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Investigation of the storage and release of oxygen in a Cu-Pt element of a high-temperature microcombustor

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Abstract. A miniature combustor for converting organic samples into CO₂ with application in carbon isotopic measurements has been manufactured and evaluated. The combustor was made of High-Temperature Co-fired Ceramic (HTCC) alumina green tapes. The device has a built-in screen printed heater and a temperature sensor made of platinum, co-sintered with the ceramic. A copper oxide oxygen supply was added to the combustor after sintering by *in-situ* electroplating of copper on the heater pattern followed by thermal oxidation. Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Thermal Gravimetric Analysis (TGA) were used to study electroplating, oxidation and the oxide reduction processes. The temperature sensor was calibrated by use of a thermocouple. It demonstrates a temperature coefficient resistance of $4.66 \times 10^{-3} / ^\circ\text{C}$ between 32 and 660 °C. The heat characterization was done up to 1000 °C by using IR thermography, and the results were compared with the data from the temperature sensor. Combustion of starch confirmed the feasibility of using copper oxide as the source of oxygen of combustion.

1. Introduction

Isotope ratio measurements of carbon have multiple applications in a wide range of disciplines, *e.g.*, earth sciences, forensic science, biomedicine, and archeology. For isotopic analysis of the ratio of ¹³C to ¹²C, the sample is usually converted to CO₂ [1]. Therefore, combustion plays an important role in sample preparation.

In, *e.g.*, biomedicine, the demand for isotopic analysis of ultra-small samples is continuously increasing [2]. One way to reduce the analyte amount necessary is to miniaturize the sample analysis and preparation system, and perhaps even integrate the two.

Using lithography techniques and wet etching, H. J. Tobias *et al.* [1] fabricated a high temperature microreactor (78×30×2 mm³) for on-line conversion of organic gas compounds in high purity fused silica. Cu and Ni wires were inserted in the reactor after manufacturing, and were thermally oxidized *in situ* to be used as the source of oxygen during the combustion. Heating was done externally with a high-temperature furnace. The combustion took place at 950 °C, and the reactor capillaries were gas tight up to 1000 °C.

Using high-precision ceramic tape casting of nanoporous alumina, T. Okamasa *et al.* [3] developed a catalytic microcombustor (25×25×5.3 mm³) with the potential to sustain 800 °C as governed by the



brazing temperature of the ceramic. However, it was evaluated only up to 390 °C. The oxygen required for combustion was fed in to the combustor through an air inlet. The combustor had an embedded tungsten igniter and was submerged in a bath to keep the temperature constant.

D. A. Merritt *et al.* [4] made a tubular microvolume reactor ($200 \times 5 \text{ mm}^2$) with nonporous alumina packed with metal wires oxidized after manufacturing (CuO/NiO) to be used for on-line combustion of gases. CuO and NiO could be used as the only source of oxygen at temperatures above 850 °C and 1150 °C, respectively.

This paper presents the fabrication and evaluation of a miniature combustor based on High-Temperature Co-fired Ceramic (HTCC) technology. The combustor has a built-in heater and temperature sensor. After sintering, the heater is Cu electroplated *in situ* and thermally oxidized in order to provide for an integrated oxygen storage.

2. Experimentals

2.1. Design, material and fabrication

The combustor, designed to be operated at up to 850 °C, consists of four ceramic layers: inlet and outlet layers (I), conductor layer, which includes the heater pattern and the temperature sensor (III & IV), and combustor wall layer (II), figure 1.

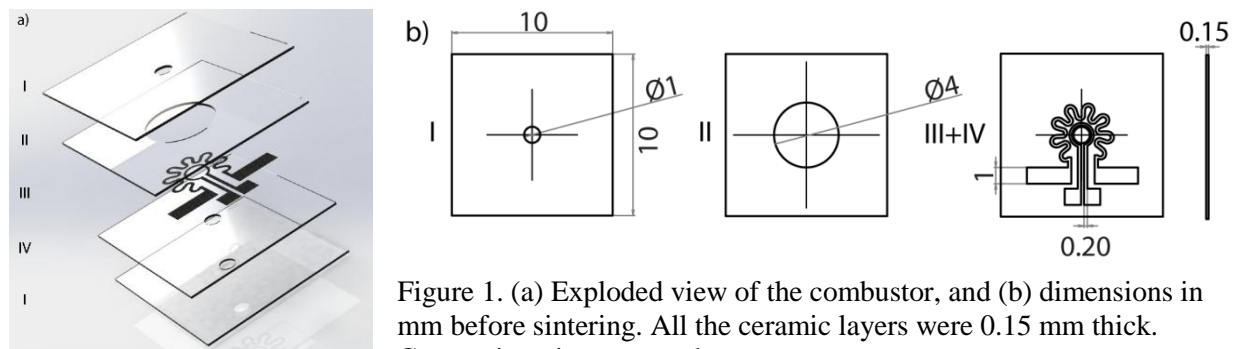


Figure 1. (a) Exploded view of the combustor, and (b) dimensions in mm before sintering. All the ceramic layers were 0.15 mm thick. Connection vias are not shown.

The connection pads for the temperature sensor and the heater are accessible through vias made between the outlet and the combustion layers (I & II) during manufacturing.

The flower shape of the heater pattern and its dimensions were chosen to be able to heat up the chamber uniformly. The temperature sensor is circular and centered inside the heater pattern.

The device was fabricated by milling and lamination of alumina green tapes (ESL 44007-150 μm , Electro Science Laboratories, USA). Conductive patterns were screen printed using platinum paste (ESL 5571, ESL Electro Science Laboratories, USA). A detailed description can be found in [5].

Copper, which is not compatible with the HTCC process, was deposited after sintering by electroplating (J-PLATE Cu 90H, J-KEM International, Germany) on the platinum heater inside the cavity, according to the manufacturer's data sheet. Electroplating durations of 7 and 46 minutes, providing two thicknesses of Cu film, were chosen.

The copper was thermally oxidized in an oven (Logotherm L5/S17, Nabertherm, Germany) at 500 °C for 10 hours, since the ratio of CuO to Cu₂O is greatest at around 500 °C, and CuO should be completely reduced at about 850 °C [6].

2.2. Characterization

The combustor sample was investigated with X-ray microscopy (XT V 130, Nikon, Japan).

In order to investigate electroplating inside the cavity, additional samples were prepared and analyzed using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The following material compositions were analyzed: (a) platinum printed on alumina, (b) Cu electroplated on top of the platinum pattern, (c) oxidized Cu electroplated pattern, and (d) Cu achieved

after reduction of the oxide. The thickness of the interfaces and the abundance of aluminum, oxygen, platinum and copper were measured from sample cross sections prepared by cutting, epoxy mounting, grinding and polishing.

The reduction of copper oxide was done in a furnace (T5HT, A.D.A.M.E.L, France) at 900 °C for an hour in presence of argon to avoid oxidation during cooling.

The study of copper oxidation and oxide reduction was complemented with Thermogravimetric Analysis (TGA) (Q500, TA Instruments, USA).

The integrated temperature sensor was calibrated by heating the combustor slowly to 660 °C in an oven (FB1410M-33, Thermo Scientific, USA), while the ambient temperature was measured by a thermocouple (K type) and the resistance of the temperature sensor was measured using 4-wire sensing technique and digital multimeter (34401A, HP, USA).

The heat distribution over the combustor floor (layers I, III, IV) during resistive heating was studied using IR imaging (Thermovision A40, FLIR Systems, Sweden), and its correlation with the temperature sensor signal was investigated.

For demonstration, corn starch was distributed over a CuO layer on a bulk alumina sample placed on a heat stage inside a soda-lime glass tube. The tube was evacuated to about 2.5 torr and surrounded by nitrogen, and the heat stage was resistively heated up to above 850 °C.

3. Results and discussion

The dimensions of the combustor after sintering were measured to be $8.3 \times 8.3 \times 0.4 \text{ mm}^3$.

The lateral and vertical shrinkage of the chip after sintering was 16% and 21%, respectively. The integrity of the realized combustor, and especially its electrical connectivity were revealed by X-ray imaging, figure 2.

3.1. SEM and EDS results

The SEM images of the Cu electroplated cross section samples before oxidation as well as after reduction are shown in figure 3. The EDS analysis confirms that the copper oxide had been completely converted to copper after reduction, figure 4(left).

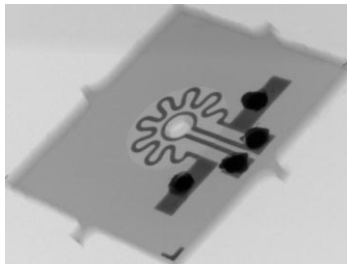


Figure 2. X-ray image of the combustor, showing the connection vias between different layers.

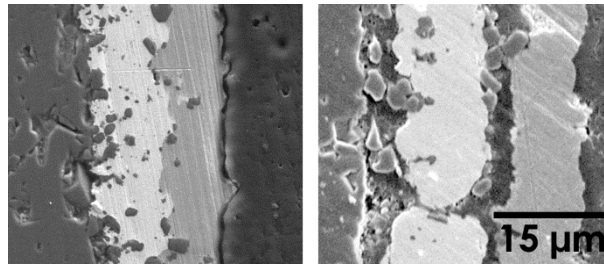


Figure 3. SEM images of the cross section of a thin layer of Cu electroplated on Pt (left) before oxidation, and (right) after oxide reduction. From left to right: alumina substrate, Pt film, Cu film and epoxy material used for cross-section preparation.

For some samples the oxidation step had caused delamination of the copper oxide and the platinum film. This was found to remain after the reduction step, figure 3(right). No delamination was observed directly after the electroplating, however.

For some of the samples, the EDS analysis shows two oxide layers with different proportions of oxygen and copper, figure 4 (center), for other samples just one, figure 4 (right).

Furthermore, migration of copper into the platinum film is noticed after the oxidation step, figure 4.

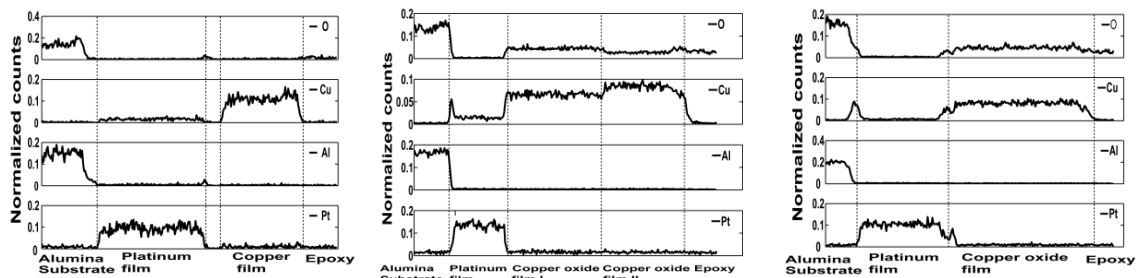


Figure 4. Composition of cross-sections. Sample with thin layer of Cu after reduction (left). Sample with thick layer of Cu after oxidation (center), and sample with thin layer of Cu after oxidation (right).

3.2. TGA results

TGA analysis results are presented in figure 5. The weight of the sample is almost constant until 500 °C, where air is introduced and oxidation is believed to start. The weight of the sample increases by more than 0.2%. At around 750 °C, the weight begins to decrease. This decrease increases at around 850 °C, which corresponds with the decomposition temperature of the oxide, and continues until the sample weight reaches its initial value.

Assuming that the weight increase of the sample at 500 °C is due to oxidation, it was calculated that 8.5 μ moles of oxygen had been absorbed, which is much less than the amount of copper (around 38.5 μ moles) in the sample. This shows that all copper had not been oxidized. However, almost all the oxide gained during oxidation had been decomposed.

3.3. Temperature sensor calibration results

Over the calibration range of 32 to 660 °C, the temperature sensor is linear (R^2 of 0.999 for the line fitted) and exhibits a temperature coefficient resistance of $4.66 \times 10^{-3} / ^\circ\text{C}$.

3.4. Heat characterization results

Figure 6 illustrates the resistive heating of a combustor floor sample with probes to 1000 °C. The heat distribution is asymmetric in the beginning of heating, (right), but becomes more symmetric at 1000 °C, (left). The power consumption at 1000 °C was around 10 W and the device was operated at that temperature for 10 minutes.

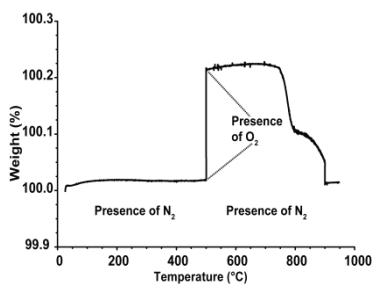


Figure 5. Results of TGA analysis of the Cu electroplated sample. (The step at 500 °C corresponds to a dwell time of six hours.)

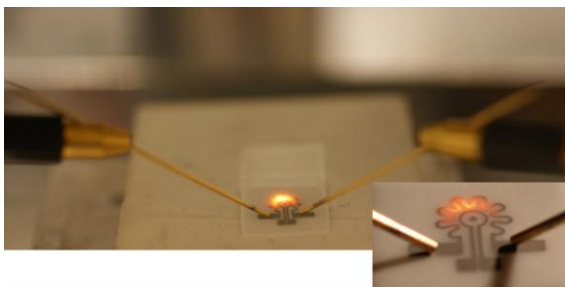


Figure 6. Resistive heating of the heater pattern using probes.



Figure 7. IR image of the heater pattern driven with 10 W.

At 1000 °C, IR imaging revealed a heat gradient resulting from cooling by the probes, figure 7. From the IR images, the average temperature of the area between the sensor and heater was extracted during three phases of heating and starch combustion in normal atmosphere. Referring to the sensor, the thermograph gave 98, 244, and 384 at 105, 243, and 316 °C, respectively, *i.e.*, a deviation increasing with temperature.

3.5. Corn starch combustion results

At temperatures below the reduction temperature of CuO (around 725 °C according to EkviCalc calculations) no combustion was observed, figure 8 (left). While heating and before the reduction, an intermediate phase of gelatinization of starch was observed, figure 8 (center). As soon as the reduction started, the combustion took place. Almost no starch was left after the combustion, figure 8 (right). Red spots appeared after the reduction, figure 8 (right), indicated that the reduction of copper had occurred. If significant leakage of oxygen had occurred, further oxidation would have happened during cooling, and the red spots would have disappeared.

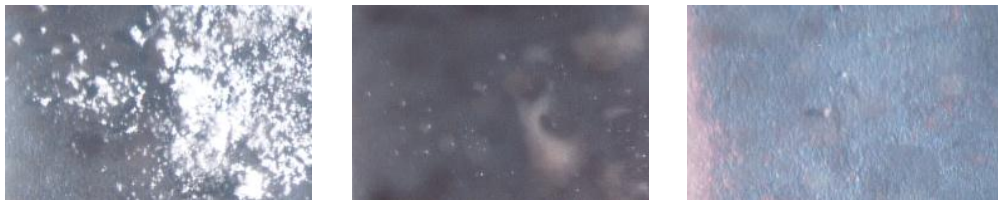


Figure 9. Left: Corn starch on CuO layer before heating, Center: Intermediate gelatinization of starch, and Right: Partially reduced CuO after combustion and cooling.

4. Conclusion and future work

A miniature high-temperature combustor has been operated to 1000 °C, although the integrity of the thick platinum and copper films suffered from the chemical and thermal cycling. EDS and TGA analysis, as well as the partial combustion of starch, verified that the *in situ* electroplating of copper and the use of copper oxide as the source of oxygen were successful.

In the future, the oxidation and decomposition recipes should be chosen more carefully in order to achieve robust and homogenous surfaces with better adhesion between the different materials. Alternatively, separate elements can be used for heating and supplying oxygen. Furthermore, the combustion should be fully studied with a residual gas analyzer in order to thoroughly measure the amount of the gases produced during the reduction and combustion, and the temperature sensor should be improved.

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