

REVIEW

by Prof. Dr. Bogdan Ranguelov, Institute of Physical Chemistry - BAS

on

PHD DISSERTATION

submitted for the award of the PhD degree in doctoral programme "Condensed matter physics" (Physical sciences),

Title: DEVELOPMENT AND STUDY OF WEAR-RESISTANT NANOCOMPOSITE COATINGS WITH MODULATED COMPOSITION FOR MULTIFUNCTIONAL APPLICATIONS

PhD candidate: **Stephan Dimitrov Kolchev**, full-time PhD student at the Central Laboratory of Applied Physics, BAS, Plovdiv, Supervisor: Prof. Dr. Lyliana Kolaklieva; Scientific consultant Prof. Dr. Roumen Kakanakov

I. Proceedings materials:

Stephan Dimitrov Kolchev was enrolled as a full-time doctoral student in Professional Field 4.1. Physical Sciences, in the doctoral program "Electrical, Optical, and Magnetic Properties of Condensed Matter" at the Central Laboratory of Applied Physics (CLAP) - BAS, Plovdiv, starting from January 1, 2020, pursuant to Order No. 41 dated December 20, 2019, issued by the Director of CLAP. With Order No. 41 dated December 15, 2022, issued by the Director of CLAP, the deadline for completing the doctoral program was extended by six months. Meanwhile, due to a change in the main activities of CLAP-BAS, in 2021, the laboratory received accreditation from the National Agency for Assessment and Accreditation for the doctoral program "Physics of Condensed Matter." In connection with this change, the National Center for Information and Documentation permitted doctoral student Stephan Kolchev to transfer from the doctoral program "Electrical, Optical, and Magnetic Properties of Condensed Matter" to the doctoral program "Physics of Condensed Matter." Stephan Kolchev was expelled with the right to defend his dissertation pursuant to Order No. 29 dated September 28, 2023, issued by the Director of CLAP. The doctoral student has passed all examinations in accordance with the individual study plan, and the materials submitted for the procedure for awarding the PhD degree comply with the requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria (ZRASRB) and its implementing regulations (attached are diplomas, an abstract, the dissertation, a certificate of passed examinations, references, and utilized publications).

The certificate of compliance with the minimum national requirements under the Law on the Development of Academic Staff in the Republic of Bulgaria (ZRASRB) for Scientific Field 4.1. Physical Sciences indicates that the candidate's assets exceed the minimum national requirements across the indicator groups G (Г), D (Д), and E(Ж). Overall, the submitted materials are presented in a complete and well-organized manner, enabling an assessment of the candidate's dissertation.

II. Education and career development:

Stephan Dimitrov Kolchev obtained secondary vocational education (Mechanical Engineering Technology) at the "Ivan Hadzhigenov" Professional High School in Kazanlak, a Bachelor's degree in Chemistry from Plovdiv University, and a Master's degree in "Chemistry and Ecology" from the same university (2013–2014). He is proficient in English. Since 2020, he has been working at the CLAP - BAS, Plovdiv, initially as a technologist, later transitioning to the position of chemist, and subsequently to the position of assistant, which he currently holds. He is a co-author of one utility model (registration effective from December 27, 2023, registration number 4658 U1) titled "Planetary Carousel for Driving Samples in a Physical Vapour Deposition Device."

III. Topic Relevance:

The topic of the doctoral dissertation of Mr. Stephan Kolchev is dedicated to the investigation of the mechanical and tribological properties, morphology, composition, and structure of hard and super hard thin layers (coatings) applied to metal surfaces using PVD (physical vapour deposition) technologies. The development of highly efficient coatings with enhanced mechanical and functional characteristics represents one of the most dynamically evolving fields in contemporary materials science and targeted surface modification. In recent years, particular attention has been drawn to thin polycrystalline coatings, which enable the purposeful combination of various phases and structural elements to achieve high wear resistance, thermal and chemical stability, as well as additional functionalities tailored to specific operational requirements. The growing demands for durability, wear resistance, and resilience to extreme loads across various industrial sectors—including mechanical engineering, aviation, micromechanics, and biomedicine—necessitate the development and detailed characterization of coatings with controlled properties at the micro- and nanoscale. Of particular significance is the fact that the research in the dissertation focuses on wear-resistant nanocomposite coatings with a variable (modulated) composition, which is fully aligned with the current scientific and applied priorities in the fields of tribology, protective coatings, and engineering nanotechnology. The potential applications of such coatings span a wide range—from mechanical engineering and energy to biomedical and electronic components—where requirements for wear resistance, chemical inertness, and structural integrity are exceptionally high.

The topic is fully aligned with the priority areas outlined in the strategic documents of the European Union, including "Horizon Europe" and the Smart Specialization Strategy. Research in the field of sustainable, intelligent, and functional materials has been identified as key to achieving goals related to ecological sustainability, energy efficiency, and digital transformation. The development of innovative nanocomposite coatings possessing multifunctional properties and enhanced durability finds a natural place within the priorities of industry, as well as in areas related to green technologies, advanced manufacturing, and sustainable engineering. In light of the above, the current topic can be defined as highly relevant, interdisciplinary, and distinctly application-oriented, holding significant potential for the development of new generations of functional materials and technologies.

IV. Dissertation-related scientific metrics:

The results published (used) in the dissertation have been published in two articles, where the candidate is the first author. The journal, MDPI Coatings, is undeniably a prestigious international publication in the field. These publications have garnered 5 (five) citations, which, for articles published in 2023 and 2025, is indicative of the timeliness and relevance of the dissertation topic. The bibliography of the two articles is as follows:

a) **Kolchev S.**, Kolaklieva L., Chitanov V., Cholakova T., Zlatareva E., Kovacheva D., Atanasova G., Kakanakov R. "The Role of Period Modulation on the Structure, Composition and Mechanical Properties of Nanocomposite Multilayer TiAlSiN/AlSiN Coatings," *Coatings*, 13 (9), 1546, (2023), DOI: 10.3390/coatings13091546;

b) **Kolchev S.**, Kolaklieva L., Kovacheva D., Atanasova G., Cholakova T., Chitanov V., Zlatareva E., Kakanakov R., Pashinski C. "Mechanical and Tribological Behavior of TiAlSiN/AlSiN Coatings Depending on the High-Temperature Treatment," *Coatings*, 15 (5), 542, (2025), DOI: 10.3390/coatings15050542.

V. Structure and content of the dissertation:

The dissertation adheres to the generally accepted rules for structure and is composed of the following sections (chapters): introduction, materials and methods, results and discussion, conclusion with a summary of the achieved results (which I consider as contributions) and conclusions. This is followed by a bibliography containing 250 titles (it is worth noting the substantial number). The dissertation (excluding the bibliography) comprises 127 pages, 64 figures, and 16 tables. A positive impression is made by the inclusion of all used abbreviations at the beginning of the dissertation—pages 6 and 7. Among these abbreviations of the employed terms, I categorically disagree that "Normal force" and "Вертикално приложена сила" (Vertically applied force) are the same thing, unless there are explicit additional clarifications. Overall, "Normal force" is not equivalent to "Vertically applied force."

In the introduction, the author emphasizes the relevance of the topic—research into the mechanical and tribological properties, morphology, composition, and structure of hard and superhard thin layers (coatings) applied to metal surfaces using PVD (physical vapor deposition) technologies. Discussed are methods for modifying surfaces aimed at improving their properties and the corresponding approaches—namely, a) surface modification under the influence of various treatments (thermal, chemical, etc.), which affect the composition and/or structure in the near-surface region, and a second approach b) where surface modification is achieved by applying coatings with specific properties, whereby the composition and structure of these coatings can differ significantly from those of the bulk material, demonstrating that this approach enables the achievement of entirely new surface properties, which cannot be realized with other methods. A review of existing methods for applying coatings in industry—galvanic and electrochemical coatings—is provided; however, these are noted to have a significant drawback, namely, that they involve processes accompanied by the release of various pollutants (largely toxic to living organisms) into the environment. The alternative and increasingly adopted method is associated with physical techniques for depositing thin polycrystalline coatings from the gas phase in a vacuum environment onto products made from various materials (so-called PVD coatings). Regarding different tools used in industry, the advantages of these PVD coatings are discussed,

including: a primary enhancement of durability and the service life of tools employed in activities such as cutting, drilling, and forming—activities related to the production of mechanical components (parts) exposed to harsh working conditions such as high temperatures and intense friction.

The coatings are characterized by high hardness, chemical inertness, thermal resistance, and a low coefficient of friction. As a result of such improvements, the following effects are achieved: a) reduced wear—the hard surface absorbs abrasive loads, preserving the geometry of the cutting edge; b) enhanced thermal protection—thermally resistant coatings reduce the heating of the substrate and prevent the so-called "tempering" of hardened steels; c) reduced friction—facilitating chip removal and minimizing local "sticking" of the processed material; and last but not least d) increased corrosion protection due to the presence of a barrier layer against oxidation and chemical attack. Discussed are multilayer PVD coatings, which find application in the automotive and other industries with regard to forming tools such as dies and punches used in drawing or shaping sheet metal—these tools are subjected to significant mechanical and thermal loads, as well as intense friction with the processed material. These coatings consist of: a) hard base layers (primarily CrN, TiN, TiCN, or TiB₂), which provide high hardness and serve as a supporting foundation that bears the majority of the mechanical load; b) relatively soft top layers with a low coefficient of friction (MoS₂ or amorphous carbon a-C), which act as dry lubricants. These top layers reduce contact friction between the tool and the processed sheet, facilitate material sliding, and prevent surface scratches or galling. Thus, the combination of a hard substrate and a "soft, lubricated" top layer allows for a significant reduction in wear, the use of lower forming forces, and operation with a reduced amount or complete absence of lubricating-cooling fluids. As a result, higher productivity, a longer service life for expensive forming tools, and improved quality of the produced components are achieved. Discussed is the necessity for multifunctional coatings capable of withstanding exceptionally high pressures, on the order of 2000 bar and more, in modern diesel injection systems, functional coatings on automotive glass, coatings on compressor blades used in aircraft gas turbines, and corresponding solutions related to the application of titanium nitride TiN-based multilayer, erosion-resistant coatings. Also commented on is the interest in creating biocompatible coatings for medicine and dentistry. A review is made of the development over the years of titanium and chromium nitride and the subsequent transition to ternary and quaternary systems. Sequentially in the exposition of this introductory part, a literature review is also conducted, which is thorough, detailed, and represents a good description of the current state in scientific-applied research in this dynamic scientific field. A detailed analysis is made of current research on multilayer PVD coatings, and the problems and challenges associated with ensuring maximum hardness, but also achieving maximum elasticity on the other hand, as well as ensuring the stability of mechanical and tribological properties at high temperatures, are discussed. The combination of titanium and chromium nitride compounds within a single coating, with the addition of alloying elements such as Al, B, C, V, and Si, has been discussed. This results in the formation of ternary or quaternary compounds with enhanced thermal stability, improved mechanical properties, and increased wear resistance. The use of the term "spinodal decomposing" would be better replaced with the more widely accepted "spinodal decomposition." It has been shown that for ternary TiAlN and CrAlN coatings, despite their

improved mechanical and tribological properties, their thermal stability is limited to temperatures on the order of 800 °C.

The introduction, as presented to the reader, prepares and establishes the objectives and tasks of the dissertation, namely: through modulating the composition of the coating, to develop and study a superhard coating for surface modification that combines enhanced mechanical and tribological properties, remains stable at high operating temperatures, and enables multifunctional industrial applications. The set tasks are ambitious and include: i) Selection of elemental composition and development of the coating architecture; ii) Development and optimization of the coating deposition technology; iii) Investigation of the mechanical properties of the optimized coating; iv) Investigation of the structure and composition of the developed coating; v) Investigation of the tribological properties of the optimized coating; vi) Investigation of the thermal stability of the mechanical and tribological properties of the optimized coating. In this introductory section, there are several (I hope unintentional) spelling errors, which do not create a favorable impression.

The first chapter begins with a description of the mechanisms of formation and growth of thin (protective) films. It would be appropriate to start with a general overview of the conditions for the formation of thin films in general, as well as a broad presentation of the mechanisms of nucleation and growth. The following should be noted as key conditions for the formation of thin films: Supersaturation (a critical parameter), the energy of nucleation and the corresponding critical cluster size of atoms/molecules (the critical size depends on the surface free energy and the degree of supersaturation); the mobility of adatoms; the substrate temperature; and the energy and angle of incidence of the arriving particles from the so-called mother phase. It would also be beneficial to mention here, in this chapter, the growth mechanisms of thin films:

a) Layer-by-layer growth mode (Frank–van der Merwe), where atoms uniformly fill the surface, layer by layer, resulting in smooth and homogeneous films; b) island growth mode (Volmer–Weber), where three-dimensional islands (clusters) form and later merge; and c) layer-plus-island growth mode (Stranski–Krastanov), where one or a few monolayers are first formed, followed by island growth. Instead, the author immediately dives into a description of more specific parameters and conditions used in the conducted experiments. Of course, this is not inherently bad, but the "narrative" in the dissertation could flow more smoothly. This is the place to make a very serious remark regarding part of the terminology used, and my remark is directed both to the candidate and to his scientific supervisors. I categorically cannot accept the use of the word "podlojka" instead of "substrate" (base/substrate in the context of thin film deposition), and the use of the word "nucleatsia" instead of "nucleation" (зародишообразуване) is unacceptable. It is noteworthy that in a doctoral dissertation I reviewed about a year ago for a doctoral candidate from Sofia University, exactly the same phraseological "errors" were identified, which raises the question of the use and training in employing the correct terminology. Regarding nucleation and the mechanisms of crystal growth, I would recommend that the doctoral candidate familiarize themselves with the book *Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy* (3rd ed.), authored by Ivan Markov, published by World Scientific Publishing Company (2017). An analysis has been conducted on the conditions for forming solid coatings with a nanocrystalline structure, the grain (crystallite) sizes, and the presence of defects (dislocations, cracks, and pores).

A class of methods for the physical vapor deposition (PVD) of thin layers has been described, including the magnetron sputtering method and the cathodic arc evaporation method.

The exposition continues with a description of the main methods for investigating coatings, namely: determining the thickness of the deposited coatings, studying mechanical properties (measuring adhesion strength, hardness assessment), investigating the surface topography, composition, and structure of the coatings (using scanning electron microscopy and energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction analysis), studying tribological properties, and investigating thermal stability. Overall, the main methods are well described; however, I have some remarks. One of them is that all figures are copied from other sources (of course, with proper citation), and the other concerns the frequent use of the degree symbol (for angle and Celsius degrees), which should be written as a superscript circle rather than the "zero" symbol used by the author. These remarks pertain solely to the formatting and visual presentation of the text and are not substantive to the content of the exposition. Regarding equation (1) on page 37, I have a question about whether P denotes pressure or force, and correspondingly, in what units the hardness is measured, since if P is pressure, as written, it results in a dimensionality of $[\text{force}/\text{distance}^4]$?

The more substantial part of the dissertation begins with Chapter 2 – Materials and Methods, and the corresponding empirical basis of the conducted research. The choice of composition for the nanocomposite coatings with modulated composition, which are to be synthesized/obtained and studied, is commented upon. The dissertation focuses on combining harder with more elastic sublayers within the composition of the multilayer coating, which is intended to achieve the desired parameters of super hardness and increased strength by deflecting cracks through the interfacial zones, causing energy dissipation without damaging the coating.

To investigate the influence of the modulation period on the properties of the developed nanocomposite multilayer structures, two groups of coatings were deposited. For the first group, the coating consists of 3 periods (ml3-TiAlSiN/AlSiN), as this is the minimum number of modulation periods required to manifest the advantages of the multilayer architecture. For the second group, we have 30 periods (ml30-TiAlSiN/AlSiN), i.e., a sufficiently large number of periods compared to the first group, to highlight effects resulting from the greater number of interfaces (boundaries) in the structure. The procedure for the preliminary preparation of the samples is also described in detail. The chapter continues with a description of the equipment used for depositing nanocomposite coatings with a modulated composition.

To achieve the selected composition of the coatings, Ti (99.99 wt.%) and alloyed AlSi (82 at.% Al, 18 at.% Si) cathodes were used and mounted in the system. For fixing the samples, a triaxial two-stage planetary system was employed. By means of a resistive heater, positioned on three sides of the chamber, temperatures up to 600 °C can be reached during the deposition of the coatings.

The developed technology for nanocomposite coatings with modulated composition is described in detail – deposition of reference single-layer coatings with different durations and corresponding thickness measurements, determination of growth rates, as well as calculation of the deposition times for each functional sublayer in multilayer structures. The technological parameters of the cathodic arc evaporation deposition process are also specified.

The chapter continues with a description of the equipment and methodologies for the investigation of nanocomposite coatings with modulated composition, which is an extension of the earlier presentation of the main methods for coating characterization, namely: determination of the thickness of the deposited coatings, investigation of mechanical properties (measurement of adhesion strength, hardness testing), examination of surface topography, composition and structure of the coatings (scanning electron microscopy and energy-dispersive elemental analysis, X-ray photoelectron spectroscopy, X-ray diffraction analysis), study of tribological properties, and evaluation of thermal stability.

The substantive part of the dissertation begins with Chapter 3, where the obtained results are presented and discussed. This chapter starts with an overview of the results concerning the morphology and elemental composition of the deposited reference (single-layer) sl-TiAlSiN and sl-AlSiN coatings, as well as the developed multilayer ml3-TiAlSiN/AlSiN and $\text{ml30-TiAlSiN/AlSiN}$ coatings. Scanning electron microscopy with energy-dispersive X-ray spectroscopy and X-ray diffraction, combined with X-ray photoelectron spectroscopy, were used—investigations were conducted both on the surface and in-depth profiles. Cross-sectional views clearly illustrate the architecture of the coatings. The light and dark layers correspond to the sublayers of the TiAlSiN and AlSiN periods. The morphology of the cross-sections reveals a dense structure. The cross-sections themselves are obtained with good fabrication accuracy, free of contaminants, and are generally smooth. The distribution of elements across the depth of the coatings is also shown with satisfactory precision. The results from X-ray diffraction indicate that changes in the modulation period do not lead to shifts in the positions of diffraction peaks but do affect their intensity. The average crystallite size is determined to be 12 nm for the ml3-TiAlSiN/AlSiN coating and 13 nm for the $\text{ml30-TiAlSiN/AlSiN}$ coating. An assessment of the quantities of the two phases yields approximately 28 mass% Ti(Al)N and 72 mass% Al(Si)N in ml3-TiAlSiN/AlSiN , and about 15 mass% Ti(Al)N and 85 mass% Al(Si)N in $\text{ml30-TiAlSiN/AlSiN}$, with the dominance of the Al(Si)N phase in the multilayer coatings being consistent with the results obtained from EDS measurements. Overall, the X-ray structural analysis of the developed coatings shows that a nanocomposite structure has been formed, and a reduction in grain size has been achieved due to the high silicon content. It is demonstrated that solid solutions of the compounds TiAl(Si)N and AlSiN have been formed. Their presence indicates that the developed multilayer coatings consist of nanocomposite sublayers, which is a prerequisite for high stability of hardness at elevated temperatures. Additionally, XPS analysis establishes that three types of bonds (Ti-N, Al-N, and Si-N) exist in the developed multilayer coatings. The stronger Ti-N bonds determine the hardness of the coatings, while the weaker Al-N bonds enhance their elasticity. The stronger Ti-N and weaker Al-N bonds primarily contribute to the hardness and elasticity of the coating.

Chapter Three continues with an investigation into the influence of temperature on the morphology, composition, and structure of ml3-TiAlSiN/AlSiN and $\text{ml30-TiAlSiN/AlSiN}$ coatings. It has been established that thermal treatment up to 900 °C does not cause changes in the structure of the coatings. No cracks or "delamination" of the interfaces were observed, indicating the presence of sufficiently strong cohesive forces up to temperatures of 900 °C. The same applies to the elemental composition of the coatings. Without delving into the detailed descriptions in the remaining part of this chapter, the conclusion that can be drawn is that, as a result of the appropriate multilayer design and developed suitable technology, a structure has been achieved

that combines the advantages of nanocomposites and multilayer coatings, suggesting a combination of superhardness with improved elasticity.

The next Chapter 4 summarizes the results from the investigation of the mechanical and tribological properties of the coatings. The thickness of the coatings has been determined. The mechanical and tribological properties include the study of hardness, elastic modulus, resistance to elastic impact and plastic deformation, as well as elastic recovery. The obtained hardness values classify the developed coatings as superhard. The higher the hardness, the greater the resistance to plastic deformation. However, superhardness is typically associated with a high elastic modulus, which makes the coating brittle. To avoid this contradiction, a low elastic modulus is necessary, which allows external loads to be distributed over a larger area. The obtained values for the elastic moduli can be considered low for these superhard coatings. Thus, the combination of superhardness with a low elastic modulus indicates improved toughness of the coating. The experiments on tribological properties, including the measurement of the friction coefficient and the determination of wear rate, are described in detail. The results show that the ml30-TiAlSiN/AlSiN coating, which possesses a greater number of interfaces, ultimately exhibits better wear resistance. The wear tracks were thoroughly investigated regarding delamination and residues at both ends of the tracks, and the wear mechanisms for the two coatings were identified. The determined hardness and adhesive strength of the two multilayer coatings suggest better tribological behavior for ml3-TiAlSiN/AlSiN; however, the obtained results from the friction coefficients, wear morphology, and wear rate indicate the opposite. The entire described set of investigations has also been applied to annealed coatings. A positive impression is made by the detailed comparison and justification of the conclusions drawn. As a main conclusion, it can be noted that the modulation period affects the coating's behavior at elevated temperatures differently due to variations in the dominant wear mechanisms. The conclusion of the dissertation includes a summary of the results. It can confidently be said that the results of the dissertation work demonstrate that the set objective has been fully and successfully achieved. A superhard, wear-resistant nanocomposite TiAlSiN/AlSiN coating has been developed, which is stable at temperatures up to 900 °C. The investigation of the mechanical and tribological properties of coatings with different modulation periods, depending on the treatment temperature, established that the three-period TiAlSiN/AlSiN coating is more suitable for high-temperature applications. This characterizes it as multifunctional and applicable in various industrial fields, including "dry" machining processes.

VI. Questions, recommendations and comments:

The remarks can be divided into two categories: the first pertains solely to formal aspects related to the formatting and structuring of the dissertation, where greater attention to detail was needed regarding the appearance of the final, completed scientific product, including the occurrence of unintentional spelling errors; the second type of remarks relates to the manner of "narrating/writing" and the style of the dissertation, though this is a process that, I am confident, the doctoral candidate will manage to improve in future work. I hope the doctoral candidate will continue their scientific activities at the Laboratory in the future.

VII. Abstract evaluation:

The abstract has been prepared in accordance with established requirements and reflects the main results of the dissertation in a clear and systematic manner. In its preparation, the practice of repeating the numbering of figures and tables, identical to that in the dissertation itself, has been followed, which facilitates the reader's orientation and establishes a direct connection between the two documents. Only a minimal discrepancy is observed in the numbering of one or two equations; however, this fact does not significantly impact the understanding of the exposition and can be considered negligible.

The abstract fulfils its primary function—providing an opportunity for a quick and comprehensive overview of the dissertation's content—by presenting the methodology, obtained results, and conclusions in a synthesized form. At the same time, it does not allow for significant omissions or distortions of the content; on the contrary, it preserves the completeness and logical coherence of the main work.

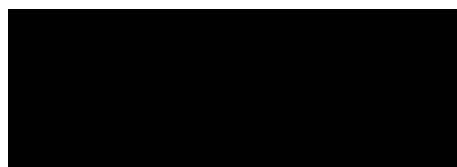
VIII. Conclusion:

Taking into account the level and scope of the conducted scientific research, as well as the high quality of the dissertation and the clearly expressed scientific and applied contributions of the doctoral candidate, I express my firmly **positive** opinion. I consider that the dissertation meets all requirements for originality, scientific value, and methodological correctness, characteristic of a work aspiring to obtain the educational and scientific degree of "Doctor."

In this context, I believe that the presented results and conclusions are of high significance for the development of research in the field of condensed matter physics and demonstrate the independence and maturity of the author's research approach.

Therefore, I confidently recommend that the esteemed Scientific Jury award the educational and scientific degree of "**PhD**" to **Stephan Dimitrov Kolchev** in Professional Field 4.1. Physical Sciences, under the doctoral program " Condensed Matter Physics."

Reviewer:



Prof. Bogdan Ranguelov,
Institute of Physical Chemistry, BAS

05/09/2025