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ABSTRACT OF THE DISSERTATION

"Nickel and molybdenum coordination complexes as metallic precursors in colloidal processing of ceramic-matrix-composites"

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The advancement of civilization is closely linked to the development of novel materials that meet the growing demands and needs of humanity. Among these, ceramic-metal composites represent a particularly significant class of materials, as they integrate the beneficial properties of both ceramics and metals, resulting in enhanced properties of the final material. For example, the presence of metallic particles in a ceramic matrix can act as a barrier to crack propagation, thereby improving the fracture toughness of the product. The effectiveness of this reinforcement depends on multiple factors, including the size, distribution, and morphology of the metallic phase. Micrometer-sized particles limit the ability to control the microstructure, as achieving uniform distribution of the metallic phase within the ceramic matrix is more difficult. This can lead to local inhomogeneities and a deterioration in the mechanical properties of the products. However, the use of metallic nanoparticles comes with certain technological challenges due to their strong tendency to agglomerate. Additionally, because of their high flammability, they require special storage conditions (in a cool, dry inert gas to prevent surface oxidation). A promising approach in the fabrication of ceramic-metal nanocomposites involves the use of metallic phase precursors, such as coordination complexes, for example metal acetylacetonates. These precursors decompose and undergo reduction at elevated temperatures, facilitating the in-situ formation of finely dispersed metallic nanoparticles within the ceramic matrix.

A particularly important stage in the production of ceramic materials and ceramic-metal composites is the shaping process. Colloidal processing, such as slip casting and gelcasting, have gained significant interest as they provide better control over the distribution of the reinforcing phase in the matrix, compared to die pressing methods. One of the most emerging techniques based on colloidal systems is digital light processing (DLP), which utilizes photopolymerization reaction to solidify suspensions. A key advantage of this method, in comparison to casting techniques, is that it doesn't require the use of moulds but only the prior preparation of a three-dimensional model using computer aided design (CAD) software is needed. The production costs of individual components are significantly reduced while enabling the fabrication of elements with high geometric complexity.

The scientific literature still lacks satisfactory solutions for the fabrication of ceramic-metal nanocomposites. Notably, a review of the literature indicates an absence of reports on the 3D printing of ceramic-metal composites from dispersions containing both ceramic and metallic particles simultaneously.

The aim of this research was to develop aqueous and organic dispersions of alumina and zirconia incorporating nickel acetylacetonate or molybdenyl acetylacetonate as metallic precursors, which, through shaping and sintering processes, enable the fabrication of ceramic-metal composites with enhanced functional properties. A complementary objective of the research was to optimize the

parameters of 3D printing using the lithographic DLP method to achieve high quality composite materials with the designed geometry.

In the study, two ceramic powders were used: alumina (TM-DAR) of the average particle size 150 nm and zirconia (TZ-PX-245) of the average particle size 40 nm. As the metallic phase, two metallic powders (Ni and Mo) with micrometer-sized particles were used, along with their precursors – nickel acetylacetonate and molybdenyl acetylacetonate. The research also involved the use of organic additives essential for preparing the suspensions, such as dispersing agents, monomers, photoinitiators, solvents, activator and initiator of the polymerization.

The first stage of the study was the characterization of ceramic powders, including measurements of true density, particle size, specific surface area, and analysis of the morphology. Subsequently, aqueous suspensions based on Al_2O_3 and ZrO_2 were prepared for shaping with the use of slip casting and gelcasting methods, as well as alumina-based suspensions for DLP printing. In each of these methods, the metallic phase was introduced in the form of precursors. Additionally, in the case of DLP printing, the research was expanded to explore the possibility of using metallic powders (nickel and molybdenum) as the metallic phase. This was motivated by the fact that the fabrication of ceramic-metal composites using DLP printing had not been previously described in the scientific literature. This approach allowed to compare the properties of composites produced using both metallic powders and precursors. For materials fabricated via slip casting and gelcasting, the results for samples produced using metallic precursors obtained in this study were compared with the literature data on ceramic-metal composites produced with the use of metallic particles.

The suspensions were subjected to rheological characterization, including oscillation tests, measurements of dynamic viscosity and shear stress as a function of shear rate, as well as the determination of the yield stress. All suspensions exhibited shear-thinning behavior, which facilitates the shaping process, and their viscosity was sufficiently low to be used in slip casting, gelcasting, and DLP printing methods. Additionally, the influence of photoinitiators and the addition of the metallic phase (in the form of powders and precursors) on the cure depth of suspensions intended for DLP printing was investigated. It was found that the addition of the metallic phase reduces the curing depths of the suspensions. However, the obtained values of cure depths (>130 μm) are sufficiently high to enable the use of the developed dispersions in the DLP printing method.

Next, the samples were formed using three different colloidal processing methods: slip casting, gelcasting, and digital light processing (DLP). For DLP printing, parameters such as layer height, base time, attach time, and light intensity were optimized. This optimization enabled the successful printing of ceramic materials from monolithic Al_2O_3 as well as Al_2O_3-Ni and Al_2O_3-Mo composites.

The next stage of the study focused on the characterization of the samples in their green state, including measurements of relative density and microstructure analysis. The relative densities of all obtained sample series ranged from 54% to 65% of the theoretical density. Microstructural analysis of the green bodies revealed that the metallic phase precursors were relatively evenly distributed throughout the samples volume. Additionally, thermal analysis (TG/DTG/DTA/MS) was performed for the green bodies, metallic powders, and metallic precursors, which enabled the selection of appropriate sintering parameters. The results indicated that sintering should be carried out in two stages: first, in air atmosphere (up to 400°C) to remove organic additives, and then in inert or reducing atmosphere to prevent metal oxidation. The samples were sintered either by pressureless sintering (1550°C, Ar/H_2) or using the SPS method (1150°C, 60 MPa, Ar).

In the final stage of the study, the sintered samples were analyzed in terms of relative density, shrinkage, Vickers hardness, and fracture toughness. Additionally, phase composition was examined using X-ray diffraction (XRD), and microstructure analysis was performed using scanning electron microscopy (SEM). It was found that even a small addition of the metallic phase (0.5 vol%) led to an increase in fracture toughness of up to approximately 50% compared to single-phase ceramics. In the samples fabricated by DLP, a more significant increase in the K_{IC} coefficient was observed for composites obtained with metallic precursors than for those produced with metallic powders. This effect may result from a more homogeneous distribution of the metallic phase within the material, as confirmed by the microstructural analysis of the sintered samples.

To sum up, new aqueous and organic suspensions were developed in which the metallic phase was introduced in the form of salts – nickel and molybdenyl acetylacetonates. Such systems had not been previously used in the fabrication of ceramic components via colloidal processing. The samples obtained from these suspensions exhibited good properties both in their green and sintered states. An additional achievement was the fabrication of ceramic-metal composites from photocurable dispersions containing both ceramic and metallic particles or metallic precursors, which had not been previously described in the scientific literature.

Keywords: ceramic-metal composites, metallic precursors, colloidal processing, digital light processing, 3D printing