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Review of the PhD dissertation of Mr. Witold Nawrot

"Application of Additive Manufacturing in Ceramic-Polymer Microsystems"

Introduction

The reviewed PhD thesis of Mr. Witold Nawrot is about the development of additive manufacturing methods and Low Temperature Co-fired Ceramic (LTCC) technologies for microsystems. Particular attention of the thesis is to utilise inexpensive commercially available stereolithography based 3D printing to enable wider exploitation and impact for field of ceramic-polymer microsystems. Ceramics has important role in different kind of microsystems especially due their electrical properties and inertness for even harsh environmental conditions. On the other hand, ceramic microsystems typically utilises complex 3D shapes, which can be difficult and laborious to produce with existing methods. In addition, functions of such systems usually require integration of multiple materials, like metals, polymers or biomaterials, for which very high fabrication temperatures of ceramics gives significant physical-chemical restrictions. Therefore, efficient and inexpensive methods to produce complex 3D ceramic structures with possibilities to reliably integrate various different materials are highly required and endeavored in the field. Therefore, I believe that the set research goals by the PhD student Witold Nawrot are highly relevant and needed in order to advance the field of the ceramic-polymer microsystems. Furthermore, parallel to technical development, the set goals have also important techno-economic aspects enabling similar capabilities with low-cost manufacturing devices compared to that of the high-end and expensive state-of-the-art tools. This makes new technological steps and utilisation of ceramic-polymer microsystems more widely available for customised solutions and new applications.

These aspects are comprehensively discussed by the PhD student and the thesis includes guidelines, novel processes, practical methods and crucial aspects to be addressed in the development of ceramic-polymer microsystems. The results are presented and interpreted by clear and conceivable manner with dozens of useful figures and graphs. The work demonstrates candidate's high knowledge and know-how in the field of additive manufacturing and microsystems.

Formal aspects of the PhD dissertation

The reviewed PhD thesis contains 208 pages, which is divided into 6 main chapters with the summary in the end of each 5 main chapters. The thesis includes also one page abstract, table of contents, list of used acronyms and list of used references. The layout of the dissertation is clear, coherent and with logical order of presentation of the subject. The thesis starts with the introduction in Chapter 1 giving general understanding about the field, current standing point on it and aims and scope of the work. It also briefly introduces content of the different chapters of the thesis for the reader. Chapter 2 describes ceramic microsystems technology and related manufacturing techniques such as LTCC, thick film and bonding methods as well as their applications.

Chapter 3 introduces a range of different additive manufacturing techniques currently available and utilised in fabrication of different 3D structures from polymers, ceramics and metals. The sub-Chapter 3.7 pays particular attention for stereolithography, which is the main additive manufacturing method in the thesis, describing related resin chemistry, equipment, manufacturing process and ceramic processing in detail. Chapter 3 gives very nice overview about different techniques, and could be used as study book material to initiate further investigations. However, some added details for example to Table 3.1 (printing speed, accuracy and resolution ranges etc.) would have enrich the content. Also for the coherence of the work's appearance, listed additive manufacturing techniques could have been in order of appearance and written same way as titles i.e. without capital letters. Title of section 3.5 is "Direct powder processing" instead of Powder Bed Fusion or Direct Energy Deposition. These are very minor things but makes reader a bit confused if terms/titles are changing.

Supposedly, author has meant that platinum has TCR ideal for temperature sensors i.e. not ideal for sensors generally (page 7) and gold melting temperature is actually a bit above 1000 ºC (page 7). For the convenience of reader and further analysis, frequency should be mentioned when discussing dielectric constant/permittivity and loss tangent e.g. $Bi_2Mo_2O_9$ (page 27) or Li_2MoO_4 (page 28).

Chapter 4 is the first original research part of the thesis describing some of it's main results. It first introduces ceramic additive manufacturing (Cer-AM) methods for microsystems and explains theoretical background i.e. generic physical behavior and equations behind the analyses and measurement methods used in the work. Subsequently, the chapter continues with materials, different internal and external structuring approaches, assembling, thermal processing and their impact for the final properties (such as porosity). Sub-Chapter 4.3 describes development of custom resin based on LTCC and photosensitive ink, one of the novel output of the thesis, and wide range of its properties. These include rheology, composition, photosensitivity, printability and properties after fabrication (surface quality, permittivity, dielectric losses, porosity) and comparing them into values found from the literature. Some minor remarks could be made i.e. Leaver effect was not explained (page 48) and P0 is for saturated gas pressure of the adsorbate instead of "vapour" (page 63). It might be worth to check nominator of equation 4.5, value of L and the variables and units resulting from the equation 4.7, as the original Brunauer-Emmet-Teller equation is using volume of adsorbate instead of quantity [cm^3/g] (page 64). There is no figure 4.28 (page 72). It is excellent that attention has been paid how to measure dielectric properties reliably, where the process for electrodes was developed, this is not always so obvious. However, in addition to stencil printed "reference" sample it would have also been interesting to see if the actual 3D stereolithography printing of similar samples has any effect for the dielectric properties (page 139).

Chapter 5 describes the development of ceramic-polymer microsystem utilising combination of different processes (LTCC, laser engraving, selective dielectric barrier discharge bonding, direct polymer additive manufacturing on ceramics) in order to accomplish integrated and reliable microfluidic system with needed electrical and optical functionalities. The chapter introduces final goal of the thesis, utilising several novel and essential sub-goals developed in the work and demonstrating them all in the single microfluidic application i.e. polymer on ceramic (PoC) electro-optical sensor system. In the chapter used analytical and measurement methods, required optical behavior and basis of PoC operation are also described. Chapter 6 concludes the thesis describing new developed processes and main achievement as well as their possible implications in the future.

The author of the thesis refers to 136 scientific papers or other references, which includes 13 papers with his participation. These include 8 conference and 5 journal papers. Contribution of the co-authors in each papers are clearly addressed and specified in each case and Mr. Nawrot is the first author in 9 papers implying clearly his adequate contribution for PhD thesis. Cited literature sources are relevant and properly chosen, although they can only scratch the surface due to vastness of the covered areas. In the text and references author of the thesis also shows that he has followed the development in the field reporting some recent advances made by other research groups during the thesis work. Thus, he is very familiar with the latest research in the topic (latest references from year 2022).

In general, text was fluent, understandable and easy to read, but some minor typos, grammatical errors or incoherency in appearance of units and acronyms (e.g. CerAM, CarAM, Cer-AM) could be found. However, all the mentioned minor errors or remarks have no impact on the scientific value and merits of the PhD thesis which is high, yet they may have slight influence for readability.

Substance of the work

The work carried out in the thesis is highly experimental while supplemented with the theorethical background and understanding of measurement principles and their interpretation. All the selected approaches, measurements and analysis methods used in the work are highly relevant and adequate to carry out the made research, analysis and followed conclusions. It contains substantial amount of manufacturing experiments and their development, which in fact are backbone to successfully realise different microsystems and especially the ones based on ceramic-polymer combination. Without solving these aspects, for example good adhesion or bonding, realisation of the reliable microsystems becomes nearly impossible. In the work several key aspects in manufacturing processes of ceramic-polymer microsystems have been solved or developed further. It was particularly impressive to see how much improved results, with proper designing and know-how, PhD student could gain with inexpensive stereolithography system in additive manufacturing even without possibility for full customisation of processing parameters. This is great example about impact of the research and gained expertise. Moreover, developed full microfluidic optoelectronic measurement system by PoC approach was highly relevant example about the possibilities of the developed techniques demonstrating also spectrum of knowledge required for development of such a system. In my opinion, in addition to the above mentioned, the greatest achievements of the PhD student were:

- development of custom resin suitable for stereolithography and with good printability, LTCC compatible properties and low surface roughness
- selective plasma bonding method for PDMS to ceramics
- high adhesion obtained between laser milled ceramic and directly stereolithography printed polymer test structure.

As a summary, in my opinion the PhD work of Mr. Nawrot contributes significantly to the development of scientific discipline of electronics and its manufacturing technologies particularly in the field of additive manufacturing and ceramic or ceramic-polymer microsystems. It is also very likely that research carried out in the thesis will be exploited by industry or research organization in further scientific research and development. Mr. Nawrot has demonstrated the necessary knowledge and skills to obtain degree of doctor in technical sciences.

Comments and questions to PhD student

- Page 28: It was stated that 90 wt.% of silver particles is difficult to achive with stereolithography or ink-jet printing which is correct with respect of printing itself. Yet on the other hand, conductive silver nanoinks traces have been successfully applied with close to 100 % of silver by utilising sintering of the prints.

- Page 28: Mentioned Li_2MoO_4 was directly 3D printed without organic additives, thus it is somewhat unclear what is meant by it's green state and related good dielectric properties?

- Page 85: What are the benefits (techno-economic) using the combination of laser engraving and stereolithography instead of just laser engraving, as was done in the case of cryocooler development?

- Page 89: How DSC measurement indicates possibility of thermal curing i.e. how curing appears in endo/exothermic processes?

- Page 101: In Chapter 3 it was stated that additive manufacturing offers greener, ecological and economical solutions, which indeed is true from the material usage perspective. However, when looking Fig. 4.28, LTCC (semi-additive manufacturing) temperature profile it seems to be much less energy consuming than that of printed ones. So how "green" are these additive manufacturing processes from the perspective of energy and emissions?

- Page 104: Although linear behavior of permittivity as a function of porosity can be seen in certain ranges, is the phenomena fundamentally linear? Is dielectric losses always increasing along with the porosity and is there any effect from frequency?

- Page 105: At what frequency SPDR measurements was made and was the porosity and its changes in these particular sample also confirmed by SEM images?

- Page 112: Improvements obtained by inexpensive stereolithographic systems are impressive and clearly result of thorough investigations and obtained know-how. Would similar level of improvements become possible with also expensive SL devices by similar research and optimisation?

- Page 123: It is not clear from Fig. 4.37 and related text what was the needed amount of light energy for curing, even though level of energy by exothermic reaction is given in the figure.

Thus, how evaluation was made which resin required the least or the highest amount of light energy?

- Page 173: Is there some confusion with the units as 9.1 kN for area with diameter of 5 mm would account for ~460 MPa as a pull-off strength?
- Page 176: Was the surface roughness and dimensions of cross-pattern realised for LTCC the same as in the case of alumina, especially depth, and if not what is possible influence of them in the results?

The above comments and questions do not hinder or undermine the merits of this PhD dissertation by any means. They should be considered merely as minor details, further clarification or as a professional discussion about the topic between reviewer and the candidate.

Reviewed PhD dissertation meets all requirements as defined by the Polish law on scientific degrees and academic titles and degrees and title in art and I request its approval to the public defence.

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