For storing large amounts of energies, the Sadoway-group at Stanford have developed batteries operating at 700 °C [72]. Although developed for large-scale applications, this demonstrates the feasibility of on-board energy storage at high temperatures. Also, the energy harvesters that are currently developed in AlN [73–75] may be an alternative in the future to support small systems with low energy budgets.

To conclude, when reaching the extremes you end up with trade-offs and compromises that will be system specific, as the environment, temperature, and pressure will put different demands on the materials, not always working in the same direction. Ceramics are well suited high-temperature materials, but the brittle nature of these materials makes them unsuitable for high pressure applications, together with the low chemical resistance to many aggressive fluids. Materials such as stainless steel are well suited for high pressure applications, but are not feasible for the high temperature applications, and being a metal alloy, steel is unsuitable for microelectronics without an insulating complement.

5. Svensk sammanfattning

Då dimensioner på komponenter minskas ner till mikroskala blir vanligtvis spröda material användbara för annars otänkbara strukturer så som flexibla membran. Även fysikens lagar beter sig annorlunda jämfört med vad vi förväntar oss i vår vardag eftersom förhållandet mellan yta och bulk ökar, vilket därmed ökar ytans betydelse. För mikrosystem som hanterar vätskor i små kanaler, även kallat mikrofluidik är detta fördelaktigt då det medför kortare transportvägar, mindre provvolymmer och en enklare hantering av värme, för att nämna några exempel.

Många mikrosystem arbetar vid atmosfärstryck och rumstemperatur och är inte anpassade för krävande tillämpningar och miljöer som innebär höga tryck och höga temperaturer. Genom att öka trycket och temperaturen öppnas dörrar till att använda analystekniker och lösningsmedel som annars inte är möjliga. Till exempel ökar reaktionshastigheter vanligtvis med både ökande temperatur och tryck.

För att kunna hantera höga tryck och höga temperaturer behövs kompatibla komponenter för dessa miljöer. Grundläggande komponenter för att påverka flöden är ventiler, pumpar och flödesbegränsare, vilka i dagsläget saknas i hög grad för att kunna hantera höga tryck. I artikel I presenteras den hittills starkaste membranbaserade mikropumpen, som visades klara att pumpa mot ett tryck på 13 MPa vilket är 130 gånger atmosfärstrycket. Även om pumpar baserade på elektroosmos har visats klara att pumpa mot högre mottryck, är den tekniken begränsad av att endast kunna pumpa elektriskt ledande vätskor. En membranpump har däremot inga sådana begränsningar, utan begränsas endast av kemisk kompatibilitet mellan vätska och strukturmaterial.

Utvecklandet av en stark mikroventil var det som blev avgörande för att kunna pumpa vid höga tryck. Ventilen, som presenteras i artikel II har visats klara av att sluta tätt mot tryck över 20 MPa och visade sig även vara gastät. Genom att kombinera tre ventiler som sekventiellt sluter tätt åstadkoms den starka pumpen. En konsekvens av att driva en pump på detta sätt är dock att pumpens flöde blir ojämnt.

För många analysmetoder där en högtrycksmikropump skulle kunna vara lämplig är ett ojämnt flöde inte önskvärt. Ett sätt att uppnå ett jämnare flöde är att använda flera pumpar som arbetar parallellt där deras flöden kompletterar varandra. Detta utnyttjades i artikel III. Där kombinerades två pumpar som dessutom hade en större mittenventil. Då den större mittenventilen levererade en större volym vätska kunde kombinationen av olika stora ventiler och parallell pumpning möjliggöra ett betydligt jämnare pumpflöde.

Genom att öka tryck och temperatur i ett system kan s.k. superkritiska fluider användas. När en fluid blir superkritisk beter den sig som ett mellanting av en vätska och en gas, med en densitet liknande en vätska men en diffusivitet och viskositet liknande en gas. En fluid blir superkritisk då både tryck och temperatur höjs över fluidens kritiska punkt, över vilken den tydliga gränsen mellan vätska och gas upphör. Fördelen med att använda superkritiska vätskor är att det gör det möjligt att använda fluider som är relativt oskadliga. Exempel på detta är koldioxid som i sitt superkritiska tillstånd blir ett användbart lösningsmedel. Tanken är att dessa skall kunna ersätta mer skadliga konventionella lösningsmedel.

I mikrofluidala system är användandet av superkritiska vätskor relativt outforskat. Därför utfördes två flödesstudier som presenteras i artikel IV och artikel V, där koldioxid i dess superkritiska tillstånd flöddes tillsammans med vatten i en mikrokanal för att studera beteendet, vilket till stor del styrs av ytspänningen mellan vätskorna och deras densitet och viskositet. Även om egenskaperna för vatten är relativt opåverkade vid de temperaturer och tryck som krävs för att koldioxid skall bli superkritiskt, varierar densiteten och viskositeten kraftigt för koldioxid kring dess kritiska punkt. Därför studerades i den första artikeln hur variationer i temperatur, tryck och flödeskvoten mellan vätskorna påverkade det uppkomna flerfasflödet mellan fluiderna. Genom att öka tryck och kvoten koldioxid relativt vatten tenderade vattnet och den superkritiska koldioxiden att flöda sida vid sida i den smala kanalen, medan för lägre tryck och en lägre kvot tenderade flödena att bryta upp till segment i kanalen. I den andra artikeln studerades inverkan av kanalens yta på flerfasflödet. Genom att använda två olika beläggningar modifierades den vanligtvis vattengillande ytan, dels till att bli koldioxidgillande och dels till att bli neutral mellan de två fluiderna. Detta visades ha stor betydelse för flerfasset. Mest noterbart var att genom att göra ytan neutral visades flödet styras av en endast fåtal μm hög vall som när den var närvarande gjorde att de två fluiderna flödade sida vid sida, istället för att som annars delades upp i segment direkt vid mynningen av kanalen.

För mikrosystem som är tänkta att arbeta vid höga temperaturer är utmaningarna annorlunda jämfört med system för höga tryck. Istället för att använda böjliga metalliska material, vilket är fördelaktigt för högtryckstillämpningar, främjas högtemperaturlåga elektroniksystem av spröda, keramiska material med ledare av ädelmetaller eller värmelåga metaller såsom wolfram. Genom att tillföra energi underlättas reaktioner och rörelser. För metalliska system är detta en utmaning då skapandet av intermetalliska föreningar (föreningar bestående av flera olika metaller) är vanligt förekommande vid högre temperaturer. Silver som har den lägsta resistansen hos alla grundämnen har länge varit av intresse att använda som elektriska ledare inom mikroelektronik och på senare tid även som fogmaterial för att fästa elektriska komponenter till monstertkort för högtemperaturrelektronik. Vid höga temperaturer i anslutning till fukt är det dock välkänt att silver rör på sig mellan elektriska ledare (s.k.

migration) och därigenom kortsluter kretsar. Därför utvecklades en testmetod inne i ett elektronmikroskop med kontrollerad atmosfär för att kunna studera silvermigring vid hög upplösning i realtid, vilken beskrivs i artikel VIII.

En av de stora utmaningarna med elektriska system som arbetar vid höga temperaturer är anslutningar för kommunikation. Genom att utnyttja trådlös kommunikation undviks många av utmaningarna relaterade till kablar och kontakter.

En av de enklare designerna av ett trådlöst system är att utnyttja en passiv resonant krets. Vid varierande temperaturer ändras dock fundamentala egenskaper hos material, så som den s.k. dielektriska konstanten. Den dielektriska konstanten styr materials lämplighet för att användas som grund för kretskort för trådlösa system och att veta hur den dielektriska konstanten varierar med en varierande temperatur är en viktig information för att kunna förutsäga hur kapacitansen i komponenter varierar med en varierande temperatur. I artikel VI studerades därför hur den dielektriska konstanten varierade för polykristallin aluminium nitrid (AlN), vilket är ett keramiskt material som är intressant för högttemperaturlämpningar.

Genom att utnyttja variationer i kapacitans, demonstrerades i artikel VII en passiv trådlös trycksensor. Trycksensorn var kapabel att mäta tryck upp till 0,3 MPa, vid temperaturer upp till 1000 °C. För trycksensorn användes förändringarna i kapacitans som dels uppkom av ett förändrat tryck, men även på grund av temperaturens inverkan på trycksensorns material. Den förstnämnda förändringen uppkom av en geometrisk förändring av en innesluten kavitet genom att ett membran tryckte ihop kaviteten vid ökande tryck vilket ger upphov till en ökande kapacitans. Materialets varierande kapacitans berodde på den tidigare nämnda dielektriska konstanten. Den trådlösa trycksensorns läsavstånd begränsades dock av den låga ledningsförmågan hos platina som användes som ledare på grund av dess högttemperaturlåglighet.

Utmaningarna för system som hanterar höga tryck skiljer sig fundamentalt från system som hanterar höga temperaturer, vilket ställer olika krav på de ingående materialen som sällan resulterar i liknande materialval för de två fallen. Väl avvägda materialval är dock attraktivt för att kunna vidga användandet av fler superkritiska vätskor med en högre kritisk punkt så som superkritiskt vatten, men även för komponenter för övervakning av exempelvis geotermiska djupborring. För dessa tillämpningar skulle ett metalliskt stål-baserat mikrosystem kunna vara en attraktiv kompromiss för tillämpningar som är krävande både med höga tryck och höga temperaturer.

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