High pressure glass microfluidics for supercritical CO_2 with aqueous solutions

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Abstract. A microfluidic system is presented to investigate interactions between supercritical CO_2 and H_2O using high-pressure glass chips. The reliability of these chips at pressures necessary to sustain CO_2 in the supercritical phase is dependent of both time and temperature. 130 bar can be kept at 38°C for more than a week. These systems can be used to investigate fluid interaction between supercritical CO_2 and aqueous solutions by the addition of pH sensitive dye and high speed absorption light imagining, making it possible to demonstrate acidification is in a multiphase chip. By the addition of integrated temperature sensors, better control of the states of the fluids inside the chips can be achieved.

1. Introduction

Supercritical fluids provide means of advanced materials handling and analytics. Being a benign, non-toxic, solvent for several types of organic compounds, while possessing gas-like viscosity and diffusivity, supercritical CO_2 has seen a lot of interest from the food and pharmaceutical industry, primarily in chromatography [1]. It is used for particle formation and loading of pharmaceutical compounds to carrier substrates [2-3]. Among such techniques, it is essential to acquire knowledge about compound solubility and partition distributions in multiphase systems. Meanwhile, in the field carbon capture for environmental sustainability, the potential of storing pressurized, high-density, CO_2 in geological formations is being explored [4]. In such conditions, it is recognized that supercritical conditions will be present and that fluids will interact with its surroundings, e.g. aqueous and mineral phases [5]. Fluid interactions between the multiphase system of high-density CO_2 and water its thus of interest in many fields. Utilizing this fluid system in microfluidics offers novel applications but the high pressures adds to equipment demands and the difficulty of operations in terms of both production and for the measurement of key parameter like solubility and partitioning constants.

Microsystems have been shown to be an effective tool for parameter characterization as equilibrium can be reached faster [6]. Scaling laws works in favour for high-pressure endurance in microsystems. Systems using supercritical CO_2 have been demonstrated for different applications. These include the extraction of compounds, for instance lignin oxidation products [7], the characterisation of micro emulsions [8], and solubility of CO_2 [9] in a H_2O-CO_2 multiphase system. Fluid properties of supercritical CO_2 like density and viscosity vary much with temperature and pressure [10-11]. Microsystems offer large surface to volume ratios, and thus great heat transfer, and the small volume lowers the contained energy of compression to safer levels. While the density variability is utilized to tune the solvent power, it also possesses challenges for the microsystem. As variations in density and viscosity also affect flow, being able to control and measure temperature, pressure and flow, inside the channels of the chips, is of great importance in high-pressure microfluidics. In this paper, means of providing extended temperature control is explored.

High-pressure microfluidic devices using anodic bonding of glass and silicon structures have been shown to sustain pressures of up to 450 bar [12]. Transparent systems, consisting of fusion bonded borosilicate glass wafers, have been shown to sustain pressures at the upper range of 260 to 690 bar [13]. The strength of any chip is depending on channel geometry and for glass; stress corrosion can with time lead to failure at much lower pressures. Transparent systems offer transmission lightning, which offer ease of use in spectroscopic determinations and enable the use of absorption spectrometry [14]. We here demonstrate a multiphase chip that offers a platform for studying fluid interactions between supercritical CO_2 and an aqueous phase. Together with light adsorption techniques and a pH sensitive dye, bromophenol blue (BPB), it is possible to extract kinetic information about the interactions between supercritical CO_2 and aqueous phases.

2. Experimental

2.1. High pressure setup and chip design

The test system consists of two high-pressure pumps containing either liquid CO_2 cooled to 4.5 °C or H_2O at room temperature, together with high pressure tubing, a sample valve, a pressure sensor and a back pressure regulator which all also are cooled. Borosilicate glass chips are mounted on a fixture for fluid and electrical interfacing and are studied with a high-speed camera (Miro 320, Phantom Vision). By mounting the camera above the chip and having high brightness, 421 and 592 nm, LEDs underneath, a transmission light path through the channels is formed.

Four different chip designs were used. Two chip types have a circular cavity of either 1.6 or 2 mm diameter and are used specifically as test structures for fracture pressure tests. In the third chip type, resistive Pt temperature sensors are embedded into the chips and exposed to the inside of the channels. The forth chip type is a multiphase chip with inlets for both aqueous solutions and CO_2, leading to a T-junction, and is used for studying interactions between the fluids.

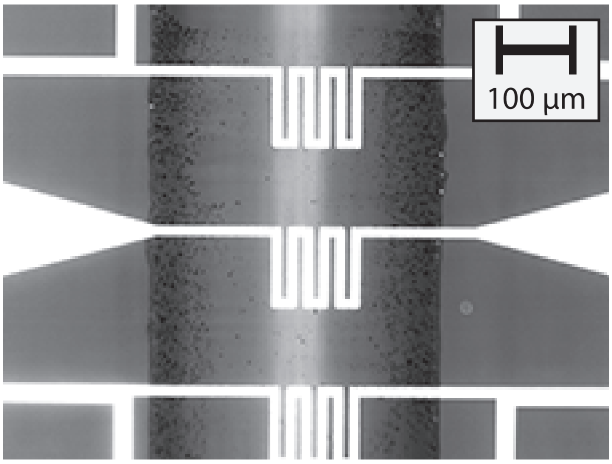

Figure 1 Three Pt temperature sensor elements embedded in the chip and exposed to the fluid inside of the channel.

2.2. Fabrication and chip assembly

The channels of the chips are fabricated with UV-lithography of a 12 μm thick resist to structure a molybdenum mask that is used with wet isotropic etching using HF to form channels. Integrated temperature sensor elements are made using a image reversal resist technique, deposition of a bimetallic layer consisting of 10 nm Ti and 100 nm Pt using sputtering and lift-off. As structures at the bond plane will hinder bonding, the metallisation is embedded downwards into the substrate as the structures first are etched before deposition of the metal layers. Thermal treatment of bonded wafers is done for 6 hours at 625 °C.

In general, fluidic channels of a width of 400 μm and a depth of 90 μm are used. Silica capillaries, glued into the channels from the side of the chips, using a 2-component epoxy glue, are used as fluidic interface connections. The electric interface is also found at the side of the chips and was connected to a printed circuit board using conductive epoxy and copper wires.

2.3. Measurements

Temperature sensing was done using 4-point measurement, connected to a data acquisition unit, and the sensor was first calibrated in an oven using a K-type thermocouple as a reference. The temperature sensor element is evaluated in subcritical CO_2. To evaluate bond strength and device reliability, pressure tests are done by a blister test method using a short-term pressurisation to fracture. The chips where pressurised using CO_2. Long-term reliability of chips is instead tested at constant pressurization at 11, 38, 80 and 125 °C, this time instead using H_2O as the pressurising medium. While operating the multiphase chip, the conditions are kept so the CO_2 is supercritical, having an average outside chip temperature of 47 °C and 80 bar backpressure.

The transmission light is chosen to have wavelength peeks at either 421 nm or 592 nm, corresponding to pH dependent absorption peeks of BPB. By such approach, a drop in pH when a neutral aqueous solution containing BPB comes in contact with high density CO_2 should give a response in terms of light intensity. The aqueous solution contains 5 mM of BPB, have a pH of 7.5 and an ion product of 15 mM by the addition of small amounts of NaOH and NaCl.

3. Results

By the use of the embedded electrodes, as seen in figure 1, it is possible to monitor the inner wall temperature of the channels, and therefore the density variations. This is exemplified in figure 2, where a sudden pressure change from 90 to 70 bar on the pumps produce a temperature drop of around 2 °C. Short-term pressure tests of the blister structures show fracture pressures in the range of 97 to 226 bar, figure 3. Chips having embedded temperature sensors reached fracture pressures in the same range.

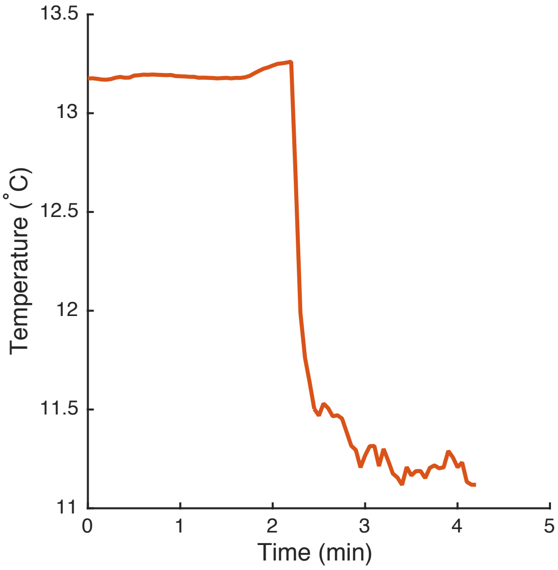

Figure 2 Temperature drop of channel wall after adjusting system pressure from 90 to 70 bar.

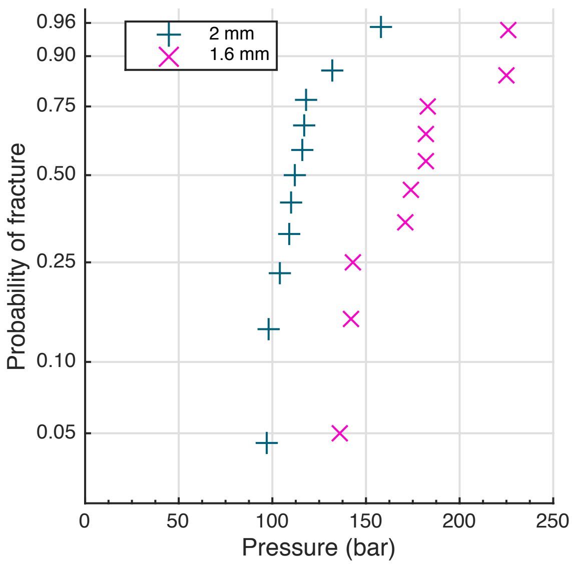

Figure 3 Fracture pressures of blister test structures with two cavity diameters.

For the 1.6 and 2.0 mm cavity, the average fracture pressure is 168 and 176 bar, respectively. Long-term pressurization test showed the presence of temperature dependent delayed fractures. For 1.6 mm cavities, pressures of 130 bar could be sustained for 1 week at 38 °C. For increased temperatures, a pressure reduction is needed to sustain the survivability. Figure 4 shows how BPB in the transparent glass chips can be utilized to detect pH changes. It shows CO_2 segment flowing in a channel. As time and length progresses, the aqueous phase becomes more acidic, expressed as an increase in light absorption.

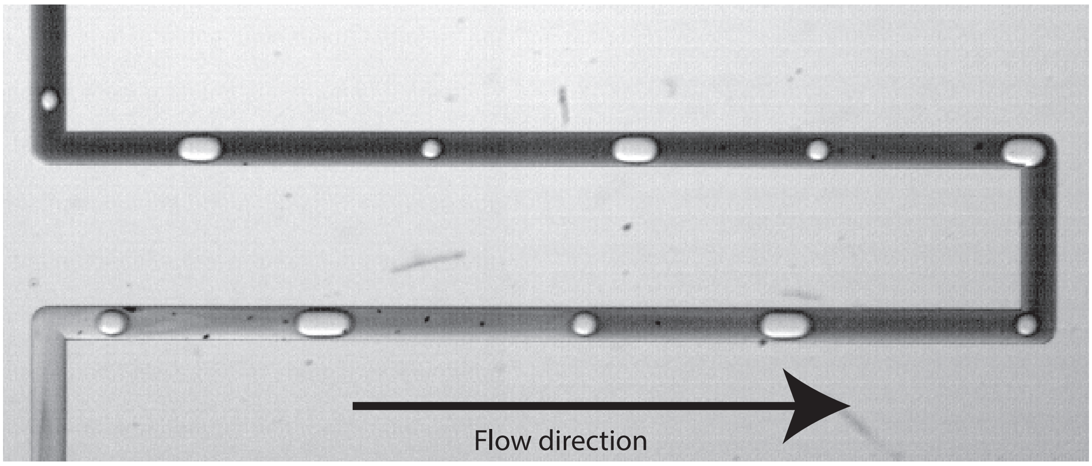

Figure 4 High-speed image at 421 nm. Flow of segments containing high density CO_2 in an aqueous solution containing BPB. As time progresses, light absorption is seen in the aqueous phase indicating a pH drop.

4. Discussion

The electrodes for the temperature sensor have successfully been operated at high-pressure conditions. It further demonstrates that the embedded electrodes do not affect the strength of the chips. Going from 90 to 70 bar at constant temperature corresponds to a density decrease of 23 kg/m^3, if however the 2 °C drop from the sensor is taken into account, the decrease is only 7 kg/m^3 [10]. With the integration of the temperature elements, added control and knowledge of the local environment in the chips is received. The chips are under constant stress and in a water rich environment, thereby exposed to stress corrosion, which affects reliability. Given that a stress corrosion mechanism is occurring, it limits the service life of devices at elevated pressures. As acidification of the aqueous phase is present when operating the multiphase chip, this indicates significant mass transport between the fluids.

5. Conclusion

A system for studying chemical interactions between H_2O and supercritical CO_2 fluid streams has been presented. Chips have been developed that are strong and reliable for more than one week of continuous measurement at 130 bar. The reliability is dependent on both time and temperature and can be linked to stress corrosion in glass. The integrated temperature sensors in the chips offer added control of the microfluidic platform. With the demonstrated multiphase system, high speed interactions of pressurised fluids can be studied using transmission lighting and indicators.

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