MANNITOL FOR HIGH TEMPERATURE PHASE CHANGE ACTUATORS

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Abstract
To enable valves for hot water microsystems, the possibility of using the volume expansion of the phase transition from solid to liquid in mannitol for strong high temperature actuators was studied. From room temperature to 160\degree C, a linear expansion of 4\% was measured, and the expansion at the phase transition from solid to liquid at 160\degree C to 180\degree C was measured to be 7\%. Stainless steel structures with a stainless steel diaphragm was filled and repeatedly heated up to 180\degree C while measuring the deflection of the diaphragm using a laser sensor. The height differences was measured to be 25 \mu m at 180\degree C.

In combination with a fluidic system, the mannitol actuator should capable as a valve for hot water microsystems.

Introduction
A research area currently with a large focus is green chemistry, where the aim is to replace toxic solvents with more environmentally friendly alternatives, e.g. pressurized and heated water or carbon dioxide [1]. By changing the temperature of a liquid, its solubility properties can be changed, e.g. at 200\degree C water has a dielectric constant comparable to methanol [2, 3]. The large ratio of area to volume in microfluidics allows for rapid heating and cooling which can be utilized for synthesis, extraction and separation with precise control. However, working under high pressures and temperatures, the corrosive nature of heated water puts high demands on the structural materials. Under these conditions, preferred materials include stainless steel and nickel alloys depending on the pH of the water [4].

To allow for fluid manipulation and low dead volumes, it is of interest to integrate valves and pumps in these systems. Thermal phase change materials (PCM), like paraffin, are associated with a large volumetric expansion during the phase transition from solid to liquid. The incompressible nature of this transition enables strong actuators, shown for paraffin micropumps capable of pressures above 100 bar [5]. However, the working temperature of the actuator is limited by the melting temperature of paraffin, and for temperatures above 100\degree C paraffin is no longer a suitable alternative. To enable valves for hot water extraction, an alternative PCM is needed that will function at higher temperatures.

Mannitol is a sugar alcohol, commonly used as a filler and artificial sweetener in pharmaceutical applications. With a melting temperature of 168\degree C, mannitol is investigated as a phase change material in stainless steel based phase change miniature actuators for hot water microsystems.

Experimental
Structured 100 \mu m thick stainless steel sheets (grade 304) was diffusionbonded [6], using the Ag-In system to a 10 \mu m thick steel foil (grade 301) to form two 200 \mu m wide channels leading to a circular cavity with a diameter of 2 mm, figure 1. To form the necessary metal layers for bonding, 3 \mu m electroplated silver was used and as a counter surface, 1.5 \mu m In was evaporated onto the steel surface, using Cr as an adhesion layer. The enclosed channels were used as a compartment for mannitol. During filling, the initially flat steel diaphragm is deformed to a concave shape, which is flattened out during actuation through melting the enclosed mannitol. The inlets were plugged by gluing a 200 \mu m thick steel stencil at the back. To add support to the structure, a second stainless steel sheet with an opening for the diaphragm was added on top of the structure.

The behavior of mannitol was characterized, first by studying the thermal expansion and investigating how it can be deposited in cavities without trapping air. As a demonstrator, an actuator was built and activated using an external heater.
**Figure 1.** A cross-section view of the actuator, consisting of three stainless steel stencils and one stainless steel foil bonded together. The middle stencil has a structured cavity, filled with mannitol.

**Figure 2.** A cross-section view of the fixture used for filling the steel structures with mannitol. The steel structure (grey) was mounted between two aluminium blocks (black). The top aluminium block has one mannitol reservoir and one reservoir acting as a waste where the excessive mannitol is collected. The filling was performed in a vacuum furnace at low pressure.

*Thermal expansion*

A glass tube was filled with mannitol grains, and to prevent contact with air, oil was added. The tube was put inside a lab furnace and a type K thermocouple was placed next to the glass tube. To account for the expansion of the oil, a second glass tube filled with only oil was also placed inside the furnace. The expansion was measured every 20°C.

*Filling of actuator*

Prior to filling, the mannitol was degassed and recrystallized by melting in a vacuum furnace at a pressure of approximately 10 mbar. The steel structure was placed in an aluminium fixture with two reservoirs, figure 2. Recrystallized mannitol grains was put in the designated reservoir, and before melting the mannitol grains, the pressure was decreased to 10 mbar. After 1 hour, the temperature was set to 190°C, and after reaching the desired temperature, the structure was allowed to slowly cool to room temperature before increasing the pressure to room atmosphere. Excessive material was gently removed and the mannitol was enclosed by gluing a 200 µm stainless steel stencil over the inlets using Epo-Tek 301-2 (Epoxy Technology).

The bonding and mannitol filling was evaluated using an X-ray inspection station (Nikon XTV 130) to identify voids in the joints and cavities of trapped air in the mannitol channel.

*Actuator measurements*

The stainless steel actuator was glued onto a ceramic board, fixated 3 cm below a laser sensor (Sick OD5). Underneath was a resistively heated Kanthal wire clamped to heat the structure, figure 3. To measure the temperature of the actuator, a Pt-100 sensor connected in a 4-wire setup was glued on top of the steel structure using a ceramic glue (Aremco 571). The diaphragm movement was measured at the center of the diaphragm by the laser sensor using triangulation, and as reference, one measurement was acquired on the top surface of the steel structure, next to the cavity.
Figure 3. A schematic of the setup for measuring the diaphragm deflection during heating using a laser displacement sensor mounted above the mannitol cavity.

Results
For the thermal expansion of mannitol, a linear expansion of 4% is seen from room temperature up to 160°C, where a shift of 7% occurs between 165°C and 185°C, figure 4.

An X-ray image of the mannitol filled cavity can be seen in figure 5, showing that there were no voids.

Figure 6 show the diaphragm movement during heating of the device and a reference measurement from a flat surface on the device approximately 1 mm next to the diaphragm. Also seen in the thermal expansion measurements, the diaphragm has a linear movement with increasing temperature up to 165°C, above which the expansion increases rapidly.

Figure 4. Thermal expansion of mannitol. A 7% increase is seen between 160°C and 180°C for mannitol.

Figure 5. X-ray images of the filled actuator.
Figure 6. Height measurement of the actuator diaphragm during heating of the device. The reference measurement was acquired approximately 1 mm from the edge of the diaphragm.

Discussion
Mannitol was demonstrated to function as a PCM, with an approximately linear expansion of 4% up to its melting temperature, where an additional 7% expansion during the phase transition was measured.

During heating, the whole structure will expand as a result of thermal expansion, and this will affect the measurements. As the diaphragm movement is expected to be 10-15 µm during actuation, this is a probable cause for the unreasonably large movements of up to 30 µm.

Also, the triangulation of the laser sensor is very sensitive to angular variations, here caused by the roughness of the steel surface during horizontal movements. This gives an error up to approximately 5 µm from the average height. This error is larger at higher temperatures, as the diaphragm starts moving vertically.

Using diffusion bonding together with structured steel stencils is a promising technique, where silver joints can be produced at low temperatures comparable to soft soldering. Thus, the structure and mechanical properties of the steel can be preserved during bonding.

The technique used for filling has proven to be very successful with a high yield. Previous attempts of placing the mannitol directly on top of the structure often resulted in bubbles, and using the fixture, more material can be supplied to the cavity.

Transferring the design of previously developed paraffin valves [7] to the mannitol actuator, we are one step closer of achieving a fluid manipulating system capable of working with hot water extraction in the 100°C to 150°C region.

Conclusion
Mannitol was demonstrated as a phase change material and an expansion of volume of 7% was measured during the phase transition from solid to liquid.

References