

REVIEW

by

Prof. Dr. Ivan NEDKOV Ivanov, regarding the dissertation submitted for the award of the educational and scientific degree “**Doctor**” in professional field 4.1. “Physical Sciences”, Doctoral program: “Condensed Matter Physics”, Specialty: “Electrical, optical and magnetic properties of condensed matter”.

Author of the dissertation: Stefan Dimitrov KOLCHEV.

Title of the dissertation: Development and research of wear-resistant nanocomposite coatings with modulated composition for multifunctional applications.

Grounds for preparing the review: Order No. 17/04.06.2025 of the Director of the Central Laboratory of Applied Physics (CLAP) BAS for the appointment of a Scientific Jury for the defense of a dissertation for the acquisition of the educational and scientific degree "**Doctor**" and the decision of the Scientific Jury approved by the Scientific Council of the Institute of Electronics (IE) BAS, Protocol No. 9/24.06.2025.

1. General description of the submitted materials and data for the doctoral student

The documents submitted by Stefan Dimitrov Kolchev under the procedure are in full compliance with the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (LDAS RB), the Regulations for the Application of the LDAS RB at Bulgarian Academy of Sciences, as well as the requirements of the Scientific Councils of the CLAP–BAS and the IE–BAS for the professional field 4.1. Physical Sciences, Specialty: Electrical, optical and magnetic properties of condensed matter. The credit table and table 3 demonstrate that the candidate meets the minimum national requirements. The subjects of this review are the candidate's thesis and the documents he has attached for theoretical scientific and applied scientific contributions and accompanying documents, including diplomas (bachelor's and master's degrees) for higher education, scientific papers, inventions, citations, etc. The attached materials meet the documentary requirements for acquiring the educational and scientific degree of "doctor" and are adequate to the professional field and specialty (topic) of the announced competition.

Master S. Kolchev graduated in 2014 with very good results - the Faculty of Chemistry of the Plovdiv University "Paisiy Hilendarski", with the educational qualification "Master's degree", specialty "Chemistry and Ecology". His scientific career began at the Central Laboratory of Applied Physics (CLAP), where on 01.07.2021 he was elected to the position of "assistant" and from 01.01.2020. he was enrolled as a full-time doctoral student at CLAP in scientific direction 4.1. “Physical Sciences”, specialty "Electrical, optical and magnetic properties of condensed

matter". After the expiration of the statutory training period, he received an extension of 6 months - until 01.07.2023 (Order of the Director of the CLAP BAS No. 41/15.12.2022) and was dismissed with the right to defense - Protocol No. 46/01.07.2023 of the Scientific Council of the Institute of Solid State Physics (ISSP) BAS, which at that time was responsible for the scientific work of the CLAP BAS. In 2025, by decision of the Management Board of the Bulgarian Academy of Sciences, protocol No. 9 of 10.04.2025, item 2, pursuant to Art. 48a, para. 2 of the Statute of the BAS, this activity was delegated to the Scientific Council of the Institute of Electronics - BAS (IE-BAS) and the documents on the procedure were submitted to the Scientific Council of the IE – BAS, Protocol No. 9/24.06.2025.

2. Relevance and importance of the topic

The subject of the dissertation is the creation of new hard and superhard thin layers (coatings) deposited on metal surfaces using PVD (Physical Vapor Deposition) technologies. Scientific research related to improving the properties of this type of coatings is generally defined by two approaches: (i) By forming a nanostructure, superhardness and temperature resistant monolayers, but as an unsolved problem with this approach is the high brittleness, respectively low elastic resistance of the temperature, which limits their application and (ii) By building a multilayer structure, to improve the elastic resistance to external influences at relatively high hardness, but the main problem with this multilayer coatings is the reduced wear resistance at high temperatures, which limits their application. These layers have a wide application in metalworking tools and the search for a satisfactory solution to these problems is the subject of research work in a number of modern laboratories. This topic is highly relevant in modern condensed matter physics and materials science, as the research for new protective and functional coatings is a priority in various high-tech industries including mechanical engineering, electronics, and energy technologies. The combination of experimental synthesis, structural characterization, and functional property assessment ensures that the thesis contributes both to fundamental knowledge and to practical applications.

3. General characteristics - aim and tasks of the dissertation

The subject of this study are nanocomposite coatings of TiAlSiN and AlSiN. The structure of the dissertation follows the conventional model typical for this type of research. The description includes an Introduction, 4 Chapters and a Conclusion, which reflect the research process, the results obtained, inform about the publication activity on the topic, citations and documents. The textual part is developed on a total of 127 pages. 250 sources are cited, the dissertation contains 64 figures and 16 tables. The author has presented extensive illustrative material, including color photographs, which well document the results achieved.

The tasks formulated in the work are logically derived from the aim, including: Selection and optimization of deposition methods for nanocomposite coatings; Investigation of structural and phase composition; Study of mechanical, tribological, optical, and magnetic properties; Establishing correlations between composition, structure, and functional performance. The tasks are well-defined, achievable, and scientifically justified.

The results of the dissertation work show that **the aims** have been achieved. An ultra-hard nanocomposite wear-resistant coating TiAlSiN/AlSiN has been developed, which is resistant at temperatures up to 900 °C. The study of the mechanical and tribological properties of coatings

with different modulation periods shows that the three-period TiAlSiN/AlSiN coating is most suitable for high-temperature applications. It is multifunctional and applicable in various areas of industry, including "dry" machining.

4. Degree of knowledge of the state of the problem, methodology of research

The literature review includes 250 titles. The use of this data in the preparation of the dissertation shows that the doctoral student can work creatively with the scientific literature. The author employs a wide range of contemporary experimental techniques: physical vapor deposition (PVD) methods for coating fabrication, The EDS, XRD, and XRS analyses revealed that the nanocomposite structure is composed of TiAlSiN and AlSiN nanocrystallites, XRD and electron microscopy for structural analysis, tribological and nanoindentation tests for mechanical characterization, as well as spectroscopic and magnetometric measurements for functional property studies are used. The chosen methods are adequate, reliable, and ensure comprehensive investigation of the problem.

5. Scientific and applied contributions

The contributions can be summarized as both enriching existing knowledge in the field of materials science and advancing the development of new materials. From an applied perspective, they include the creation of materials with enhanced properties and promising potential for practical applications. The main contributions of the dissertation can be summarized as follows:

PVD technology for the application of TiAlSiN/AlSiN multilayer nanocomposite coatings has been optimized. Two modifications of the cathodic arc technology have been developed, incorporating original technical solutions suitable for practical implementation, and a **Utility Model** has been patented.

Development of **novel nanocomposite coatings and establishment of structure–property correlations**. A multilayer TiAlSiN/AlSiN nanocomposite coating was obtained, consisting of two main sublayers: one composed of nanocrystals of the solid solution TiAlN (general formula $Ti_{1-x}Al_xN$) and the other of AlSiN (general formula $Al_{1-x}Si_xN$). The layers are embedded in an amorphous Si_3N_4 matrix; their structure is dense, and no columnar growth has been observed. Maximum hardness values of 49.5 GPa and 43.4 GPa were achieved for 3 (ml3) and 30 (ml30) periodic coatings respectively, classifying them as **superhard**. This part of investigations presents systematic studies, conducted with modern methods, on the morphology, composition, and structure of the coatings depending on the modulation period. The results show that the observed superhardness arises from three factors: the nanocomposite structure, solid solution formation in the crystallites, and their size. It has also been demonstrated that the lower elastic modulus of the sublayer contributes to improved elasticity of the entire coating. It has been established that the mechanical properties depend on the modulation period, with a decrease in the modulation period leading to reduced hardness. Analysis of the phase and chemical composition indicates that a higher Al content results in a dominant influence of the weaker Al–N chemical bonds (297 kJ/mol) compared with the stronger Ti–N bonds (464 kJ/mol), which in turn lowers the overall elastic modulus of the modulated TiAlSiN/AlSiN nanocomposite coating. This contribution can be

defined as highly scientifically applied. The results concerning the role of modulation periods in determining the structure, composition, and mechanical properties of nanocomposite TiAlSiN/AlSiN layers have been published in *Coatings* (2023, 13, 1546). The work has already received 4 independent citations, which clearly illustrates the significance of the contribution.

Systematic **high-temperature tests** were conducted to study the properties of multilayer nanocomposite coatings in the temperature range of 700 °C – 900 °C, with parallel monitoring of the morphology, structure, and architecture of the coatings. XPS spectra revealed that the multilayer ml3- and ml30-TiAlSiN/AlSiN coatings are composed of the nitrides TiN, AlN, TiAlN, and Si₃N₄. After annealing, partial oxidation was observed on the surface, specifically the presence of Ti–O–N and Si–O bonds, along with the formation of TiO₂ and Al₂O₃ oxides in the solid solution. The studies demonstrated that these compositional changes lead to a reduction in the amount of nitrides on the surface, in good agreement with literature data (Zou C.W. et al., 2011). An ultrahard nanocomposite wear-resistant ml3-TiAlSiN/AlSiN coating has been developed, which remains stable at temperatures up to 900 °C. The results show that after heating to 900 °C, hardness decreases—well explained by the spinodal decomposition of the TiAlN solid solution—but remains sufficiently high for industrial applications. The thermally stable structure prevents interdiffusion and ensures stability of the interfaces between the sublayers and periods. This represents a significant advantage of the developed coatings, since structural stability during high-temperature processing is a prerequisite for maintaining reliable mechanical and tribological properties. The results obtained demonstrate that it possesses high strength, combining superhardness with improved elasticity, both of which remain sufficiently stable to 900 °C. These findings represent a clearly defined scientific and applied contribution and *were presented at a conference* with international participation, and place the CLAP BAS team among serious competitors in the development of a new generation of superhard metalworking tools capable of operating at high temperatures without the use of lubricants.

Results were obtained on **the tribological properties** of the developed multilayer nanocomposite TiAlSiN/AlSiN coating. The adhesion–cohesion strength, coefficient of friction, and wear resistance of the coating were investigated. The studies established a dependence of these parameters on the composition of the sublayers and on the modulation period. It was also found that the wear mechanism depends on the modulation period. The results of this research were published in the journal *Coatings* 2025, 15, 542, and this year they attracted interest, with 1 citation from independent foreign authors.

6. Publication activity and data on the doctoral student's credit rating

The dissertation work of Master S. Kolchev is of a good scientific level. The results have been published in **2 scientific journals** with an impact factor (IF) - *Coatings* (IF: 2.864, Q2, reference 2024) and he has co-authorship in a **Utility Model** - Certificate Reg. No. 4658 U1, Application No. 5985 dated 27/12/2023, with priority from 27/12/2023. As mentioned above, **4 independent citations** of the 2023 article and **1** of the work published in 2025 were noted. *Coatings* magazine focuses the interest not only of scientists, but also of specialists with applied interests, and the rapid appearance of citations is a good testament to the importance of the research. The doctoral candidate also has **3 participations in scientific conferences** (INFRAMAT 2021, 2022 and 2023).

By completing his educational program, the doctoral **student collects 267 credits with a requirement of ≥ 200 .**

7. Critical remarks

These remarks are of a recommendatory nature and do not diminish the overall quality of the dissertation. In some sections, the discussion of experimental results could benefit from a deeper theoretical interpretation. In some places, a literal translation from English is used (e.g. "multilayers/мултислоеве", etc.), although there are completely appropriate terminological analogues in Bulgarian. When discussing the results of the dissertation during the defense, a significant weakness of the experimental work became apparent, namely the lack of data on the repeatability of some experimental results. I would recommend that the doctoral student pay more attention to this problem in his future scientific activities, especially since the results of his work are emerging with visible applications in industry.

Conclusion

Analysis of the dissertation work presented above shows that according to the indicators it formally fulfills the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria (LDAS RB), the Regulations for the Application of the LDAS at Bulgarian Academy of Sciences, as well as the requirements of the Scientific Councils of the CLAP–BAS and the IE–BAS for the professional field 4.1. The dissertation by S. Kolchev is a valuable contribution to the field of condensed matter physics and applied materials science. It demonstrates the author's ability to conduct independent scientific research, to obtain significant results, and to present them in a systematic and convincing manner.

I confidently propose that the Scientific Jury award **Stefan Dimitrov Kolchev** the educational and scientific degree “**Doctor**” in the professional field **4.1. Physical Sciences**, specialty: **Electrical, optical and magnetic properties of condensed matter**.

Prepared:

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Reviewed: (signature)

/Prof. DSc I. Nedkov/