Functional ceramic materials by sustainable $scCO_2$ processing

Erkki Levänen[1]

[1] Laboratory of Materials Science, Tampere University of Technology, Korkeakoulunkatu 6, FI-33101 Tampere, Finland.

Introduction

The ceramic materials has new interesting functional properties and applications via miniaturization of structures and surfaces, utilizing plastic behaviour of thin films, photoactive effects, biological response and adjustable surface adhesion properties. New manufacturing techniques are capable to produce well-defined dense thin films, nanoparticles and ordered structures and surface topographies. At the same time, there is urgent need for manufacturing of complex structures and large surfaces with sustainable ways. Hybrid manufacturing technologies combining one or more approaches might have answer to that requirement. The examples of hybrid manufacturing technologies are ceramic lithography printing, Zn-based nanowire growth in supercritical carbon dioxide ($scCO_2$) and particle synthesis by laser ablation in supercritical conditions to laser patterning and growth in reactive environment.
This study introduces the latest trends in functional ceramics and their hybrid manufacturing techniques and focuses on plastic behaviour of thin films and supercritical carbon dioxide processing.

Results and Discussion

Thin film technologies such as ALD, PLD, PVD, CVD and sol-gel can produce dense, defect free and microstructurally well-defined coatings. We have tested PLD coated amorphous thin films by in-situ TEM compression and tensile tests and results showed 100% plastic deformation in compression and 10 % plastic deformation in tensile testing. The experimental results were verified also by force field molecular simulations and calculate yield stress 4.8 GPa fits well with experiments. The plastic behaviour predicts that the reliability of thin film structures can be significantly better as usually expected and the design principles can be modified accordingly. It would be very interesting to see,if the plastic behaviour mechanism can be utilized in larger 3D structures. One possible route for manufacturing of such reliable structures could be ceramics 3D printing.

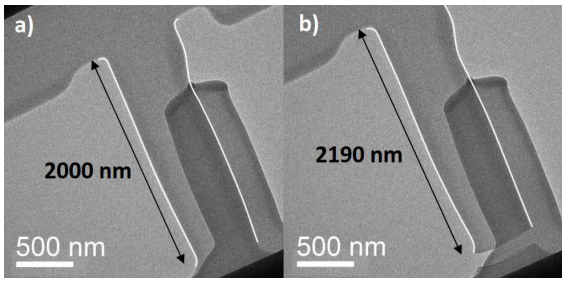

Figure 1. Tensile test of thin alumina film showing plastic deformation [1]

Multifunctional semiconductors such as TiO_2 and ZnO with offer vast application field from photovoltaic applications to antimicrobial surfaces and controlled adhesion. We used supercritical carbon dioxide atmosphere for manufacturing of Zn- bases nanowires, which can be further treated to ZnO structures and which have potential as antimicrobial surfaces, photovoltaic electrodes or as artificial patina on hot dip galvanized steel. Antimicrobiality of ZnO is originating from photoactivity under light, but ZnO works also in dark conditions. With CO_2 assisted manufacturing, Zn-based nanowires can be produced uniformly over the large areas, fast and environmentally friendly way. Nanowires can be used as artificial patina, but after heat treatment to ZnO they have photoactive properties.

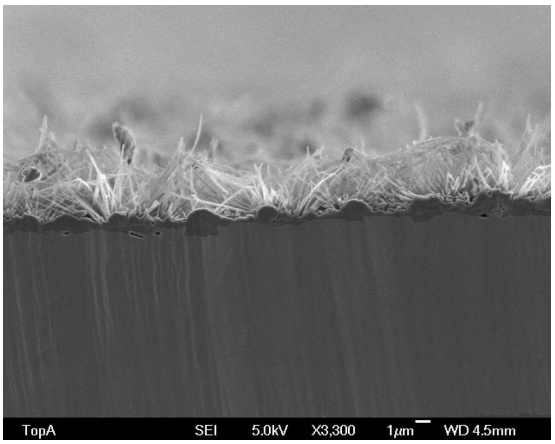

Figure 2. Zn based nanowires on the surface of hot dip galvanized steel after scCO2 treatment [2]

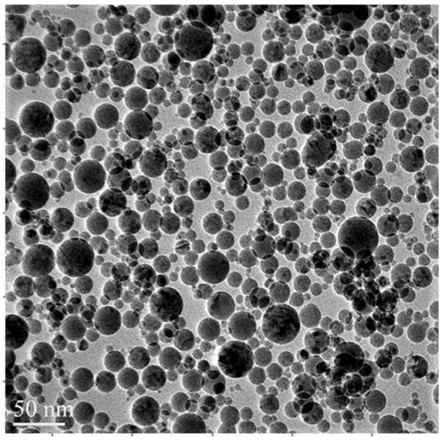

Figure 3. Ti_xO_y nanoparticles from laser ablation in supercritical carbon dioxide

We have prepared TiO_2 and Ti_xO_y nanoparticles by laser ablation in $ScCO_2$ environment and due to the nonstoichiometric, metastable structures they have promising photoactive properties. On to ablated target surface it is also possible to create corresponding oxide structures. By laser beam movement it is also possible to create different patterned and ordered oxide surfaces.

$ScCO_2$ can also be used as clean, nonpolar solvent in emulsion based synthesis. We have demonstrated TiO_2 sol-gel synthesis in water-in-oil emulsion, where oil is replaced by carbon dioxide. The TiO_2 powders has perfectly round shape originating from the water droplet where synthesis from precursors to oxides occurs, while CO_2 is acting as continuous carrier around water droplets. The primary particle size, surface area and phase structure can be varied by process parameters as temperature.

Conclusions

The functionalities of ceramic materials will raise from the combination of the unique properties of nanostructures such as unexpected mechanical properties, optimal optical and electrical properties and especially they combinations but especially through efficient and sustainable manufacturing methods. Understanding and adapting the plastic deformation methods may open totally new applications of nanostructured ceramics. Green processing with the help of nontoxic, recyclable solvent, CO_2, will have potential when upscaling of manufacturing processes.

References

[1] Erkka J. Frankberg, Plastic deformation of Amorphous Aluminium oxide – Flow of Inorganic glass at room temperature *Dr. Thesis, TUT* **2018**, 144 pages
[2] Ville Saarimaa, Aaretti Kaleva, Juha-Pekka Nikkanen, Saara Heinonen, Erkki Levänen, Pasi Väisänen, Antti Markkula, Jyrki Juhanoja, *Surface & Coatings Technology*, **2017**, 331, 137-142