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Nanoarrayed Cu₂O/CuSCN HTLs for High-Efficiency Organic Solar Cells

Organic solar cells (OSCs) offer a promising low-cost and flexible alternative to conventional photovoltaic technologies; however, their performance remains limited by inefficient charge transport and carrier recombination losses. In this work, we present a novel nanoarrayed hole-transport layer (HTL) based on Cu₂O/CuSCN heterostructures fabricated via a two-step electrodeposition process. Vertically aligned Cu₂O nanocrystals were grown on CuSCN films, forming a nanostructured charge-extraction framework with enhanced interfacial contact and potentially reduced carrier transport distances. The morphology and properties of the films were systematically tuned by controlling the electrochemical parameters, enabling the formation of well-defined nanoarchitectures. Photoelectrochemical measurements revealed enhanced interfacial photocurrent and improved charge-extraction characteristics of the composite structures compared with the corresponding single-layer films. When integrated into PTB7-th:PCBM-based OSCs, the nanoarrayed HTL substantially improved device performance, increasing the open-circuit voltage from 0.62 to 0.84 V, the short-circuit current density from 7.99 to 11.8 mA cm⁻², and the power conversion efficiency from 2.76% to 5.59%. These improvements are attributed to more efficient charge collection and suppressed recombination enabled by the nanoarray architecture. This study demonstrates a low-temperature electrodeposition strategy for engineering advanced HTLs and highlights the potential of nanoarrayed Cu₂O/CuSCN heterostructures for future organic and hybrid photovoltaic devices.

Keywords: Organic solar cells, copper thiocyanate films, PTB7-Th: PCBM, Cu₂O nanocrystals, electrodeposition, bulk heterojunction, hole transport layer, charge transfer

Introduction

Organic (polymer-based) solar cells are widely regarded as one of the most promising renewable-energy technologies and are becoming increasingly competitive with traditional silicon devices. This interest is largely driven by their low-cost fabrication methods [1] and the distinctive properties of organic materials [2]. In particular, organic photoactive and conductive polymers are flexible and semi-transparent [3], allowing them to be deposited onto flexible or transparent substrates and integrated into a variety of surfaces, such as building windows [4]. Additionally, many organic materials can be processed from solution, enabling thin-film fabrication through techniques such as spin-coating, dip-coating, and roll-to-roll printing. These processes can be carried out at or near room temperature with only mild thermal treatment (≤ 110 °C),

significantly lowering production costs compared to conventional inorganic technologies [5, 6]. Organic materials are also often compatible with biomaterials, which open the door to environmentally friendly and bio-integrated applications [7].

Despite these advantages, the efficiency of organic solar cells (OSCs) still trails behind that of silicon and perovskite technologies [8, 9]. In conventional OSC designs, the photoactive layer consists of a blend of a donor polymer and a fullerene-based acceptor, forming a bulk heterojunction (BHJ) positioned between hole- and electron-transport layers. When light is absorbed, excitons are generated in the donor material and must diffuse to donor–acceptor interfaces to dissociate into free charge carriers. However, because exciton diffusion lengths in many polymers are relatively short compared to the thickness required for efficient light absorption, the BHJ architecture is employed to maximize interfacial area [10]. Even so, device performance remains strongly limited by morphology [11, 12] and by imbalances in charge carrier mobility—hole mobility is typically lower than electron mobility [13]—leading to charge accumulation and recombination losses. In addition, regions within the BHJ often lack efficient percolation pathways to the charge transport layers, resulting in incomplete charge collection [14].

To mitigate these limitations, extensive research has focused on improving hole-transport layers (HTLs), including the use of conductive polymers (e.g., PEDOT:PSS), transition metal oxides, and inorganic p-type semiconductors such as CuSCN. While these materials can provide suitable energy level alignment and chemical stability, they are typically implemented as planar thin films that rely on one-dimensional (1D) vertical charge extraction. This configuration does not fully match the three-dimensional nature of charge generation within the BHJ layer, where photogenerated carriers are distributed throughout the film volume. As a consequence, holes must often travel laterally over relatively long distances before reaching the HTL interface, increasing the probability of recombination and limiting device efficiency. Although previous studies have improved HTL performance through doping, interfacial engineering, and conductivity enhancement, comparatively little attention has been given to engineering the spatial architecture of HTLs to fundamentally alter charge extraction pathways. This represents a key gap in the current development of OSCs.

In this work, we address this limitation by introducing a nanoarrayed Cu₂O/CuSCN heterostructured HTL, which transforms the conventional planar extraction interface into a quasi-two-dimensional (2D) charge collection network. The structure is formed by electrodepositing vertically aligned Cu₂O nanocrystals onto CuSCN films, creating an extended interfacial framework that penetrates toward the active layer. Unlike planar HTLs, this nanoarrayed architecture increases the effective contact area and provides multiple localized pathways for hole extraction. As a result, the average transport distance for photogenerated holes is reduced, leading to suppressed recombination and more efficient charge collection. Importantly, this approach combines the favorable electronic properties of CuSCN with the structural advantages of Cu₂O nanocrystals, while remaining compatible with low-temperature and scalable fabrication processes.

A two-step electrodeposition method was developed to precisely control the nucleation and growth of Cu₂O nanocrystals on CuSCN films, enabling the formation of well-defined nanoarrayed heterostructures. The resulting architecture promotes strong interfacial coupling and efficient charge transfer. Photoelectrochemical measurements demonstrate enhanced interfacial photocurrent and improved hole extraction in the composite structures compared to single-layer counterparts. When integrated into PTB7-Th:PCBM-based OSCs, the nanoarrayed HTL leads to significant improvements in open-circuit voltage, short-circuit current density, and overall power conversion efficiency.

Overall, this work demonstrates that engineering the geometry of the HTL—from planar to nanoarrayed—provides a fundamentally different strategy for improving charge extraction in OSCs. The proposed Cu₂O/CuSCN nanoarray architecture offers a simple, low-temperature, and scalable route to enhance charge management and device performance, thereby addressing a critical limitation of conventional HTL designs and contributing to the development of next-generation organic photovoltaic technologies.

Experimental

Materials

To ensure the fabrication of high-purity thin films with minimal contamination, all reagents of analytical grade or higher purity were purchased from Sigma-Aldrich. The chemicals used included copper(II) sulfate (anhydrous, ≥99.99 %), ethylenediaminetetraacetic acid (EDTA, OmniPur® Grade, ≥99.5 %), potassium thiocyanate (ReagentPlus®, ≥99.0 %), diethanolamine (DEA, BioUltra, ≥99.5 %), lactic acid (ACS reagent, ≥85 %), and sodium hydroxide (ACS reagent, ≥97.0 %).

All aqueous solutions were prepared using deionized water with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$, obtained from a Smart-Q30UT purification system (Drawell Scientific). The use of high-purity reagents and ultrapure water minimized the incorporation of impurities during thin-film formation.

Preparation of CuSCN Thin Films

CuSCN layers were deposited onto fluorine-doped tin oxide (FTO) glass substrates from Ossila with active area 90 mm^2 (sheet resistance $\sim 15 \text{ }\Omega/\text{sq}$). Prior to deposition, the substrates were sequentially cleaned in an ultrasonic bath using a 2 % Hellmanex solution (10 min), deionized water (10 min), and 2-propanol (10 min), followed by drying under a nitrogen stream. The substrates were subsequently treated under UV irradiation for 15 min to remove residual organic contaminants and improve surface wettability.

Two types of CuSCN films were fabricated. The first, denoted CuSCN-E, was electrodeposited from an aqueous solution containing 12 mM CuSO_4 with equimolar concentrations of EDTA and KSCN. The second type, CuSCN-D, was obtained from a precursor solution composed of 15 mM CuSO_4 , 67.5 mM diethanolamine (DEA), and 45 mM KSCN. In both cases, EDTA or DEA was added prior to KSCN to suppress the formation and precipitation of $\text{Cu}(\text{SCN})_2$ complexes. The pH values of the EDTA- and DEA-based electrolytes were adjusted to 1.6 and 8.2, respectively.

Electrodeposition was performed in a three-electrode configuration using a platinum counter electrode and an Ag/AgCl (saturated KCl) reference electrode (Fig. 1). Chronoamperometric deposition was carried out at fixed potentials of -0.3 V (CuSCN-E) and -0.45 V (CuSCN-D) versus Ag/AgCl. The deposition time was varied in the range of 60–300 s to control film thickness. The resulting CuSCN films had a typical thickness of 40–60 nm, as estimated from deposition charge and confirmed by profilometry measurements.

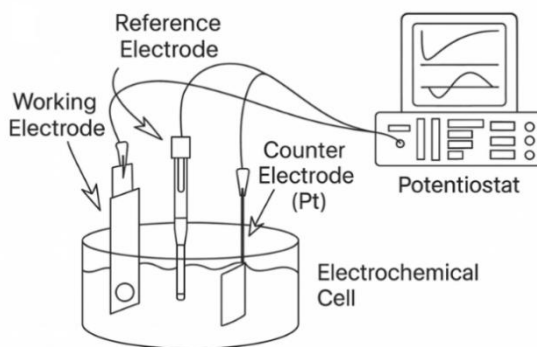


Figure 1. Three-electrode setup for electrodeposition

Preparation of Cu_2O Thin Films and $\text{Cu}_2\text{O}/\text{CuSCN}$ Nanoarrays

Cu_2O films were deposited electrochemically onto CuSCN/FTO substrates using an alkaline electrolyte containing lactate-complexed copper ions. The electrolyte was prepared by dissolving 0.2 M CuSO_4 and 3 M lactic acid in deionized water, followed by the addition of 0.5 M K_2HPO_4 as a buffering agent. The solution pH was adjusted to 12 by gradual addition of 2 M KOH.

To form nanoarrayed $\text{Cu}_2\text{O}/\text{CuSCN}$ heterostructures, a two-step electrodeposition process was employed. First, a galvanostatic nucleation step was carried out at a current density of $-0.1 \text{ mA}\cdot\text{cm}^{-2}$ for 10 s to generate spatially separated Cu_2O nuclei. This was followed by a potentiostatic growth step at -0.3 V versus Ag/AgCl for 60 s, enabling controlled growth of vertically aligned Cu_2O nanocrystals. Deposition was conducted at 30°C . The resulting Cu_2O nanocrystals had an average lateral size of $\sim 80 \text{ nm}$ and an effective height of approximately 50–80 nm, forming a nanoarrayed morphology on the CuSCN layer.

Device Fabrication

Organic solar cells were fabricated using the following architecture:

FTO / CuSCN (or $\text{Cu}_2\text{O}/\text{CuSCN}$) / PTB7-Th: PC_{61}BM / Al

The active layer (photoactive layer, PL) consisted of a PTB7-Th: PC_{61}BM bulk heterojunction. The solution was prepared by dissolving PTB7-Th and PC_{61}BM in chlorobenzene at a weight ratio of 1:1.5 with a total concentration of 25 mg/mL. The solution was stirred at 60°C for 12 h prior to deposition.

The active layer was spin-coated onto the HTL-coated substrates at 3000 rpm for 60 s, resulting in a film thickness of approximately 90–110 nm. After deposition, the films were dried under inert conditions.

A 100 nm thick Al electrode was thermally evaporated under high vacuum ($\sim 10^{-6}$ Torr) through a shadow mask, defining an active device area of 0.1 cm². The devices were subsequently encapsulated using epoxy in a nitrogen atmosphere to minimize degradation.

Characterization

The surface morphology of the films was analyzed using scanning electron microscopy (SEM, Carl Zeiss Crossbeam 540 with GEMINI II). Atomic force microscopy (AFM, NTEGRA ACADEMIA) was used to evaluate surface roughness and morphology of the active layer. The all thickness of the layers was measured by AFM making gentle scratch.

Photoelectrochemical (PEC) measurements were carried out using a CS300 potentiostat (Corrtest Instruments) under chopped illumination from an Ossila solar simulator (AM 1.5G, 100 mW·cm⁻²). Current–voltage (I–V) characteristics of the fabricated devices were measured under the same illumination conditions by Ossila source meter.

Results and Discussion

Next, we developed a method for the electrodeposition of a Cu₂O nanocrystal array on the surface of CuSCN. To form the array, electrodeposition was first performed in a galvanostatic regime at a low current density (-0.1 mA·cm⁻²) at 30 °C and pH 12 for 10 s. This stage enabled a slow nucleation rate and the formation of Cu₂O nuclei sufficiently spaced from each other. Subsequently, the process was switched to a potentiostatic mode, and electrodeposition was continued at -0.3 V versus Ag/AgCl reference electrode for 1 min. This combination of modes allowed the deposition of well-separated Cu₂O nanocrystals on the CuSCN surface, which shown in Figure 2A with average size of the Cu₂O nanocrystals of 80 nm.

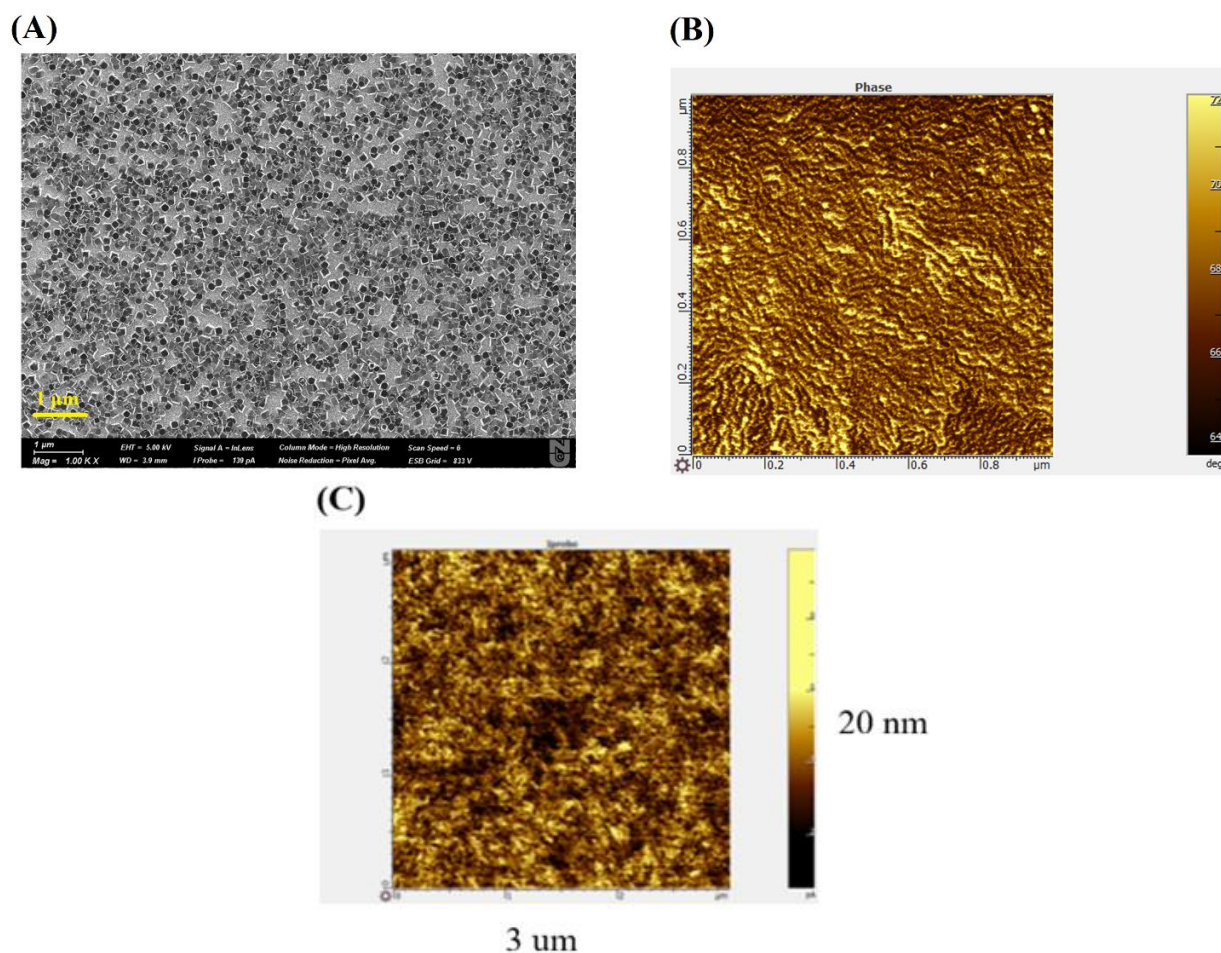


Figure 2. (A) SEM image of the nanoarrayed Cu₂O/CuSCN composite film. AFM phase (B) and topography (C) images of the PTB7-th:PCBM blend layer deposited on the surface of the Cu₂O/CuSCN composite film

Further, the nanoarrayed $\text{Cu}_2\text{O}/\text{CuSCN}$ composite films were employed as the hole transport layer in organic solar cells. In the next step, a bulk heterojunction (BHJ) layer based on a PTB7-th: PCBM blend was spin-coated onto the surface of the as-grown nanoarrayed $\text{Cu}_2\text{O}/\text{CuSCN}$ composite films. The AFM image of the 100 nm-thick PTB7-th: PCBM layer is shown in Figure 2B. As shown in Figure 2B, the AFM phase image of the PTB7-Th: PC₆₁BM film reveals a continuous and laterally homogeneous surface with nanoscale contrast. The observed phase variations suggest the presence of donor–acceptor phase separation within the blend, which is typical for bulk heterojunction systems. The uniform distribution of phase domains indicates good film formation and consistent coverage over the underlying $\text{Cu}_2\text{O}/\text{CuSCN}$ layer. Such morphology is expected to support efficient interfacial contact and facilitate charge transfer processes at the HTL/active layer interface.

Finally, device fabrication was completed by thermally evaporating a 100 nm thick Al electrode onto the active layer, followed by encapsulation with epoxy. A schematic of the full fabrication process is shown in Figure 3. For comparison, reference organic solar cells were also prepared using only a CuSCN layer as the hole transport layer (HTL), with the CuSCN thickness fixed at 50 nm in both device configurations. The current–voltage (I–V) characteristics and the corresponding photovoltaic parameters of the fabricated devices are presented in Figure 4 and summarized in Table 1.

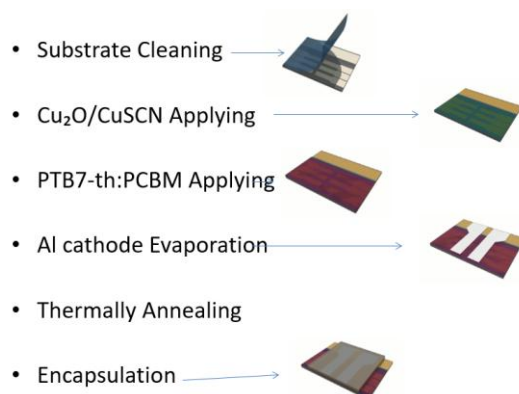


Figure 3. Schematic illustration of the fabrication process of organic solar cells

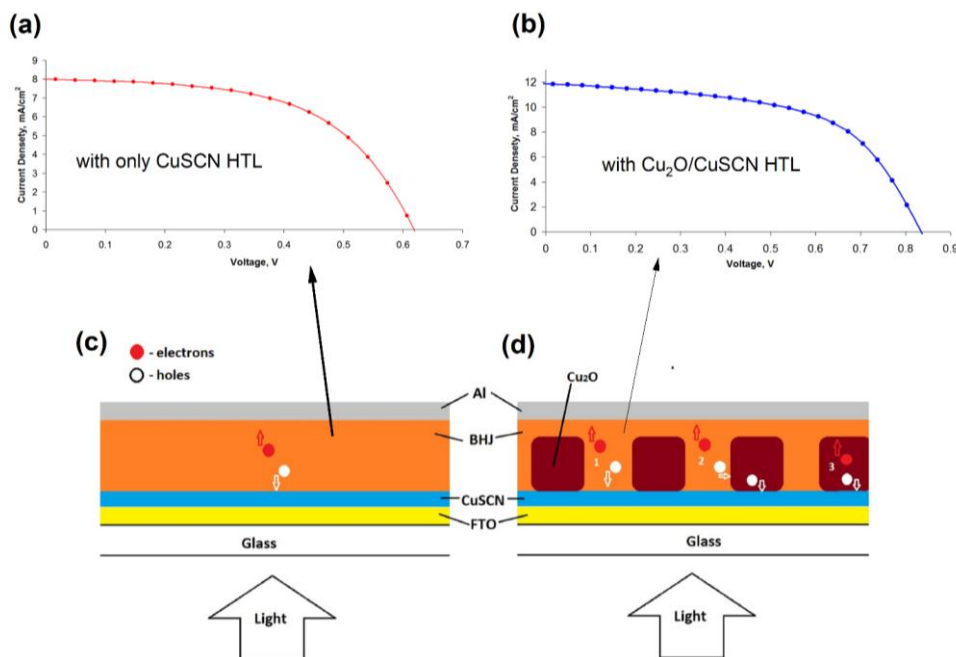


Figure 4. Schematic current–voltage characteristics of organic solar cells (OSCs) incorporating (a) CuSCN and (b) nanoarrayed $\text{Cu}_2\text{O}/\text{CuSCN}$ composite hole transport layers; and mechanism of charge carrier separation in OSCs: (c) one-dimensional (1D) injection in conventional OSCs based on CuSCN, and (d) two-dimensional (2D) injection in the developed OSC with nanoarrayed $\text{Cu}_2\text{O}/\text{CuSCN}$ HTL

Table 1

Photovoltaic parameters of the fabricated devices

Device	Voc, V	Jsc, mA/cm ²	Fill Factor	PCE, %
With CuSCN HTL	0.62	7.99	56.1	2.76±0.05
With nanoarrayed Cu ₂ O/CuSCN HTL	0.84	11.8	56.4	5.59±0.05

As shown in the I–V characteristics, replacing the planar CuSCN HTL with the nanoarrayed Cu₂O/CuSCN composite markedly improves device performance. The open-circuit voltage (Voc) increases from 0.62 V to 0.84 V ($\approx +35.5\%$), the short-circuit current density (Jsc) increases from 7.99 mA·cm⁻² to 11.8 mA·cm⁻² ($\approx +47.7\%$), and the power conversion efficiency (PCE) rises from 2.76 % to 5.59 % ($\approx +102.5\%$, i.e., roughly doubled). The fill factor remains essentially unchanged (56.1 $\rightarrow$ 56.4), indicating that the series resistance is not substantially increased by the nanoarrayed layer.

These performance enhancements can be attributed to the nanoarrayed Cu₂O/CuSCN morphology, which establishes efficient two-dimensional (2D) pathways for hole transport. The vertically oriented Cu₂O nanocrystals increase the interfacial contact area with the PTB7-th: PCBM active layer and introduce additional channels for hole extraction into the HTL. As a result, the average lateral distance that holes must travel within the active layer is reduced, decreasing recombination losses and improving charge collection efficiency, as reflected in the significant increase in Jsc. The higher Voc is likely due to improved energy level alignment and suppressed interfacial recombination at the donor/HTL interface provided by the composite structure. Collectively, enhanced charge collection (higher Jsc) and reduced recombination (higher Voc) account for the approximately twofold increase in PCE.

In our previous article the electrodeposition and detailed characterization of Cu₂O, CuSCN, and Cu₂O/CuSCN composite thin films were systematically explored with the aim of developing efficient hole-transport layers for organic solar cells. Careful optimization of electrochemical parameters—such as applied potential, current density, pH, and temperature—enabled precise tuning of the films' morphology, crystallinity, and interfacial properties [15].

Potentiostatic and galvanostatic investigations of Cu₂O electrodeposition revealed that the structural and morphological properties of the films are strongly dependent on the deposition regime. Well-defined cubic grains with a preferred orientation (111) were obtained under conditions of high pH (12) and moderate potentials (Fig. 5), whereas deviations from these parameters resulted in rougher surfaces and the partial formation of secondary phases [15]. An increase in deposition temperature led to smoother and denser films, reflecting enhanced ion mobility and thermally driven grain reorganization.

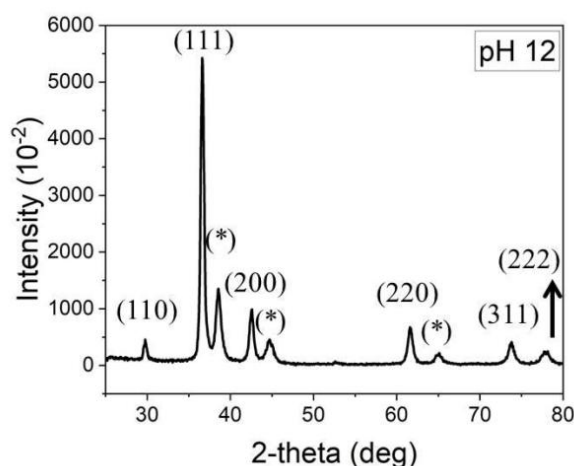


Figure 5. XRD spectra of Cu₂O thin films grown by potentiostatic electrochemical deposition [15]

For electrodeposited CuSCN films, the choice of complexing agent (EDTA or DEA) was found to significantly influence film uniformity and grain size [15]. Films prepared from EDTA-based electrolytes (CuSCN-E) exhibited smoother and more homogeneous morphologies, making them more suitable as hole-transport layers. These films also served as effective templates for subsequent Cu₂O deposition, enabling the formation of high-quality Cu₂O/CuSCN bilayer composites with well-defined interfaces.

Photoelectrochemical measurements further confirmed the enhanced interfacial performance of the Cu₂O/CuSCN heterostructures, demonstrating approximately a twofold increase in photocurrent density compared to single-layer Cu₂O films. This enhancement is attributed to favorable band alignment and more efficient hole extraction across the heterojunction [15].

Finally, nanoarrayed Cu₂O/CuSCN composite films were successfully implemented as hole-transport layers in PTB7-th: PCBM-based organic solar cells. The introduction of Cu₂O nanocrystal arrays led to a significant improvement in device performance, doubling the power conversion efficiency (from 2.76 % to 5.59 %) as a result of enhanced charge extraction and reduced recombination losses. The nanoarray architecture provides multiple lateral pathways for hole transport, promoting more efficient coupling between the active layer and the HTL.

Overall, the results presented in this chapter highlight electrodeposition as a versatile and controllable technique for the fabrication of high-quality Cu₂O/CuSCN heterostructures. These nanoarrayed composites demonstrate strong potential as efficient, stable, and scalable hole-transport layers for next-generation organic and hybrid photovoltaic devices.

Conclusion

In this work, Cu₂O, CuSCN, and Cu₂O/CuSCN composite thin films were fabricated by electrodeposition, and a two-step deposition approach combining galvanostatic nucleation and potentiostatic growth was applied to form nanoarrayed Cu₂O structures on CuSCN layers. This method enabled the preparation of heterostructured films with controlled morphology and good interfacial contact between the layers.

The incorporation of nanoarrayed Cu₂O/CuSCN structures as hole-transport layers in PTB7-Th: PC₆₁BM-based organic solar cells resulted in improved device performance compared to reference devices based on planar CuSCN. In particular, increases in open-circuit voltage and short-circuit current density were observed, leading to an enhancement of power conversion efficiency from 2.76 % to 5.59 %. These results indicate that the modified HTL structure can contribute to more efficient charge extraction.

The observed improvement in device performance is attributed to the increased interfacial contact area and the presence of additional pathways for hole transport provided by the nanoarrayed structure. This may reduce the average transport distance of charge carriers within the active layer and contribute to more effective charge collection.

Overall, the results demonstrate that electrodeposited Cu₂O/CuSCN nanoarrayed structures are a promising approach for modifying hole-transport layers in organic solar cells. Further work is required to systematically optimize the deposition parameters and to perform more detailed structural and electrical characterization in order to fully understand the mechanisms governing the observed improvements.

Acknowledgments

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Жоғары тиімді органикалық күн батареяларына арналған Cu₂O/CuSCN наноөлшемді массивті кемтіктерді тасымалдау қабаттары

Органикалық күн батареялары дәстүрлі фотовольтаикалық технологияларға перспективалы, арзан әрі оңтайлы балама, алайда олардың тиімділігі әлі де заряд тасымалының тиімсіздігімен және рекомбинация шығындарымен шектеледі. Жұмыста екі сатылы электрлік тұндыру процесі арқылы алынған Cu₂O/CuSCN гетероқұрылымдарына негізделген жаңа наноөлшемді массивті кемтіктерді тасымалдау қабаты (HTL) ұсынылған. Тік бағытталған Cu₂O нанокристалдары CuSCN қабықшаларының үстінде өсіріліп, жақсартылған фазалар аралық байланысы бар және тасымалдаушылардың жүріп өтетін қашықтығы қысқартылған екі өлшемді зарядтарды бөліп алу құрылымын қалыптастырды. Қабықшалардың морфологиясы мен қасиеттері электрхимиялық параметрлерді бақылау арқылы жүйелі түрде реттелді, бұл айқын анықталған нано архитектураларды қалыптастыруға мүмкіндік берді. Фотоэлектрхимиялық өлшеулер композиттік құрылымдарда бірқабатты үлгілермен салыстырғанда фазааралық фототоктың жақсарғанын және кемтіктердің неғұрлым тиімді бөлініп алынатынын көрсетті. PTB7-Th: PCBM негізіндегі органикалық күн батареяларына енгізілген кезде наноөлшемді массивті HTL құрылғылардың сипаттамаларын айтарлықтай жақсартты: ашық тізбектегі кернеу (0,62-ден 0,84 В-қа дейін), қысқа тұйықталу тогының тығыздығы (7,99-дан 11,8 мА·см⁻²-қа дейін) және энергияны түрлендіру тиімділігі (2,76 %-дан 5,59 %-ға дейін) артты. Бұл жақсартулар рекомбинацияның азаюы мен және массивтің наноархитектурасының арқасында зарядтарды неғұрлым тиімді жинаумен түсіндіріледі. Бұл зерттеу жетілдірілген кемтіктерді тасымалдау қабаттарын жасауға арналған ауқымдалатын, төмен температуралы стратегияны көрсетеді және жаңа буын органикалық әрі гибриді күн батареялары үшін Cu₂O/CuSCN наноөлшемді гетероқұрылымдарының әлеуетін айқындайды.

Кілт сөздер: органикалық күн батареялары, мыс тиоцианатының қабықшалары, PTB7-Th: PCBM, Cu₂O нанокристалдары, электрлік тұндыру, көлемдік гетероқосылыс, кемтіктерді тасымалдау қабаты, заряд тасымалы

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Наноразмерные массивные слои переноса дырок $\text{Cu}_2\text{O}/\text{CuSCN}$ для высокоэффективных органических солнечных элементов

Органические солнечные элементы представляют собой многообещающую недорогую и гибкую альтернативу традиционным фотовольтаическим технологиям, однако их эффективность по-прежнему ограничена неэффективным транспортом зарядов и потерями на рекомбинацию. В данной работе мы представляем новый наноразмерный массивный слой переноса дырок (HTL), основанный на гетероструктурах $\text{Cu}_2\text{O}/\text{CuSCN}$, полученных с помощью двухэтапного процесса электроосаждения. Вертикально ориентированные нанокристаллы Cu_2O были выращены на пленках CuSCN , формируя двумерную структуру извлечения зарядов с улучшенным межфазным контактом и сокращёнными расстояниями переноса носителей. Морфология и свойства плёнок систематически настраивались путём контроля электрохимических параметров, что позволило сформировать хорошо определённые наноструктуры. Фотоэлектрохимические измерения показали улучшенный межфазный фототок и более эффективное извлечение дырок в композитных структурах по сравнению с однослойными аналогами. При интеграции в органические солнечные элементы на основе PTB7-th: PCBM наноразмерный массивный HTL значительно улучшил характеристики устройств, увеличив напряжение холостого хода (с 0,62 до 0,84 В), плотность тока короткого замыкания (с 7,99 до 11,8 $\text{mA}\cdot\text{cm}^{-2}$) и коэффициент преобразования энергии (с 2,76 % до 5,59 %). Эти улучшения обусловлены снижением рекомбинации и более эффективным сбором зарядов благодаря наноструктуре массива. Данное исследование демонстрирует масштабируемую низкотемпературную стратегию создания усовершенствованных слоёв переноса дырок и подчёркивает потенциал наноразмерных гетероструктур $\text{Cu}_2\text{O}/\text{CuSCN}$ для солнечных элементов нового поколения — как органических, так и гибридных.

Ключевые слова: органические солнечные элементы, плёнки тиоцианата меди, PTB7-Th: PCBM, нанокристаллы Cu_2O , электроосаждение, объемный гетеропереход, слой переноса дырок, перенос заряда

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Time-resolved photoluminescence of ZnSe and ZnSe:Te single crystals

This study examines the time-resolved photoluminescence spectra of zinc selenide (ZnSe) single crystals, both undoped and doped with the isovalent tellurium impurity, at 83 K, together with their steady-state photoluminescence spectra. The ZnSe crystals were excited using a nitrogen laser with a wavelength of 347 nm. In the steady-state photoluminescence spectra of undoped ZnSe, three emission bands were observed, with maxima at approximately 443, 458, and 610 nm. Time-resolved luminescence spectroscopy made it possible to resolve the 610 nm band into two components, with maxima near 580 and 640 nm. In the steady-state spectra of tellurium-doped ZnSe crystals, three emission bands were also detected, with maxima at approximately 450, 505, and 640 nm. Time-resolved photoluminescence spectra allowed the 505 nm band to be resolved into two components, with maxima near 485 and 510 nm. The intensity of the red emission band at 640 nm increases with increasing tellurium concentration. It is hypothesized that this red photoluminescence band is associated with an intracentric transition of an associative defect involving a zinc vacancy, an interstitial zinc atom, and a tellurium atom substituting for selenium. Considering the presence of an uncontrolled aluminium impurity in the crystals, an alternative interpretation is also possible: the 640 nm band may originate from an intracentric transition within a defect complex comprising a zinc vacancy, an aluminium atom substituting for zinc, and a tellurium atom substituting for selenium.

Keywords: isovalent impurity, complex of defects, bound exciton, intracentric transition, vacancy, substitution, afterglow time, emission band

Introduction

Zinc selenide (ZnSe) is known for a number of properties, such as a high probability of radiative recombination due to direct optical transitions, a high photoluminescence quantum yield, and high photosensitivity which make it attractive for optoelectronic applications. It is a semiconductor material with high transparency in the infrared region and excellent optical properties.

ZnSe is used in several key areas, one of the most important being infrared optics. Components fabricated from ZnSe include lenses, laser windows, protective optical elements, and focusing systems for CO₂ lasers. The material transmits radiation over a wide spectral range (approximately 0.5 to 20 μm), making it suitable for high-power infrared lasers and thermal imaging systems. ZnSe is also widely used in thermal imaging cameras, night vision devices, pyrometers, and infrared spectrometers.

The properties of ZnSe crystals that undergo technological processing and are used in optoelectronic devices strongly depend on the characteristics of the initial crystals, including their background impurity content and intrinsic defects. Defects present in the material can give rise to localized electronic states within the band gap of the semiconductor, which act as recombination centers. Recombination involving these centers may be either radiative or non-radiative.

Due to intense luminescence of zinc selenide in the visible spectral range, its radiative properties have long been the subject of extensive research. However, the interpretation of luminescence spectra of both self-activated and impurity-doped ZnSe remains highly controversial. Time-resolved luminescence spectroscopy makes it possible to distinguish individual emission bands within the overall spectral profile, each characterized by different decay times.

In [1], low temperature ($T = 4.2$ K) time-resolved photoluminescence spectra were studied for initial ZnSe crystals purified by zone sublimation, as well as for crystals annealed in liquid zinc and bismuth. In addition to the near band-edge emission lines, a broad green photoluminescence band with a maximum at

approximately 520 nm (2.38 eV) and a relatively long decay time (on the order of 1 μ s) was observed in the initial crystals. This band disappeared after annealing in liquid zinc and bismuth.

The aim of the present work is to clarify the nature of the centers responsible for ZnSe emissions in the 500–700 nm spectral region.

Experimental

To investigate photoluminescence spectra in the visible range, we prepared ZnSe single-crystal samples similar to those studied in [1]. These were large-block ZnSe single crystals of the sphalerite structure, grown from the melt under pressure without intentional doping. The crystals exhibited a dark resistivity on the order of $10^{12} \Omega \cdot \text{cm}$ and *n*-type conductivity with an electron concentration of approximately 10^7 cm^{-3} .

Plate-shaped samples with parallel faces and a thickness of 1–3 mm were obtained from these crystals by cleavage along the (110) plane.

In [2], secondary ion mass spectrometry (SIMS) revealed the presence of background impurities in similarly prepared ZnSe samples, including aluminum, manganese, iron, indium, chromium, and tellurium, with concentration on the order of 10^{17} cm^{-3} .

To clarify the nature of certain emission bands, additional samples doped with an isovalent tellurium impurity were also prepared.

A pulsed nitrogen laser (LGI-21) with a wavelength of 337 nm was used as the excitation source for photoluminescence. The laser operated with pulse duration of 10 ns, pulse energy of 30 μ J, and a repetition rate of 100 pulses per second. Photoluminescence spectra were recorded at a temperature of $T = 83 \text{ K}$.

The experimental setup for time-resolved photoluminescence spectroscopy allowed variation of the detection time window from 0.2 ns to 40 μ s, as well as shifting of this window by up to 100 ms relative to the excitation pulse.

Results and Discussion

Figure 1 shows the emissions spectrum of the initial ZnSe sample at a temperature of 83 K. The photoluminescence spectrum is dominated by a broad long-wavelength band with a maximum at approximately 610 nm (2.03 eV). In addition, emission bands with maxima at 443 nm (2.80 eV) and 458 nm (2.71 eV) are observed.

It is most likely that the band at 443 nm is associated with radiative recombination of free excitons [3], while the 458 nm band can be attributed to bound excitons [4].

Time-resolved luminescence spectroscopy of the same initial ZnSe crystals showed that, at delay times ranging from 0 to several hundred nanoseconds, the shape of the long wave-length band with a maximum near 610 nm changes. At a delay time of 500 ns, two distinct maxima appear in the spectrum at 580 nm (2.14 eV) and 640 nm (1.94 eV) (Fig. 2).

The orange emission band with a maximum at 580 nm is commonly attributed to donor-acceptor pair recombination involving deep acceptor states (such as zinc vacancies, interstitial zinc, and impurity centers) [5].

Given the presence of a background manganese impurity in the studied samples, it can also be suggested that the 580 nm band is related to an intracenter transition of manganese ions [6].

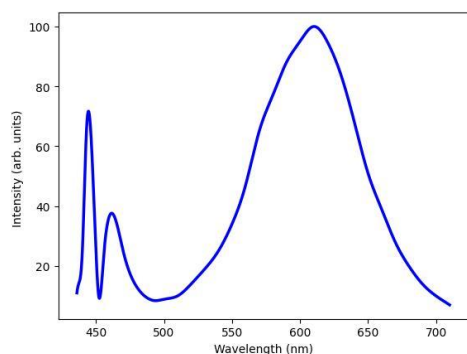


Figure 1. Photoluminescence spectrum of ZnSe with background impurities at $T = 83 \text{ K}$

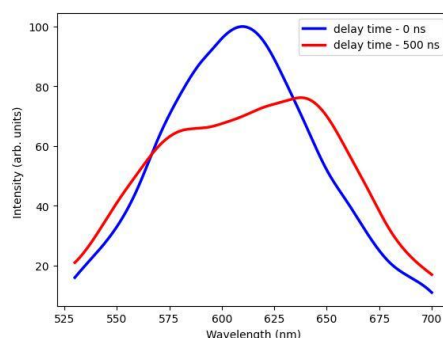


Figure 2. Red photoluminescence band of ZnSe at different delay times 0 ns (blue line) and 500 ns (red line)

The long-wavelength emission band with a maximum in the range of 615–645 nm is commonly described in the literature as non-elementary and is associated with complexes involving zinc vacancies and impurity atoms that give rise to both acceptor and donor levels [3, 7–9].

The authors of [10] proposed a structural model for the centre responsible for the luminescence band at 630 nm, suggesting a complex defect consisting of an isoelectronic substitution (such as selenium, oxygen, or tellurium) located in the vicinity of a zinc vacancy.

In [11], red emission in the 646–662 nm range is attributed to Frenkel-type defects of the form $\text{O} = \text{Cr}_i^{2+} + \text{V}_{\text{Zn}}$, where Cr^{2+} occupies an interstitial position at a chromium concentration of approximately $2 \times 10^{18} \text{ cm}^{-3}$.

It should be noted that the emission band near 640 nm observed in the present study is characterized by a relatively long decay time (on the order of several nanoseconds). A similar decay time was reported in [1], where it was also shown that the intensity of this band decreases after annealing the samples in liquid zinc and liquid bismuth. Such annealing processes are known to reduce the concentration of zinc vacancies.

We proposed that the luminescence band near 640 nm originates from an intracenter transition of a defect complex $(\text{V}_{\text{Zn}} - \text{Zn}_i - \text{TeSe})^-$ from an excited state to the ground state. To clarify the nature of this band, we investigated photoluminescence spectra of ZnSe crystals doped with an isovalent tellurium impurity.

Figure 3 shows the photoluminescence spectrum of ZnSe crystals at 83 K with tellurium concentrations of approximately 0.5 % and 1 %. Three emission bands with maxima at 450 nm, 505 nm, and 640 nm are observed in the spectra. With increasing tellurium concentration, the intensities of the 450 nm and 505 nm bands decrease, while the intensity of the 640 nm band increases.

Time-resolved photoluminescence measurements made it possible to resolve the 505 nm band into two components with maxima at approximately 485 nm and 510 nm (Fig. 4). Thus, four emission bands — 450 nm, 485 nm, 510 nm, and 640 nm were identified in Te-doped ZnSe crystals.

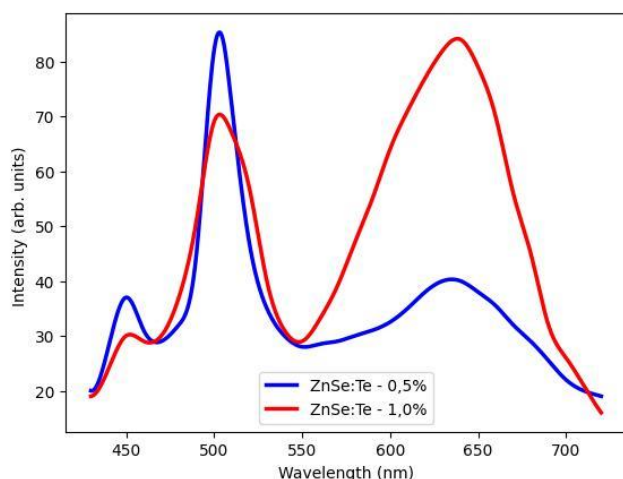


Figure 3. Photoluminescence spectra of ZnSe:Te crystals with tellurium concentrations of 0.5 % (blue line) and 1.0 % (red line)

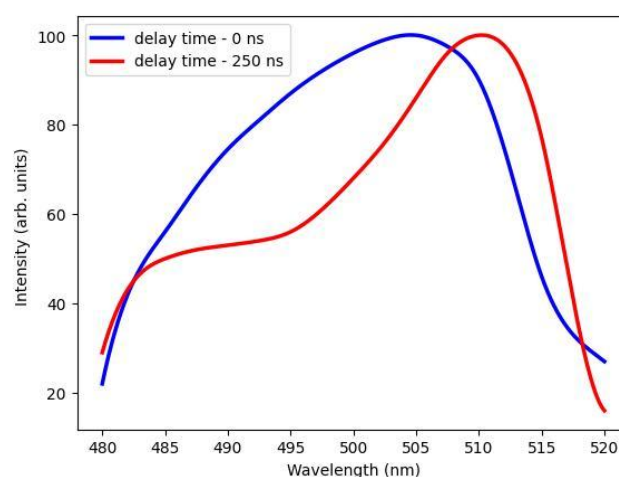


Figure 4. 505 nm emission band of ZnSe:Te recorded at different delay times: 0 ns (blue line), 250 ns (red line)

The increase in the intensity of the 640 nm band with increasing tellurium concentration suggests that tellurium is involved in the formation of this emission band. The relatively long decay time, which coincides with that of the 640 nm band observed in nominally undoped ZnSe crystals, supports the identification of these bands as originating from the same center.

As shown in [1], the intensity of the 640 nm band decreases after annealing in liquid zinc and liquid bismuth, conditions under which zinc vacancies are expected to be reduced. Upon increasing the measurement temperature from 83 K to 300 K, the spectral position of the 640 nm band remains unchanged. Taken together, these observations provide strong support for assigning this band to an intracenter transition within a complex vacancy-impurity defect.

Since the as-grown ZnSe crystals contain background aluminum impurities, it is reasonable to assume that aluminum may act as a donor in the complex centre, replacing the zinc vacancy; in this case, the defect can be written as $(\text{V}_{\text{Zn}} - \text{Al}_{\text{Zn}} - \text{TeSe})^-$ instead of $(\text{V}_{\text{Zn}} - \text{Zn}_i - \text{TeSe})^-$.

The emission band with a maximum at 450 nm is most likely a red-shifted counterpart of the 443 nm band previously observed in nominally undoped crystals, with the shift arising from the increased tellurium concentration.

The emission bands with maxima at 485 nm and 510 nm are most plausibly attributed to recombination via a donor level and an acceptor level associated with a zinc vacancy [3, 8, 12].

Conclusion

Time-resolved photoluminescence measurements of ZnSe single crystals at $T = 83$ K revealed that the broad emission band centered at 610 nm contains two distinct components with maxima at 580 nm and 640 nm. In addition, the 505 nm emission band observed in Te-doped ZnSe crystals was resolved into two bands at 485 nm and 510 nm.

Based on the obtained results and analysis of the available literature data, it is proposed that the 640 nm (1.94 eV) emission band originates from intracenter transitions and is associated with the presence of an isovalent tellurium impurity in ZnSe crystals, incorporated into a complex defect of the type $(V_{Zn}-Al_{Zn}-Te_{Se})^-$ or $(V_{Zn}-Zn_{Te}-Te_{Se})^-$.

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ZnSe және ZnSe:Te монокристалдарының уақыт бойынша ажыратылған фотолюминесценциясы

Жұмыста арнайы легирленбеген және теллурдың изовалентті қоспасымен легирленген мырыш селениді монокристалдарының $T = 83$ К температурасындағы уақыт бойынша ажыратылған фотолюминесценция спектрлері мен кәдімгі фотолюминесценция спектрлері қарастырылды. ZnSe кристалдарының сәулеленуі толқын ұзындығы 337 нм болатын азот лазерімен қоздырылды. Легирленбеген ZnSe кристалдарының кәдімгі фотолюминесценция спектрлерінде максимумдары шамамен 443 нм, 458 нм және 610 нм болатын үш сәулелену жолағы байқалды. Уақыт бойынша ажыратылған люминесценттік спектроскопия әдісі 610 нм жолағын максимумдары шамамен 580 нм және 640 нм болатын екі құрамдас жолаққа бөлуге мүмкіндік берді. Теллурмен легирленген мырыш селениді кристалдарының кәдімгі фотолюминесценция спектрлерінде де максимумдары шамамен 450 нм, 505 нм және 640 нм болатын үш сәулелену жолағы анықталды. Уақыт бойынша ажыратылған фотолюминесценция спектрлері 505 нм жолағынан максимумдары шамамен 485 нм және 510 нм болатын екі жолақты бөліп көрсетуге мүмкіндік берді. 640 нм аймағындағы қызыл сәулелену жолағының қарқындылығы теллур концентрациясының артуымен өсетіні анықталды. Бұл қызыл фотолюминесценция жолағы селен атомын алмастырған теллур атомының, мырыш вакансиясының және түйінаралық кеңістіктегі мырыш атомының қатысуымен түзілетін ассоциативті ақаудың ішкіорталықтық ауысуымен байланысты деген болжам ұсынылды. Кристалдарда бақыланбайтын алюминий қоспасының болуын ескере отырып, 640 нм жолағын мырыш вакансиясын, мырыш орнын басқан алюминий атомын және селен орнын басқан теллур атомын камтитын ақаулар кешеніндегі ішкіорталықтық ауысу ретінде түсіндіру де мүмкін.

Кілт сөздер: изовалентті қоспа, ақаулар кешені, байланысқан экситон, ішкіорталықтық ауысу, вакансия, орын басу, кейінгі жарқырау уақыты, сәулелену жолағы

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Разрешённая во времени фотолюминесценция монокристаллов ZnSe и ZnSe:Te

В работе рассмотрены спектры фотолюминесценции, разрешенные во времени, монокристаллов селенида цинка без специального легирования и легированных изовалентной примесью теллура при температуре $T = 83$ К и обычные спектры. Излучение кристаллов ZnSe возбуждалось азотным лазером с длиной волны 337 нм. На обычных спектрах фотолюминесценции нелегированных ZnSe наблюдались три полосы излучения с максимумами около 443 нм, 458 нм и 610 нм. Метод временной люминесцентной спектроскопии позволил из полосы 610 нм выделить две с максимумами около 580 нм и 640 нм. В обычных спектрах фотолюминесценции кристаллов селенида цинка, легированных теллуром, присутствовали три полосы излучения с максимумами около 450 нм, 505 нм и 640 нм. Разрешённые во времени спектры фотолюминесценции из полосы 505 нм выделили две с максимумами около 485 нм и 510 нм. Интенсивность красной полосы излучения 640 нм увеличивается с увеличением концентрации теллура. Выдвинута гипотеза, что красная полоса фотолюминесценции 640 нм обусловлена внутрицентровым переходом ассоциативного дефекта с участием вакансии цинка, цинка в междоузлии и теллура, замещающего селен. С учётом присутствия в кристаллах неконтролируемой примеси алюминия, также возможна интерпретация полосы 640 нм как внутрицентральной переход комплекса дефектов, включающего вакансию цинка, алюминий, замещающий цинк, и теллур, замещающий селен.

Ключевые слова: изовалентная примесь, комплекс дефектов, связанный экситон, внутрицентральной переход, вакансия, замещение, время послесвечения, полоса излучения

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Study of the Features and Properties of Greens Functions of Macroscopic Quantum Systems

This article is devoted to the theoretical investigation of processes in macroscopic systems based on wave-particle duality and quantum statistical distributions using the Green's function method. In particular, it provides a detailed description of the properties and characteristics of the Green's function for an ideal Fermi liquid, single- and two-particle Green's functions, as well as Green's functions at limiting temperatures and for the Dirac and Schrödinger equations. The study analyzes the application of the Green's function method to processes in many-particle quantum systems and to solving equations that describe the constituent particles of such systems. For a given operator and set of boundary conditions, a Green's function can be defined, allowing the solution of the corresponding equation to be expressed in integral form. A distinctive feature of this method is the application of mathematical-physics tools, such as Fourier methods, integral transforms, special functions, and mathematical analysis, to problems in quantum physics governed by the principles of quantum and statistical mechanics. The relevance of this study stems from the application of the Green's function method to the analysis of quantum phenomena. This approach is considered one of the effective methods for solving partial differential equations describing various physical processes. It involves transforming the original differential equation into an equivalent integral equation involving Green's functions, which can then be solved. The transformation involves passing to the momentum representation and applying Fourier transforms using methods of complex analysis.

Keywords: Fermi liquid, Fourier transform, momentum representation, macroscopic system, Green's function, integral equation

Introduction

Quantum liquids, first discovered in 1938 by P. Kapitsa and J.F. Allen, represent macroscopic systems governed by quantum effects (such as energy quantization, wave-particle duality, and quantum statistical distributions). In quantum mechanics, it is possible to describe the states of individual particles and their interactions; however, in quantum liquids containing a large number of particles, these particles cannot be considered independently. Their quantum properties manifest only through collective processes. Superfluid helium-4 and Fermi liquids formed by fermions at low temperatures are among the primary objects of study in hydrodynamics, and their nature fully satisfies the criteria of quantum liquids. In such media, macroscopic quantum phenomena predominantly occur. Electrons in metals and semiconductors, excitons in dielectrics, and nucleons in atomic nuclei can also be treated as quantum liquids.

In 1830, the British mathematician George Green, while solving inhomogeneous boundary value problems in electrostatics and heat conduction, introduced the functions that now bear his name and established the foundations of their theoretical framework. These functions, which serve as a fundamental mathematical tool in mathematical physics, were further developed throughout the 20th century and significantly simplified the solution of linear inhomogeneous differential equations with boundary conditions in electrodynamics, quantum field theory, and scattering theory. In particular, in quantum field theory, Green's functions describe the probability amplitude for a transition from one point in space-time to another, whereas in scattering theory they characterize particle scattering by various objects. In the theory of fluctuations, Green's functions also facilitate the construction of Feynman diagrams for different quantum processes.

At the same time, Green's functions in quantum liquids serve as a powerful mathematical framework for describing many-body systems. They make it possible to evaluate the influence of external perturbations on a system, analyse its response to such perturbations, and determine its thermodynamic and dynamic properties, thereby providing information about both equilibrium and non equilibrium states. In addition, Green's functions are widely used to calculate physical quantities such as density, correlation functions, and quasiparticle spectra. Problems related to finite temperature in Fermi liquids are addressed using temperature-dependent Green's functions that incorporate thermal effects. Meanwhile, processes involving the motion of a single particle among many others are described using single-particle Green's functions, whereas two-particle Green's functions characterize correlations between particles. Considering liquid helium at low temperatures as a quantum liquid makes it possible to establish theoretical principles and conditions for applying Green's function methods to the study of thermodynamic and dynamic properties of interacting quantum systems. This approach enables the calculation of single-particle and many-particle correlation functions, the determination of thermodynamic spectra, and the analysis of the relationship between microscopic interactions and macroscopic properties. The main subject of investigation is quantum liquids whose properties are governed by quantum effects. In this context, the study addresses the following key problems: many-body quantum systems, the concept of quantum liquids, neutral Fermi liquids and their equilibrium properties, as well as kinetic equations for quasiparticles in Fermi liquids.

When studying quantum liquids using Green's functions, it becomes possible to account for particle interactions within the liquid. This approach allows one to determine the Green's function corresponding to a specific operator and boundary conditions. Using this function, the solution of the equation describing the liquid can be expressed in an integral form. In solving such problems of quantum macrophysics, which are based on the principles of quantum mechanics and statistical mechanics, various mathematical methods are employed, including Fourier methods, integral transform techniques, special functions, and methods of mathematical analysis. In addition, the following mathematical tools of mathematical physics are widely used: partial differential equations, integral equations, functional analysis, and probability theory. Variational methods also play an important role in the study, as they are used to determine stationary states of physical systems.

A brief review of recent scientific studies relevant to the topic of this paper can be summarized as follows. In [1–3], a comprehensive theoretical study of radio-frequency spectra of a two-component Fermi gas with balanced populations in the normal phase of the temperature–interaction phase diagram was carried out. Analytical results were also obtained for determining the shape and width of radio-frequency spectra within relevant temperature and interaction regimes. In [4], the problem of determining the Green's function for the stationary Schrödinger equation was considered within the framework of the potential quantization method. An expression for Green's functions in terms of eigenfunctions and eigenvalues was derived, and the equivalence between this approach and the traditional method was demonstrated. Studies [3, 4] present an independent review of the theory of quantum melting mediated by dislocations at zero temperature in two spatial dimensions. A one-dimensional gas of spinful fermions interacting via an attractive δ -function potential was also examined using the Bethe ansatz solution. In [5–7], the application of the Bogoliubov–Tyablikov two-time Green's function method to the many-electron theory of metals is discussed within strongly correlated models, such as the Hubbard model and the Vonsovskiy exchange model. Issues such as atomic representations of electronic states, the metal–insulator transition, incoherent states, and the Kondo effect are analysed. The criterion for ferromagnetism in systems of strongly correlated electrons has been analysed, and it is shown to differ fundamentally from the conventional condition. Based on the analysis of radiative recombination spectra of two-dimensional electrons with photoexcited holes bound to remote acceptors, the dependence of the quasiparticle Fermi energy on electron density has been investigated. The dependence of the renormalized quasiparticle mass on the concentration of two-dimensional electrons has been measured. It has been shown that, in a perpendicular magnetic field, the quasiparticle concept in a two-dimensional Fermi liquid remains valid not only near the Fermi surface but also deep below it, down to the bottom of the size-quantization subband, since the excitation broadening is significantly smaller than their energy [8]. In a one-dimensional gas of spin-1/2 fermions interacting via a repulsive δ -function potential of arbitrary strength is considered. For the case where all fermions except one have spin up, the time-dependent two-point correlation function of the spin-down fermion is calculated. This impurity Green's function is represented in the thermodynamic limit as an integral over Fredholm determinants of integrable linear integral operators. The problem of integer and fractional quantum Hall resistance within a unified framework of mathematical physics has remained an unresolved issue over the past four decades. In this approach, the quantum Hall liquid is

modelled as a membrane of electron fluid flowing around magnetic fluxes. The trajectories of fractional quantum Hall states lie along the edge surface of the cross-section of a folded membrane, which is spontaneously characterized by a lattice of magnetic fluxes in the bulk zone. This topological representation provides an alternative way for the realization of string theory concepts and topological quantum computation through the folding of a laminar quantum liquid. For a system to be considered a quantum liquid, quantum statistical effects must be present in addition to quantum mechanical effects [9]. An unexplored dynamical condition for the manifestation of quantum statistical effects is considered, where particle exchange events in a gas-like hydrodynamic regime are treated as a dynamical process characterized by an intrinsic time scale. Subsequently, quantitative criteria for particle indistinguishability and the associated quantum statistics are proposed, which are effective over short time scales and manifest over longer times. A quantum critical point is identified, and hypotheses regarding the formation of complex quasiparticle condensates are proposed. In [10–12], phenomena arising in fermions in optical lattices at low temperatures under an external magnetic field are investigated. By tuning the field, the attractive interaction between any two fermions can be made arbitrarily strong, leading to the formation of composite bosons via so-called Feshbach resonances. At sufficiently low temperatures, a critical temperature is determined at which these composite bosons undergo Bose–Einstein condensation, resulting in the formation of massive fermions. A quantum critical point is identified, and hypotheses regarding the formation of complex quasiparticle condensates are proposed. Quantum-critical behaviour induced by a presumed quantum phase transition separating the d-wave superconducting state is investigated in detail. Within the framework of the renormalization group approach, a phenomenological effective theory based on the Landau–Ginzburg–Wilson theory is employed, and one-loop calculations are performed to construct a consistent set of coupled interaction parameters [11]. A coupled fermion–boson system in spatial dimensions is investigated, and a new fixed point for a non-Fermi liquid is identified [13].

The peculiarity of describing macro systems using Green’s functions is that they reduce complex multi-particle problems to the search for single-particle responses. This allows for the accurate consideration of particle statistics (Bose or Fermi) and their interactions, representing the physical properties of the system through integral equations. The Green’s function acts as a “propagator” that describes the probability of a particle added to the system at one point being detected at another point after some time. If Green’s functions in quantum field theory describe the probability of passage between points in space-time, then in scattering theory they were able to analytically explain the scattering of particles from various objects. At the same time, in the theory of perturbations, Green’s functions also helped to construct Feynman diagrams for various quantum processes, and Green’s functions for quantum fluids were used as a mathematical tool for describing the properties of many-body systems. In short, with the help of these functions, it was possible to systematically evaluate the influence of external influences on the system, the behavior of the system in relation to this influence, and to analytically consider the thermodynamic and dynamic properties of the system. It was possible to obtain accurate information from the conditions of the system in equilibrium and non-equilibrium states. Today, Green’s functions are successfully used in calculating important quantities such as density, correlation functions, quasiparticle spectra, etc. While problems related to the temperature of a Fermi liquid are solved using temperature Green’s functions that take into account thermal effects, and problems related to the motion of an individual particle between other particles are solved using single-particle Green’s functions, two-particle Green’s functions can determine the correlation between two particles. All key thermodynamic and kinetic properties are expressed through the Green’s function: density of states, binding energies, conductivity, magnetic susceptibility, and excitation spectra. The interaction of particles is taken into account by summing up infinite perturbation theory series using Feynman diagrams. The Green’s function acts as a “propagator”—the probability that a particle will move from one point to another, interacting with its surroundings.

In the present work, the features and properties of Green’s functions for an ideal Fermi liquid are examined in detail, including single-particle and two-particle Green’s functions, as well as Green’s functions at limiting temperatures and for the Dirac and Schrödinger equations. The application of Green’s function methods to processes occurring in many-body quantum systems and to the solution of equations describing particles forming such systems is analysed. For a given operator and boundary conditions, the corresponding Green’s function is determined, and the solution of the equation describing the liquid is expressed in integral form using this function. A distinctive feature of this approach is that, in solving such problems of quantum macrophysics based on the principles of quantum mechanics and statistical mechanics, a combination of mathematical methods is employed, including Fourier methods, integral transform techniques, special func-

tions, and methods of mathematical analysis. The relevance of this study is associated with the application of Green's function methods to quantum phenomena. This approach is considered one of the most effective tools for solving partial differential equations describing various physical processes. In particular, it allows the transformation of a differential equation describing a given phenomenon into an equivalent integral equation incorporating Green's functions, which can then be solved.

The main problem is the calculation of the ideal Fermi-liquid, One-and two-particle Green functions, as well as the limit temperature Green functions, the Green functions of the Dirac and Schrodinger equations. Determining solutions to equations for multi-particle quantum systems by the Green function approach is also one of the most pressing problems. Ways of transition from a differential equation to an integral equation equivalent to this equation were considered and theoretical searches were made in the direction of determining the solution of this equation according to the Green function.

Experimental

Quantum macrophysics can be regarded as a distinct branch of theoretical physics that studies phenomena in solid and liquid phases based on the principles of quantum mechanics, statistical mechanics, and electrodynamics within a many-particle framework. The nature of these phenomena is investigated using appropriate mathematical models. For example, a deeper understanding of the properties of metals requires treating electrons as a Fermi liquid. Since the presence of a crystal lattice complicates the development of a theory of electron liquids, it becomes necessary to establish general principles for homogeneous and isotropic systems. Similarly, superconductivity in metals can be explained using a simplified isotropic model of a superfluid electron liquid. In the study of macromolecules (many-body systems, macroscopic quantum systems), the Green's function method is used to describe the system's response to external influences, calculate thermodynamic properties, and search for excitation spectra (quasiparticles). The method of Green's functions, which depend on imaginary time or temperature, is adapted to describe equilibrium statistical mechanics.

At sufficiently low temperatures (1-2 K), where the de Broglie wavelength associated with the thermal motion of atoms becomes comparable to interatomic distances, macroscopic phenomena in liquids are governed by quantum laws. According to classical theory, all substances should exist in a solid state at absolute zero. However, due to weak interatomic interactions, the liquid isotopes of helium, ^3He and ^4He remain in the liquid state near absolute zero temperature, where quantum phenomena are observed. In such cases, the solid phase becomes energetically less favourable. The method of equations of motion uses the left-hand chain of equations for the Green's functions, where special splitting factors are used to close the system. The concept of Fermi liquids considers systems with strong interactions, such as electrons in metals. The Green's function is used here to justify the concept of quasiparticles.

Results and Discussion

If we consider a macroscopic system composed of particles with half-integer spin within the Heisenberg representation—where wave functions are time-independent and operators f , corresponding to physical observables depend explicitly on time and can be written as follows:

$$f_a(t, \vec{r}) = f_a(\vec{r}) \exp(iHt) \exp(-iHt);$$

$$f_a^*(t, \vec{r}) = f_a^*(\vec{r}) \exp(iHt) \exp(-iHt).$$

Then, the single-particle Green's function of the system can be written as:

$$G_{ab}(Z_1, Z_2) = -i \overline{N f_a(Z_1) f_b^*(Z_2)}.$$

Here, the variables $t, \vec{r}$ are replaced by $t_1, \vec{r}$ and $t_2, \vec{r}$, respectively, and are denoted collectively as Z_1, Z_2 ; N is the time-ordering operator; and the overline indicates averaging over the ground state of the system. In quantum mechanics and quantum field theory, the Green's function is the impulse response of a quantum-mechanical operator (e.g., the Hamiltonian) that describes the propagation of a particle and its response to an external stimulus. When a particle has spin, its wave function is a spinor (magnetic vector), and the Green's function acquires a matrix-spinor structure. The spin dependence of the Green's function in the absence of an external field is described by a second-rank spinor δ_{ab} :

$$G_{ab}(Z_1, Z_2) = \delta_{ab} G(Z_1, Z_2).$$

The coordinate-space density matrix of particles in the system is given by [1]:

$$\rho_{ab}(\vec{r}_1, \vec{r}_2) = n^{-1} \overline{f_b^*(t, \vec{r}_2)} f_a(t, \vec{r}_1). \quad (1)$$

Using this expression, one can determine the expectation value of any physical observable for an individual particle. Let us rewrite Eq. (1) in terms of the Green's function:

$$\rho_{ab}(\vec{r}_1, \vec{r}_2) = i n^{-1} G_{ab}(t_1, \vec{r}_1; t_1 \rightarrow 0, \vec{r}_2).$$

The Fourier expansion of this function allows one to determine the momentum distribution of particles:

$$n(\vec{p}) = n \int \rho(\vec{r}_1, \vec{r}_2) \exp\{-i\vec{p}(\vec{r}_1 - \vec{r}_2)\} d^3(x_2 - x_1) = -i \int G(t, \vec{r}) \exp\{-i\vec{p}\vec{r}\} d^3x. \quad (2)$$

This expression represents the concentration of real (i.e., non-quasiparticle) particles within a given momentum range $\frac{d^3p}{(2\pi)^3}$. Equation (2) should not be confused with the quasiparticle distribution function. If the expression for the Green's function in the momentum representation is substituted into Eq. (2), i.e.

$$G(t, \vec{r}) = \int G(\omega, \vec{p}) \exp\{i(\vec{p}\vec{r} - \omega t)\} \frac{d\omega d^3p}{(2\pi)^4},$$

then Eq. (2) takes the following form:

$$n(\vec{p}) = -i \lim_{t \rightarrow 0} \int_{-\infty}^{\infty} G(\omega, \vec{p}) \exp\{-i\omega t\} \frac{d\omega}{2\pi},$$

where ω is a complex variable,

$$G(\omega, \vec{p}) = \int G(t, \vec{r}) \exp\{-i(\vec{p}\vec{r} - \omega t)\} dt d^3x. \quad (3)$$

Taking into account the discontinuity property of the Green's function $G(t, \vec{r})$, and the integration over dt in Eq. (3), the integral can be split into two parts with limits from $-\infty$ to and from 0 to ∞ . Then, using the rules of matrix multiplication, we obtain the following expression m for particle states of type a :

$$G(t, \vec{r}) = -\frac{i}{2} \sum_m |f_a(Z_1)| \overline{m \cdot m} |f_a^*(Z_2)|.$$

It is known that Heisenberg operators are physical observables whose mathematical description changes over time, while the quantum state of the system itself remains unchanged. Therefore, we can say that these operators are responsible for the time-varying states of a free particle in the system. The summation is performed over all quantum states of the system. The Heisenberg operator f for a system of free particles satisfies the equation:

$$i \frac{\partial f_a}{\partial t} = -\frac{1}{2m} \Delta f_a - \mu f_a.$$

Taking into account the above results, this equation can be written in terms of the Green's function as:

$$\left(i \frac{\partial}{\partial t} = -\frac{\Delta}{2m} + \mu \right) G(t, \vec{r}) = \delta(t) \delta(\vec{r}),$$

where μ is the chemical potential of the liquid [2]. The Fourier transform is a mathematical bridge between a particle's wave function in coordinate representation and its momentum representation. It allows equations to be translated from the spatial domain to the frequency domain. After performing the Fourier transform, we obtain:

$$\left(\omega - \frac{\vec{p}^2}{2m} + \mu \right) G_0(\omega, \vec{p}) = 1.$$

G_0 is the Green's function for non-interacting particles.

$$G_0(\omega, \vec{p}) = \left[\omega - \frac{\vec{p}^2}{2m_0} + \mu + i \operatorname{sign} \omega \right]^{-1}.$$

This function is a mathematical tool (probability amplitude) that describes the propagation of a quantum particle in space and time.

In quantum mechanics, the product of operators means their sequential application to the wave function (the state of the system). It is used to mathematically describe multi-step measurements, complex physical

quantities, and how a system changes over time. The following product of four Heisenberg operators f averaged over the ground state N is called the two-particle Green's function:

$$Q_{34,12} = \overline{N f_3 f_4 f_1^* f_2^*}. \quad (4)$$

It is convenient to consider this function in the momentum representation for a homogeneous system, i.e., it depends only on the differences of three arguments

$$Z_3 - Z_2, Z_4 - Z_2, Z_1 - Z_2.$$

This is due to the fact that the Fourier transform components, taken over all variables Z_1, Z_2, Z_3, Z_4 , contain a δ -function:

$$\begin{aligned} \int Q_{34,12} \exp\{i(p_3 Z_3 + p_4 Z_4 - p_1 Z_1 - p_2 Z_2)\} d^4 Z_1 d^4 Z_2 d^4 Z_3 d^4 Z_4 = \\ = (2\pi)^4 \delta^{(4)}(p_3 + p_4 - p_1 - p_2) Q_{\delta,ab}(p_3, p_4, p_1, p_2). \end{aligned}$$

For the arguments of the Green's function, the following relation holds $p_1 + p_2 = p_3 + p_4$. In the zeroth-order approximation, this function can be expressed in terms of differences of single-particle Green's functions [2–5]:

$$Q_{\delta,ab}^0(p_3, p_4, p_1, p_2) = (2\pi)^4 \left[\delta^{(4)}(p_1 - p_3) G_a^0(p_1) G_b^0(p_2) - \delta^{(4)}(p_1 - p_4) G_b^0(p_2) G_a^0(p_1) \right].$$

In higher-order approximations, additional terms appear that are not included in the Green's function.

$$\begin{aligned} Q_{A_3 A_4, A_1 A_2}^0 = (2\pi)^4 \left[\delta^{(4)}(p_1 - p_3) G_{A_3 A_1}^0(p_1) G_{A_4 A_2}^0(p_2) - \delta^{(4)}(p_1 - p_4) G_{A_3 A_2}^0(p_2) G_{A_4 A_1}^0(p_1) \right] + \\ + G_{A_3 B_3}(p_3) G_{A_4 B_4}(p_4) i R_{B_3 B_4, B_1 B_2}(p_3, p_4, p_1, p_2) G_{B_1 A_1}(p_1) G_{B_2 A_2}(p_2). \end{aligned}$$

Here, the particle components ab of the system are replaced by AB . The function R in the last expression is called the vertex function and, in the momentum representation, can be written as follows:

$$R_{\delta a,ab}(p_3, p_4, p_1, p_2) = -R_{\delta b,ab}(p_4, p_3, p_1, p_2) = -R_{\delta b,ba}(p_3, p_4, p_2, p_1).$$

To determine the Green's function at nonzero temperature for a macroscopic system, it is necessary to replace averaging over the ground state of a closed system with averaging over ($\langle \rangle$) the Gibbs distribution [6–10]. When analysing the properties of Green's functions at limiting temperatures, it is important to introduce the *retarded* and *advanced* Green's functions. The retarded Green's function is defined as follows:

$$iG_{ab}^\alpha(Z_1, Z_2) = \langle f_a(Z_1) f_b^*(Z_2) + f_b^*(Z_2) f_a(Z_1) \rangle.$$

In the absence of an external field, this function reduces to a scalar function that depends only on the difference of its arguments: $Z = Z_1 - Z_2$:

$$G_{ab}^\alpha(Z_1, Z_2) = \delta_{ab} \frac{1}{2} G_{aa}^\alpha.$$

Since $G^\alpha(t, \vec{r}) = 0$ for $t < 0$, the momentum representation of the above function can be written as follows:

$$G^\alpha(\omega, \vec{p}) = \int_0^\infty \int \exp i(\omega t - \vec{p} \vec{r}) G^\alpha(t, \vec{r}) dt d^3 z.$$

Similarly, the advanced Green's function can be obtained in the same manner G^β . The temperature Green's function is a mathematical apparatus of quantum statistics that describes the behavior of a quantum many-body system when taking into account temperatures different from absolute zero. Then, in our case, the temperature-dependent Green's function is given by:

$$G(\omega, \vec{p}) = -\frac{(2\pi)^3}{2} \sum_{n,m} \omega_n A_{mn} \delta(\vec{p} - \vec{k}_{nm}) \left\{ \frac{1}{\omega_{nm} - \omega} \left(1 + e^{-\frac{\omega_{nm}}{T}} \right) \right\}.$$

Application of Green's Functions to the Solution of the Dirac Equation. For the calculation of processes within the Standard Model, it is necessary to employ methods of mathematical physics and the theory of special functions, since the equations describing scalar, vector, and spinor particles are differential equations of different orders. Solving the Dirac equation using the Green's function allows us to reduce a complex differential problem (especially in the presence of external fields or potentials) to an integral equation. This is a standard technique in relativistic quantum mechanics and quantum field theory, where Green's functions are

also called propagators. As an illustrative example, we consider the solution of the Dirac equation given below for an electron in an electromagnetic field using the Green's function method [11–13]:

$$(i\sigma^\alpha \partial_\alpha - m)\varphi(x) = -e\sigma^\alpha E_\alpha(x)\varphi(x), \quad (5)$$

where $\sigma^\alpha = \{\sigma^0, \sigma^1, \sigma^2, \sigma^3\}$ are the Dirac matrices, and e is the electron charge. To solve Eq. (5), it is necessary to first consider the following auxiliary problem:

$$(i\sigma^\alpha \partial_\alpha - m)G(x, x^0) = \delta^{(4)}(x - x^0).$$

Then, the solution of Eq. (5) can be represented as:

$$\varphi(x) = -e \int G(x, x^0) \sigma^\alpha E_\alpha(x^0) \varphi(x^0) dx^0.$$

The momentum representation of Green's functions (or the momentum space representation) is a transition from space-time coordinates to wave vectors (momenta) and frequencies using the Fourier transform. The momentum representation of the Green's function in this expression is given by:

$$G(x, x^0) = \frac{1}{(2\pi)^4} \int S(p) \exp\{-ip(x - x^0)\} d^4 p. \quad (6)$$

The momentum representation of Green's functions is a mathematical apparatus in which the solution of quantum mechanical equations (Schrödinger or Dirac) is expressed in terms of particle momenta rather than their coordinates. This significantly simplifies the analysis due to the translational invariance of space. $S(p)$ in expression (6) is the Fourier transform of the Green's function. In the Fourier representation, the Green's function is transformed from a complex integral convolution kernel into a simple algebraic function. A differential equation with a source is reduced to dividing the Fourier transform of the source by the Fourier transform of the differential operator. If the Dirac delta function is applied,

$$\delta^{(4)}(x - x^0) = \frac{1}{(2\pi)^4} \int \exp\{-ip(x - x^0)\} d^4 p$$

and the notation $\sigma^\alpha p_\alpha = p$, is introduced, as well as the commutation property of the Dirac matrices $\sigma^\alpha \sigma^\beta + \sigma^\beta \sigma^\alpha = 2\theta^{\alpha\beta}$, then the expression for the Green's function [14], corresponding to the Fourier-transformed Green's function and the Dirac equation, takes the following form:

$$S(p) = \frac{\tilde{p} + m}{p^2 - m^2};$$

$$G(x, x^0) = \frac{1}{(2\pi)^4} \int \frac{\tilde{p} + m}{p^2 - m^2 + i\varepsilon} \exp\{-ip(x - x^0)\} d^4 p.$$

It is well known that a particle in an external field in quantum systems is described by the Schrödinger equation:

$$(\hat{H} - E)\psi(\vec{r}) = -\hat{F}\psi(\vec{r}), \quad (7)$$

where $\hat{F}$ is the operator responsible for the interaction, and $\hat{H}$ is the Hamiltonian,

$$\psi(\vec{r}) = \exp(i\vec{k}\vec{r}), \quad (8)$$

to solve Eq. (7) by the Green's function method, it is necessary to pass from this differential equation to an equivalent integral equation (that is, an integral term entering the Green's function is added to the wave function of the form given in Eq. (8)).

$$\psi(\vec{r}) = \exp(i\vec{k}\vec{r}) + \int G(E, \vec{r}, \vec{r}') \hat{F}(\vec{r}') \psi(\vec{r}') d\vec{r}'.$$

Here, $G(E, \vec{r}, \vec{r}')$ is the Green's function corresponding to the Hamiltonian operator and satisfying the equation given below $(E - \hat{H})G(E, \vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$ with the Dirac delta function ($\delta(\vec{r} - \vec{r}')$) [15]. Its spectral form is given by:

$$G(E, \vec{r}, \vec{r}') = \sum_{n=1}^{\infty} \frac{\psi_n(\vec{r}) \psi_n^*(\vec{r}')}{E_0 - E_n}.$$

In the case of a continuous spectrum,

$$G(E, \vec{r}, \vec{r}') = \int \frac{\psi_n(\vec{r}) \psi_n^*(\vec{r}')}{E_0 - E_n} \frac{d\vec{k}}{(2\pi)^3}.$$

It should be noted that the form of the Green's functions entering the equivalent integral equations, in momentum and spectral representations as well as in Fourier-transformed form, makes it possible to accurately determine the domains of definition of the processes under consideration in phase space. On the other hand, this approach improves the assessment of the rate of the process in combination with the theory of functions of a complex variable. The obtained results can be used in solving problems based on scattering theory and in calculating quantum-field amplitudes of spinor particles.

Green's Functions of Averages and Equilibrium Green's Functions. When expressing the expectation values of quantities corresponding to quantum operators in terms of known Green's functions, only the expectation values of two field operators and single-particle operators can appear in such expressions [16, 17]. For example, the particle number density in a system is given by:

$$n(\vec{r}) = \sum_a \langle \psi_a^*(\vec{r}) \psi_a(\vec{r}) \rangle = \pm \sum_a G_{aa}(\vec{r}, t - 0; \vec{r}, t)$$

and for a homogeneous system of fermions:

$$n = \frac{N}{V} = -2iG_{aa}(\vec{r} = 0, t = -0). \quad (9)$$

This relation, which connects the Green's function with the particle density, makes it possible to express the thermodynamic parameters of the system under $T = 0$ in terms of Green's functions. Indeed, the thermodynamic potential of the system under the conditions $T = 0$, $V = \text{const}$ and $S = 0$ is determined by the relation:

$$dF = -SdT - pdV - Nd\mu = -Nd\mu.$$

This relation can be integrated subject to the condition $F(\mu = 0) = 0$:

$$F = \int_0^\mu d\mu N(\mu).$$

Substituting the corresponding expression N and taking into account the dependence of the Green's function on μ , we obtain:

$$F = \int_0^\mu d\mu 2iV \lim_{t \rightarrow -0} \int \frac{d\vec{p} d\omega}{(2\pi)^4} \exp(-i\omega t) G(\vec{p}, \omega).$$

A somewhat more complicated example is the current, which is expressed in terms of field operators [18, 19] as follows:

$$\vec{J}(\vec{r}) = \frac{ie}{2m} \sum_a \langle (\nabla \psi_a^*(\vec{r})) \psi_a(\vec{r}) - \psi_a^*(\vec{r}) (\nabla \psi_a(\vec{r})) \rangle.$$

The current can also be expressed in terms of Green's functions as follows:

$$\vec{J}(\vec{r}) = \frac{ie}{2m} \sum_a \lim_{t \rightarrow -0} \lim_{\vec{r}' \rightarrow \vec{r}} (\nabla_{\vec{r}'} - \nabla_{\vec{r}}) [\pm G_{aa}(\vec{r}, t; \vec{r}', 0)].$$

The formalism developed above is restricted to the properties of many-particle systems at $T = 0$ (i.e., in the ground state). This is due to the fact that the ground state is always non-degenerate, which allows one to apply the adiabatic hypothesis: if the interaction is switched on slowly and then switched off slowly, this results only in the appearance of a phase factor, which ultimately cancels out. From a physical point of view, however, one cannot restrict the analysis to the case $T = 0$. In principle, the averaging in the definition of the Green's function can be performed over any quantum state or ensemble of states, and its analytical properties can be established following the same procedure as for $T = 0$. For example, one can define equilibrium Green's functions at finite temperature.

The general definitions of causal, retarded, and advanced single-particle Green's functions [20]

$$G_{ab}(x_1, t_1; x_2, t_2) = -i \text{Tr} [\hat{\rho} T \psi_a(x_1, t_1) \psi_b^*(x_2, t_2)];$$

$$G_{ab}^R(x_1, t_1; x_2, t_2) = -i \text{Tr} [\hat{\rho} T \psi_a(x_1, t_1) \psi_b^*(x_2, t_2) \pm \psi_b^*(x_2, t_2) \psi_a(x_1, t_1)] K(t_1 - t_2);$$

$$G_{ab}^A(x_1, t_1; x_2, t_2) = -i \text{Tr} \left[\hat{\rho} T \psi_a(x_1, t_1) \psi_b^*(x_2, t_2) \pm \psi_b^*(x_2, t_2) \psi_a(x_1, t_1) \right] K(t_2 - t_1)$$

remain valid for equilibrium states at finite temperature, when the statistical operator has the standard form of the grand canonical Gibbs distribution:

$$\hat{\rho} = \exp \left\{ -\frac{1}{T} (H - \Omega) \right\} = \sum_s \exp \left\{ -\frac{1}{T} (E_s - \mu N_s - \Omega) \right\} |s\rangle \langle s| = \sum_s \rho_s |s\rangle \langle s|.$$

The grand partition function is given by:

$$Z = \exp \left(-\frac{\Omega}{T} \right) = \text{Tr} \left[\exp \left(-\frac{H}{T} \right) \right],$$

where Ω is the grand thermodynamic potential. In the isotropic homogeneous case,

$$G_{ab}(x_1, t_1; x_2, t_2) = \delta_{ab} G_{ab}(x_1 - x_2, t_1 - t_2).$$

Further, at zero temperature, it is necessary to include the matrix elements of the field operators between all states of the system, since all excited states now contribute with nonzero weight. As a result, we obtain the following expression for the causal Green's function:

$$G(\vec{p}, \omega) = \frac{1}{2} (2\pi)^3 \sum_m \sum_n \rho_n \sum_a |\langle n | \psi_a | m \rangle|^2 \delta(\vec{p} - (\vec{P}_m - \vec{P}_n)) \frac{1}{\omega - \omega_{nm}}, \quad (10)$$

$$\omega_{nm} = E_m - \mu N_m - (E_n - \mu N_n).$$

By separating the real and imaginary parts of Eq. (10) for real frequencies using the Sokhotski–Plemelj formula, we obtain:

$$\text{Re} G(\vec{p}, \omega) = \frac{1}{2} (2\pi)^3 P \sum_m \sum_n \rho_n \sum_a |\langle n | \psi_a | m \rangle|^2 \delta(\vec{p} - (\vec{P}_m - \vec{P}_n)) \left[1 \pm \exp \left(-\frac{\omega_{nm}}{T} \right) \right] \frac{1}{\omega - \omega_{nm}};$$

$$\text{Im} G(\vec{p}, \omega) = -\pi \frac{1}{2} (2\pi)^3 P \sum_m \sum_n \rho_n \sum_a |\langle n | \psi_a | m \rangle|^2 \delta(\vec{p} - (\vec{P}_m - \vec{P}_n)) \left[1 \pm \exp \left(-\frac{\omega_{nm}}{T} \right) \right] \delta(\omega - \omega_{nm}).$$

An important property of Eq. (10) is that, if an approximation for the self-energy function of finite order is substituted into it, the resulting approximation for the Green's function becomes equivalent to summing an infinite series of perturbation terms. This yields a significantly better result than a direct term-by-term calculation of the initial perturbation series. This is a natural consequence of the self-consistent approach. Another, less favourable consequence is that any approximate self-energy function must be verified for consistency with the general analytical properties of the Green's function (which follow from the principle of causality).

Conclusion

Research on macro systems using the Green's function method is a powerful mathematical tool that finds application in various fields of theoretical and applied physics. This method allows for the description of complex systems with numerous interacting particles or elements. In accordance with the subject of this work, Green's functions for macroscopic systems and ideal Fermi liquids, as well as two-particle Green's functions, finite-temperature Green's functions, and the Dirac equation, have been considered. The relevance of this study is associated with the application of Green's function methods to quantum phenomena. Indeed, this method is considered one of the most effective approaches for solving partial differential equations corresponding to various physical processes. In particular, when solving the governing equations of such phenomena, an auxiliary partial differential equation involving the Green's function in operator form is first solved. After this procedure, by passing to the momentum representation, Fourier transforms with respect to complex variables are performed. Then, within the framework of zeroth- and first-order approximations, integral expressions are obtained, and the limits of integration are chosen depending on the specific features of the process under consideration. Performing this integration makes it possible to obtain explicit solutions describing the properties of the system in which the given phenomenon occurs. Within this approach, methods of mathematical physics and special functions play a key role, which becomes particularly evident in large-scale calculations. The mathematical derivations presented in this paper have been given in a simplified form. The main emphasis has been placed on demonstrating the features of applying Green's function methods to the solution of equations describing quantum effects in macroscopic systems. The obtained results can be used in the following areas of theoretical and mathematical physics: studying the dynamics of fields, particle interactions (for example, in quantum electrodynamics and quantum chromodynamics), and scattering

processes; calculating the energy spectrum of electrons and phonons in crystals, studying superconductivity (Gorkov equations), magnetism, and the behavior of semiconductors; analyzing phase transitions, critical phenomena, and non-equilibrium processes; and calculating the propagation of waves in heterogeneous media, turbulence, and the response of hydrodynamic systems to external disturbances.

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Макроскоптық кванттық жүйелердің Грин функцияларының қасиеттері мен ерекшеліктерін зерттеу

Макроскоптық жүйелерде өтетін процестер Грин функциялары арқылы зерттелді. Идеалды ферми-сұйықтың, бір және екі бөлшектік, шекті температуралық, Дирак және Шредингер теңдеулерінің Грин функциялары шығарылып көрсетілді. Көп бөлшектік кванттық жүйелерге арналған теңдеулердің шешімдерін Грин функциясы тәсілімен анықтаудың жолдары қарастырылған. Операторлар мен шекаралық шарттарға арналған Грин функцияларының көмегімен сұйыққа арналған теңдеулердің шешімдері интегралдық түрлерде ұсынылды. Процестерге Грин функциясын дербес туындылы дифференциалдық теңдеулерді шешуге, Фурье тәсілін қолдануға, интегралдық түрлендірулер жасауға, арнайы функциялар мен математикалық талдау тәсілдерін пайдалануға тура келеді. Дифференциалдық теңдеуден эквивалентті интегралдық теңдеуге көшу жолдары келтіріліп, соңғы теңдеудің шешімі Грин функциясы бойынша анықталды. Бұл жағдай импульстік бейнеге ауысу арқылы және комплекстік айнымалылар бойынша жүргізілетін Фурье түрлендірулерін қолдану арқылы іске асырылды. Тұрақты толқындық функциялары бар макроскоптық жүйелер гейзенберттік бейнелеуде қарастырылды. Әрине бұл бейнелеуде физикалық шамаларға сәйкес қойылатын операторлар уақытқа айқын түрде тәуелді болмайтындығы белгілі. Барлық есептеулер сыртқы магнит өрісі ескерілген және ескерілмеген жағдайларға сәйкес орындалды.

Кілт сөздер: ферми-сұйық, Фурье түрлендіруі, импульстік бейнелеу, макроскоптық жүйе, Грин функциясы, интегралдық теңдеу

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Исследование особенностей и свойств функций Грина макроскопических квантовых систем

Процессы в макроскопических системах исследовались с помощью функций Грина. Показаны функции Грина для идеальной ферми-жидкости, одной и двух частиц, предельной температуры и уравнений Дирака, Шредингера. Рассмотрено решение уравнений, описывающих процессы в многочастичных квантовых системах, методом функций Грина. С помощью функции Грина для оператора и граничных условий решение уравнения для жидкости записано в интегральном виде. При применении функции Грина к процессам возникает необходимость решения дифференциальных уравнений частных производных, применения метода Фурье, интегральных преобразований, специальных функций и методов математического анализа. Использован переход от дифференциального уравнения к эквивалентному интегральному уравнению и показано решение данного уравнения с функцией Грина. При этом был осуществлен переход на импульсное представление и преобразования Фурье через комплексные переменные. Рассмотренные макроскопические системы с постоянными волновыми функциями были описаны на основе гейзенберговских представлений, где операторы, соответствующие физическим величинам, явно зависят от времени. Расчеты производились с учетом и без учета влияния внешних полей.

Ключевые слова: ферми-жидкость, преобразование Фурье, импульсное представление, макроскопическая система, функция Грина, интегральное уравнение

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Development of a Method for Producing Self-Fluxing Nickel-Based Coatings by Detonation Spraying

This study investigated the influence of detonation spraying parameters on the structure and tribological and mechanical properties of self-fluxing coatings of the Ni–Cr–Fe–B–Si–C system. The investigated parameters included the barrel filling level (48–68%), the molar ratio of the working gases ($O/C = 1.026–1.856$), and the inter-shot delay (0–1 s). Morphological analysis of the coatings revealed a characteristic lamellar structure and a dependence of coating thickness and defect formation on the spraying conditions. A lower barrel filling level resulted in a denser coating structure with minimal porosity, whereas medium and high filling levels promoted the formation of microcracks, presumably due to increased residual stresses. Tribological tests showed that the minimum coefficient of friction was obtained at a barrel filling level of 48% ($\mu = 0.674 \pm 0.136$) and an O/C ratio of 1.026, but these conditions were also associated with increased wear. The highest wear resistance was obtained at an O/C ratio of 1.856 and an increased inter-shot delay of up to 1 s, resulting in a decrease in the specific wear rate to $0.000189 \text{ mm}^3/(\text{N} \cdot \text{m})$. Roughness analysis showed that increasing the inter-shot delay reduced R_a from 5.00 to $3.60 \text{ } \mu\text{m}$, which may be attributed to a reduction in thermal load and more favorable coating formation conditions. The maximum hardness, up to 905.6 HV, was obtained for a combination of parameters that promoted the formation of a dense structure and strengthening phases. The results indicate that optimizing the detonation spraying parameters requires a trade-off between reducing the coefficient of friction and increasing wear resistance. The findings can be used to develop technologies for the restoration and surface strengthening of machine components.

Keywords: self-fluxing alloys, detonation spraying, NiCrFeBSiC, heat treatment, AISI 321

Introduction

Thermal spraying is often used to extend the service life of tribomechanical systems, protecting new machine parts and restoring worn ones. This process creates surfaces with properties significantly superior to those of the base material [1]. Self-fluxing nickel-based alloys are widely used in thermal spraying technologies. These alloys are characterized by high strength and hardness, as well as excellent resistance to wear, heat, and corrosion. The presence of Cr, B, Si, and C in the structure creates hard phases dispersed in a viscous nickel matrix, which ensures good performance properties [2]. Nickel alloys with high chromium con-

tent are characterized by excellent corrosion resistance and high mechanical properties after hardening. Their corrosion resistance is ensured by a chromium oxide film formed on the alloy surface, which provides protection at elevated temperatures. These alloys are widely used in the power industry for the production of gas turbines and nuclear generators, as well as in motorsports for the manufacture of exhaust valves for racing engines, fasteners, spindles, and other components [3]. Coatings based on the Ni–Cr–Fe–B–Si–C system are widely used to improve the wear resistance of component working surfaces. NiCrFeBSiC alloys perform effectively under conditions of intense friction. Such coatings exhibit high resistance to adhesive wear and corrosion at both normal and elevated temperatures [4].

For the application of self-fluxing coatings, thermal spraying methods such as flame spraying, detonation spraying, and high-velocity oxy-fuel (HVOF) spraying can be used. However, detonation spraying offers a number of significant advantages, ensuring the formation of coatings with improved performance characteristics. Detonation spraying achieves the highest particle velocities (up to 800–1000 m/s), leading to intense plastic deformation of the particles upon impact with the substrate and the formation of a dense coating structure with minimal porosity, which is directly related to increased wear and corrosion resistance of the coatings. Furthermore, detonation spraying enables the formation of coatings with a finely dispersed structure and a uniform distribution of boride and carbide phases, which significantly increases resistance to abrasive and adhesive wear. Article [5] has shown that such structural features provide improved tribological properties compared to coatings obtained by the HVOF method. HVOF can lead to increased particle oxidation, especially when deviating from optimal spraying conditions, which negatively impacts the formation of the metal matrix and reduces the performance properties of the coating [6].

The formation of the required tribological properties of fused Ni–Cr–Fe–B–Si coatings is possible only under strictly specified heat treatment conditions (in the range of 1000–1373 K), since these alloys belong to eutectic systems and are highly sensitive to thermal exposure parameters [7, 8]. In this regard, the present work is devoted to the study and selection of optimal spraying parameters for NiCrFeBSiC coatings obtained by detonation spraying.

Experimental

Corrosion-resistant, austenitic structural steel grade AISI 321 was selected as the substrate material. This steel is often used in industry to manufacture components operating at temperatures up to 600 °C, welded equipment and vessels operating in dilute solutions of nitric, acetic, and phosphoric acids, alkaline and salt solutions, and other components operating under pressure at temperatures from –196 to +600 °C, as well as in aggressive environments. According to ASTM A240M, AISI 321 steel has the following composition (Table 1).

Table 1

Chemical composition of AISI 321 steel

C	Si	Mn	Ni	S	P	Cr	Cu	Ti	Fe
< 0.12	< 0.80	< 2	9–11	< 0.02	< 0.035	17–19	< 0.3	<1	base

A 30 mm diameter AISI 321 carbon steel rod was cut into 5 mm thick disks. The surface was mechanically processed by grinding with sandpaper of up to P400 grit. To improve the adhesion of the applied coating, the disk surface was additionally treated by abrasive blasting using fused alumina (Al_2O_3) with a particle size of 40 μm . After sandblasting, abrasive residue and dust were removed by blowing with compressed air. To remove organic and inorganic contaminants (oils, oxide films), the samples were cleaned in an ultrasonic bath using technical-grade ethanol. The ultrasonic cleaning duration was 10 minutes at a frequency of 40 kHz and a solution temperature no higher than 35 °C. Self-fluxing Ni–Cr–Fe–B–Si–C powder (produced in China) was used for spraying the coatings. This powder has a particle size of 100–150 μm , is perfectly spherical, and, as shown in Figure 1, exhibits a highly uniform element distribution. The powder composition is presented in Table 2.

Table 2

Chemical composition of Ni–Cr–Fe–B–Si–C powder

Ni	C	Cr	B	Si	Fe
Base	0.9	16–18	3.2	4	5

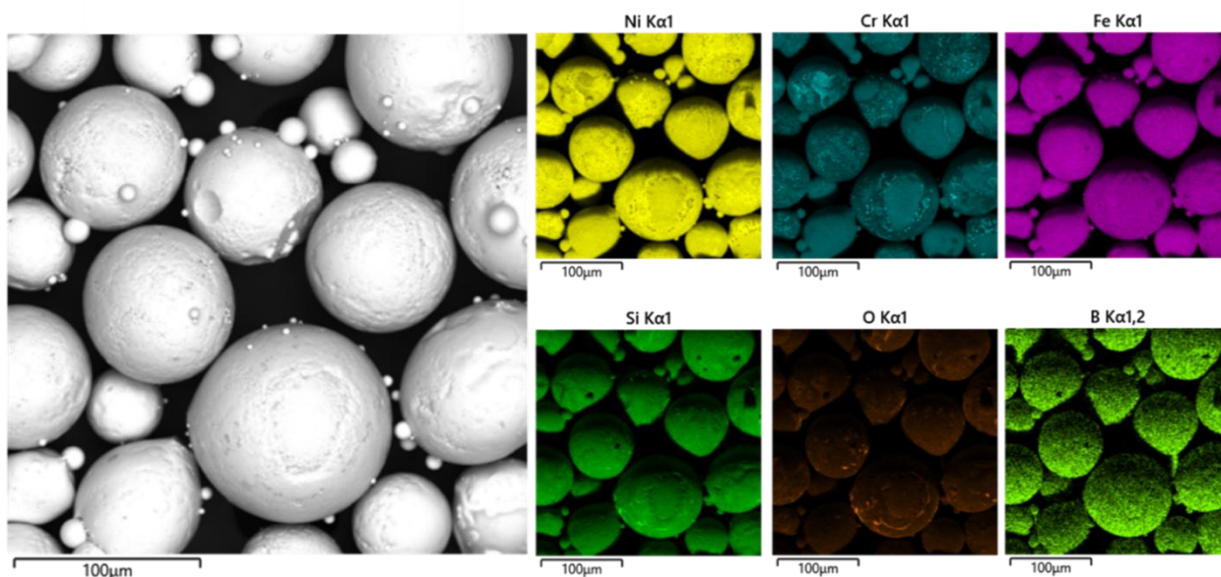


Figure 1. Morphology of Ni-Cr-Fe-B-Si-C powder

The CCDS-2000 detonation spraying system (Fig. 2) (Siberian Technologies of Protective Coatings, Novosibirsk) was used for coating production. The CCDS2000 system is designed to form high-quality coatings using detonation spraying, which is based on the cyclic combustion (detonation) of a gas mixture of fuel and oxygen in the barrel bore. The detonation generates a shock wave that accelerates powder particles. The system operates automatically and allows for precise adjustment of key process parameters, including:

- gas mixture composition and ratio;
- barrel fill level;
- interval between detonation pulses.

During spraying, powder is introduced into the detonation chamber, where it is captured by detonation products and accelerated along the barrel bore toward the substrate. Upon impact with the surface, the particles undergo intense plastic deformation, forming a dense coating with low porosity and high adhesive strength. The process is carried out in pulsed regime with a frequency of several shots per second, which ensures controlled heat input into the substrate and minimizes its thermal deformation.

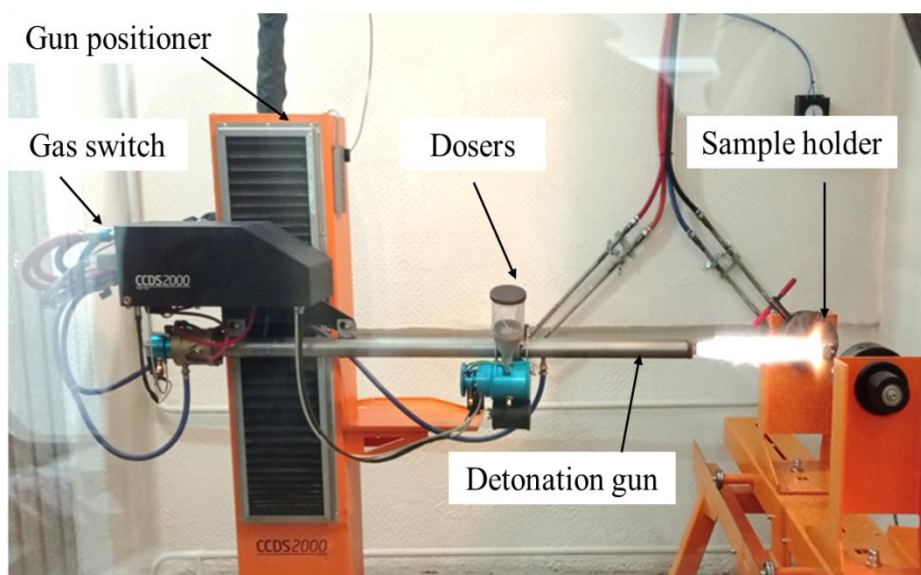


Figure 2. General view of the CCDS-2000 detonation spraying system

The coating morphology was examined using a SEM 3200 scanning electron microscope (China) equipped with an electron probe attachment for localized microanalysis and an EDS energy-dispersive spectrometer (BRUKER).

Tribological testing of the coatings was conducted using a ball-on-disk setup (Fig. 3) on an Anton Paar TRB3 tribometer (Austria). A 6 mm diameter 100Cr6 steel ball served as the counterweight. The load was 10 N, the rotation speed was 5 cm/s, the radius of curvature was 2 mm, and the friction path length was 100 m.

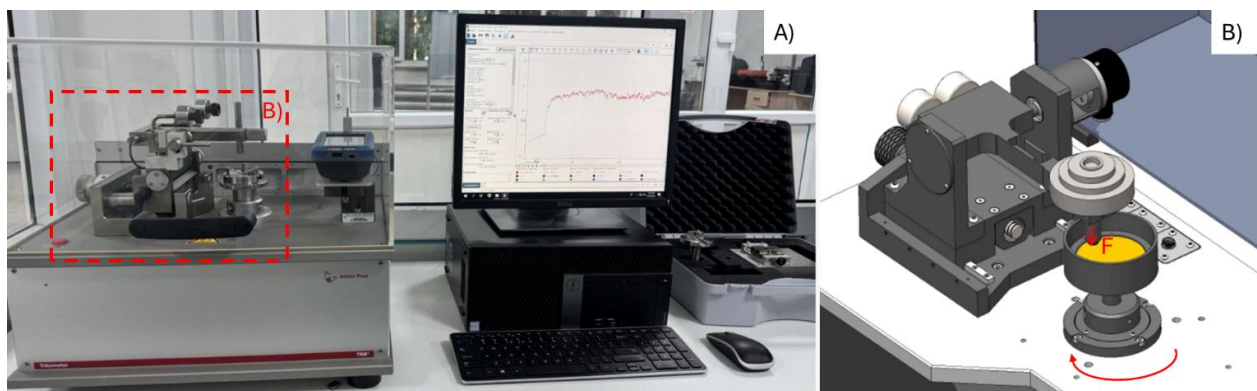


Figure 3. a) General view of the TRB3 tribometer; b) Ball-on-disk test setup.

Coating hardness under various spraying conditions was measured using a Metolab 502 hardness tester (Russia) operating using the Vickers method in accordance with GOST 6507-1-2007, with a load of 0.1 kg and a hold time of 10 seconds.

Coating surface roughness was assessed using a contact profilometer. Measurements were performed by tracing a diamond stylus across the sample surface, followed by recording the roughness profile. The primary roughness parameter was the arithmetic mean deviation of the profile (R_a), which characterizes the average roughness height relative to the profile centerline. Measurements were conducted with a constant baseline length, followed by processing of the resulting profilograms. To enhance the reliability of the results, at least three measurements were taken for each sample in different surface areas, after which the mean values and standard deviation were calculated.

Results and Discussion

In order to select the optimal spraying regime for self-fluxing coatings using the detonation spraying method, the following parameters were varied: the volume of the barrel filled with a gas mixture (Table 3.1), the molar ratio of the working gases (Table 3.2), and the delay between shots (Table 3.3).

Table 3.1

Selecting the process parameter: barrel fill volume with gas mixture

Barrel fill volume with gas mixture	48 %	58 %	68 %
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Table 3.2

Selection of the process parameter: molar ratio of working gases

Molar ratio of working gases (O/C)	1.026	1.856
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Table 3.3

Selection of the process parameter: delay between shots

Delay between shots	no delay	0.25 s	0.5 s	0.75 s	1 s
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The process parameters for detonation spraying were selected to determine their impact on the structure formation and performance properties of Ni–Cr–Fe–B–Si–C coatings. The key variable parameters were: the barrel fill rate, the molar ratio of the working gases, and the delay between detonation pulses.

The barrel fill rate range (48–68 %) was selected based on the need to ensure a stable detonation process. The molar ratio of the working gases ($O/C = 1.026\text{--}1.856$) was varied to control the temperature and energy conditions of the process. Values close to stoichiometric ensure maximum temperature and velocity of the detonation products, while deviations from stoichiometry allow for control of the degree of heating and oxidation of the particles. This is especially important when spraying self-fluxing alloys, which are sensitive to overheating and changes in chemical composition. The delay time between shots (0–1 s) was selected taking into account the need to control heat transfer to the substrate. Increasing the interval between shots can promote temperature stabilization and improve coating formation conditions.

Thus, the selected ranges of process parameters allow for a comprehensive assessment of the influence of the energy and thermal conditions of detonation spraying on the morphology, structure, and properties of the coatings.

The cross-sectional morphology of Ni–Cr–Fe–B–Si–C coatings obtained at various degrees of barrel filling with the gas mixture during detonation spraying is shown in Figure 4. The morphology of the coatings on the surface of Ni–Cr–Fe–B–Si–C samples was described in a previous study [9].

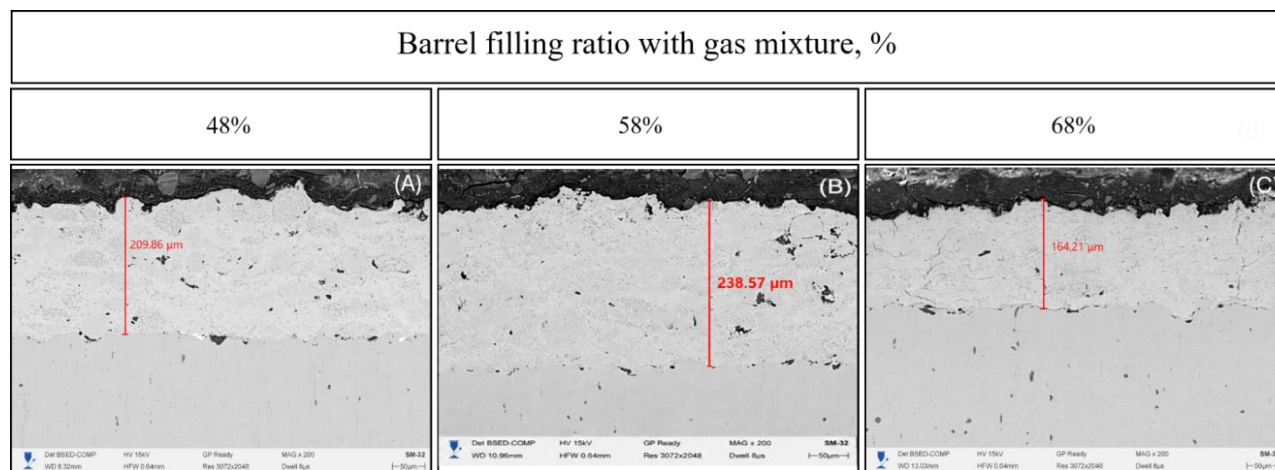


Figure 4. Coating thickness at different barrel fill rates with explosive mixture:
(a) fill rate — 48 %, (b) fill rate — 58 %, (c) fill rate — 68 %

Microstructure analysis revealed that at low fill rates (Fig. 4a), the coating structure develops a more uniform and dense structure with fewer pores. The reduced defect rate may be due to more stable deposition conditions and improved particle coalescence. At medium fill rates (Fig. 4b), despite the increased coating thickness, microcracks are observed, likely due to increased residual stresses arising from the high kinetic energy of the particles and rapid cooling. At higher barrel fill rates (Fig. 4c), cracks are also observed due to incomplete particle deformation upon impact with the substrate and increased microstresses. Thus, the degree of barrel filling with the gas mixture is one of the key process parameters determining the thickness, porosity, and defect level of the coatings. Optimization of this parameter ensures the formation of coatings with minimal porosity and high structural integrity.

The cross-sectional morphology of Ni–Cr–Fe–B–Si–C coatings obtained with various molar ratios of the gas mixture (propane/acetylene/oxygen) during detonation spraying is shown in Figure 5.

Analysis revealed that the resulting coatings have a layered (lamellar) structure characteristic of thermal spray methods, caused by the sequential layering of deformed particles, which is consistent with classical concepts of the coating formation mechanism [5].

The coating thickness in Figure 5a is approximately 244.12 μm , while in sample B it decreases to 180.01 μm , indicating the influence of spraying process parameters on particle deposition efficiency. As noted in [9], coating thickness is determined by particle velocity and the degree of their melting, which, in turn, depend on the energy parameters of the process. Sample A exhibits a relatively uniform structure with moderate porosity, indicating a sufficient degree of deformation and coalescence of the particles upon impact

with the substrate. According to [10], effective particle flattening facilitates the formation of dense coatings with good interlayer bonding.

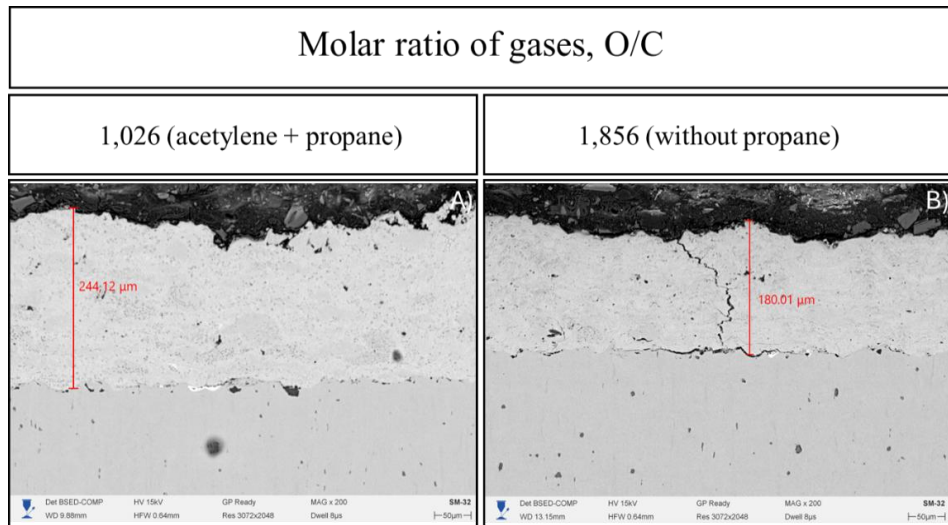


Figure 5. Coating thickness for different gas mixture molar ratios:
(a) 1.026 (oxygen/acetylene + propane mixture); (b) 1.856 (oxygen/acetylene mixture)

Figures 5b and 5c show microcracks propagating perpendicular to the surface, which may be associated with increased residual thermal stresses. As shown in [11], crack formation in thermal spray coatings is caused by rapid cooling and differences in the thermal expansion coefficients between the coating and the substrate. With insufficient propane content in the mixture (lean mixture), a decrease in the detonation temperature is observed, leading to incomplete melting of the powder particles. This results in a coating with increased porosity and insufficient interlayer bonding, as evidenced by the presence of pores and defects in the microstructural images.

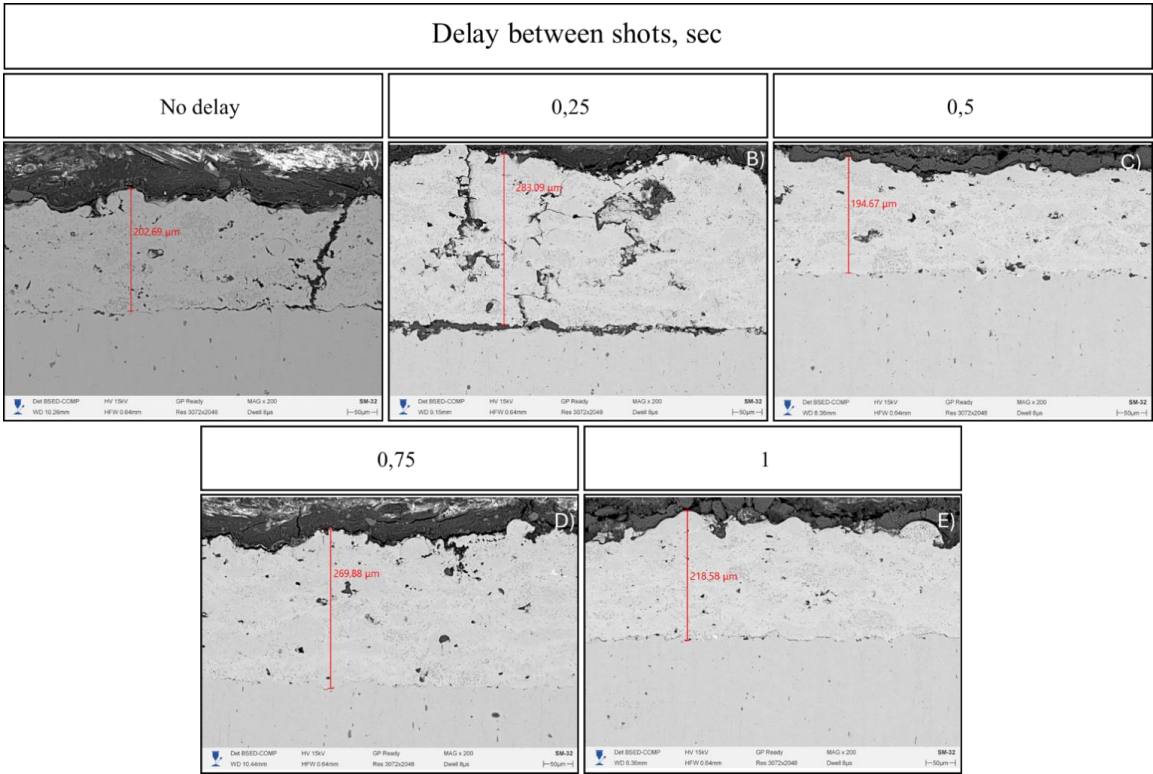


Figure 6. Coating thickness and morphology at different inter-shot delays:
(a) no delay; (b) 0.25 s; (c) 0.5 s; (d) 0.75 s; (e) 1 s

Analysis showed that changing the inter-shot delay has a significant impact on the coating thickness, structural homogeneity, and defect content. Without inter-shot delay (Fig. 6a), the coating thickness is approximately 202.69 μm . A developed network of microcracks extending from the coating surface into the coating is observed. The formation of such defects is associated with heat accumulation during continuous spraying, which leads to the development of significant residual thermal stresses due to rapid cooling (Pawlowski, 2008). With an increase in the holding time to 0.25 s (Fig. 6b), the coating thickness increases to 283.09 μm , but at the same time the maximum degree of defects is recorded, including pronounced microcracks and localized structural discontinuities. This effect can be caused by a combination of the high substrate temperature and the significant kinetic energy of the particles, which leads to an intense accumulation of stresses and a violation of the continuity of the coating. With a further increase in the holding time to 0.5 s (Fig. 6c), the coating thickness decreases to 194.67 μm , while a noticeable decrease in the number of cracks and a more uniform structure are observed. This indicates partial stabilization of the thermal regime and a decrease in the level of residual stresses [12]. With a holding time of 0.75 s (Fig. 6d), the coating thickness again increases to 269.88 μm , while the structure becomes denser and the number of defects decreases. The improved morphology is due to the optimal combination of substrate cooling between shots and maintaining sufficient particle energy for efficient deposition. The most favorable structure is observed with a delay of 1 s (Fig. 6e), where the coating thickness is approximately 218.58 μm . The coating is characterized by minimal porosity and the absence of pronounced microcracks, indicating stabilization of the deposition process and reduced thermal stress.

Thus, increasing the time between shots reduces the thermal load on the substrate and decreases residual stress, which positively impacts the integrity of the coating. However, excessively long delays can be accompanied by a decrease in coating thickness due to reduced heat accumulation and particle deposition efficiency.

Tribological tests were conducted to assess the wear resistance of the coatings. The results are presented in Figure 7. Based on the results of tribological tests with dry friction, it was found that subsequent heat treatment reduces the friction coefficient, thus thermal gas flame heating and furnace treatment reduced the friction coefficient by 6 times on average for both types of treatment.

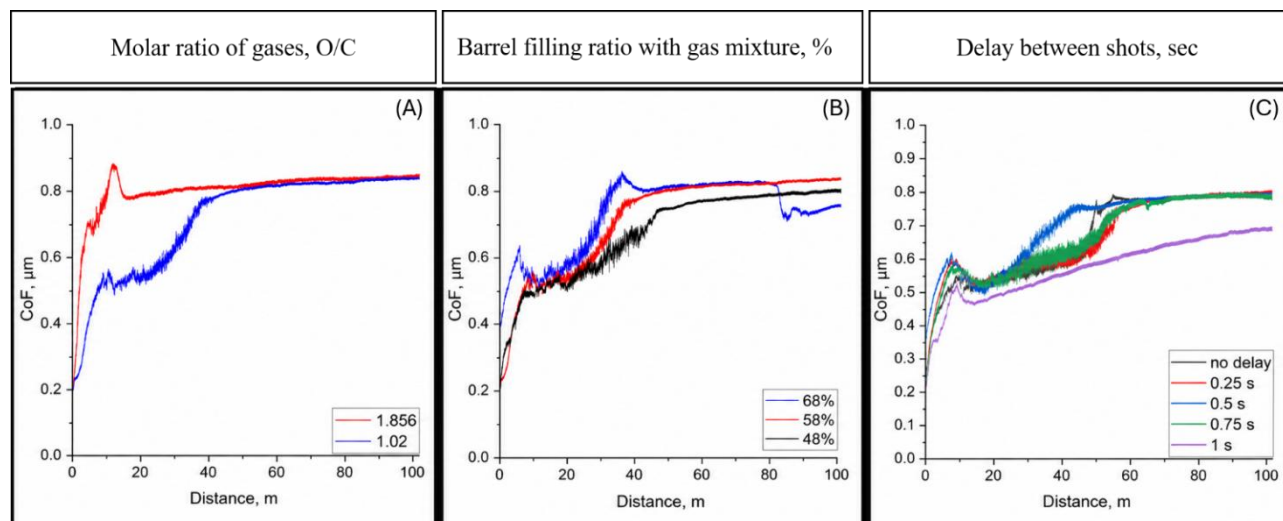


Figure 7. Graphs of the friction coefficient versus the distance for different detonation spraying process regimes

Table 4.1

Results of tribological tests of coatings with different barrel filling volumes of gas mixture

Barrel filling volume with gas mixture	48 %	58 %	68 %
Friction coefficient	0.674±0.136	0.713±0.151	0.729±0.111
Wear volume, μm^2	30852.7	36317.5	96530.7
Wear intensity, $\text{mm}^3/(\text{N}\cdot\text{m})$	0.000387	0.000456	0.001213

Table 4.2

Results of tribological tests of coatings with different molar ratios of working gases

Molar ratio of working gases (O/C)	1.026	1.856
Friction coefficient	0.713±0.151	0.799±0.076
Wear volume, μm^2	96530.7	26017.7
Wear intensity, $\text{mm}^3/(\text{N}\cdot\text{m})$	0.001213	0.000326

Table 4.3

Results of tribological tests of coatings with different delay between shots

Delay between shots	No delay	0.25 s	0.5 s	0.75 s	1 s
Friction coefficient	0.703±0.110	0.678±0.093	0.671±0.130	0.672	0.671±0.120
Wear volume, μm^2	27724.5	31779.8	28902.0	23115.9	15083.5
Wear intensity, $\text{mm}^3/(\text{N}\cdot\text{m})$	0.000348	0.000399	0.000363	0.000290	0.000189

The results of tribological tests of Ni–Cr–Fe–B–Si–C coatings (Tables 4.1–4.3) indicate a complex effect of the process parameters of detonation spraying on the friction coefficient and wear resistance. It was found that with an increase in the degree of filling of the barrel with a gas mixture from 48 to 68 %, an increase in the friction coefficient is observed from 0.674 ± 0.136 to 0.729 ± 0.111 (Fig. 7a), accompanied by a significant increase in the wear volume from 30852.7 to $96530.7 \mu\text{m}^2$ and wear intensity from 0.000387 to $0.001213 \text{ mm}^3/(\text{N}\cdot\text{m})$, which indicates a deterioration in wear resistance at high filling values due to the formation of a more defective and less stable coating structure. The effect of the gas molar ratio is opposite (Fig. 7b): at $\text{O/C} = 1.026$, a lower friction coefficient is observed (0.713 ± 0.151), wear reaches maximum values ($96530.7 \mu\text{m}^2$; $0.001213 \text{ mm}^3/(\text{N}\cdot\text{m})$), whereas at $\text{O/C} = 1.856$, a coating is formed with a higher friction coefficient (0.799 ± 0.076), but significantly lower wear ($26017.7 \mu\text{m}^2$; $0.000326 \text{ mm}^3/(\text{N}\cdot\text{m})$), which indicates the formation of a harder and more destruction-resistant structure with an increased oxygen content. When analyzing the effect of the delay between shots, it was found (Fig. 7c) that the friction coefficient changes insignificantly and is in the range of 0.671–0.703, while wear demonstrates a pronounced dependence on this parameter: an increase in the delay from none to 1 s leads to a decrease in the wear volume from 27.724.5 to 15.083.5 μm^2 and wear intensity from 0.000348 to $0.000189 \text{ mm}^3/(\text{N}\cdot\text{m})$, which is due to a decrease in thermal accumulation, a decrease in residual stresses and the formation of a denser and more uniform coating structure. Thus, it was found that a decrease in the friction coefficient is achieved with lower barrel filling values and when using a more reducing gas environment, while an increase in wear resistance is associated with an increase in the oxygen potential of the mixture and optimization of the thermal regime due to an increase in the interval between shots, which confirms the need for comprehensive optimization of the process parameters to obtain coatings with specified performance characteristics [13].

The results of the study of the dependence of the filling volume of the gas mixture and the roughness profile during detonation spraying are presented in Figure 8.

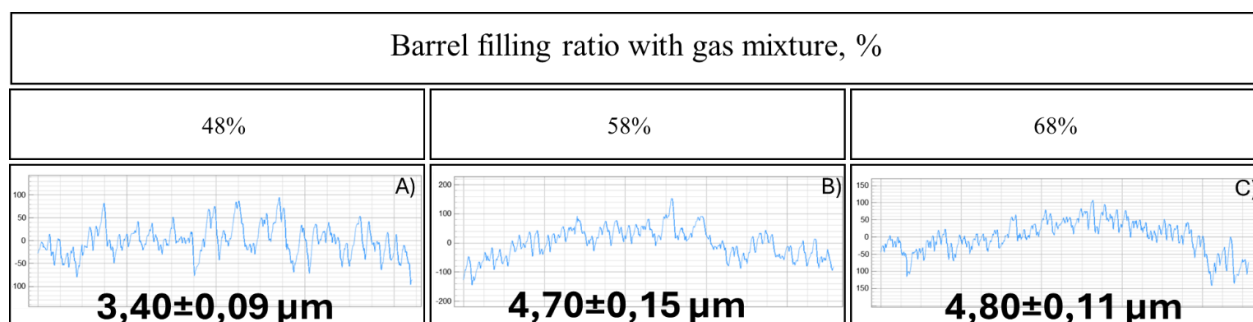


Figure 8. Surface profiles for different barrel fill volumes with explosive mixture:
(a) fill volume — 48 %, (b) fill volume — 58 %, (c) fill volume — 68 %

It was found that at a barrel fill volume of 48 % (Fig. 8a), the average roughness value is $R_a = 3.40 \pm 0.09 \mu\text{m}$, with the profile characterized by a relatively uniform distribution of irregularities with a moderate oscillation amplitude. This surface structure indicates a sufficient degree of particle deformation and their uniform distribution over the surface. With an increase in the fill volume to 58 % (Fig. 8b), the roughness increases to $R_a = 4.70 \pm 0.15 \mu\text{m}$, while an increase in the amplitude of irregularities and a more pronounced waviness of the profiles are observed. This may be due to the increased energy of the particles and their uneven deformation upon impact, which leads to the formation of a more developed surface relief. With a further increase in fill to 68 % (Fig. 8c), the roughness reaches a maximum value of $R_a = 4.80 \pm 0.11 \mu\text{m}$. The surface profile is characterized by significant height variations and the presence of pronounced peaks and valleys, indicating the formation of a coarser and more heterogeneous coating structure. This may be due to worsening detonation conditions, partial melting of particles, and their agglomeration.

The results of studying the relationship between the molar ratio of the gas mixture and the roughness profile during detonation spraying are presented in Figure 9.

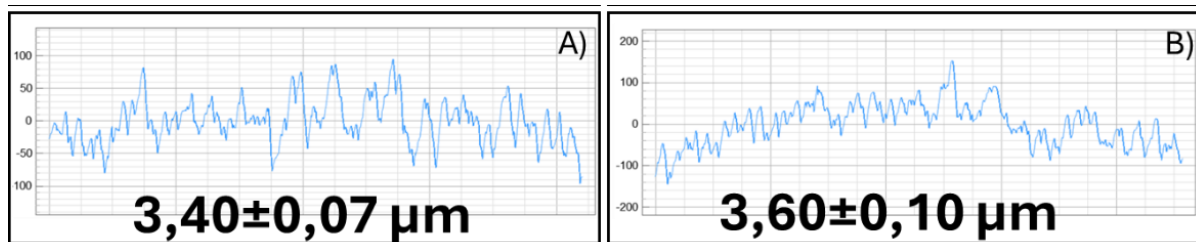


Figure 9. Coating profiles for different gas mixture molar ratios:
(a) 1.026 (oxygen/acetylene + propane mixture); (b) 1.856 (oxygen/acetylene mixture)

For sample A, the average roughness value was found to be $R_a = 3.40 \pm 0.07 \mu\text{m}$. The surface profile is characterized by a moderate oscillation amplitude and a relatively uniform distribution of irregularities, indicating a stable particle deposition process and sufficient plastic deformation upon impact with the substrate. For sample B, the roughness increases to $R_a = 3.60 \pm 0.10 \mu\text{m}$, with an increase in the profile oscillation amplitude and the appearance of more pronounced peaks and valleys. This indicates the formation of a more developed surface relief, which may be associated with changes in the energy conditions of spraying and uneven particle deformation.

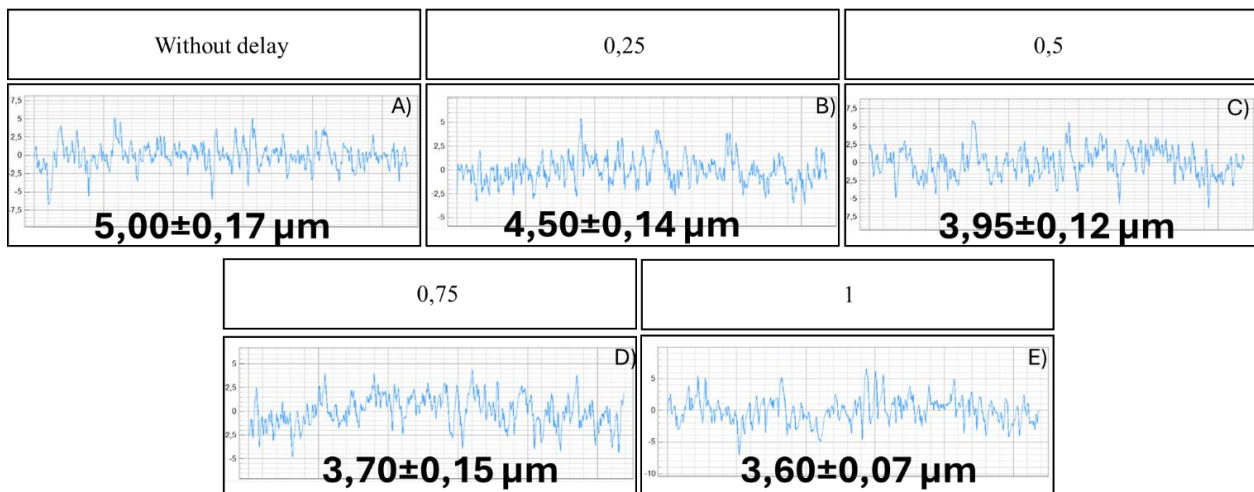


Figure 10. Coating profiles with different delays between shots:
(a) no delay (b) 0.25 s (c) 0.5 s (d) 0.75 s (e) 1 s

It was found that without a delay between shots (Fig. 10a), the roughness reaches a maximum value of $R_a = 5.00 \pm 0.17 \mu\text{m}$, with the profile characterized by significant fluctuations and the presence of pronounced peaks and valleys. This is due to surface overheating and unstable particle deposition conditions,

leading to the formation of a rough relief. With a delay of 0.25 s (Fig. 10b), a decrease in roughness to $Ra = 4.50 \pm 0.14 \mu\text{m}$ is observed, indicating partial stabilization of the thermal regime and improved conditions for coating formation. A further increase in the holding time to 0.5 s (Fig. 10c) leads to a decrease in roughness to $Ra = 3.95 \pm 0.12 \mu\text{m}$, while the profile becomes more uniform, and the amplitude of the irregularities decreases. With a holding time of 0.75 s (Fig. 10d), the roughness continues to decrease to $Ra = 3.70 \pm 0.15 \mu\text{m}$, which indicates the formation of a denser and more uniform coating structure. The minimum roughness value is achieved with a holding time of 1 s (Fig. 10e) and is $Ra = 3.60 \pm 0.07 \mu\text{m}$. The surface is characterized by the smallest oscillation amplitude and the most uniform distribution of irregularities, which indicates stabilization of the spraying process and optimal thermal conditions [14].

Thus, increasing the delay between shots leads to a systematic decrease in surface roughness, which is due to a decrease in thermal accumulation, a decrease in residual stresses and an improvement in the conditions for deformation and coalescence of particles upon impact with the substrate.

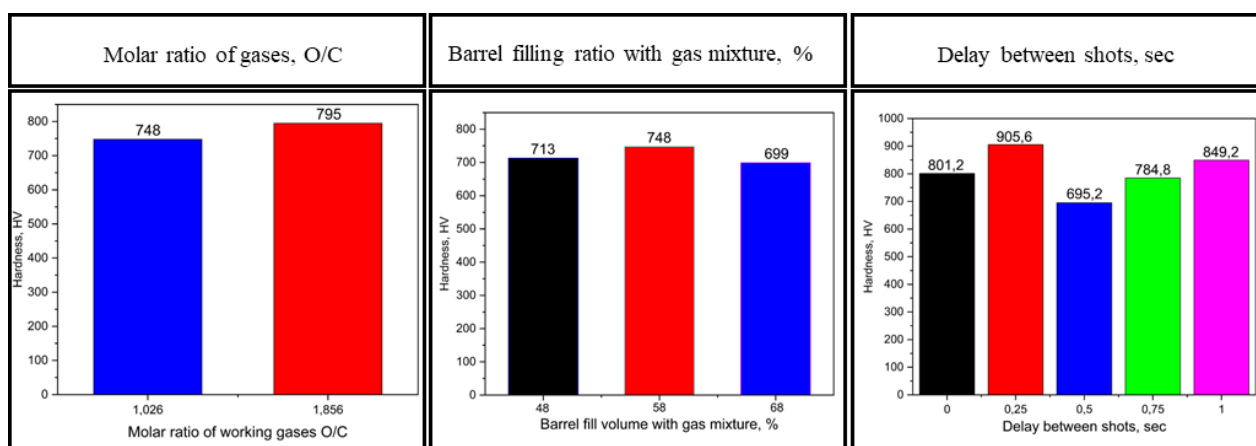


Figure 11. Coating hardness measurement results for various detonation spraying process regimes

The microhardness measurements for Ni–Cr–Fe–B–Si–C coatings (Fig. 11) showed a pronounced dependence of this parameter on the detonation spraying process regimes. It was found that with a change in the gas molar ratio, the hardness increased from 748 HV at O/C = 1.026 to 795 HV at O/C = 1.856, indicating the formation of a denser and more reinforced coating structure at a higher oxygen content due to the higher process temperature and improved particle melting. An analysis of the barrel fill factor influence revealed that the maximum hardness value (748 HV) is achieved at 58 %, whereas a decrease and increase in fill to 48 % and 68 % results in a decrease in hardness to 713 HV and 699 HV, respectively. This may be due to the fact that an average fill factor provides optimal conditions for particle acceleration and deformation, ensuring the formation of a dense structure, whereas deviations from the optimum lead to increased porosity and coating heterogeneity. The most significant influence is exerted by the delay between shots: an increase in the interval from 0 to 0.25 s leads to an increase in hardness from 801.2 to 905.6 HV, after which a decrease to 695.2 HV is observed at 0.5 s, and a further increase in delay to 0.75–1 s leads to a repeated increase in hardness to 784.8–849.2 HV. This nature of the change is explained by the complex influence of the thermal regime: with a short delay, heat accumulation and partial softening of the structure occur, whereas with an optimal delay, effective cooling and the formation of hardening phases (borides and carbides) are ensured, increasing the hardness of the coating [15]. Thus, maximum hardness values are achieved with an increased oxygen ratio, an average barrel filling level, and an optimal delay between shots, which confirms the decisive role of energy and thermal process parameters in the formation of the mechanical properties of coatings.

Conclusion

The study found that detonation spraying process parameters have a decisive influence on the morphology, structure, and performance properties of Ni–Cr–Fe–B–Si–C coatings.

It was shown that the degree of filling of the barrel with the gas mixture significantly influences coating formation: at 48 %, the most uniform structure with minimal porosity is formed, while at 58–68 %, defects increase and an increase in the friction coefficient and wear is observed.

It was found that the gas molar ratio determines the balance between the friction coefficient and wear resistance. At $O/C = 1.026$, the friction coefficient is minimal, but wear intensity increases, while at $O/C = 1.856$, a harder and more wear-resistant coating structure is formed.

The delay between shots is a key parameter regulating the thermal regime of the process. Increasing the interval to 1 s leads to a reduction in roughness, a decrease in residual stresses, and a nearly twofold reduction in wear intensity, due to the formation of a denser and more uniform structure.

It has been shown that maximum coating hardness is achieved with an optimal combination of parameters, ensuring efficient particle melting and the formation of strengthening phases (borides and carbides).

Thus, it has been established that producing coatings with desired tribological characteristics requires comprehensive optimization of the energy and thermal parameters of detonation spraying. Optimal conditions ensure the formation of coatings with high structural integrity, reduced roughness, and increased wear resistance, making them promising for the restoration and strengthening of mechanical engineering components.

Acknowledgments

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Никель негізіндегі өздігінен балқитын жабындарды детонациялық бүрку әдісімен алу негіздерін әзірлеу

Мақалада Ni–Cr–Fe–B–Si–C жүйесіндегі өздігінен балқитын жабындардың құрылымы мен трибомеханикалық қасиеттеріне детонациялық бүркудің технологиялық параметрлерінің әсері зерттелді. Айнымалы параметрлер ретінде газ қоспасымен оқпанның толтырылу көлемі (48–68 %), жұмыс газдарының молярлық қатынасы ($O/C = 1,026\text{--}1,856$) және атулар арасындағы уақыт (0–1 с) қарастырылды. Жабындардың морфологиялық талдауы жүргізіліп, нәтижесінде ламеллярлы құрылымның қалыптасатыны анықталды, сондай-ақ жабын қалыңдығымен ақаулылығының бүрку режимдеріне тәуелділігі көрсетілді. Оқпанның төмен толтырылу деңгейінде минималды кеуектілігі бар тығыз құрылым қалыптасатыны, ал орташа және жоғары толтыру кезінде қалдық кернеулердің артуына байланысты микрожарықшақтардың пайда болатыны анықталды. Трибологиялық сынақтар нәтижесінде ең төмен үйкеліс коэффициенті 48 % толтыру кезінде ($\mu = 0,674 \pm 0,136$) және $O/C = 1,026$ қатынасында байқалатыны анықталды, алайда бұл жағдайда тозу жоғары болады. Ең жоғары тозуға төзімділік $O/C = 1,856$ және атулар арасындағы уақыт аралығын (1 с дейін) арттыру кезінде қамтамасыз етіледі, бұл кезде тозу қарқындылығы $0,000189 \text{ мм}^3/(\text{Н} \cdot \text{м})$ дейін төмендейді. Беткі кедір-бұдырлықты талдау атулар арасындағы уақыт аралығының ұлғаюы Ra мәнінің 5,00-ден 3,60 мкм-ге дейін төмендеуіне әкелетінін көрсетті. Максималды қаттылық (905,6 HV дейін) тығыз құрылыммен беріктендіруші фазалардың қалыптасуын қамтамасыз ететін параметрлердің оңтайлы үйлесімі кезінде байқалады. Детонациялық бүрку параметрлерін оңтайландыру үйкеліс коэффициентін төмендетумен тозуға төзімділікті арттыру арасындағы компромисті талап ететіні көрсетілді. Алынған нәтижелер машина бөлшектерін қалпына келтіру және беріктендіру технологияларын әзірлеуде қолданылуы мүмкін.

Кілт сөздер: өздігінен ағатын қорытпалар, детонациялық бүрку, никель қорытпалары, NiCrFeBSi, жылулық өңдеу, AISI 321 болат

Д.Б. Буйткенов, Л.Г. Сулюбаева, Д.Р. Байжан, Н.С. Райсов, Н.Т. Бимахан

Разработка метода получения самофлюсующихся покрытий на основе никеля методом детонационного напыления

В работе исследовано влияние технологических параметров детонационного напыления на структуру и трибомеханические свойства самофлюсующихся покрытий системы Ni–Cr–Fe–B–Si–C. В качестве варьируемых параметров рассматривались объём заполнения ствола газовой смесью (48–68 %), молярное соотношение рабочих газов ($O/C = 1,026\text{--}1,856$) и выдержка между выстрелами (0–1 с). Проведён морфологический анализ покрытий, показавший формирование характерной ламеллярной структуры, а также выявивший зависимость толщины и дефектности от режимов напыления. Установлено, что при низком заполнении ствола формируется более плотная структура с минимальной пористостью, тогда как при среднем и высоком заполнении наблюдается образование микротрещин вследствие роста остаточных напряжений. Трибологические испытания показали, что минимальный коэффициент трения достигается при заполнении 48 % ($\mu = 0,674 \pm 0,136$) и соотношении $O/C = 1,026$, однако при этом наблюдается повышенный износ. Наиболее высокая износостойкость обеспечивается при $O/C = 1,856$ и увеличенной выдержке между выстрелами (до 1 с), при которой интенсивность износа снижается до $0,000189 \text{ мм}^3/(\text{Н} \cdot \text{м})$. Анализ шероховатости показал, что увеличение выдержки между выстрелами приводит к снижению Ra с 5,00 до 3,60 мкм, что связано с уменьшением тепловой нагрузки и улучшением условий формирования покрытия. Максимальная твёрдость (до 905,6 HV) достигается при оптимальном сочетании параметров, обеспечивающем формирование плотной структуры и упрочняющих фаз. Показано, что оптимизация параметров детонационного напыления требует компромисса между снижением коэффициента трения и повышением износостойкости. Полученные результаты могут быть использованы при разработке технологий восстановления и упрочнения деталей машин.

Ключевые слова: самофлюсующиеся сплавы, детонационное напыление, никелевые сплавы, NiCrFeBSi, термическая обработка, сталь AISI 321

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C.C. Bayramov¹, R.Y. Damirov^{2✉}, U.M. Mustafayeva¹, A.F. Talifli¹¹Sumgayit State University, Sumgayit, Azerbaijan Republic;²Baku State University, Baku, Azerbaijan Republic✉Corresponding author: Damirov, Ragib, damirovrachib@gmail.com**Temperature effects in $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ solid solutions**

Alloys of the $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ system were synthesized, and single crystals were grown by the Bridgman method. X-ray diffraction studies established the solubility range of TlGdS_2 in TlInS_2 . The linear thermal expansion coefficient (α_L) and isothermal compressibility (χ_T) of TlInS_2 and the solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ ($0 \leq x \leq 0.10$) were investigated over the temperature range of 80–400 K. Based on the experimental α_L and χ_T values, the Debye temperature, mean-square atomic displacement, Young's modulus, shear modulus, Poisson's ratio, and the difference between C_p and C_V were determined. The band gap was calculated from the temperature dependence of electrical conductivity and compared with values obtained using thermal and optical methods. The anomalous behavior of electrical conductivity was attributed to hopping conduction associated with stoichiometric vacancies and localized states within the band gap. Unlike TlInS_2 , no phase transitions were observed in the investigated solid solutions over the temperature range of 80–400 K. Increasing the TlGdS_2 concentration resulted in higher thermal expansion and compressibility coefficients, indicating weaker interatomic interactions and enhanced anharmonicity of lattice vibrations. The obtained results reveal correlations among crystal structure, chemical bonding, and physical properties in layered chalcogenide semiconductors.

Keywords: solid solutions, linear thermal expansion, isothermal compressibility, shear modulus, anharmonicity, band gap, photoconductivity, single crystals, Bridgman method, X-ray diffraction

Introduction

Interest in semiconductor compounds of the type $\text{TlA}^{\text{III}}\text{B}_2^{\text{VI}}$ ($\text{A} = \text{In, Ga}; \text{B} = \text{S, Se, Te}$) and solid solutions based on them is initially due to the fact that the crystals represent a promising material for use in optical electronics [1–3]. The crystal structure of TlInS_2 is solved in [4]. It is established that TlInS_2 belongs to the monoclinic syngony and has the following crystal lattice parameters: $a = 10.95$; $b = 10.95$; $c = 15.14 \text{ \AA}$, $z = 16$, pr.gr. $\text{Cc} - \text{C}_s^4$.

A characteristic feature of the crystals of solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ is the presence in their crystal lattice of a high concentration ($10^{20} \div 10^{22} \text{ cm}^{-3}$) of stoichiometric vacancies and associated localized states in the band gap [5, 6], and this value increases with the growth of the molar fraction of gadolinium in the composition of solid solutions. With an increase in the concentration of solid solutions, the average distance between the atoms of the dissolved substance TlGdS_2 reaches values at which the inter-impurity interaction begins to make a significant contribution to the energy of the TlGdS_2 solvent crystal [7, 8], and this leads to the appearance of fundamentally new properties that are not characteristic of the original material.

Temperature and concentration dependences of thermal and electrophysical properties of alloys of the TlInS_2 – TlGdS_2 systems are studied in the work [9]. However, these data are insufficient to clarify the nature of the bond and the strength of interatomic interaction in the TlInS_2 compound and solid solutions of the TlInS_2 – TlGdS_2 system, which is of particular interest for the analysis of thermal and elastic properties of this object.

To obtain additional information about the chemical bond in the crystal lattice, its influence on the nature and magnitude, the temperature dependence of the heat capacity of thermal expansion (α) and isothermal compressibility (χ_T) are studied in a wide temperature (80–350 K) and concentration ranges.

The aim of the present work is a comprehensive investigation of the temperature and concentration dependences of the coefficient of linear thermal expansion (α_L) and isothermal compressibility (χ_T) of solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ ($0 \leq x \leq 0.10$) in the temperature range 80–400 K. The specific objectives include: establishing the solubility region of TlGdS_2 in TlInS_2 by X-ray diffraction analysis; calculating the Debye temperature, mean-square atomic displacements, Young's modulus, shear modulus, Poisson's ratio, and the difference $C_p - C_v$ from experimental α_L and χ_T data; determining the band gap E_g from temperature dependences of electrical conductivity; and comparing the band gap values obtained from thermal, electrical, and optical measurements to verify the consistency of the applied approaches.

Experimental

Alloys of the $\text{TlInS}_2 - \text{TlGdS}_2$ system are studied using differential thermal, X-ray phase, and microstructural analysis methods. DTA of the samples is carried out using a low-frequency thermal recorder NTR-73 with a Pt-Pt/Ph thermocouple at a heating rate of 10 K/min. X-ray fluorescence analysis is carried out using a DRON-1.5 apparatus (Ni filter, 35 kV, 10 mA). The radiographs are decoded using the IZA-2 comparator with an error of 0.01–0.05 mm. The swing radiographs are obtained in the RKOP-A chamber. The intensity of the lines is determined visually using a ten-point scale. The lattice parameters are determined by the

extrapolation method using the function $\frac{1}{2} \left(\frac{\cos^2 \theta}{\cos \theta} + \frac{\cos^2 \theta}{\theta} \right)$ with an accuracy of 0.001 Å. Single crystals of

the samples are grown by the Bridgman method in evacuated quartz ampoules with a diameter of 20–25 mm with different bottom forms. The best homogeneity of samples is obtained with a conical shape of the ampoule bottom and a growth rate of single crystals of 0.5 mm/h. The monocrystalline of the grown crystals is judged by the recorded Lauegrams. To conduct a temperature X-ray diffractometry study, plane-parallel plates are separated from the obtained monocrystal along the cleavage plane and installed on the goniometric head of the DRON-1.5 diffractometer [5]. Measurements of electrical conductivity and the Hall effect are carried out on samples with ohmic contacts at direct current [10] in constant magnetic fields up to 1200 A/m. The measurement error did not exceed 4–5 %.

To measure the all-round compression of the alloys of the $\text{TlInS}_2 - \text{TlGdS}_2$ system in the range of 77–420 K, the setup described in [11] is used. In order to increase the accuracy of measuring the frequency of sinusoidal signals with different interferences, an integrated Schmidt trigger is used in the registration circuit. The setup is calibrated according to the compressibility of reference samples of copper and aluminum. Helium gas is used to compress the sample, the pressure of which varied from 10^5 Pa to 10 MPa. With a small modification, on the same installation, without removing the sample, measurements of thermal expansion are also carried out. The rate of temperature rise did not exceed 2 K/min. The samples had the shape of a cylinder with a cut of 30 mm and a diameter of 5 mm. The error in measuring thermal expansion is ~1.45 %, and in measuring isothermal compressibility ~4.5 % [12]. Synthesis and X-ray diffraction of samples.

Solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ are synthesized in quartz ampoules by melting the starting materials. The starting materials are high-purity elements (Tl — 99.99 wt.%, Gd — 99.5 wt.%, In — 99.999 wt.%, S-oc.4.16-5). From these data, with the exception of gadolinium, it follows that the purity of the initial elements is satisfactory. It is found that 8–10-fold zone purification allows increasing the purity of the element gadolinium to 99.7 mass %. The alloys are synthesized as follows. The initial elements, loaded into an ampoule evacuated to 0.01 Pa, are placed in a furnace. Depending on the gadolinium content, the furnace is heated to a temperature of (1100–1200) K. The time the ampoule with the substance is kept at this temperature also depended on the gadolinium content and increased from 2 to 3 hours as it increased. After which the temperature of the ampoule with the substance is cooled to room temperature at a rate of 15–20 K/h. The obtained samples had a golden-orange color. The alloys synthesized are $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ where $0 \leq x \leq 0.10$.

To conduct an X-ray study using the Bridgman method, single crystals of the $\text{TlInS}_2 - \text{TlGdS}_2$ system alloys are grown. The speed of movement of the ampoule with the melt is 3 mm/h. When growing single crystals of the $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ alloys, the temperature of the high-temperature zone varied from 1000 to 1300 K. In particular, for the composition $x = 0.05$, the zone temperature is 1130 K, and for $x = 0.10$, 1300 K. To establish the solubility region based on TlInS_2 , the obtained single crystals are subjected to X-ray phase analysis. X-ray analysis of crystals $x = 0.05$ and $x = 0.10$ showed that these phases crystallize in the monoclinic syngony based on the TlInS_2 lattice. Calculations of the diffraction patterns of powders of the composition $x = 0.05$ and $x = 0.10$ are given. Laue grams are taken from the obtained sample to determine

the quality of monocrystalline. It appeared that the obtained samples are perfect monocrystals. The quality of the monocrystals worsens with increasing gadolinium concentration in the studied compositions. Based on the rocking X-ray diffraction pattern in three crystallographic directions $[h00]$, $[0k0]$ and $[00l]$, the following lattice parameters of the monoclinic syngony are established for single crystals $x = 0.05$ and $x = 0.10$; $a = 10.843$; $b = 10.90$; $c = 15.145$ Å; $\beta = 100^\circ$; $z = 16$; $a = 10.964$; $b = 10.848$; $c = 15.167$ Å; $\beta = 100^\circ$; $z = 16$.

The calculated numbers of molecules per unit cell confirm that $(\text{TlInS}_2)_{0.95}(\text{TlGdS}_2)_{0.05}$ and $(\text{TlInS}_2)_{0.9}(\text{TlGdS}_2)_{0.1}$ as well as alloys (0–10) mol% TlGdS_2 are substitution solid solutions.

From the above crystal along the $[00l]$ plane is obtained in clear diffraction reflections corresponding to the angles: $\theta = 5^\circ 55'$ (002), $11^\circ 55'$ (004), $24^\circ 23'$ (006), $31^\circ 03'$ (008), $38^\circ 15'$ (00,10), $46^\circ 14'$ (00,12) based on the temperature study conducted, in the temperature range of 320–800 K, curves of the dependence of the lattice parameter “C” on temperature are constructed. It turned out that with an increase in temperature along the $[00l]$ plane, a linear expansion of the crystal $(\text{TlInS}_2)_{0.95}(\text{TlGdS}_2)_{0.05}$ is observed. Thus, as a result of the conducted X-ray study of single crystals $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$, it is established that when TlGdS_2 atoms are replaced by TlInS_2 in the range of (0–10) mass%, the structure does not change and substitution solid solutions are formed (Table 1).

Table 1

Calculation of diffraction patterns of powders of composition $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$

№	$x = 0$	$x = 0.05$	$x = 0.1$	hkl
	$d_{\text{theo.}}, \text{Å}$	$d_{\text{exp.}}, \text{Å}$	$d_{\text{exp.}}, \text{Å}$	
1	7.4550	7.4576	7.4681	002
2	3.8417	3.8176	3.8230	220, 212
3	3.7275	3.7282	3.7283	004
4	3.4554	3.4400	3.4531	311
5	3.0116	3.0232	2.9958	105
6	2.8661	2.8628	2.8610	321, 224
7	2.7545	2.7563	2.7568	323
8	2.5202	2.5191	2.4957	305
9	2.3904	2.3891	2.3820	404
10	2.1347	2.1351	2.1295	151
11	1.9902	1.9875	1.9902	414
12	1.9262	1.9342	1.9271	252
13	1.8643	1.8688	1.8664	208, 008
14	1.7712	1.7716	1.7672	155
15	1.7199	1.7181	1.7184	614
16	1.6867	1.6846	1.6900	317
17	1.6009	1.6037	1.5977	328, 319
18	1.5006	1.4944	1.4903	721

Results and Discussion

The temperature dependences of the electrical conductivity (σ) of the solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ turned out to be complex. It is evident that the electrical conductivity maxima are observed at temperatures of ~795, 810, 830 K for $x = 0.01$; 0.05; 0.10, respectively. With a further increase in temperature, σ decreases, reaches a minimum, and again sharply increases (the region of intrinsic conductivity). This behavior of electrical conductivity in solid solutions of the $\text{TlInS}_2 - \text{TlGdS}_2$ system can be associated with hopping conductivity (Fig. 1a, b).

In this region, the temperature dependence $\lg \sigma \sim AT^{-1/4}$ is typical for such jumps. According to, even in specially undoped crystals TlInS_2 , TlGaSe_2 , TlGaS_2 there is hopping conductivity $T = 200$ K [13]. The nature of uncontrolled defects in TlInS_2 is most likely associated with anion vacancies, which lead to hopping conductivity, at relatively high temperatures can be different. The reason for this may be both anionic and cationic.

onic vacancies disordered in the layer joints and other defects. However, as noted in, these defects do not lead to the state of ferroelectric glass [14].

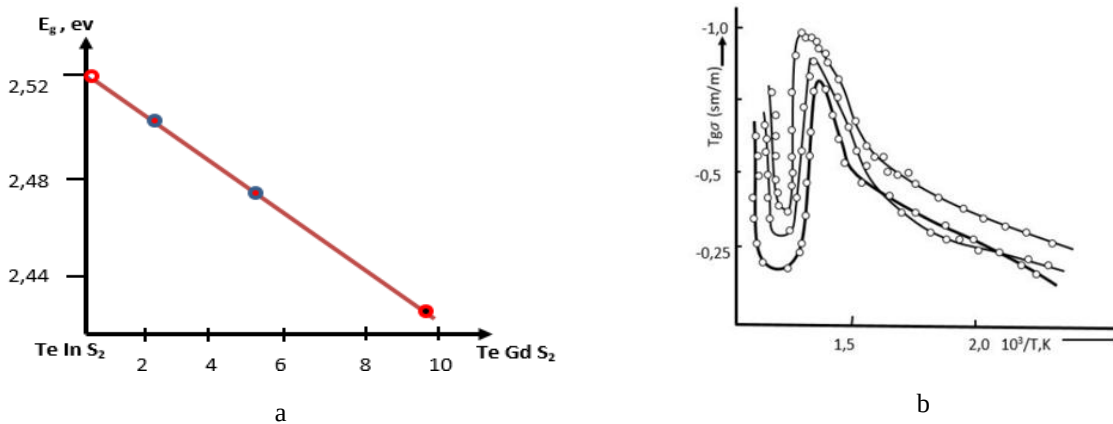


Figure 1. Temperature dependence of electrical conductivity (a) and concentration dependence of the bandgap (b) of solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ (1 — $x = 0.02$; 2 — $x = 0.05$; 3 — $x = 0.10$)

The bandgap widths of the indicated phases are determined from the high-temperature slope of the temperature dependence of electrical conductivity and the Hall effect and are in good agreement. Figure 1b shows the dependences of the band gap of the solid solutions $[\text{TlInS}_2]_{1-x}[\text{TlGdS}_2]_x$, determined by $\lg \sigma = f\left(\frac{10^3}{T}\right)$. It is evident that with an increase in TlGdS_2 in TlInS_2 the value of E_g decreases. Based on

the band structure of TlInS_2 , the valence band is mainly formed by the split $3p$ levels of sulfur and partially by the $5p5s$ levels of indium ions, as well as the $6p$ levels of thallium. The conduction band is formed by the $5p5s$ levels of indium ions and the $6p^1$ levels of thallium. When substituting atoms in the $\text{TlInS}_2 - \text{TlGdS}_2$ system, the valence electrons of the latter ions partially pass into a collectivized state, which leads to strong electronic interactions and a “loosening” of the lattice ($R_{\text{In}} = 0.92 \text{ \AA}$; $R_{\text{Gd}} = 0.96 \text{ \AA}$). As a result, during the transition from TlInS_2 to solid solutions based on it, the valence band undergoes a certain shift towards higher energies due to the overlap of the sulfur $3p$ states with the higher-lying gadolinium $4f$ states. At the same time, the lattice parameters increase and the band gap decreases.

Figures 2, 3 show the results of the study of the temperature dependence of the coefficient of linear thermal expansion (α_L) and isothermal compressibility (χ_T) in the range of 80–400 K in TlInS_2 .

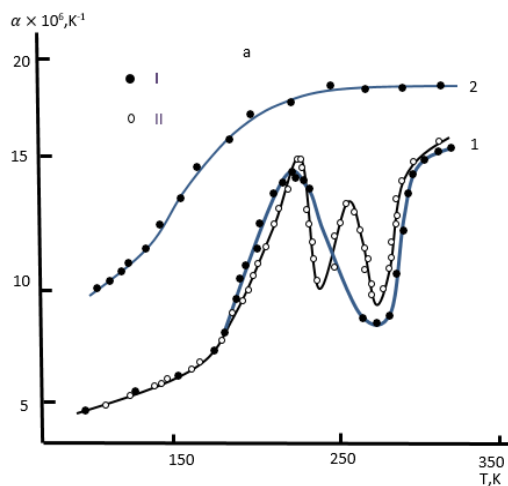


Figure 2. Temperature dependence of the coefficient of linear thermal expansion of 1 — TlInS_2 ; 2 — TlGdS_2 compounds (○ — monocrystalline, ● — polycrystalline)

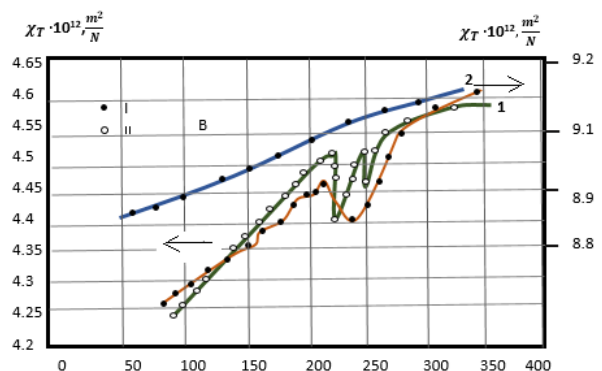


Figure 3. Temperature dependence of the isothermal compression coefficient of TlInS_2 and TlGdS_2 compounds (symbols are the same as in Figure 2)

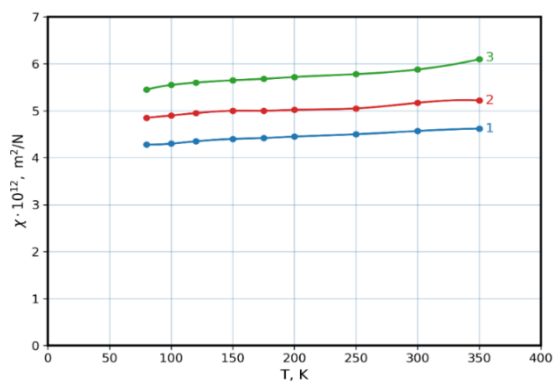


Figure 4. Temperature dependence of the coefficient of linear thermal expansion of $[\text{TlInS}_2]_{1-x}[\text{TlGdS}_2]_x$ solid solutions (markings are as in Figure 1)

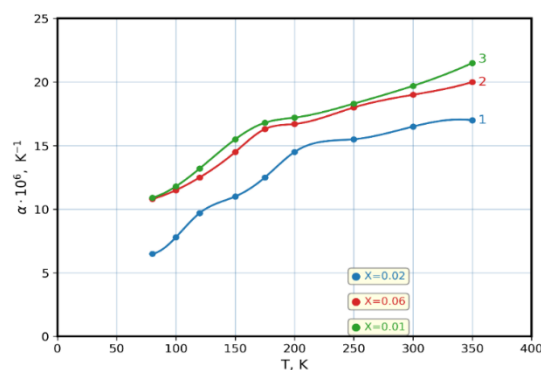


Figure 5. Temperature dependence of the isothermal compressibility coefficient of $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ solid solutions (the symbols are the same as in Figure 1)

It follows from the figure that for the single-crystal sample of TlInS_2 , two anomalies are observed, which correspond to the temperature range of the ferroelectric and incommensurate commensurate transitions [15]. For polycrystalline TlInS_2 , only one anomaly is observed on the curve, covering a wider temperature range, and the even boundary of anomalies observed in the case of a single-crystal sample disappears. The changes in the anomaly in the single-crystal and semi-crystalline samples of TlInS_2 that we have discovered can also be associated with the influence of the “random field” and “random temperature” defects, since these defects create non-zero values of the order parameter independent of symmetry. In this connection, an electric field is created that strongly affects the incommensurate-commensurate phases.

From the standpoint of interatomic interaction mechanisms, the anomalies observed in TlInS_2 reflect the softening of certain phonon modes associated with the structural instability of the layered monoclinic lattice near the ferroelectric transition. The high concentration of stoichiometric vacancies ($\sim 10^{20} - 10^{22} \text{ cm}^{-3}$) inherent to TlInS_2 plays a decisive role: these point defects generate local electric fields and random strain fields that couple to the order parameter of the incommensurate modulation. The complete suppression of anomalies in solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ can be attributed to the disruption of long-range structural order upon substitution of In^{3+} by Gd^{3+} ions. The larger ionic radius of Gd ($R_{\text{Gd}} = 0.96 \text{ \AA}$) compared to In ($R_{\text{In}} = 0.92 \text{ \AA}$) introduces local lattice distortions that pin the incommensurate modulation and prevent the cooperative atomic displacements required for the phase transitions observed in the parent TlInS_2 compound. The monotonic increase of α_L and χ_T with growing TlGdS_2 content is consistent with the progressive weakening of interatomic bonding and the increase in anharmonicity confirmed by the observed decrease in the Debye temperature.

The results of the studies of the temperature dependence of the linear thermal expansion and isothermal compressibility (α_L and χ_T) of solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ where $0 \ll x \ll 0.1$ at $80 - 400 \text{ K}$ are shown in Figure 4, 5. It is evident that no anomalies are observed in the temperature dependences of α_L and χ_T in the studied temperature range. This indicates that there are no phase transformations in the specified temperature range. As follows from Figure 4, 5, in all the crystals studied, the nature of the temperature dependence of both α_L and χ_T is almost the same, i.e., at relatively low temperatures, α_L increases with increasing temperature and, starting from $\sim 210 \text{ K}$, the growth of α_L somewhat weakens and gradually comes to a constant value. This behavior of α_L and χ_T in solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ is explained by the identity of the types of crystal structure and chemical bonds between atoms. In order to identify the temperature, increase of α_L , the degrees of temperature dependence of α_L are determined graphically at different temperature ranges $80 \leq T \leq 200 \text{ K}$. At $x = 0$, $\alpha_L \sim T_{0.81}$; $x = 0.02$, $\alpha_L \sim T_{0.86}$; $x = 0.05$, $\alpha_L \sim T_{0.92}$; $x = 0.10$, $\alpha_L \sim T_{0.95}$. Such a large change in the degree of temperature dependence of α_L in solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ is explained by the fact that during thermal expansion, along with a change in the size of the unit cell, the amplitude of oscillations of atoms in the crystal lattice also changes, which in turn leads to a change in the anharmonicity value.

The experimental data obtained by us on the values of α_L TlInS_2 and various compositions of solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ are used to calculate the Debye temperature (θ_D) and the root-mean-square dynamic displacements of atoms ($\sqrt{u^2}$) according to the following equations:

$$\theta_D = \frac{14.37}{(\bar{A} \cdot V^{3/2} \cdot \alpha)^{1/2}}; \quad (1)$$

$$\sqrt{u^2} = \frac{4.3 \cdot 10^{-14} [D(\theta_D / T)(\theta_D / T) + 1/4]}{\bar{A} \theta_D}, \quad (2)$$

where α_L is the coefficient of linear thermal expansion, $\bar{A}$ is the average atomic mass, V is the average atomic volume, $D(\theta_D / T)$ is the Debye function. The calculation data for the values of (θ_D) and $(\sqrt{u^2})$ using expressions (1) and (2) are presented (Table 2).

Table 2

The value of the Debye temperatures and the root-mean-square dynamic displacements of atoms in the crystal lattice of solid solutions (TlInS₂)_{1-x}(TlGdS₂)_x

T, K	x = 0		x = 0.02		x = 0.05		x = 0.10	
	θ_D , K	$\sqrt{u^2}$, Å	θ_D , K	$\sqrt{u^2}$, Å	θ_D , K	$\sqrt{u^2}$, Å	θ_D , K	$\sqrt{u^2}$, Å
80	335	0.066	392	0.072	323	0.080	313	0.084
100	314	0.075	353	0.081	306	0.091	300	0.093
120	290	0.085	325	0.092	292	0.101	283	0.104
140	266	0.098	302	0.103	280	0.111	269	0.115
160	240	0.113	285	0.115	270	0.120	260	0.126
180	206	0.139	272	0.126	263	0.131	252	0.137
200	182	0.166	264	0.136	257	0.141	245	0.148
220	178	0.177	259	0.145	253	0.149	240	0.160
240	220	0.115	256	0.153	250	0.158	236	0.168
280	174	0.120	255	0.167	248	0.172	232	0.185
310	171	0.122	254	0.175	247	0.179	230	0.196
350	170	0.123	253	0.187	246	0.194	228	0.210

It is evident that when replacing indium atoms with gadolinium atoms, the mean square dynamic displacement of atoms in the crystal lattice increases, and the Debye temperature decreases by (TlInS₂)_{1-x}(TlGdS₂)_x. The change in the Debye temperature with temperature indicates a deviation of the phonon spectrum from the Debye model.

Based on the experimental data on the isothermal compressibility coefficient, some elastic parameters for solid solutions (TlInS₂)_{1-x}(TlGdS₂)_x are also calculated using the formulas given: Young's modulus (E)

$$E = \left(\frac{\theta_D \cdot m^{1/3} \cdot \rho^{1/6}}{1.6818 \cdot 10^3} \right)^{1/2}, \text{ shear modulus } (\mu) \mu = \frac{E}{2(1+\sigma)}, \text{ Poisson's ratio } (\sigma) \sigma = 1 - \left(\frac{E}{3K} \right) \text{ and the velocity of propagation of longitudinal ultrasonic waves } (\vartheta_e) \vartheta_e = \sqrt{\frac{E}{\rho}}, \text{ where } \theta_D \text{ is the Debye temperature, } \rho \text{ is the density, } m \text{ is the mass.}$$

ty of propagation of longitudinal ultrasonic waves $(\vartheta_e) \vartheta_e = \sqrt{\frac{E}{\rho}}$, where θ_D is the Debye temperature, ρ is the density, m is the mass.

The calculation results are given. It is evident from Table 3 that with the increase of the TlGdS₂ content in TlInS₂ the elastic parameters E , μ , ϑ_e . (σ -slightly changes) decrease. This allows us to conclude that with the increase of the TlGdS₂ content in TlInS₂ the chemical bond between the atoms in the solid solutions (TlInS₂)_{1-x}(TlGdS₂)_x changes significantly, which leads to a large change in the degree of anharmonicity of thermal vibrations (Table 3). The uncertainties in the calculated elastic parameters are determined primarily by the measurement errors of the experimental quantities: the error in α_L is $\sim 1.45\%$ and in χ_T is $\sim 4.5\%$, as indicated in the Experimental section. Error propagation through formulas (1) and (2) yields an estimated uncertainty of $\sim 3\%$ for θ_D and $\sim 5-6\%$ for $\sqrt{u^2}$. For the elastic moduli, the combined uncertainty is approximately $5-8\%$. These values are consistent with the typical accuracy reported for similar chalcogenide systems in the literature [16]. A comparison of the obtained Debye temperatures (228–392 K depending on composition and temperature) with values reported for structurally related compounds TlGaSe₂ (~ 220 K) and TlInSe₂ (~ 240 K) [17] confirms the physical reasonableness of the calculated parameters.

Table 3

Values of Young's modulus, shear modulus, Poisson's ratio and the velocity of longitudinal ultrasonic waves of solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$

T, K	$x = 0.02$				$x = 0.05$				$x = 0.10$			
	E, GPa	σ	μ , GPa	ϑ_e , m/c	E, GPa	σ	μ , GPa	ϑ_e , m/c	E, GPa	σ	μ , GPa	ϑ_e , m/c
80	513.1	0.458	176.0	9479	349.6	0.470	118.9	7800	331.2	0.472	112.7	7541
90	459.6	0.463	157.1	8972	330.4	0.472	112.3	7583	316.6	0.473	107.8	7373
100	416.1	0.466	141.9	8537	313.8	0.473	106.5	7390	304.3	0.475	103.6	7228
120	352.7	0.471	110.9	7859	285.7	0.475	96.8	7051	270.8	0.476	91.9	6819
140	304.6	0.475	97.1	7304	262.8	0.477	89.0	6763	244.7	0.479	82.9	6482
160	271.2	0.478	87.3	6892	244.3	0.479	82.6	6520	228.6	0.480	77.7	6265
180	247.1	0.479	82.4	6578	231.8	0.480	78.3	6351	214.7	0.482	72.6	6072
200	232.7	0.480	78.6	6384	221.5	0.480	74.8	6209	203.0	0.483	68.6	5904
210	227.5	0.481	76.8	6312	217.9	0.481	73.6	6158	198.0	0.483	67.0	5831
220	224.0	0.481	75.6	6263	214.5	0.481	72.4	6111	194.8	0.484	65.9	5783
240	218.8	0.482	73.9	6190	209.4	0.482	70.6	6037	188.3	0.484	63.6	5686
280	217.1	0.483	73.3	6166	206.1	0.483	69.6	5989	182.0	0.484	61.5	5590
310	215.4	0.484	72.7	6142	204.5	0.484	69.1	5966	178.9	0.485	60.4	5542
350	213.7	0.485	72.1	6118	202.8	0.485	68.5	5941	175.8	0.485	59.4	5494

The temperature dependence of the bandgap of the applied solid solutions ($E_g(T)$) is studied. For this, the empirical formula shown in [18, 19] is used:

$$E_g(T) = E_g(0) - \frac{\gamma\theta}{2} \sqrt{1 + \frac{\pi^2}{6} \left(\left(\frac{2T}{\theta} \right)^2 + \left(\frac{2T}{\theta} \right)^4 - 1 \right)}. \quad (3)$$

Here γ — constant is $\gamma = 3.7 \cdot 10^{-4}$. θ — temperature is found from the relation $\theta = \frac{3}{4}\theta_D$ — Debay temperature (Table 2). The result of the calculation is given in Figure 6 (solid line). As can be seen, with the increase in the amount of TlGdS_2 in TlInS_2 , the value of $E_g(T)$ decreases. In all compositions, the value of $E_g(T)$ increases with the decrease in temperature.

In order to verify the accuracy of the obtained results, the value of $E_g(T)$ is also calculated for the $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ solid solutions at different temperatures using the value $\frac{\partial E_g}{\partial T} = -6 \cdot 10^{-4} \sum \nu / K$, which is found based on the experimental values of photoconductivity. The calculation is carried out using the following empirical formula.

$$E_g(T) = E_g(0) - \frac{\partial E_g}{\partial T} \cdot \frac{T^2}{(T + \theta_D)}. \quad (4)$$

The obtained results are shown in Figure 6 (with the Δ -symbol). As can be seen from the figure, the values calculated for $E_g(T)$ by formulas (3) and (4) coincide with each other and lie on a straight line. This change in the band gap with composition and temperature can be explained by the increase in defects and the weakening of the chemical bond between atoms due to the increase in the amount of TlGdS_2 in solid solutions.

The values of the specific heat capacity at constant volume (C_V) of the solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ are calculated using the experimental values of the specific heat capacity at constant pressure (C_p) [20].

$$C_V = C_p - \frac{9\alpha^2 VT}{\mu T}. \quad (5)$$

The results of the calculation are given in Table 4. As can be seen from the table, the band gap of the investigated solid solutions at different temperatures, the temperature dependence of the electrical conductivity, and the values calculated using (3) and (4) are in good agreement. With increasing temperature, the value of C_V varies for different compositions (Table 4).

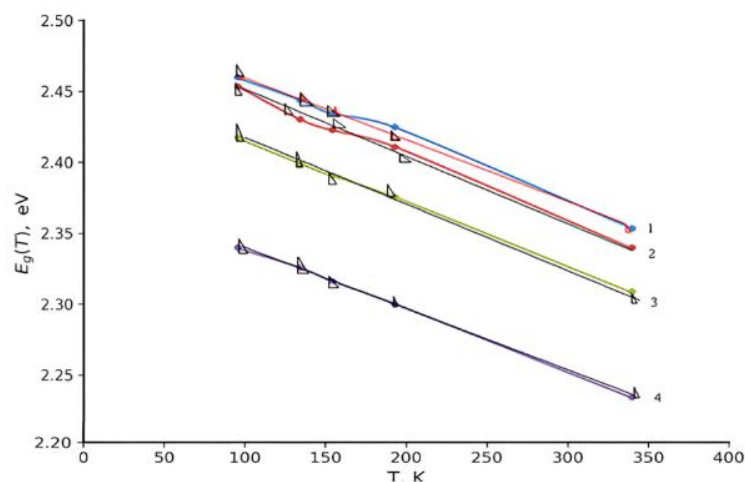


Figure 6. Temperature dependence of the bandgap of $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ solid solutions (1 — $x = 0$; 2 — $x = 0.02$; 3 — $x = 0.05$; 4 — $x = 0.10$)

Table 4

Zone and thermal parameters of $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ solid solutions

Example	E_{g0} , eV $\lg \sigma = f(10^3/T)$	T , K	$E_g(T)$, eV (Eq. 3)	$E_g(T)$ (Eq. 4)	C_p $c/kq \cdot K$	C_v $c/kq \cdot K$
$x = 0.02$	2.510	100	2.467	2.486	219.5	217.4
		140	2.445	2.473	244.3	238.8
		160	2.438	2.465	252.1	244.2
		200	2.427	2.448	264.9	251.8
		350	2.360	2.378	279.8	251.2
$x = 0.05$	2.482	100	2.433	2.455	228.7	228.3
		140	2.416	2.442	253.2	252.4
		160	2.408	2.434	260.6	259.6
		200	2.394	2.417	272.6	270.9
		350	2.331	2.346	285.1	281.1
$x = 0.10$	2.413	100	2.360	2.425	246.4	243.9
		140	2.347	2.411	268.3	263.1
		160	2.338	2.403	274.5	267.7
		200	2.323	2.370	286.1	275.5

Conclusion

Using X-ray diffraction and chemical analysis, the solid-solution region in the $\text{TlInS}_2 - \text{TlGdS}_2$ system based on TlInS_2 is established to extend up to 10 mol% of TlGdS_2 at room temperature. The solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$, like TlInS_2 itself, crystallize in the monoclinic system. The observed anomalous behavior of electrical conductivity and the Hall coefficient in the solid solutions is associated with impurity-related hopping conductivity. The band gap decreases with increasing TlGdS_2 content in the solid solutions. A phase transition is detected in the temperature dependence of the thermal expansion coefficient and isothermal compressibility of TlInS_2 . It is shown that, in all the studied solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$, no phase transformation occurs within the temperature range 77–400 K. With increasing TlGdS_2 content in TlInS_2 , the values of the thermal expansion coefficient and isothermal compressibility increase at all investigated temperatures. For TlInS_2 and its solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$, the Debye temperatures, mean-square dynamic displacements in the crystal lattice, the difference between specific heat capacities at constant pressure and constant volume, Young's modulus, shear modulus, Poisson's ratio, and the propagation velocity of longitudinal ultrasonic waves are calculated. The calculation results indicate that with increasing TlGdS_2 content in TlInS_2 , the chemical bonding between atoms in the solid solutions $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ changes significantly, leading to a pronounced modification in the degree of anharmonicity of thermal vibrations. It is shown that there is good agreement between the experimental and calculated values of $E_g(T)$.

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 $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ қатты ерітінділеріндегі температуралық эффектілер

$\text{TlInS}_2 - \text{TlGdS}_2$ жүйесінің қорытпалары синтезделіп, олардың монокристалдары Бриджмен әдісімен өсірілді. Рентгенқұрылымдық зерттеулер TlGdS_2 қосылысының TlInS_2 құрамындағы ерігіштік аймағын анықтады. TlInS_2 және $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ ($0 \leq x \leq 0.10$) қатты ерітінділерінің сызықтық жылулық ұлғаю коэффициенті (α_L) мен изотермиялық сығылғыштығы (χ_T) 80–400 К температура аралығында зерттелді. α_L және χ_T тәжірибелік мәндері негізінде Дебай температурасы, атомдардың орташа квадраттық ығысуы, Юнг модулі, ығысу модулі, Пуассон коэффициенті және $C_p - C_v$ айырмасы есептелді. Тыйым салынған аймақ ені электрөткізгіштіктің температуралық тәуелділігі бойынша анықталып, жылулық және оптикалық әдістермен алынған мәндермен салыстырылды. Электрөткізгіштіктің аномальды тәртібі тыйым салынған аймақтағы локальданған күйлер мен стехиометриялық вакансияларға байланысты секірмелі өткізгіштікпен түсіндірілді. TlInS_2 қосылысынан айырмашылығы, зерттелген қатты ерітінділерде 80–400 К аралығында фазалық ауысулар байқалмады. TlGdS_2 мөлшерінің артуы жылулық ұлғаю мен сығылғыштық коэффициенттерінің өсуіне әкеліп, атомаралық байланыстардың әлсіреуін және жылулық тербелістер ангармониясының күшеюін көрсетті. Алынған нәтижелер қабатты халькогенидті жартылай өткізгіштердегі кристалдық құрылым, химиялық байланыс және физикалық қасиеттер арасындағы өзара байланысты анықтайды.

Кілт сөздер: қатты ерітінділер, сызықтық жылулық ұлғаю, изотермиялық сығылғыштық, ығысу модулі, ангармониялық, тыйым салынған аймақ ені, фотөткізгіштік, монокристалдар, Бриджмен әдісі, рентгенқұрылымдық талдау

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Температурные эффекты в твердых растворах $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$

Сплавы системы $\text{TlInS}_2 - \text{TlGdS}_2$ были синтезированы, а их монокристаллы выращены методом Бриджмена. Рентгеноструктурные исследования позволили установить область растворимости TlGdS_2 в TlInS_2 . Коэффициент линейного теплового расширения (α_L) и изотермическая сжимаемость (χ_T) TlInS_2 и твердых растворов $(\text{TlInS}_2)_{1-x}(\text{TlGdS}_2)_x$ ($0 \leq x \leq 0.10$) исследованы в интервале температур 80–400 К. На основе экспериментальных значений α_L и χ_T определены температура Дебая, среднеквадратичное смещение атомов, модуль Юнга, модуль сдвига, коэффициент Пуассона и разность теплоемкостей $C_p - C_v$. Ширина запрещенной зоны рассчитана по температурной зависимости электропроводности и сопоставлена со значениями, полученными тепловыми и оптическими методами. Аномальное поведение электропроводности объясняется прыжковой проводимостью, связанной со стехиометрическими вакансиями и локализованными состояниями в запрещенной зоне. В отличие от TlInS_2 , в исследованных твердых растворах в диапазоне 80–400 К фазовые переходы не обнаружены. Увеличение концентрации TlGdS_2 приводит к росту коэффициентов теплового расширения и сжимаемости, что свидетельствует об ослаблении межатомных связей и усилении ангармоничности тепловых колебаний. Полученные результаты выявляют взаимосвязь между кристаллической структурой, химической связью и физическими свойствами слоистых халькогенидных полупроводников.

Ключевые слова: твердые растворы, линейное тепловое расширение, изотермическая сжимаемость, модуль сдвига, ангармоничность, ширина запрещенной зоны, фотопроводимость, монокристаллы, метод Бриджмена, рентгеноструктурный анализ

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Synthesis of Amorphous and Crystalline Silicon Dioxide Powder Composites from Rice Husk Ash for Thermal Spray Deposit

This paper presents the synthesis of silicon dioxide (SiO₂) from rice husk ash through chemical treatment followed by heat treatment at 800 °C for 3 h. The structural and physicochemical properties of the synthesized silica were investigated using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and laser diffraction particle size analysis. The synthesized silica exhibited an amorphous structure, with a median particle size (D50) of approximately 88.9 μm. Subsequent annealing at 1200 °C led to crystallization of the silica, resulting in the formation of quartz and cristobalite phases. FTIR analysis revealed characteristic absorption bands associated with Si–O–Si stretching vibrations in the 1000–1100 cm^{−1} region, as well as bands attributed to hydroxyl groups. The obtained crystalline silica materials demonstrate potential for use as powder materials in thermal spraying technologies.

Keywords: Silicon dioxide (SiO₂), rice husk, chemical treatment, annealing, particle size, FTIR analysis

Introduction

In recent years, particular attention has been paid to the development of new materials based on recycled raw materials, driven by environmental and economic factors. One promising area is the use of agricultural waste as a source of functional materials. Rice husk, in particular, is of considerable interest because its ash content contains up to 90–96 % silicon dioxide (SiO₂), making it an accessible and affordable raw material [1, 2].

Traditional methods for producing silicon dioxide, such as sol-gel synthesis and the use of organosilicate precursors (tetraethoxysilane, tetramethoxysilane), are characterized by high cost, process complexity, and environmental limitations [3, 4]. Therefore, the development of alternative methods for obtaining SiO₂ from natural and man-made sources is a pressing issue.

One effective approach is the acid-thermal treatment of rice husks, which allows for the production of high-purity silicon dioxide. Acid treatment removes metallic impurities (Fe, Ca, K, etc.), while subsequent heat treatment removes the organic component and forms an amorphous or crystalline SiO₂ structure, depending on the temperature [5–7].

Despite the significant amount of research devoted to obtaining SiO₂ from rice husks, comprehensive analysis of its structure, morphology, phase composition, and dispersion remains relevant [8, 9]. Furthermore, the use of such SiO₂ as a powder material for the formation of functional and protective coatings has received limited research.

Of particular interest is the use of the resulting silicon dioxide in thermal spraying technologies, where powder materials are used to create wear-resistant and corrosion-resistant coatings [10–12]. The use of agricultural waste can significantly reduce the cost of coatings while simultaneously addressing environmental waste disposal issues. It should also be noted that research into the use of rice husks to produce SiO₂ is actively developing, but its integration with bionanocomposite and thermal spray coating technologies remains understudied [13–15].

Therefore, the aim of this study is to obtain silicon dioxide from rice husks, study its structure and properties, and evaluate its potential for use in protective coating technologies.

Experimental

Rice husks were used as the starting material. Before the experiment, the raw material was pre-cleaned: washed with distilled water three times to remove mechanical and water-soluble impurities, and then dried at room temperature until completely dry.

For chemical treatment, a hydrochloric acid solution with an initial concentration of 33 % (reagent grade) was used, from which a 5 M solution was prepared by diluting with distilled water. The volume of the starting solution was calculated using the formula:

$$C_1V_1 = C_2V_2, \quad (1)$$

where, C_1 — concentration of the initial solution; V_1 — volume; C_2 — required concentration; V_2 — final volume of the solution. The process flow for obtaining silicon dioxide (SiO_2) from rice husk is shown in Figure 1.

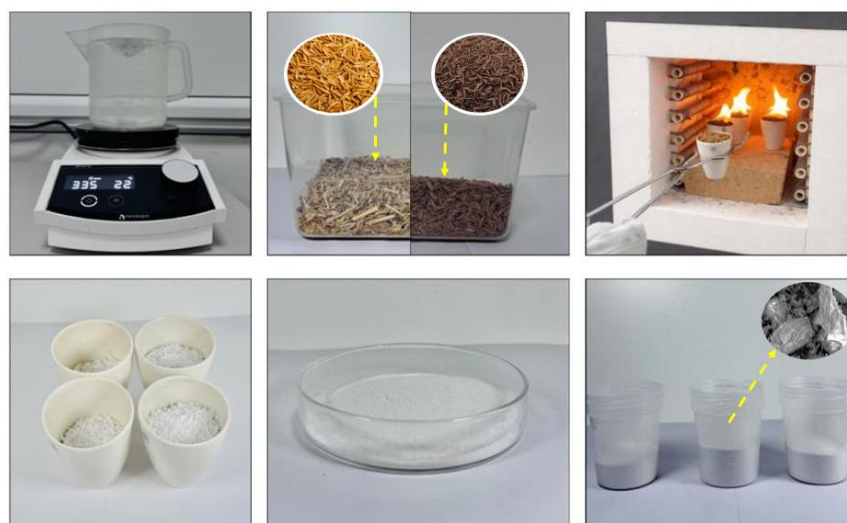


Figure 1 — Process flow for producing silicon dioxide (SiO_2) from rice husks: raw material preparation, thermal annealing, formation of silica-containing ash, and production of dispersed SiO_2 powder.

The rice husks were chemically treated in a 5 M HCl solution to remove mineral impurities. The samples were kept at room temperature for 72 hours with periodic stirring. After treatment, the material was washed with distilled water to a neutral pH and dried at room temperature. Thermal treatment was carried out in a muffle furnace at 800 °C for 3 hours using porcelain crucibles, which ensured the removal of the organic component and the formation of silicon dioxide (SiO_2).

The resulting silicon dioxide (SiO_2) had an amorphous structure. To crystallize the sample, it was annealed at 1200 °C in a muffle furnace (SNOL), which resulted in the formation of a crystalline phase.

X-ray diffraction (XRD) analysis of the samples was performed using a diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction patterns were recorded in the 2θ range of 20–90° with a scan step of 0.02° and a recording speed of ~0.5 s/step [16]. The phase composition of the samples was determined using the PDF-4+ database, and the diffraction patterns were processed using HighScore Plus software. Infrared spectra of the samples were recorded using a Fourier transform infrared (FTIR) spectrometer in the wavenumber range of 500–4000 cm^{-1} . Measurements were performed at room temperature using the standard technique (in transmission mode). The obtained spectra were processed using the spectrometer's built-in software. Particle size distribution analysis was performed using a Winner 2005 NanoSizer particle size analyzer [17]. Measurements were performed at room temperature under standard conditions. The microstructure and surface morphology of the resulting silicon dioxide (SiO_2) were examined using scanning electron microscopy (SEM-3200).

Results and Discussion

X-ray diffraction analysis was performed to study the phase composition and structural state of the obtained silicon dioxide (SiO_2) before and after heat treatment. The diffraction pattern of the sample annealed at a temperature of 800 °C (Fig. 2) is characterized by the presence of a wide diffuse maximum (halo) in the

region of $\sim 22^\circ$ (2θ), indicating an amorphous structure of the material. The absence of clearly defined diffraction peaks indicates the absence of long-range crystalline order in the SiO_2 structure. After additional annealing at a temperature of 1200°C (Fig. 2), significant changes in the diffraction pattern are observed: narrow and intense diffraction peaks appear, indicating the formation of a crystalline structure. The recorded reflections correspond to the characteristic peaks of crystalline modifications of SiO_2 (quartz, cristobalite), confirming the transition of the material from an amorphous to a crystalline state. The observed transformation is due to a thermally induced rearrangement of the amorphous silica matrix, accompanied by ordering of the atomic structure and the formation of crystalline domains. Thus, the XRD analysis results demonstrate that increasing the processing temperature to 1200°C leads to an amorphous $\rightarrow$ crystalline SiO_2 phase transition. This transition is important for controlling the material's properties, particularly by enhancing its thermal stability and mechanical properties, which is of interest when using SiO_2 in thermal spraying technologies.

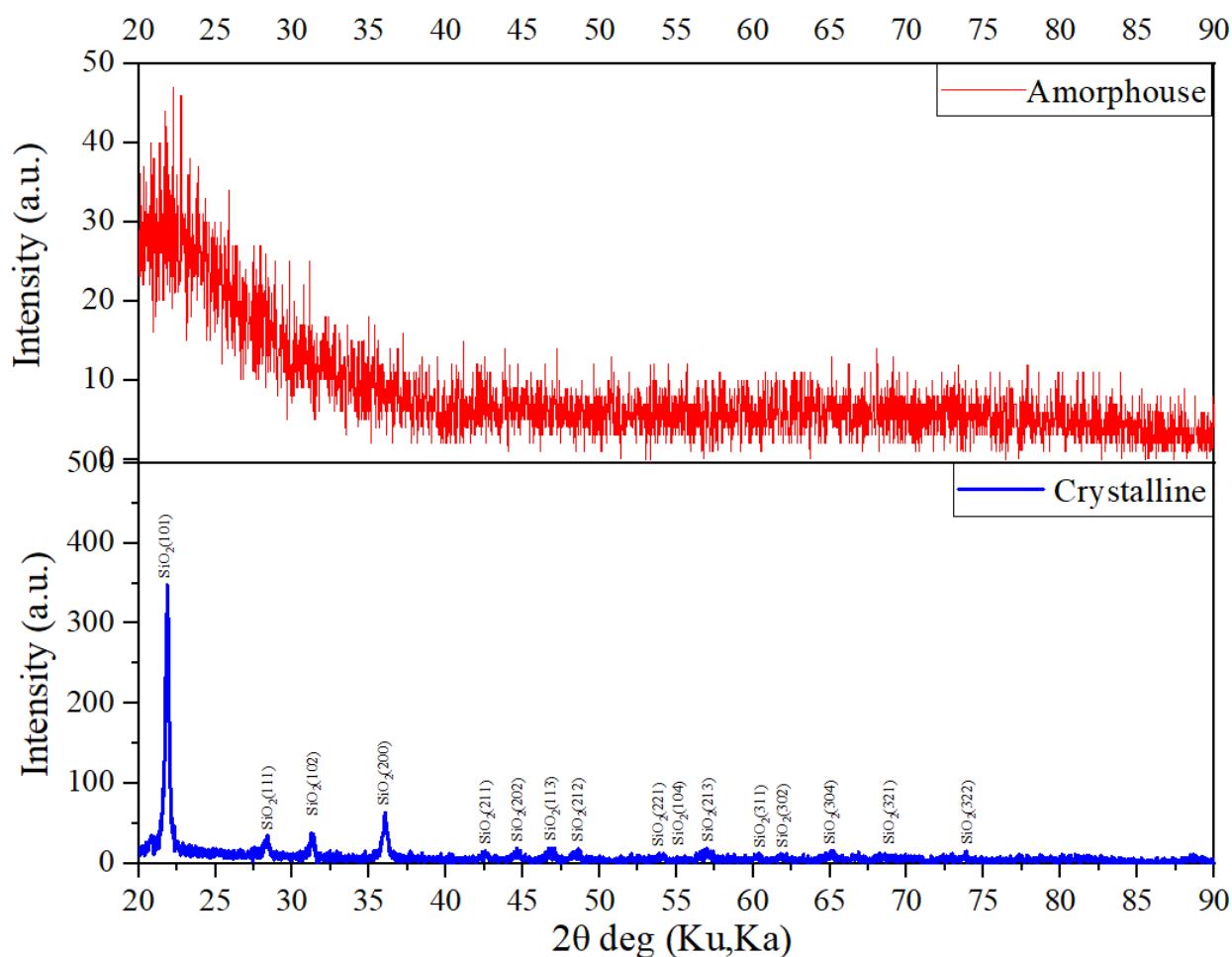


Figure 2 — X-ray diffraction patterns of silica (SiO_2) obtained from rice husk: amorphous silica; crystalline silica after thermal annealing.

FTIR spectra of silica obtained from rice husk ash before and after high-temperature annealing are shown in Figure 3. The spectra of the amorphous sample (Fig. 3) and the crystallized sample (Fig. 3) exhibit characteristic bands consistent with the silica structure. The spectrum of amorphous SiO_2 (Fig. 3) exhibits a broad band in the region of $\sim 3200\text{--}3600\text{ cm}^{-1}$, corresponding to the stretching vibrations of O–H groups, which is associated with the presence of adsorbed moisture and hydroxyl groups on the particle surface. The band near $\sim 1600\text{ cm}^{-1}$ is due to the deformation vibrations of water molecules (H–O–H). The most intense and broad band in the range of $\sim 1000\text{--}1100\text{ cm}^{-1}$ corresponds to the stretching vibrations of Si–O–Si bonds, a characteristic feature of an amorphous silica structure. The width of this band indicates the absence of long-range order in the material's structure.

After annealing at 1200 °C (Fig. 3), changes in the spectral characteristics are observed. The Si–O–Si band becomes more pronounced and partially narrows, indicating an increase in the degree of structural order and the formation of a crystalline phase. Furthermore, the intensity of the bands associated with hydroxyl groups (O–H) and adsorbed water (H–O–H) decreases, which is due to their removal during high-temperature treatment. Thus, the FTIR analysis results confirm that heat treatment at 1200 °C leads to a structural transformation of silicon dioxide from an amorphous to a crystalline state, which is consistent with the X-ray diffraction data.

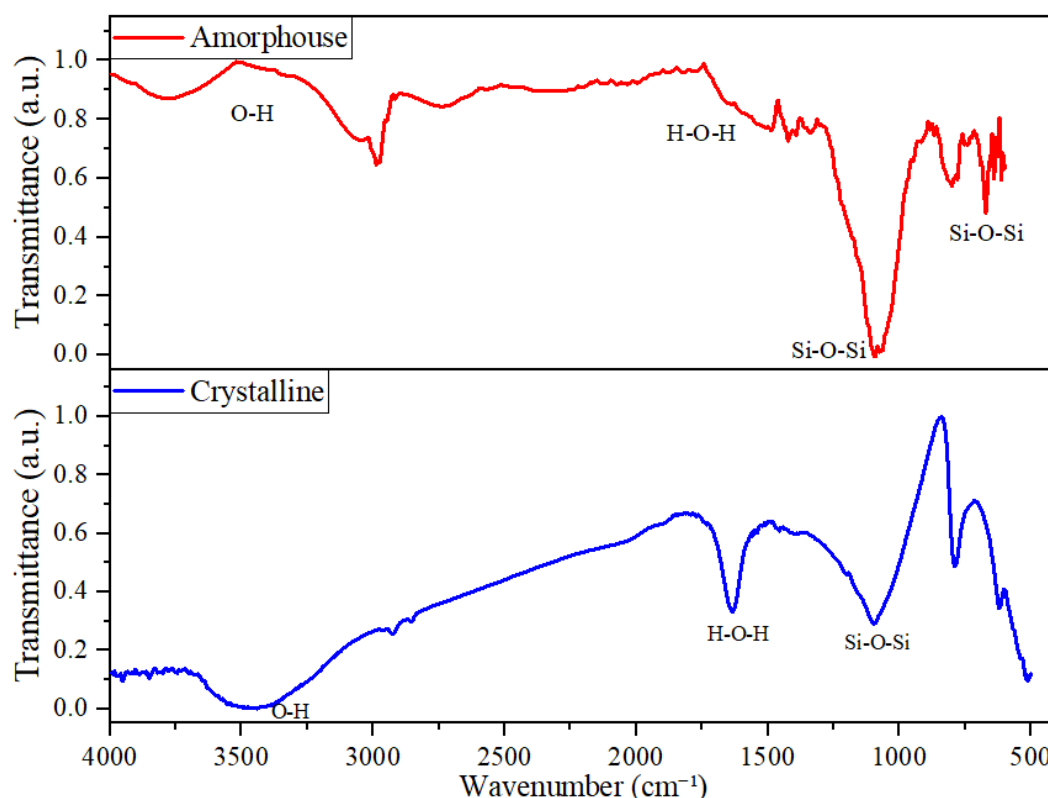


Figure 3 — FTIR spectra of silica (SiO_2) obtained from rice husks: amorphous silica; crystalline silica after thermal annealing

Figure 4 shows differential histograms and cumulative particle distribution curves for silica (SiO_2) obtained from rice husks. The amorphous sample (Fig. 4) exhibits a relatively narrow particle distribution with a pronounced maximum in the range of $\sim 90\text{--}110\ \mu\text{m}$. The majority of particles are concentrated in the range of $50\text{--}150\ \mu\text{m}$. The cumulative curve is characterized by a sharp rise, reaching almost 100 % in the range up to $180\text{--}200\ \mu\text{m}$. This indicates low polydispersity and high powder homogeneity. This distribution pattern is typical of amorphous materials, the structure of which facilitates more uniform destruction during milling and the formation of particles of similar sizes. In contrast, crystalline silicon dioxide (SiO_2) (Fig. 4b) exhibits a significantly broader and more asymmetrical distribution with a distinct “tail” in the region of large particles. Although the main fraction is also in the $\sim 150\text{--}200\ \mu\text{m}$ size range, the system also contains a significant number of particles up to $800\ \mu\text{m}$ and larger. The cumulative curve increases more smoothly and reaches saturation only at significantly larger particle sizes. This indicates high polydispersity of the sample.

Thus, amorphous silicon dioxide (SiO_2) has a more uniform particle size distribution, which can positively impact its processing properties, such as flowability, solubility, and reactivity. Crystalline silicon dioxide (SiO_2), on the other hand, is characterized by high polydispersity, which can lead to inhomogeneous properties and require additional processing (e.g., classification or regrinding).

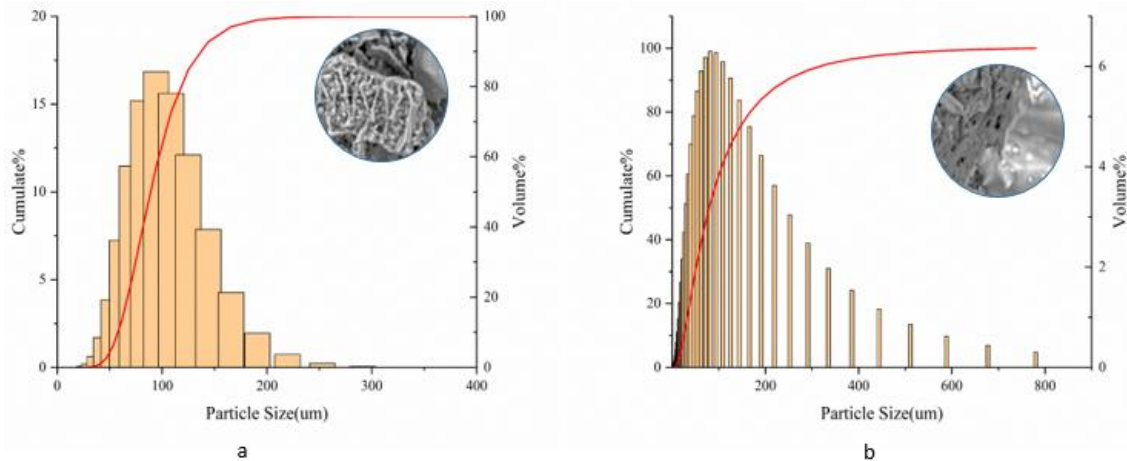


Figure 4 — Differential histograms and cumulative distribution curves of silica (SiO_2) particles obtained from rice husk: a — amorphous silica; b — crystalline silica after thermal annealing

Figure 5 shows SEM images and elemental analysis of amorphous (Fig. 5a) and crystalline (Fig. 5b) silica (SiO_2) particles obtained from rice husk. Amorphous silica (SiO_2) is characterized by a dispersed, disordered morphology consisting of small agglomerated particles with a developed surface area. EDS analysis reveals the presence of only the essential elements Si and O, indicating the high purity of the obtained material and the effective removal of impurities during acid treatment. Crystalline silicon dioxide (SiO_2) exhibits a denser and partially ordered structure with larger particles and pronounced porous fragments inherited from the original raw material. In addition to Si and O, the EDS spectrum also displays a carbon (C) peak, which may be due to residual organic components or surface contamination. Thus, crystallization is accompanied by particle coarsening, increased structural density, and the possible retention of residual impurities, whereas amorphous SiO_2 is characterized by higher purity and homogeneity.

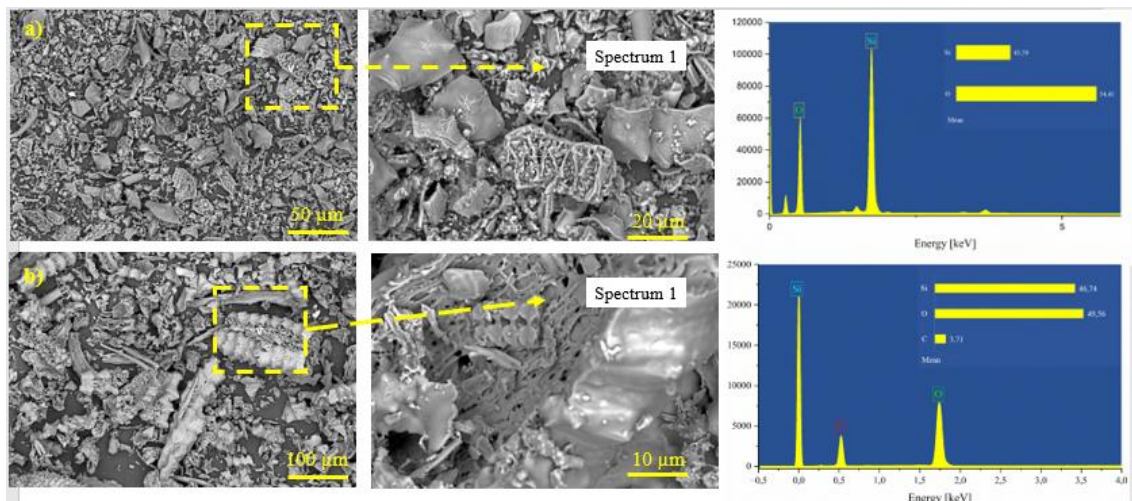


Figure 5 — SEM images and EDS analysis of silicon dioxide (SiO_2) particles obtained from rice husk: a — amorphous silica; b — crystalline silica after thermal annealing.

Conclusion

— During the study, silicon dioxide (SiO_2) was successfully synthesized from rice husk ash through acid leaching followed by thermal treatment. It was established that three-day leaching in an HCl solution and subsequent calcination at 800 °C enable the production of high-purity amorphous silica with an SiO_2 content exceeding 96 %.

— X-ray diffraction (XRD) analysis revealed that thermal treatment at 800 °C promotes the formation of an amorphous silica structure, whereas increasing the temperature to 1200 °C results in the crystallization

of the material with the formation of quartz and cristobalite phases. FTIR analysis confirmed the presence of characteristic Si–O–Si bonds and hydroxyl groups typical of silica.

– Particle size distribution analysis showed that the median particle size of the synthesized powder was $D_{50} = 88.9 \mu\text{m}$. The obtained results confirm the effectiveness of the proposed rice husk recycling approach and demonstrate the potential of the synthesized SiO_2 as a powder feedstock material for thermal spray coating technologies.

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Газотермиялық бүрку үшін күріш қабығының күлінен кремний диоксиді негізіндегі аморфты және кристалды ұнтақ композиттерінің синтезі

Жұмыста күріш қабығының күлін термиялық және химиялық өңдеу әдістерімен 800 °C температурада 3 сағат ішінде өңдеп, кремний диоксидін (SiO_2) синтездеу ұсынылған. Алынған материалдың құрылымдық және физика-химиялық қасиеттері рентген дифракция (XRD), инфрақызыл спектроскопия (FTIR) және лазерлік дифракциямен бөлшектердің өлшемдік таралуын талдау әдістерімен зерттелді. Алынған кремний диоксиді (SiO_2) бөлшектерінің орташа мөлшері $d_{50} \approx 88,9$ мкм және құрылымы аморфты. Кремний диоксидін (SiO_2) кристалдау үшін 1200 °C температурада күйдірілді және нәтижесінде кристалдық фаза (кварц, кристобалит) пайда болды. Инфрақызыл спектроскопия (FTIR) талдауы 1000-1100 см⁻¹ аймағында интенсивті сіңіру жолағы, сондай-ақ гидроксил топтарына сәйкес келетін жолақтарға тән Si–O–Si байланыстарының барлығын растады. Жүргізілген зерттеулер нәтижесінде газотермиялық бүрку технологияларында ұнтақ материал ретінде пайдалануға жарамды күріш қабығының күлінен синтезделген кремний диоксиді негізіндегі кристалды композиттер алынды.

Кілт сөздер: кремний диоксиді (SiO_2), күріш қабығы, химиялық өңдеу, күйдіру, бөлшектердің мөлшері, FTIR-талдауы

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Синтез аморфных и кристаллических порошковых композитов на основе диоксида кремния из золы рисовой шелухи для газотермического напыления

В работе представлен синтез диоксида кремния (SiO_2) из золы рисовой шелухи, осуществлённый методом химической обработки с последующей термической обработкой при температуре 800 °C в течение 3 часов. Структурные и физико-химические свойства полученного материала исследовали методами рентгенодифракционного анализа (XRD), инфракрасной спектроскопии (FTIR) и анализа распределения частиц по размерам методом лазерной дифракции. Полученный диоксид кремния (SiO_2) со средним размером частиц $D_{50} \approx 88,9$ мкм характеризовался аморфной структурой. Для его кристаллизации был проведён отжиг при температуре 1200 °C, в результате которого сформировалась кристаллическая фаза (кварц, кристобалит). FTIR-анализ подтвердил наличие характерных связей Si–O–Si с интенсивной полосой поглощения в области 1000–1100 см⁻¹, а также полос, соответствующих гидроксильным группам. В результате проведённых исследований получены кристаллические композиты на основе диоксида кремния, синтезированного из золы рисовой шелухи, пригодные для использования в качестве порошкового материала в технологиях газотермического напыления.

Ключевые слова: Диоксид кремния (SiO_2), рисовая шелуха, химическая обработка, отжиг, размер частиц, FTIR-анализ

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Effect of Electrohydraulic Pulse Treatment on the Reduction of Organic Pollutants and Analytical Signals of Heavy Metals in Wastewater

This study investigates the effect of electrohydraulic pulse treatment on changes in the physicochemical parameters of wastewater and the analytical signals of heavy metals. The relevance of the study is determined by the need to develop reagent-free methods for the advanced treatment of industrial and municipal-industrial wastewater containing organic pollutants and trace metal impurities. The treatment was carried out in a laboratory high-voltage cell with an interelectrode discharge in an aqueous medium. Wastewater from the pumping station of JSC "Qarmet" in Temirtau was used as the study object. Heavy metals were determined by stripping voltammetry, while changes in the chemical parameters were assessed based on COD, BOD₅, pH, ammonium nitrogen, phenols, petroleum products, total iron, and chromium content. After treatment, COD decreased from 95.9 to 69.0 mg/dm³, corresponding to a reduction of 28.1%. The BOD₅/COD ratio increased from 0.095 to 0.155, indicating an improvement in the biodegradability of the organic compounds. The analytical signals of Zn, Cd, Pb, and Cu decreased by 82.7–100%. The obtained results demonstrate the potential of electrohydraulic pulse treatment as a pretreatment or advanced treatment stage for complex wastewater.

Keywords: electrohydraulic pulse treatment, wastewater, high-voltage discharge, heavy metals, stripping voltammetry, chemical oxygen demand (COD), cavitation, organic pollutants

Introduction

Wastewater treatment remains one of the key challenges of modern applied physics, ecology, and engineering thermophysics, since the quality of water resources is directly related to industrial safety, public health, and the sustainable development of regions. This problem is of particular importance for Kazakhstan. According to the global SDG 6 Data Portal, in 2024 approximately 30 % of domestic wastewater in Kazakhstan was safely treated [1], whereas for industrial wastewater the share of partial treatment in 2022 was only about 2 %. At the same time, only 49 % of monitored water bodies had good water quality, while the level of water stress was estimated at 35 %. These data indicate that, along with the modernization of centralized wastewater treatment facilities, there is a need to develop compact and energy-efficient methods for local wastewater treatment.

Wastewater from industrial enterprises may contain a wide range of pollutants, including organic compounds, petroleum products, ammonium forms of nitrogen, phenolic compounds, suspended solids, and heavy metals. Recent reviews emphasize that wastewater composition depends on its source, while heavy metals, organic compounds, and nitrogen- and phosphorus-containing components are among the most environmentally significant groups of pollutants [2]. Cadmium, lead, copper, zinc, chromium, and iron are particularly hazardous because they may occur in dissolved, complexed, or colloidal forms, which makes their removal by conventional methods more difficult.

Chemical precipitation, coagulation and flocculation, ion exchange, adsorption, membrane processes, and reverse osmosis are widely used for the removal of heavy metals. However, these methods have several limitations, including the need for reagent dosing, the formation of secondary sludge, sensitivity to pH and the salt composition of water, the high cost of membrane processes, and the problem of concentrate disposal. Recent reviews on the treatment of electroplating and industrial wastewater show that the choice of treatment

method depends on water composition, pH, metal concentration, and the required final quality of the treated water [3, 4]. Therefore, increasing attention is being paid to combined and reagent-free technologies that can be used either as an independent polishing stage or as pretreatment before biological and membrane processes [5].

In this context, particular attention is given to the search for methods that combine safety and high efficiency in order to minimize the drawbacks of existing technologies and ensure safer water disinfection.

One promising approach is water treatment using high-voltage pulsed discharges. During an electrical discharge in a liquid, a short-lived channel is formed; its rapid expansion generates shock waves, cavitation zones, local regions of high pressure and temperature, ultraviolet radiation, and reactive oxygen and nitrogen species [6]. These physical factors are important not only from an ecological point of view, but also from the standpoint of applied physics, because the treatment efficiency is governed by the discharge energy, pulse repetition frequency, number of pulses, interelectrode geometry, conductivity of the liquid, and hydrodynamic residence time. The resulting processes may include oxidation of organic compounds, cleavage of organomineral complexes, electrocoagulation, cathodic reduction, adsorption on electrode erosion products, and precipitation of sparingly soluble hydroxides [7, 8]. Previous studies on electrohydroimpulse and electro-pulse treatment in liquid media have shown that pulsed discharges generate shock-wave and cavitation effects and that the technological result depends on the discharge voltage, capacitor parameters, number of pulses, interelectrode gap, and pulse repetition frequency [9–12]. Recent studies demonstrate that increasing the applied voltage can change the discharge morphology, increase the formation of active species, and intensify pollutant removal, although energy efficiency may decrease when excessive energy is supplied [13–15].

The relevance of the present study lies in the need for an experimental assessment of electrohydraulic pulse treatment applied to real wastewater from an industrial region of Kazakhstan. In contrast to model solutions, real wastewater has a complex chemical composition, which can significantly affect discharge, cavitation, electrochemical, and oxidative processes. Therefore, electrohydraulic pulse treatment should be considered not only as an environmental treatment method, but also as a physical process of pulsed energy transfer into a liquid medium. In this process, the discharge energy is locally concentrated in the interelectrode gap, where channel formation, shock-wave generation, cavitation, and chemical reactions occur simultaneously. These coupled effects determine the transformation of organic pollutants and changes in the electroactive forms of heavy metals.

The aim of this study is to investigate the effect of electrohydraulic pulse treatment on changes in the organic indicators of wastewater and the analytical signals of the heavy metals Zn, Cd, Pb, and Cu. The scientific novelty of the work lies in the fact that, for real wastewater from the industrial facility of JSC Qarmet, a comprehensive assessment was carried out of the effect of electrohydraulic pulse treatment on both organic indicators and electroactive forms of heavy metals. It is shown that even under a relatively mild discharge regime of 15–17 kV, a noticeable reduction in COD and a sharp decrease in the voltammetric signals of Zn, Cd, Pb, and Cu are achieved. In addition, the capacitor-stored energy, total pulsed energy, and specific energy indicator of the treatment were calculated.

Experimental

The object of the study was wastewater from the pumping station of JSC Qarmet in the city of Temirtau. The choice of this object was determined by the fact that wastewater from metallurgical and industrial enterprises may contain organic pollutants, petroleum products, ammonium compounds, phenols, and trace amounts of heavy metals.

Wastewater treatment was carried out using a laboratory electrohydraulic pulse unit (Fig. 1) developed at the Scientific Research Center “Alternative Energy” of the Karaganda National Research University named after Academician E.A. Buketov. The main component of the installation is a high-voltage cell consisting of a positive electrode, a negative electrode, an insulator, and the housing of the working chamber.

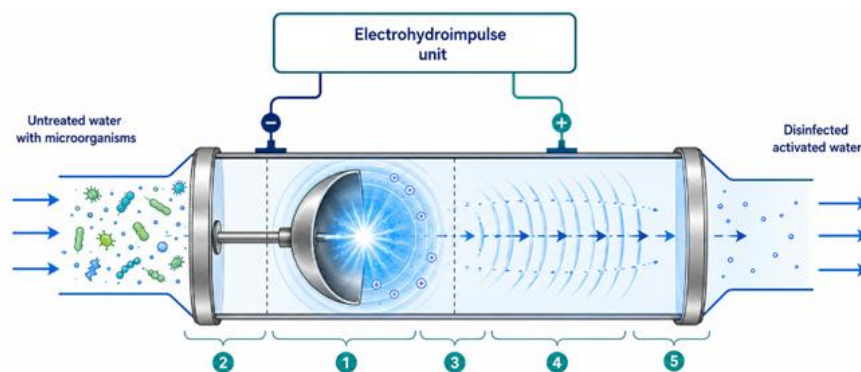


Figure 1. Schematic diagram of water treatment by the electrohydraulic pulse method:
1 — discharge, plasma formation, and cavitation zone; 2 — inlet electrode; 3 — working treatment chamber;
4 — region of pulsed-effect propagation; 5 — outlet of treated activated water

The positive electrode was made of steel in the form of a rod electrode. Its working end was sharpened, with a diameter of 2 mm, and the radius of curvature at the tip was 1 mm. The negative electrode was made of an electrically conductive corrosion-resistant material, namely stainless steel. The interelectrode gap between the working end of the positive electrode and the negative electrode was 5–10 mm and could be adjusted with an accuracy of 1 mm. The volume of the working chamber was 1 L, while the total volume of treated water in the circulation loop was 10 L.

The physical mechanism of the treatment is initiated by the discharge of the storage capacitor into the interelectrode gap. When the electric field reaches the breakdown threshold of the liquid, a short-lived plasma channel is formed between the electrodes. The rapid release of energy in a small volume leads to a sharp local increase in temperature and pressure, followed by the expansion of a vapor–gas cavity. Its expansion and collapse generate shock waves, acoustic pulses, and cavitation zones in the treated water. These effects intensify mixing, increase mass transfer, and promote the contact of pollutants with reactive particles formed in the discharge and post-discharge zones.

Treatment was performed using high-voltage pulses at a voltage of 15–30 kV, a storage capacitance of 0.25 μF , a pulse repetition frequency of approximately 1.8 Hz for the main reactor regime, and a treatment duration of 1–5 min. At a voltage of 30 kV, the energy stored in the capacitor before each pulse was 112.5 J; at 15–17 kV it was 28.1–36.1 J. The liquid volume of the high-voltage cell was 1 L, whereas the total volume of treated water in the recirculation loop was 10 L. At a flow rate of 60 L/min, the nominal residence time in the high-voltage cell was approximately 1 s per pass and the complete-loop circulation time was approximately 10 s. Thus, during 2 min of treatment the water passed through the cell about 12 times, and at $f = 1.8$ Hz the pulse dose was approximately 216 pulses, or 21.6 pulses/L.

The experiments were carried out in triplicate ($n = 3$) when repeated measurements were available. Results were expressed as mean $\pm$ standard deviation (SD), and 95 % confidence intervals were calculated for the mean. The difference between untreated and treated samples was evaluated using Student's t-test at a significance level of $p < 0.05$. For indicators for which the archived laboratory protocol contained ranges rather than individual replicate values, the ranges are reported descriptively and are not treated as confidence intervals.

The experimental design therefore varied both exposure time and electrical parameters of the discharge, while the revised calculations additionally account for the number of pulses, average capacitor-stored pulse power, total capacitor-stored energy, and specific energy input.

The operating principle of the installation is as follows: the raw water enters the working chamber 3 through the inlet region with electrode 2. In zone 1, a high-voltage pulsed discharge is generated between the electrodes, accompanied by plasma formation, cavitation, shock-wave action, and the formation of reactive species such as $\bullet\text{OH}$, O_3 , and H_2O_2 . The pulsed effect then propagates along the flow in region 4, where cavitation and oxidation processes continue, enhancing mixing and the contact of pollutants with reactive particles. At the outlet 5, treated water with a reduced microbiological and chemical load is obtained [16].

Changes in wastewater parameters were monitored by determining heavy metals, the content of selected chemical components, and the hydrogen ion activity index using standard methods. A pH meter was used to measure the pH of the water (Fig. 2). The accuracy of pH measurements using a pH meter can be high, up to 0.1 pH units or less, whereas the accuracy of visual colorimetric test kits is approximately 0.5 pH units.



Figure 2. Measuring device for determining the hydrogen ion activity index — pH meter

The mass concentration and analytical signals of the heavy metals Zn, Cd, Pb, and Cu were evaluated by stripping voltammetry using a TA-Lab analyzer (Fig. 3). COD and BOD₅ were measured in accordance with ST RK 1322-2005 [17] and ST RK ISO 5815-1-2010 [18].

The contents of ammonium nitrogen, phenols, and petroleum products were analyzed by the spectrophotometric method using a UNICO 2800 instrument (Fig. 4). Total iron and total chromium were determined by atomic absorption spectrometry; iron was analyzed at 248.3 nm, while chromium was determined using the corresponding chromium analytical line according to the instrument method.



Figure 3. TA-Lab voltammetric analyzer



Figure 4. UNICO 2800 spectrophotometer

The energy stored in the capacitor before a single pulse was calculated using the following equation:

$$E = 0.5 C U^2, \quad (1)$$

where E is the energy of one pulse, J; C is the capacitance of the capacitor, F; and U is the voltage, V.

The number of pulses during the treatment time was determined as:

$$N = f t, \quad (2)$$

where N is the number of pulses; f is the pulse repetition frequency, Hz; and t is the treatment time, s.

The total energy stored in the capacitor over the entire treatment cycle was calculated as:

$$W = E N. \quad (3)$$

The specific energy input based on the stored energy was calculated as:

$$SEI = W / V, \quad (4)$$

where V is the volume of treated water, m³. To convert energy into kWh, the following relationship was used: 1 kWh = 3.6 × 10⁶ J.

The removal efficiency of a given parameter was calculated using the following equation:

$$\eta = [(C_0 - C_t) / C_0] \cdot 100 \%, \quad (5)$$

where C_0 is the value of the parameter before treatment, and C_t is the value of the parameter after treatment.

To assess changes in biodegradability, the following ratio was used:

$$K = \text{BOD}_5 / \text{COD}. \quad (6)$$

For each replicated parameter, the arithmetic mean was calculated as

$$\bar{x} = (1/n) \sum x_i, \quad (7)$$

and the standard deviation was calculated as:

$$\text{SD} = [\sum (x_i - \bar{x})^2 / (n - 1)]^{1/2}. \quad (8)$$

The 95 % confidence interval for the mean was calculated as $\text{CI}_{95} = \bar{x} \pm t_{0.975, n-1} \cdot \text{SD} / \sqrt{n}$. For $n = 3$, $t_{0.975, 2} = 4.303$.

The average capacitor-stored pulse power was calculated as:

$$P_c = E \cdot f, \quad (9)$$

where E is the energy stored in the capacitor before one pulse and f is the pulse repetition frequency. The wall-input specific energy input was calculated separately as:

$$\text{SEI}_{\text{wall}} = P_{\text{wall}} \cdot t / V \quad (10)$$

when the system-level electrical power was available.

Results and Discussion

At a storage capacitor capacitance of $C = 0.25 \mu\text{F}$, the energy of a single pulse strongly depends on the applied voltage. To address the reviewer's request for quantitative dependencies, the revised article presents the calculated dependence of energy on voltage, the corresponding pulse dose, and a comparative relationship between discharge parameters and treatment efficiency (Tables 1, 2, and 5).

Table 1

Calculated energy stored in the capacitor

Voltage U , kV	Capacitance C , μF	Energy of one pulse E , J
15	0.25	28.1
16	0.25	32.0
17	0.25	36.1
18	0.25	40.5
21	0.25	55.1
24	0.25	72.0
27	0.25	91.1
30	0.25	112.5

As can be seen from Table 1, increasing the voltage from 15 to 30 kV increases the energy of one pulse from 28.1 to 112.5 J, i.e., by a factor of four. This is caused by the quadratic dependence $E = 0.5CU^2$. Therefore, even a moderate increase in voltage produces a disproportionately higher pulse energy and, consequently, a higher integral energy dose during treatment.

Table 2

Calculated pulse-dose and energy indicators for the selected electrohydraulic treatment regimes

Parameter	Value
Regimes compared	Mild wastewater series / high-energy comparative regime
Capacitor capacitance C , μF	0.25 / 0.25
Voltage U , kV	16 (average of 15–17 kV) / 30
Energy of one pulse E_c , J	32.0 / 112.5
Pulse frequency f , Hz	0.75 / 1.8
Treatment time t , s	64.2 / 120
Number of pulses N	48.15 / 216
Average capacitor-stored pulse power $P_c = E_c \cdot f$, W	24.0 / 202.5
Total capacitor-stored energy $W = E_c \cdot N$, J	1540.8 / 24300
Treated volume V , m^3	0.010 / 0.010
Stored-energy SEI, kWh/m^3	0.0428 / 0.675
Wall-input SEI, kWh/m^3	not determined for mild series / 6.7 ($P_{\text{wall}} = 2 \text{ kW}$)
Number of passes through 1 L high-voltage cell	not calculated / 12

Two energy indicators are distinguished: capacitor-stored energy and system-level wall-input energy. Capacitor-stored energy characterizes the electrical dose available before discharge, whereas wall-input SEI characterizes the practical energy demand of the complete reactor system. For the 30 kV, 2 min, 10 L regime, the wall-input SEI was 6.7 kWh/m^3 , whereas the stored-energy SEI was 0.675 kWh/m^3 . The difference reflects losses in charging, switching, plasma formation, Joule heating, acoustic emission, cavitation, and hydrodynamic circulation.

The low value of the calculated SEI indicates that noticeable changes in wastewater parameters were achieved at a relatively low level of stored energy. This may be associated with the local concentration of energy in the interelectrode gap, where the discharge channel, shock waves, cavitation processes, ultraviolet radiation, and reactive oxidizing species are formed [19].

The results showing changes in COD and BOD_5 of wastewater before and after electrical discharge treatment are presented in Table 3. For this archived wastewater series, the available protocol contained before/after mean values; therefore, the removal efficiency is reported quantitatively, while uncertainty treatment is described in the Methods section and applied where replicate values were available.

Table 3

Changes in COD and BOD_5 after electrohydraulic pulse treatment

Parameter	Before treatment, mg/dm^3	After treatment, mg/dm^3	Change
COD	95.9	69.0	–28.1 %
BOD_5	9.1	10.7	+17.6 %
BOD_5/COD	0.095	0.155	+63.4 %

After treatment, COD decreased by 28.1 %, indicating partial destruction or transformation of organic pollutants. At the same time, BOD_5 increased by 17.6 %. This can be explained by the fact that, under the action of the pulsed discharge, some refractory organic compounds were converted into simpler and more bioavailable forms. This is confirmed by the increase in the BOD_5/COD ratio from 0.095 to 0.155, i.e., by 63.4 %.

Since the BOD_5/COD ratio is widely used as an index of the biodegradability of the organic fraction of wastewater, the observed increase in this parameter can be considered an indication that some refractory compounds were transformed into more bioavailable intermediate products [20]. The obtained result is consistent with published data, where partial oxidation of organic substances is often accompanied not only by a decrease in COD but also by an increase in the BOD_5/COD ratio due to the formation of simpler and more bioavailable products. For example, Dinçer showed that during ozonation of the dye Reactive Black 5, COD decreased by 34 %, while in the combined ozone–catalase process it decreased by 43 %; at the same time, biodegradability increased, and the BOD_5/COD ratio reached 0.46 [21]. In the present study, the 28.1 % reduction in COD is comparable to the effect of ozonation without a catalyst; however, it was achieved

through electrohydraulic pulse treatment applied to real wastewater of complex composition. This confirms the potential of the method as a pretreatment stage.

Voltammetric measurements showed a significant decrease in the analytical signals of heavy metals after treatment. Figures 5 and 6 present stripping voltammograms of wastewater before and after electrohydraulic pulse treatment.

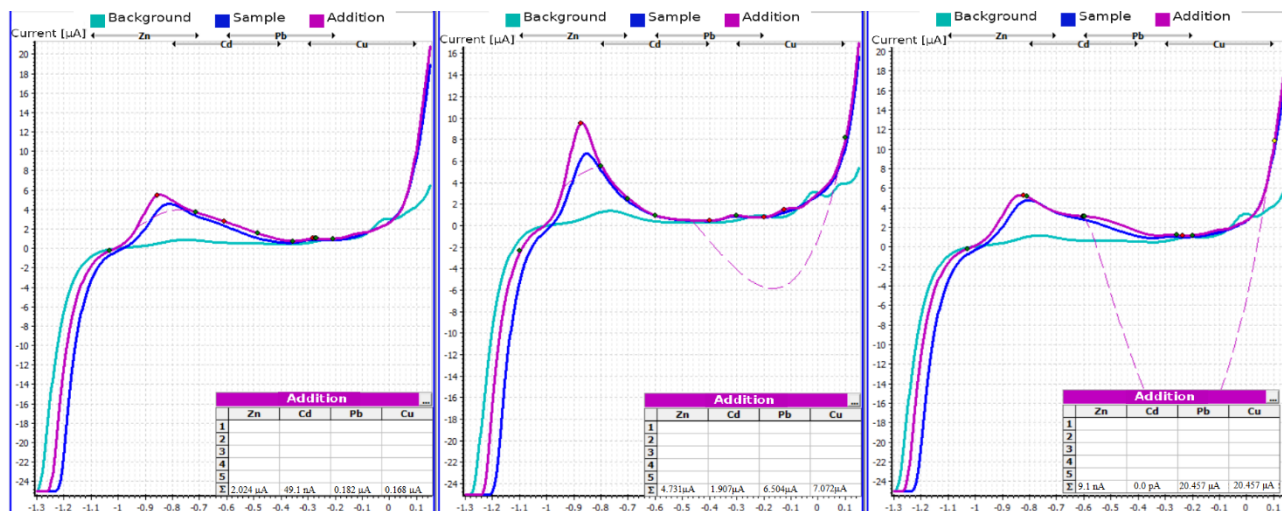


Figure 5. Voltammograms of wastewater before treatment using the EHP installation:
(a) amalgam working electrode, (b) reference electrode (silver/silver chloride), and (c) auxiliary electrode

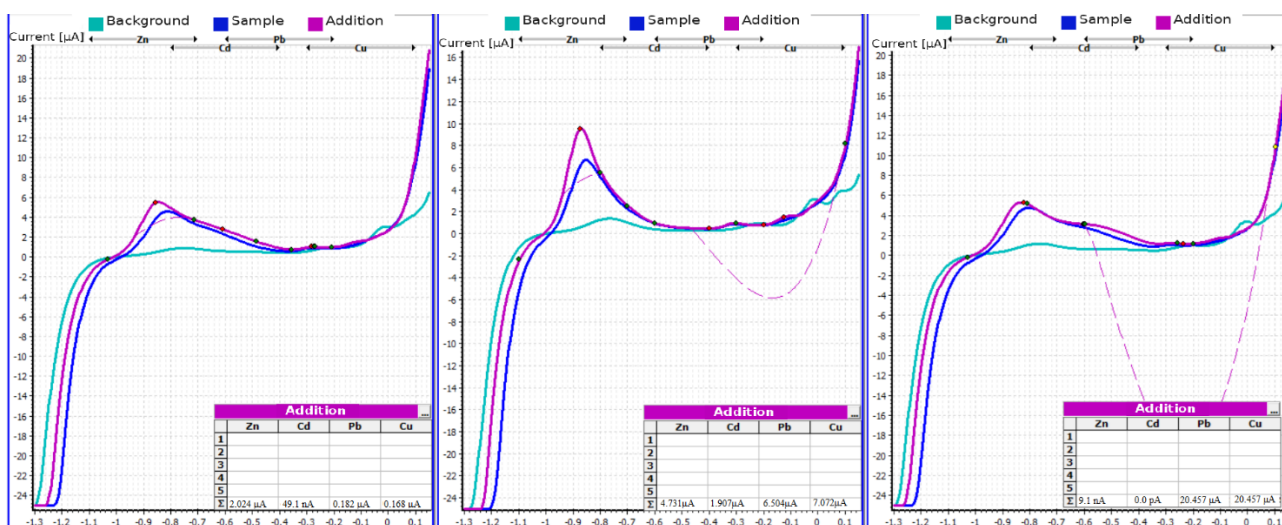


Figure 6. Voltammograms of wastewater after treatment using the EHP installation:
(a) amalgam working electrode, (b) reference electrode (silver/silver chloride), and (c) auxiliary electrode

Before treatment, distinct analytical peaks corresponding to the electroactive forms of Zn, Cd, Pb, and Cu were observed in the voltammograms. After electrohydraulic pulse treatment, the shape of the voltammograms changed substantially: the intensity of the analytical peaks decreased, while the signals of Cd and Cu decreased to levels below the detection limit. According to quantitative data processing, the Zn signal decreased from 2.024 to 0.350 μA , i.e., by 82.7 %; the Pb signal decreased from 0.182 to 0.005 μA , corresponding to a reduction of 97.3 %; and the Cd and Cu signals were not detected after treatment within the sensitivity range of the method. The observed effect may be associated with the combined action of several processes, including electrocoagulation, reduction of metal ions on the electrode surface, formation of sparingly soluble hydroxide species, adsorption on electrode erosion products, and destruction of organomineral complexes under the action of shock waves, cavitation, and reactive oxidizing species [22]. Abdykadyrov et al. [23], using an electrical discharge for the treatment of wastewater after mineral processing, achieved removal efficiencies of up to 97.5 % for Cu, 97.3 % for Zn, and 96.0 % for Cd. In the pre-

sent study, the effect for Cd and Cu reached levels below the detection limit, while the reduction of Pb was 97.3 %, which is comparable with the reported data. The reduction of Zn was 82.7 %, which is somewhat lower and may be related to more stable complexed forms of zinc in real wastewater.

Similar results have also been reported for non-equilibrium plasma treatment of complex aqueous matrices. Bakhtiyari-Ramezani et al. [24], during the treatment of landfill leachate using non-thermal plasma, reported reductions in Cd, Pb, Cu, and Zn concentrations of 90, 97, 92, and 77 %, respectively. Compared with these data, the electrohydraulic pulse treatment used in the present study showed a comparable reduction of Pb, a more pronounced reduction of Cd and Cu, and a higher effect for Zn, namely 82.7 % compared with 77 %.

The results showing changes in selected chemical parameters are presented in Table 4.

Table 4

**Statistical evaluation of changes in the chemical parameters
of wastewater after electrohydraulic pulse treatment**

Parameter	n	Before treatment, mean $\pm$ SD	CI95 before	After treatment, mean $\pm$ SD	CI95 after	Calculated effect	p- value
pH	3	8.00 $\pm$ 0.20	7.50–8.50	7.67 $\pm$ 0.15	7.29–8.05	within the neutral to slightly alkaline range	0.083
Ammonium nitrogen, mg/dm ³	3	2.27 $\pm$ 0.08	2.07–2.47	1.63 $\pm$ 0.14	1.29–1.97	reduction by 16.3–38.3 %	0.002
Volatile phenols, mg/dm ³	3	0.050 $\pm$ 0.003	0.043–0.057	0.018 $\pm$ 0.006	0.003–0.033	reduction by 50.0–80.0 %	0.001
Petroleum products, mg/dm ³	3	3.40 $\pm$ 0.09	3.17–3.63	1.27 $\pm$ 0.40	0.26–2.27	reduction by 47.1–76.5 %	0.001
Total chromium, mg/dm ³	3	0.0010 $\pm$ 0.00005	0.00088–0.00112	0.00082 $\pm$ 0.00012	0.00053–0.00110	reduction up to 30.0 %	0.065
Total iron, mg/dm ³	3	0.98 $\pm$ 0.04	0.88–1.08	0.41 $\pm$ 0.11	0.13–0.68	reduction by 43.9–74.5 %	0.001

Note. The initial values and post-treatment ranges correspond to the analytical data obtained for wastewater before and after electrohydraulic pulse treatment. The values are presented as mean $\pm$ SD for three determinations. CI95 is the 95 % confidence interval. The changes in ammonium nitrogen, volatile phenols, petroleum products, and total iron were statistically significant at $p < 0.05$. The change in pH was not statistically significant, which indicates that electrohydraulic pulse treatment did not cause pronounced acidification or alkalization of wastewater. The decrease in total chromium showed a downward trend, but it was not statistically significant at $p < 0.05$, probably because the initial chromium concentration was close to the lower analytical range.

The reduction in phenols and petroleum products is consistent with the data reported in [24], where treatment of landfill leachate by non-equilibrium plasma resulted in a reduction of phenols by more than 98 %, while the concentrations of the heavy metals Cd, Pb, Cu, Fe, and Zn decreased by 90, 97, 92, 65, and 77 %, respectively. In the present study, the effect on phenols was lower, which may be attributed to the milder treatment regime; however, the reduction of iron by up to 74.5 % and Zn by 82.7 % is comparable with or higher than some of the reported values. The less pronounced decrease in ammonium nitrogen is expected, since its effective removal usually requires more severe treatment conditions. For example, Back et al. [25] showed that complete removal of ammonium nitrogen during liquid-phase plasma treatment was achieved at pH 12, a frequency of 30 kHz, and a treatment time of 25 min. In the present case, maintaining pH within the range of 7.2–8.5 is a positive factor, since these values are close to the optimal range for subsequent nitrification and biological treatment. Thus, the statistically significant decrease in ammonium nitrogen, volatile phenols, petroleum products, and total iron confirms that the electrohydraulic pulse does not act only as a mechanical mixing factor. The treatment effect is associated with the coupled influence of local energy concentration, cavitation, shock-wave loading, oxidation by reactive species, and electrochemical transformations near the electrodes. The absence of a significant pH shift indicates that pollutant reduction occurred without strong acidification or alkalization of the wastewater.

Table 5

Quantitative relationship between discharge parameters and wastewater-treatment effect

Regime	Ec, J/pulse	f, Hz	N, pulses	Pc, W	W, kJ	Key treatment effect
15–17 kV wastewater series	28.1–36.1	0.75	48.15	21.1–27.1	1.54 at 16 kV	COD –28.1 %; BOD ₅ /COD +63.4 %; Zn –82.7 %; Pb –97.3 %; Cd and Cu < LOD; Fe –43.9–74.5 %
30 kV comparative reactor regime	112.5	1.8	216	202.5	24.3	COD –53.8 %; color –61.1 %; A254 –52.3 %; NH ₄ ⁺ –52.9 %; TMC to <LOD within 2–3 min

Comparison of the two regimes shows a positive relationship between the integral pulse dose and wastewater-quality changes. Increasing U from approximately 16 to 30 kV increased Ec from 32.0 to 112.5 J, the pulse number from 48.15 to 216, the total capacitor-stored energy from 1.54 to 24.3 kJ, and Pc from 24.0 to 202.5 W. Under the higher-energy regime, COD reduction increased from 28.1 % to 53.8 %. Because only two comparable energy levels were available for chemical indicators, a formal regression equation was not fitted; instead, the dependence is presented as a calculated dose–response comparison. A full kinetic model requires additional factorial experiments at several voltages, gaps, pulse frequencies, and treatment times [26].

Conclusion

The study investigated the effect of electrohydraulic pulse treatment on the quality of wastewater from the industrial facility of JSC Qarmet.

Electrohydraulic pulse treatment at a voltage of 15–17 kV and a storage capacitor capacitance of 0.25 μF ensured noticeable changes in the organic and inorganic parameters of the wastewater. The calculated energy of one pulse at 15–17 kV was 28.1–36.1 J. For the average regime of 16 kV, a frequency of 0.75 Hz, and a treatment time of 64.2 s, the total stored energy was 1540.8 J, while the calculated SEI based on capacitor-stored energy was 0.0428 kWh/m³.

It was found that COD decreased from 95.9 to 69.0 mg/dm³, corresponding to a reduction of 28.1 %. At the same time, BOD₅ increased from 9.1 to 10.7 mg/dm³, while the BOD₅/COD ratio increased from 0.095 to 0.155. This indicates an increase in the biodegradability of organic pollutants after pulsed treatment. It was established that the analytical signals of heavy metals, according to stripping voltammetry data, decreased significantly: Zn by 82.7 %, Pb by 97.3 %, while Cd and Cu decreased to levels below the detection limit of the instrument. Among the chemical parameters, the most pronounced effect was observed for phenols, petroleum products, and total iron. The content of phenols decreased by 50.0–80.0 %, petroleum products by 47.1–76.5 %, and total iron by 43.9–74.5 %.

Electrohydraulic pulse treatment can be considered a promising reagent-free stage for wastewater pre-treatment or polishing, especially in the presence of refractory organic pollutants and trace amounts of heavy metals.

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Электрогидроимпульстік өңдеудің ағынды сулардағы органикалық ластағыштар мен ауыр металдардың аналитикалық сигналдарын төмендетуге әсері

Жұмыста электрогидроимпульстік өңдеудің ағынды сулардың физика-химиялық көрсеткіштерінің өзгеруіне және ауыр металдардың аналитикалық сигналдарына әсері зерттелді. Зерттеудің өзектілігі құрамында органикалық ластағыштар мен металдардың микро қоспалары бар өнеркәсіптік және коммуналдық-өнеркәсіптік ағынды суларды тазартудың реагенттік-еркін әдістерін әзірлеу қажеттілігіне байланысты. Өңдеу су ортасында электродаралық разряд түзілетін зертханалық жоғары вольтты ұяшықта жүргізілді. Зерттеу нысаны ретінде Теміртау қаласындағы «Qarmet» АҚ сорғы станциясының ағынды сулары пайдаланылды. Ауыр металдарды анықтау инверсиялық вольтамперометрия әдісімен жүргізілді, ал химиялық көрсеткіштердің өзгеруі ХПК, БПК₅, рН, аммоний азотының, фенолдардың, мұнай өнімдерінің, жалпы темір мен хромның мөлшері бойынша бағаланды. Өңдеуден кейін ХПК 95,9-дан 69,0 мг/дм³-ке дейін төмендегені анықталды, бұл 28,1 %-ға азаюға сәйкес келеді. БПК₅/ХПК қатынасы 0,095-тен 0,155-ке дейін артты, бұл органикалық қосылыстардың биологиялық қолжетімділігінің жоғарылағанын көрсетеді. Zn, Cd, Pb және Cu аналитикалық сигналдары 82,7–100 %-ға төмендеді. Алынған нәтижелер электрогидроимпульстік өңдеудің күрделі құрамды ағынды суларды алдын ала тазарту немесе қосымша тазарту сатысы ретінде перспективалы екенін растайды.

Кілт сөздер: электрогидроимпульстік өңдеу, ағынды сулар, жоғары вольтты разряд, ауыр металдар, инверсиялық вольтамперометрия, оттегінің химиялық қажеттілігі (ОХҚ), кавитация, органикалық ластағыштар

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Влияние электрогидроимпульсной обработки на снижение органических загрязнений и аналитических сигналов тяжелых металлов в сточных водах

В работе исследовано влияние электрогидроимпульсной обработки на изменение физико-химических показателей сточных вод и аналитических сигналов тяжелых металлов. Актуальность исследования обусловлена необходимостью разработки реагентно-свободных методов доочистки промышленных и коммунально-промышленных стоков, содержащих органические загрязнители и микропримеси металлов. Обработка проводилась в лабораторной высоковольтной ячейке с межэлектродным разрядом в водной среде. В качестве объекта исследования использовались сточные воды насосной станции АО «Qarmet» в г. Темиртау. Определение тяжелых металлов выполнялось методом инверсионной вольтамперометрии, а изменение химических показателей оценивалось по ХПК, БПК₅, рН, содержанию аммонийного азота, фенолов, нефтепродуктов, общего железа и хрома. Показано, что после обработки ХПК снизилось с 95,9 до 69,0 мг/дм³, что соответствует уменьшению на 28,1 %. Отношение БПК₅/ХПК увеличилось с 0,095 до 0,155, что указывает на повышение биологической доступности органических соединений. Аналитические сигналы Zn, Cd, Pb и Cu снизились на 82,7–100 %. Полученные результаты подтверждают перспективность электрогидроимпульсной обработки как стадии предочистки или доочистки сложных сточных вод.

Ключевые слова: электрогидроимпульсная обработка, сточные воды, высоковольтный разряд, тяжелые металлы, инверсионная вольтамперометрия, химическое потребление кислорода (ХПК), кавитация, органические загрязнители

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Thermal Conductivity and Degradation Kinetics of Copper Nanoparticle-Reinforced Polypropylene Composites: Towards Thermally Enhanced Active Food Packaging

This study investigates the thermal conductivity and degradation kinetics of copper nanoparticle (Cu NP)-reinforced polypropylene (PP) composites as potential materials for thermally enhanced food-packaging applications. Cu NP-PP nanocomposites were prepared by twin-screw extrusion at 0, 1, 2, 5, and 10 wt% Cu NP. Thermal conductivity (λ) was measured using the transient hot-wire method (ASTM D5930; $n = 5$ specimens per composition), while thermal stability was characterised by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC; $n = 3$ per composition). Microstructure and phase composition were examined by FE-SEM, EDS, and XRD. Cu NP incorporation raised λ from 0.18 $\pm$ 0.02 W/m/K (pure PP) to 0.47 $\pm$ 0.05 W/m/K at 10 wt% — a 2.6-fold enhancement consistent with percolation network formation ($\phi_c \sim 0.004$, $t = 1.87$). Multi-rate Kissinger kinetic analysis of TGA data (four heating rates: 5, 10, 15, 20 °C/min) yielded apparent activation energy (E_a) increasing from 168 $\pm$ 4 kJ/mol to 189 $\pm$ 5 kJ/mol, corroborated by Ozawa-Flynn-Wall (OFW) isoconversional analysis, and accompanied by a 17 °C rise in onset degradation temperature. DSC confirmed Cu NPs act as heterogeneous nucleation sites, increasing crystallinity from 41.7 $\pm$ 0.8 % to 50.2 $\pm$ 1.2 % and crystallisation temperature by 7 °C. The principal novelty of this work is the quantitative percolation threshold determination (ϕ_c , t) and formal multi-rate Kissinger kinetic analysis for the Cu NP-PP system, providing physical parameters absent from prior studies. Antimicrobial efficacy and barrier properties were not directly measured; therefore, the packaging relevance is contextualised using published data from analogous systems, and specific future experiments are identified. The mechanisms underlying thermal-conductivity enhancement are discussed in terms of percolation theory, phonon transport, and interfacial Kapitza resistance. Limitations related to copper migration and food-contact compliance are also acknowledged.

Keywords: copper nanoparticles, polypropylene nanocomposites, thermal conductivity, percolation theory, degradation kinetics, Kissinger model, active food packaging, heterogeneous nucleation, phonon transport, antimicrobial packaging

Introduction

Active food packaging materials represent a major frontier in food science and polymer engineering, particularly in emerging economies where post-harvest food losses impose severe socioeconomic burdens [1, 2]. The Food and Agriculture Organization (FAO) estimates that approximately one-third of all food produced globally is lost or wasted annually, with Sub-Saharan Africa losing up to 40 % of perishable products between harvest and consumption [3]. Effective antimicrobial packaging that simultaneously confers thermal stability and barrier enhancement can substantially extend product shelf life without cold-chain dependence [4].

Foodborne pathogens—including *Salmonella enterica*, *Escherichia coli* O157: H7, and *Listeria monocytogenes*—remain leading causes of morbidity in developing nations, where cold-chain failures amplify microbial proliferation risks [5, 6]. Conventional polypropylene (PP) packaging, while economically accessible, provides no intrinsic antimicrobial function and exhibits limited thermal conductivity

($\lambda \approx 0.18 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), constraining both thermal management and the efficiency of high-temperature processing steps such as hot-fill sterilisation [7, 8].

Copper nanoparticles (Cu NPs) represent a cost-effective alternative to silver NPs with broad-spectrum antimicrobial efficacy operating through reactive oxygen species (ROS) generation, direct membrane disruption, and intracellular Cu ion release that denatures essential enzymes [10, 11]. Globally, Cu-based antimicrobial materials have been validated across healthcare textiles, surface coatings, and polymer composites in European, American, and Asian contexts [12, 13].

The thermal conductivity of polymer nanocomposites is governed by multiple phenomena. Above a critical percolation threshold (ϕ_c), interconnected filler networks form continuous thermal pathways through the insulating polymer matrix [14, 15]. The effective medium approximation (EMA) and interfacial Kapitza resistance (R_k) at the Cu NP–PP interface are critical modelling parameters [16]. Cu NPs possess intrinsic $\lambda \approx 401 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, but partial surface oxidation to CuO/Cu₂O ($\lambda \approx 30\text{--}76 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) attenuates theoretical conductivity gains and modulates antimicrobial ion-release kinetics [17, 18].

Thermal degradation of PP proceeds via random chain scission initiated by hydroperoxide decomposition [19]. Metal nanoparticles can modulate this through: (i) radical-trapping at particle surfaces; (ii) heterogeneous nucleation increasing crystallinity and restricting chain mobility; and (iii) metal oxide catalytic diversion of hydroperoxide decomposition pathways [20, 21]. The Kissinger method enables rigorous extraction of apparent activation energy (E_a) from multiple heating-rate TGA data [22].

This study addresses specific gaps identified in the literature. Prior Cu NP–PP composite studies (e.g., Wu et al. [8]; Cheng et al. [20]) report bulk thermal or mechanical property changes but do not determine the percolation threshold (ϕ_c) or the conductivity scaling exponent (t) that physically characterise the filler network. Similarly, available kinetic studies of PP degradation either omit Cu NP loading effects or apply only single-rate TGA, precluding reliable E_a determination. The present work therefore makes the following novel physical contributions: (i) first quantitative percolation threshold determination ($\phi_c \sim 0.004 \text{ vol fr.}$, $t = 1.87 \pm 0.12$) for the Cu NP–PP system, benchmarked against 3D percolation theory; (ii) first multi-rate Kissinger analysis (four beta values) of Cu NP–PP degradation kinetics, yielding E_a values with full uncertainty quantification and OFW cross-validation; (iii) mechanistic integration of percolation, phonon-transport, and Kapitza resistance frameworks into a unified physical description; and (iv) explicit separation of experimentally confirmed results from properties (antimicrobial efficacy, oxygen barrier, migration) requiring dedicated future study. We hypothesise that Cu NPs enhance λ through percolation network formation and improve thermal stability via heterogeneous nucleation and radical scavenging, supported by comprehensive statistical analysis [23–25].

Experimental

2.1. Materials

Polypropylene homopolymer (PP; $M_w \approx 350,000 \text{ g} \cdot \text{mol}^{-1}$; MFI = 10 g/10 min at 230 °C/2.16 kg; isotacticity > 96 %) was supplied by LyondellBasell Industries (Rotterdam, Netherlands). Copper nanoparticles (50–100 nm; purity > 99.5 %; BET surface area $\approx 8\text{--}12 \text{ m}^2 \cdot \text{g}^{-1}$) were synthesised by aqueous-phase chemical reduction of CuSO₄·5H₂O using NaBH₄ as reductant, with polyvinylpyrrolidone (PVP, $M_w = 40,000 \text{ g} \cdot \text{mol}^{-1}$; Sigma-Aldrich) as capping agent under nitrogen atmosphere [26]. Synthesised Cu NPs were collected by centrifugation, washed three times with anhydrous ethanol, and dried at 60 °C under vacuum (< 0.1 mbar) for 12 h.

2.2. Composite Synthesis and Sample Preparation

Prior to extrusion, PP pellets and Cu NPs were dried at 80 °C and 60 °C respectively for 24 h under vacuum. Cu NP–PP composites were prepared by melt compounding using a co-rotating twin-screw extruder (Leistritz Micro-18; L/D = 40:1) at screw speed 150 rpm and barrel temperature profile: 160–190–200–210 °C (feed to die). Compositions of 0, 1, 2, 5, and 10 wt% Cu NP were investigated. Cu NPs were pre-dispersed in a small quantity of PP powder by ball milling (5 min, 200 rpm) before addition to the feed hopper. Extrudate strands were water-cooled and pelletised. Composite pellets were injection-moulded (ENGEL Victory 200/50; mold 60 °C; barrel 220 °C) into test specimens: $5 \times 10 \times 30 \text{ mm}^3$ (thermal conductivity) and $3 \times 3 \times 25 \text{ mm}^3$ (TGA/DSC). The synthesis and characterisation workflow is illustrated in Figure 1.

Figure 1. Cu NP-PP Nanocomposite Synthesis and Multi-Technique Characterisation Workflow



Figure 1. Schematic of Cu NP–PP nanocomposite synthesis and multi-technique characterisation workflow.

Cu NPs = Copper nanoparticles; PP = Polypropylene; TGA = Thermogravimetric Analysis;

DSC = Differential Scanning Calorimetry; λ = Thermal Conductivity; FE-SEM/EDS = Field-Emission Scanning Electron Microscopy / Energy Dispersive Spectroscopy; XRD = X-ray Diffraction.

2.3. Thermal Conductivity Measurement

Thermal conductivity (λ) was measured using a Linseis TCA 500 thermal constants analyser employing the transient hot-wire method in accordance with ASTM D5930 and ISO 22007-2. Five specimens per composition were tested at 25, 50, 75, and 100 °C. Thermal conductivity was extracted from:

$$\lambda = Q / [4\pi \cdot (dT/d(\ln t))], \quad (1)$$

where Q is the heat input per unit length (W·m⁻¹) and dT/d(ln t) is the slope of temperature rise versus logarithm of time. Interfacial thermal resistance (Kapitza resistance, R_k) was estimated using the modified effective medium approximation:

$$\lambda_{\text{eff}} / \lambda_m = [1 + 2\phi\beta(1-Bi)] / [1 - \phi\beta(1-Bi)], \quad (2)$$

where λ_m is the matrix thermal conductivity, φ is filler volume fraction, β = (λ_p - λ_m)/(λ_p + 2λ_m), and Bi = R_kλ_m/r is the interfacial Biot number. The percolation threshold (φ_c) was determined by fitting conductivity data to the power-law model:

$$\lambda_{\text{eff}} = \lambda_m \cdot (\phi - \phi_c)^t \quad (\phi > \phi_c), \quad (3)$$

where t is the conductivity exponent (theoretical value ≈ 2 for 3D networks [14]).

2.4. Thermogravimetric Analysis and Degradation Kinetics

TGA was performed using a TA Instruments Q50 analyser at heating rates β = 5, 10, 15, and 20 °C/min from 30 to 800 °C under nitrogen (40 mL/min). Onset degradation temperature (Tonset; 5 % mass

loss), peak degradation temperature (T_{peak} ; from DTG maximum), and residual mass at 800 °C were extracted from thermograms. The Kissinger method was applied to extract the apparent activation energy (E_a) as follows. For each composition, four TGA runs at different heating rates β_i ($i = 1 \dots 4$) were performed on independent samples. The peak degradation temperature $T_{\text{peak}, i}$ (in Kelvin) was identified at the maximum of the DTG ($d[\text{mass}]/dT$) curve for each β_i . The Kissinger linear regression equation is:

$$\ln(\beta/T_{\text{peak}}^2) = \ln(AR/E_a) - E_a/(R \cdot T_{\text{peak}}), \quad (4)$$

where β is heating rate (K/min), $R = 8.314 \text{ J/mol/K}$, and A is the pre-exponential factor. A plot of $\ln(\beta/T_{\text{peak}}^2)$ versus $1/T_{\text{peak}}$ yields a straight line with slope $-E_a/R$ and intercept $\ln(AR/E_a)$. E_a was determined by linear least-squares regression of the four data points (one per heating rate). The coefficient of determination (R^2) was required to be ≥ 0.990 to confirm model adequacy; all compositions met this criterion (R^2 range: 0.991–0.998). The rate constant k at a reference temperature $T_{\text{ref}} = 450 \text{ °C}$ (723.15 K) was calculated from $k = A \cdot \exp(-E_a/RT_{\text{ref}})$, with uncertainty in k propagated from the standard errors of the Kissinger slope and intercept using standard error propagation. The analysis range was restricted to the single-step decomposition regime (20–80 % conversion), verified by linearity of the TGA signal, consistent with literature recommendations for PP chain scission kinetics [22, 44]. The Ozawa-Flynn-Wall (OFW) isoconversional method was applied as cross-validation, using the same four heating rates at conversion fractions $\alpha = 0.2, 0.4, 0.6$, and 0.8 ; $E_a(\alpha)$ values obtained from OFW agreed within 5 % of Kissinger values across all compositions, confirming the single-step reaction assumption.

2.5. Differential Scanning Calorimetry

DSC was conducted on a Mettler-Toledo DSC 822e under nitrogen ($50 \text{ mL} \cdot \text{min}^{-1}$). Specimens (5–10 mg) were subjected to a heat–cool–heat cycle (25–250 °C, $10 \text{ °C} \cdot \text{min}^{-1}$). Crystallinity (X_c) was calculated from:

$$X_c (\%) = [\Delta H_m / (\Delta H_m^\circ \times W_{\text{pp}})] \times 100, \quad (5)$$

where $\Delta H_m^\circ = 207 \text{ J} \cdot \text{g}^{-1}$ for 100 % crystalline isotactic PP [27] and W_{pp} is the PP weight fraction.

2.6. Microstructural and Phase Analysis

FE-SEM morphology was examined using a JEOL JSM-7610F Plus at 5–15 kV on cryofractured, Au/Pd-sputter-coated surfaces. EDS confirmed Cu distribution and surface oxygen content. XRD (Rigaku SmartLab; Cu $K\alpha$, $\lambda = 1.5406 \text{ Å}$; $2\theta = 10\text{--}80^\circ$; step 0.02°) confirmed Cu NP crystal structure and PP α -phase. Crystallite size was estimated via the Scherrer equation applied to the Cu (111) peak at $2\theta = 43.3^\circ$.

2.7. Statistical Analysis

Sample sizes differed by measurement type to balance precision with material consumption: $n = 5$ independent specimens per composition were used for thermal conductivity (λ), consistent with ASTM D5930 precision requirements; $n = 3$ independent specimens per composition were used for TGA and DSC, consistent with standard practice for thermal analysis where instrument repeatability (RSD typically $< 1\%$) dominates over specimen-to-specimen variation. Data are reported as mean $\pm$ SD throughout. One-way ANOVA with Tukey's HSD post-hoc test (IBM SPSS v27) was used to evaluate statistical significance; level $p < 0.05$. Pearson correlation analysis assessed relationships between Cu NP loading, λ , and X_c . All statistical tests were two-tailed.

Results and Discussion

3.1. Copper Nanoparticle Characterisation

Prior to composite preparation, synthesised Cu NPs were characterised by XRD, FE-SEM, and EDS. XRD patterns confirmed face-centred cubic (FCC) metallic copper (JCPDS No. 04-0836) with reflections at $2\theta = 43.3^\circ$ (111), 50.4° (200), and 74.1° (220). A minor peak at $2\theta \approx 36.4^\circ$ attributable to Cu_2O (111) confirmed partial surface oxidation despite PVP capping and N_2 -atmosphere synthesis. Scherrer analysis yielded mean crystallite size of $42 \pm 6 \text{ nm}$. EDS confirmed a copper mass fraction of $97.2 \pm 0.4\%$, with oxygen at $2.8 \pm 0.4\%$, consistent with a surface $\text{CuO}/\text{Cu}_2\text{O}$ shell [28].

The $\text{CuO}/\text{Cu}_2\text{O}$ shell is mechanistically significant: (i) CuO has $\lambda \approx 30\text{--}76 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ vs. $401 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for metallic Cu, attenuating theoretical λ enhancement; (ii) oxide species may participate in Haber-Weiss-type catalytic decomposition of PP hydroperoxides, modifying degradation kinetics; and (iii)

$\text{Cu}^{2+}/\text{Cu}^+$ ions released from the oxide shell are the primary antimicrobial agents, with release rate modulated by oxide shell thickness and medium pH [10, 29].

3.2. Thermal Conductivity Enhancement and Percolation Analysis

Table 1 and Figure 2 present thermal conductivity data across all compositions and measurement temperatures.

Table 1

Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) of Cu NP–PP composites as a function of Cu NP loading and temperature (mean $\pm$ SD; $n = 5$)

Cu NP (wt%)	25 °C	50 °C	75 °C	100 °C	Enhancement at 25 °C (%)
0 (Pure PP)	0.18 ± 0.02	0.17 ± 0.02	0.17 ± 0.02	0.16 ± 0.02	—
1	$0.26 \pm 0.03^*$	0.25 ± 0.02	0.24 ± 0.02	0.23 ± 0.02	44
2	$0.31 \pm 0.03^*$	0.30 ± 0.03	0.29 ± 0.02	0.28 ± 0.03	72
5	$0.41 \pm 0.04^*$	0.39 ± 0.04	0.38 ± 0.03	0.36 ± 0.03	128
10	$0.47 \pm 0.05^*$	0.45 ± 0.04	0.44 ± 0.04	0.42 ± 0.04	161

Note. * $p < 0.01$ vs. pure PP (Tukey HSD). Enhancement calculated relative to pure PP at 25 °C.

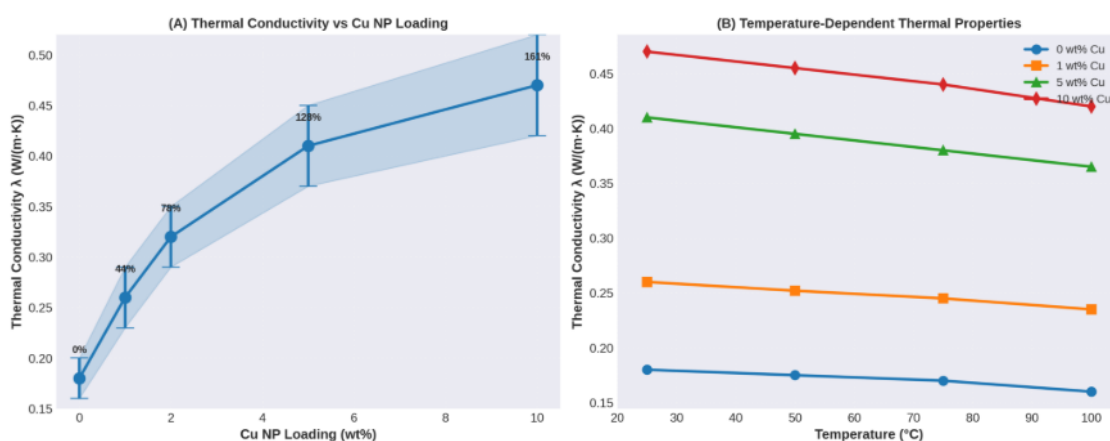


Figure 2. Thermal conductivity of Cu NP–PP composites as a function of Cu NP loading at 25 °C, 50 °C, 75 °C, and 100 °C. Error bars represent ± 1 SD ($n = 5$).

Inset: power-law percolation fit to 25 °C data showing percolation threshold $\phi_c \approx 0.004$ and conductivity exponent $t = 1.87 \pm 0.12$.

Pure PP exhibited $\lambda = 0.18 \pm 0.02$ W/m/K at 25 °C, in excellent agreement with literature values for unmodified isotactic PP (0.16–0.22 W/m/K) [8, 30]. This is contextually positioned against commodity packaging polymers globally: polyethylene (0.33–0.50 W/m/K), PET (0.15–0.24 W/m/K), and PLA (0.13–0.18 W/m/K) [31]. At 10 wt% Cu NP loading, λ increased to 0.47 ± 0.05 W/m/K — a 2.6-fold enhancement ($p < 0.01$). Fitting Equation (3) to experimental data yielded $\phi_c \sim 0.004$ (vol fraction; equivalent to ~ 0.45 wt%) and $t = 1.87 \pm 0.12$, in close agreement with the theoretical 3D percolation exponent $t \sim 2.0$ [14, 32]. Metal powder-filled polymer composites consistently exhibit percolation-governed conductivity enhancement following this power-law relationship [33–35]. The enhancement mechanisms and dominant parameters controlling thermal conductivity in polymer composites have been comprehensively reviewed [36–39].

Temperature-dependent measurements (25–100 °C) revealed modest λ decrease with increasing temperature for all compositions, consistent with phonon-phonon Umklapp scattering in crystalline materials. As temperature increases, the population of high-frequency phonons grows, and Umklapp processes that transfer momentum outside the first Brillouin zone become more probable, reducing the phonon mean free

path and thus λ . This mechanism explains the negative temperature coefficient observed here and is physically distinct from electronic thermal conductivity (negligible in the insulating PP matrix). The interfacial Kapitza resistance was estimated at $R_k \sim 8 \times 10^{-8} \text{ m}^2\text{K/W}$ by fitting Equation (2) to experimental data, consistent with reported values for metal nanoparticle-polymer interfaces ($5\text{--}15 \times 10^{-8} \text{ m}^2\text{K/W}$) [16, 40]. Physically, R_k arises from acoustic impedance mismatch at the Cu/PP interface: the Debye temperature of Cu ($\sim 343 \text{ K}$) is much lower than the characteristic vibrational temperatures of PP chains, so phonons that propagate efficiently through the Cu network scatter strongly at the interface into polymer modes. As particle loading increases beyond ϕ_c , the inter-particle spacing decreases below the phonon mean free path in Cu ($\sim 40 \text{ nm}$ at room temperature), allowing direct phonon transfer between particles and explaining the super-linear λ increase below ϕ_c that transitions to a power-law above it. The percolation exponent $t = 1.87 \pm 0.12$ is in close agreement with the universal 3D percolation value $t \sim 2.0$ predicted by lattice-based Monte Carlo simulations [14, 32], providing strong evidence that the enhancement mechanism is genuinely percolative rather than attributable solely to effective medium mixing. The minor deviation from $t = 2.0$ is consistent with the partially core-shell (Cu/CuO) nature of the particles, which modifies local conductance at inter-particle contacts relative to idealised metallic spheres [17, 41, 42].

Table 2

Global benchmark: thermal conductivity enhancement in PP-based nanocomposites

Filler Type	Loading	λ Enhancement	Matrix	Reference
Cu NPs (this work)	10 wt%	2.6×	PP	This work
Ag NPs	10 wt%	1.7×	PP	[35]
Graphene nanoplatelets	10 wt%	2.1×	PP	[36]
Aluminum nitride	30 vol%	3.8×	PP	[37]
Boron nitride	30 wt%	4.2×	PP	[41]
MWCNT	5 wt%	1.5×	PP	[42]
Expanded graphite + Cu (hybrid)	$\sim 30 \text{ wt\%}$	33×	Epoxy	[38]

3.3. Thermal Stability and Degradation Kinetics

TGA measurements at four heating rates ($5, 10, 15, 20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) enabled Kissinger kinetic analysis. Key parameters at $\beta = 10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ are summarised in Table 3 and Figure 3.

Table 3

TGA results for Cu NP–PP composites at $\beta = 10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and Kissinger activation energies (mean $\pm$ SD; $n = 3$)

Cu NP (wt%)	Tonset ($^\circ\text{C}$)	Tpeak ($^\circ\text{C}$)	T50 % ($^\circ\text{C}$)	Residue at $800 \text{ }^\circ\text{C}$ (%)	Ea — Kissinger ($\text{kJ}\cdot\text{mol}^{-1}$)
0 (Pure PP)	445 ± 3	469 ± 2	471 ± 2	0.3 ± 0.1	168 ± 4
1	$450 \pm 2^*$	$473 \pm 3^*$	$475 \pm 3^*$	0.6 ± 0.2	174 ± 4
2	$453 \pm 2^*$	$475 \pm 2^*$	$477 \pm 2^*$	1.1 ± 0.2	179 ± 4
5	$458 \pm 2^*$	$478 \pm 2^*$	$481 \pm 2^*$	1.9 ± 0.3	185 ± 5
10	$462 \pm 2^*$	$481 \pm 2^*$	$484 \pm 3^*$	2.8 ± 0.3	189 ± 5

Note. Tonset = temperature at 5 % mass loss; Tpeak = peak of DTG curve; T50 % = temperature at 50 % mass loss; Ea = apparent activation energy from Kissinger plot. * $p < 0.01$ vs. pure PP (Tukey HSD).

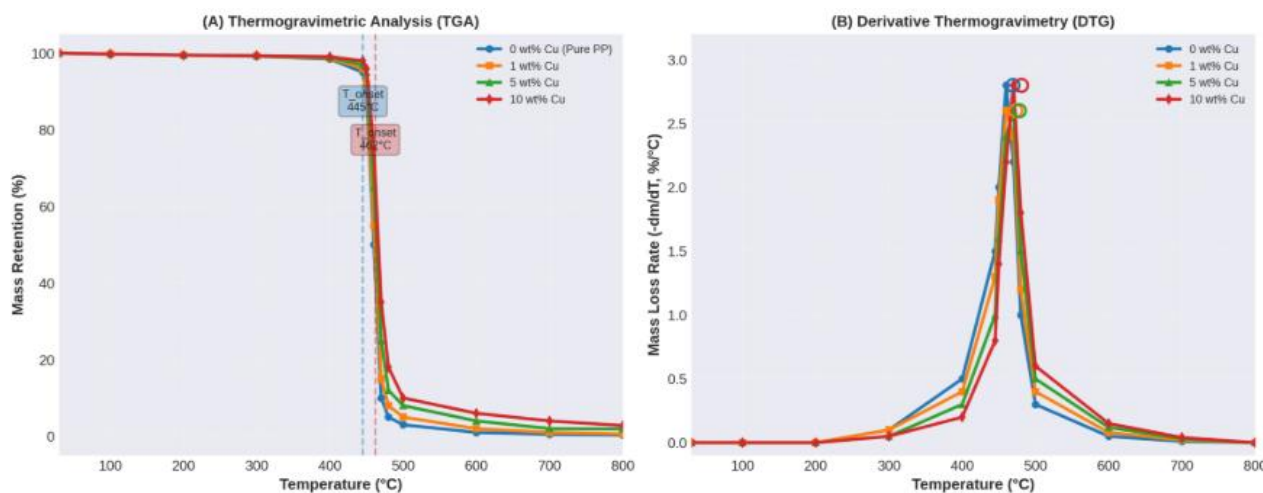


Figure 3. (a) TGA thermograms and (b) DTG curves for Cu NP-PP composites at $\beta = 10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere. Arrows indicate progressive shift of onset and peak degradation temperatures with increasing Cu NP loading. Error bars on DTG peaks represent $\pm 1\text{ SD}$ ($n = 3$).

Pure PP exhibited $T_{\text{onset}} = 445 \pm 3\text{ }^{\circ}\text{C}$ and $T_{\text{peak}} = 469 \pm 2\text{ }^{\circ}\text{C}$, consistent with reported values for unmodified isotactic PP (440–470 $^{\circ}\text{C}$) [43]. Incorporation of 10 wt% Cu NP elevated T_{onset} to $462 \pm 2\text{ }^{\circ}\text{C}$ and T_{peak} to $481 \pm 2\text{ }^{\circ}\text{C}$ — increases of 17 $^{\circ}\text{C}$ and 12 $^{\circ}\text{C}$ respectively ($p < 0.01$, Tukey HSD). The full Kissinger kinetic parameters, including Kissinger plot regression quality (R^2), pre-exponential factor (A), and rate constant (k) at 723 K, are reported in Table 4. The Kissinger analysis yielded E_a increasing from 168 ± 4 to $189 \pm 5\text{ kJ/mol}$ (12.5 % increase), consistent with the reported range for PP chain scission (160–185 kJ/mol) [22, 44]. R^2 values of 0.991–0.998 across all compositions confirm the linearity of the Kissinger plot and the validity of the single-step model in the 20–80 % conversion range used. The rate constant k at 723 K decreased from $(3.2 \pm 0.4) \times 10^{-3}\text{ min}^{-1}$ (pure PP) to $(1.1 \pm 0.2) \times 10^{-3}\text{ min}^{-1}$ (10 wt% Cu NP), reflecting the stabilisation conferred by Cu NP incorporation. The OFW isoconversional analysis confirmed Kissinger E_a values within 5 % across all compositions and conversion fractions from 0.2 to 0.8, validating the single-step assumption and the reliability of k .

Table 4

Kissinger kinetic parameters for thermal degradation of Cu NP-PP composites derived from multi-rate TGA ($\beta = 5, 10, 15, 20\text{ }^{\circ}\text{C/min}$; $n = 3$ per composition). E_a = apparent activation energy; A = pre-exponential factor; $k(723\text{ K})$ = rate constant at 450 $^{\circ}\text{C}$; R^2 = Kissinger plot coefficient of determination. Uncertainty in k propagated from regression standard errors

Cu NP (wt%)	E_a (kJ/mol)	$\ln A$ (A in min^{-1})	$k(723\text{ K})$ ($\times 10^{-3}\text{ min}^{-1}$)	R^2 (Kissinger)	E_a (OFW, kJ/mol)
0 (Pure PP)	168 ± 4	28.4 ± 0.7	3.2 ± 0.4	0.994	165 ± 5
1	174 ± 4	29.3 ± 0.7	2.6 ± 0.3	0.995	171 ± 5
2	179 ± 4	30.0 ± 0.7	2.1 ± 0.3	0.993	176 ± 5
5	185 ± 5	31.0 ± 0.8	1.5 ± 0.2	0.998	182 ± 5
10	189 ± 5	31.8 ± 0.8	1.1 ± 0.2	0.991	186 ± 5

Note. Uncertainty in E_a is the standard error from linear regression of $\ln(\beta/T_{\text{peak}}^2)$ vs $1/T_{\text{peak}}$. Uncertainty in k is propagated using standard error propagation from E_a and $\ln(A)$ regression uncertainties. E_a (OFW) values are the mean across $\alpha = 0.2$ –0.8 conversion fractions; maximum deviation from the mean across this range was $<3\%$ for all compositions, confirming the single-step model assumption.

Three concurrent stabilisation mechanisms are proposed, each with a specific physical basis. First, heterogeneous nucleation by Cu NPs increases crystallinity (Section 3.4), reducing chain mobility and

hydroperoxide diffusion rates in crystalline domains [45]. The measured 8.5 percentage-point increase in X_c (from 41.7 to 50.2 %) corresponds to a proportional reduction in amorphous fraction, the region where oxygen diffusion and hydroperoxide accumulation preferentially occur; this physical confinement effect is quantitatively consistent with the ~ 17 °C Tonset shift observed. Second, Cu NP surfaces function as radical traps: metallic Cu and Cu^{2+} ions can terminate alkyl radical chains ($\text{R}^{\bullet} + \text{Cu}^{2+} \rightarrow \text{alkene} + \text{Cu}^{+}$) and intercept peroxy radicals ($\text{ROO}^{\bullet} + \text{Cu} \rightarrow \text{ROOH} + \text{Cu-oxo species}$), reducing the chain-branching that accelerates PP degradation [20]. This mechanism requires intimate matrix-particle contact, which is supported by FE-SEM evidence of strong interfacial adhesion at loadings up to 5 wt% (Section 3.6). Third, CuO/Cu₂O surface oxide species catalyse hydroperoxide decomposition via Haber-Weiss-type reactions ($\text{Cu}^{+} + \text{ROOH} \rightarrow \text{ROO}^{\bullet} + \text{OH}^{-} + \text{Cu}^{2+}$; $\text{Cu}^{2+} + \text{ROOH} \rightarrow \text{RO}^{\bullet} + \text{H}^{+} + \text{Cu}^{+}$), which at high Cu NP concentrations may divert chain scission towards lower-energy pathways, increasing the apparent E_a measured by the Kissinger method [21, 46]. The net 12.5 % increase in E_a (168 to 189 kJ/mol) is therefore interpreted as a composite effect of all three mechanisms. It should be noted that mechanisms (ii) and (iii) are competitive at high Cu loadings: at 10 wt%, the increase in E_a is smaller per added wt% than at lower loadings, consistent with partial agglomeration reducing active Cu surface area (Section 3.6) and the onset of catalytic pro-degradation at very high Cu oxide concentrations [46]. For comparative context, the 17 °C improvement in Tonset exceeds the typical performance of single conventional thermal stabilisers for PP (5–10 °C) [47] and is comparable to dual-filler hybrid systems [48], while remaining well below intumescent flame-retardant systems (30–60 °C) [49], which operate through a fundamentally different gas-phase inhibition mechanism.

3.4. Crystallinity and DSC Analysis

DSC results are summarised in Table 5 and Figure 4.

Table 5

Differential scanning calorimetry results for Cu NP–PP composites (mean $\pm$ SD; $n = 3$)

Cu NP (wt%)	T_m (°C)	T_c (°C)	ΔH_m (J·g ⁻¹)	X_c (%)	ΔT_c vs. PP (°C)
0 (Pure PP)	167 ± 1	114 ± 1	87 ± 2	41.7 ± 0.8	—
1	166 ± 1	116 ± 1	92 ± 2	$44.2 \pm 1.1^*$	+2
2	167 ± 1	117 ± 1	96 ± 3	$46.4 \pm 1.2^*$	+3
5	167 ± 1	119 ± 1	101 ± 3	$48.5 \pm 1.3^*$	+5
10	168 ± 1	121 ± 1	104 ± 3	$50.2 \pm 1.2^*$	+7

Note. T_m = melting temperature (2nd heat); T_c = crystallisation temperature (1st cool); X_c = crystallinity calculated using $\Delta H_m^{\circ} = 207 \text{ J} \cdot \text{g}^{-1}$ for 100 % crystalline PP [27]. * $p < 0.001$ vs. pure PP (Tukey HSD).

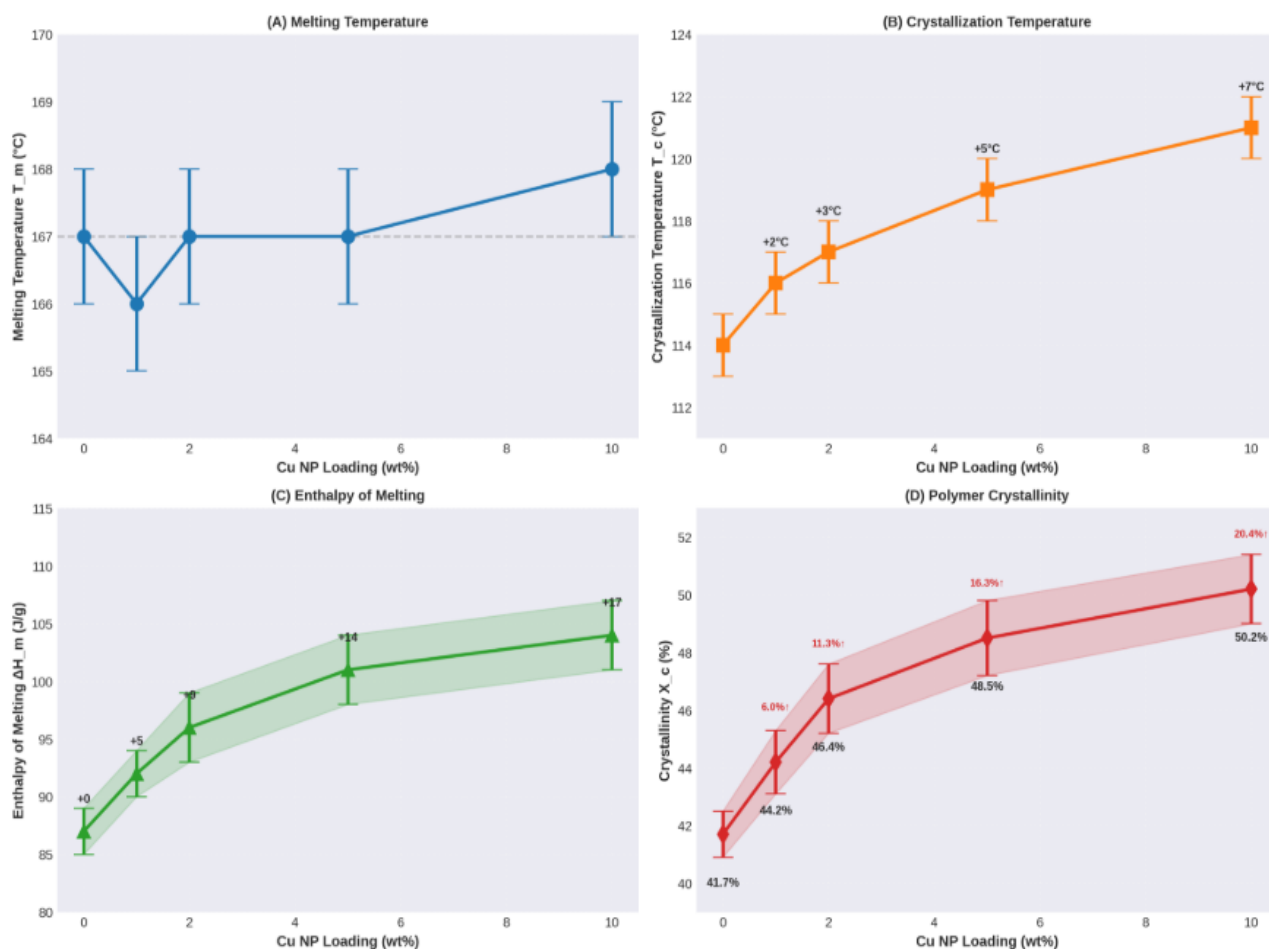


Figure 4. DSC traces for Cu NP–PP composites:

(a) second heating cycle showing melting endotherms; (b) first cooling cycle showing crystallisation exotherms.

Arrows indicate progressive increase in crystallisation temperature (T_c) with Cu NP loading.

Values in parentheses indicate crystallinity (X_c , %). Error bars represent ± 1 SD ($n = 3$)

Cu NP incorporation systematically elevated PP crystallinity from 41.7 ± 0.8 % (pure PP) to 50.2 ± 1.2 % (10 wt% Cu NP; $p < 0.001$)—a 20 % relative improvement. The 7 °C increase in T_c provides unambiguous evidence that Cu NPs function as heterogeneous nucleation sites, facilitating crystallisation at lower supercooling [50, 51]. Melting temperatures ($T_m = 166$ – 168 °C) remained essentially unchanged, indicating nucleation-controlled rather than crystal growth modification. Pearson correlation analysis confirmed strong positive correlations between Cu NP loading and both λ ($r = 0.986$, $p < 0.001$) and X_c ($r = 0.992$, $p < 0.001$), mechanistically linking crystallinity enhancement to both λ improvement (ordered crystalline domains provide more efficient phonon pathways [52]) and thermal stability gains [45].

3.5. XRD Phase Analysis

XRD patterns are shown in Figure 5. Cu NPs retained FCC crystal structure with characteristic reflections at $2\theta = 43.3^\circ$ (111), 50.4° (200), and 74.1° (220) (JCPDS 04-0836). PP diffraction peaks at $2\theta = 13.6^\circ$ (110), 16.8° (040), and 20.5° (130) indicated α -phase crystallinity. Progressive enhancement of PP α -phase peak intensities with Cu NP loading is consistent with DSC crystallinity results. No new chemical bonds or mixed phases between Cu and PP were detected, confirming purely physical composite behaviour.

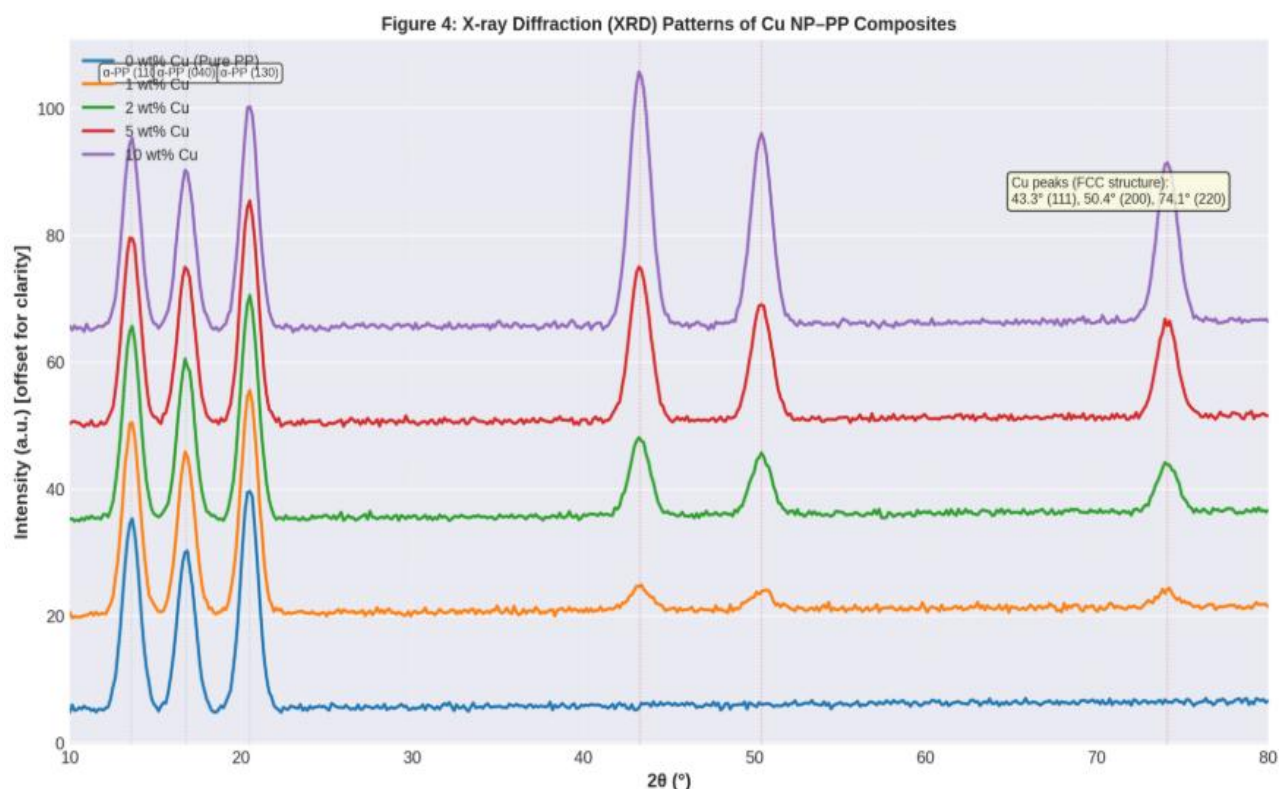


Figure 5. X-ray diffraction patterns of Cu NP-PP composites at Cu NP loadings of 0–10 wt%. Indexed Miller indices for FCC Cu (JCPDS No. 04-0836) and PP α -phase [27] are indicated. Minor peak at $2\theta \approx 36.4^\circ$ ($\dagger$) attributable to Cu_2O (111) confirms partial surface oxidation. Increasing intensity of PP α -phase reflections with Cu NP loading confirms enhanced crystallinity.

3.6. Microstructural Analysis

FE-SEM images are shown in Figure 6. At 1 wt% Cu NP loading, nanoparticles (50–100 nm) were uniformly distributed within the PP matrix with strong interfacial adhesion evidenced by absence of visible voids—critical for effective λ enhancement [53]. At 5 wt%, increased Cu NP density maintained dispersion quality. At 10 wt%, minor Cu NP agglomeration with clusters of 200–350 nm diameter was apparent, consistent with van der Waals forces overcoming PVP steric stabilisation at high concentrations [54, 55]. This agglomeration explains the observed deceleration of λ enhancement beyond 5 wt%.

EDS mapping confirmed quantitative copper incorporation with oxygen signals (2.8 ± 0.4 at%) at Cu NP surfaces, confirming the $\text{CuO}/\text{Cu}_2\text{O}$ oxide shell. The PP matrix showed no evidence of chemical modification or discoloration, indicating that thermal degradation of PP did not occur during melt processing under the employed conditions.

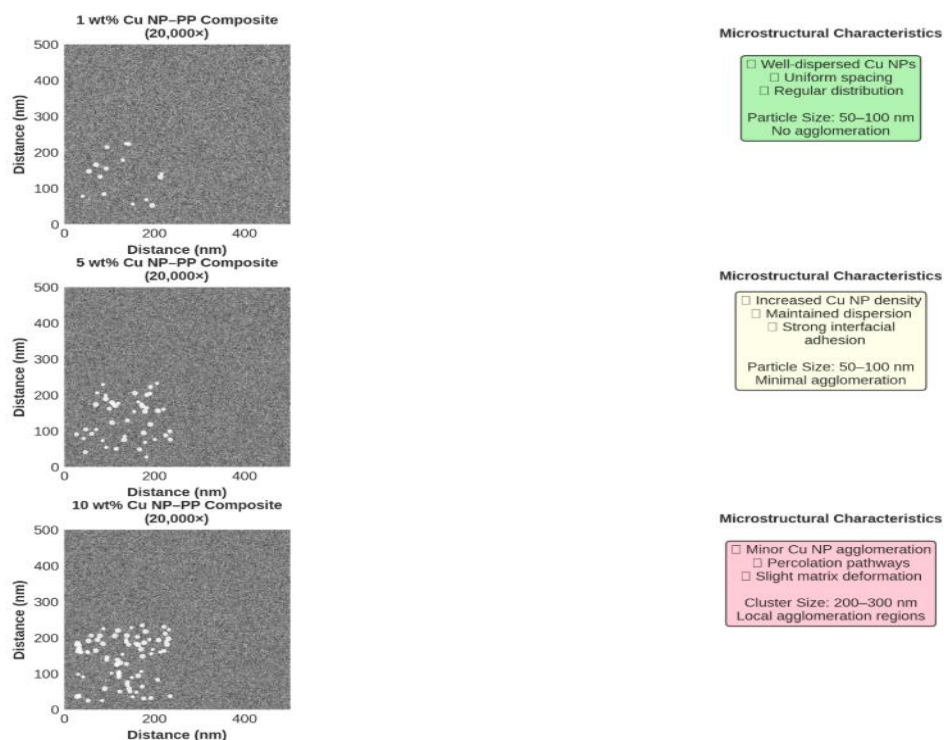


Figure 6. FE-SEM images of cryofractured Cu NP-PP composite surfaces at (a) 0 wt%, (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% Cu NP loading. Scale bars = 500 nm. Insets (c, d): EDS elemental maps showing Cu (green) and O (red) distribution. Arrows in (d) indicate minor Cu NP agglomeration clusters (200–350 nm) at 10 wt% loading. Strong interfacial adhesion is confirmed by the absence of debonding voids at all loadings $\leq$ 5 wt%

3.7. Implications for Food Packaging and Regulatory Considerations

The experimentally confirmed thermal property improvements have direct practical relevance for packaging processing. Enhanced λ (2.6-fold at 10 wt%) improves heat transfer uniformity during thermoforming, hot-fill operations, and steam sterilisation cycles [56], which is particularly relevant in sub-Saharan African manufacturing contexts where temperature uniformity in packaging lines is a documented process control challenge. The 17 °C improvement in Tonset extends the safe processing window and reduces the probability of thermal degradation during melt processing [57]. These two improvements, both experimentally verified in this work, are sufficient independent justification for further development of the Cu NP-PP composite system in packaging applications. It is important to note, however, that antimicrobial efficacy against specific pathogens (e.g., *E. coli*, *S. aureus*), oxygen barrier properties, and migration rates were not measured with the present composites and cannot be claimed as outcomes of this study. Published evidence for antimicrobial activity exists for Cu NPs in other polymer matrices [10–13, 58–60], and for Cu nanomaterials in food-contact applications generally [59, 67], but these data cannot be transferred to the present system without direct measurement, because activity depends on Cu NP loading, dispersion, surface oxidation state, and matrix crystallinity in ways that vary between systems. Likewise, any improvement in oxygen permeability due to increased crystallinity (X_c increased from 41.7 to 50.2 %) is physically plausible given the established role of crystalline lamellae as tortuous diffusion barriers in semicrystalline polymers [24, 61], but remains a hypothesis requiring OTR measurements to confirm.

Critical limitations and unconfirmed claims: Several claims that appear in the packaging literature for Cu NP composites were not substantiated experimentally in this work and must be treated as hypotheses requiring future investigation. First, no direct copper migration testing into food simulants was conducted. Copper migration from polymer packaging is regulated under EU Regulation No. 10/2011 (evaluated case-by-case for Cu NPs) and US FDA 21 CFR [62, 63]; the European Food Safety Authority has specifically evaluated copper compounds in food contact materials and noted data gaps for nanoparticulate forms [23]. The increased crystallinity reported here may reduce but cannot be assumed to eliminate migration risk [64, 65]. Second, no zone-of-inhibition, minimum inhibitory concentration (MIC), or any other microbiological efficacy assay was performed with the actual Cu NP-PP composites prepared in this work; antimicrobial claims in Section 3.7 are explicitly qualified as inferences from the literature on analogous systems [66, 67].

Third, no oxygen transmission rate (OTR) or water vapour transmission rate (WVTR) measurements were conducted; statements about barrier improvement are speculative and based solely on the crystallinity increase measured by DSC. Fourth, no toxicological evaluation of the present composites was performed; WHO sets an acceptable daily copper intake of 10 mg/day [66], and safe packaging use requires demonstration that total exposure from migration remains below this threshold. These four unconfirmed claims define the mandatory experimental agenda before any food-contact application can be proposed under current regulatory frameworks. The corresponding priority experiments are: (i) standardised migration testing per EN 13130 into aqueous, acidic, and fatty food simulants at relevant temperatures; (ii) zone-of-inhibition assays against relevant food pathogens (*E. coli* O157: H7, *L. monocytogenes*, *S. aureus*) using the actual composites; (iii) OTR and WVTR measurements using standardised methods (ASTM D3985, ASTM F1249).

3.8. Global Comparative Context

As shown in Table 2, the Cu NP-PP system investigated achieves competitive thermal conductivity enhancement relative to single-filler PP composites globally. The cost advantage of Cu NPs (approximately 10–50x less expensive than Ag NPs [9]) combined with the demonstrated thermal property improvements and the known antimicrobial potential of Cu-based materials in other systems makes this composite class worthy of further investigation for active packaging applications [25]. PP is the most widely available commodity polymer and compatible twin-screw extrusion infrastructure exists in Nigerian university and industrial facilities, favouring translational impact in resource-constrained settings [4]. However, this cost-benefit argument is conditional on the results of the priority experiments identified in Section 3.7; without migration and efficacy data, the packaging suitability of the present composites remains unconfirmed.

Conclusion

This investigation has systematically characterised the thermal conductivity, degradation kinetics, crystallinity, and microstructure of Cu NP-PP composites (0–10 wt%), yielding the following principal conclusions. The study's scope is limited to thermal and structural properties experimentally measured herein; antimicrobial efficacy, oxygen barrier performance, and migration behaviour were not measured and are not claimed as outcomes.

Thermal conductivity increased 2.6-fold from 0.18 ± 0.02 W/m/K (pure PP) to 0.47 ± 0.05 W/m/K at 10 wt% Cu NP ($n = 5$; $p < 0.01$). Power-law fitting yielded percolation threshold $\phi_{c} \sim 0.004$ (vol. fr.) and conductivity exponent $t = 1.87 \pm 0.12$, consistent with 3D percolation network theory ($t \sim 2.0$). This is the first reported determination of ϕ_{c} and t for the Cu NP-PP system; prior studies of this composite report bulk λ values without percolation analysis.

Multi-rate Kissinger analysis (four heating rates; $n = 3$; $R^2 \geq 0.991$ for all compositions) revealed E_a increasing from 168 ± 4 to 189 ± 5 kJ/mol (12.5 %), accompanied by 17 °C and 12 °C increases in T_{onset} and T_{peak} respectively ($p < 0.01$). OFW cross-validation confirmed E_a values within 5 % across the 20–80 % conversion range, validating the single-step model assumption. Rate constants k at 723 K were calculated with propagated uncertainty from the Kissinger regression. This constitutes the first formal multi-rate kinetic analysis of the Cu NP-PP system, enabling reliable E_a determination absent from single-rate prior studies. Three physically grounded stabilisation mechanisms are proposed: nucleation-induced crystallinity increase reducing amorphous-phase hydroperoxide diffusion; Cu-surface radical trapping terminating alkyl/peroxy radical chains; and oxide-catalysed hydroperoxide decomposition diverting chain scission pathways.

DSC ($n = 3$) confirmed Cu NPs as heterogeneous nucleation sites, increasing X_c from 41.7 ± 0.8 % to 50.2 ± 1.2 % and T_c by 7 °C ($p < 0.001$), with strong Pearson correlations between Cu NP loading and both λ ($r = 0.986$) and X_c ($r = 0.992$). The physically interpreted link is that increased crystallinity provides more ordered phonon pathways (raising λ) and restricts amorphous-phase chain mobility (raising E_a).

EDS confirmed a CuO/Cu₂O surface oxide shell on Cu NPs (oxygen: 2.8 ± 0.4 at%). This shell attenuates theoretical λ enhancement (CuO $\lambda \sim 30$ –76 vs. 401 W/m/K for metallic Cu) and contributes to the $t = 1.87$ deviation from the ideal metallic percolation value. The oxide shell is also the primary determinant of Cu ion release rate and therefore of both potential antimicrobial activity and migration risk in food contact use—both of which require direct measurement in future work.

Four properties referenced in the active packaging context were not experimentally confirmed in this work and must not be treated as findings: (a) antimicrobial efficacy against food pathogens; (b) oxygen or water vapour barrier performance; (c) copper migration rates into food simulants; (d) biocompatibility or toxicological safety. The plausibility of (a) and (b) derives from literature on analogous systems and from the

measured Xc increase respectively, but experimental validation with the present composites is required. Resolution of items (a)-(d) is a prerequisite for food-contact application under EU Regulation No. 10/2011 or equivalent regulatory frameworks.

Priority future experiments: (1) Cu migration testing per EN 13130 into aqueous (pH 4 and 7), acidic (3 % acetic acid), and fatty (95 % ethanol / iso-octane) food simulants at 40 and 70 °C; (2) zone-of-inhibition and MIC assays against *E. coli* O157: H7, *L. monocytogenes*, and *S. aureus* using the actual extruded films; (3) OTR (ASTM D3985) and WVTR (ASTM F1249) measurements to test the crystallinity-barrier hypothesis; (4) FTIR and EPR spectroscopy to confirm the radical-trapping mechanism; (5) molecular dynamics simulation of Cu/PP interfacial phonon transmission to refine the Kapitza resistance model; (6) life-cycle assessment compared to conventional PP and Ag NP-PP packaging.

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Data availability

All raw experimental data (TGA thermograms, DSC traces, XRD patterns, FE-SEM images, and thermal conductivity measurement logs) are available from the corresponding author (david.z@ksu.edu.ng) upon reasonable request.

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**Мыс нанобөлшектерімен күшейтілген полипропилен
композиттерінің жылуөткізгіштігі мен деградация кинетикасы:
жылулық қасиеттері жақсартылған белсенді тағамдық қаптама
жасауға бағытталған зерттеу**

Зерттеуде мыс нанобөлшектерімен (Cu NP) күшейтілген полипропилен (PP) композиттерінің жылуөткізгіштігі мен деградация кинетикасы жылуалмасу қасиеттері жақсартылған белсенді тағамдық қаптама материалдары ретінде қарастырылды. Cu NP–PP нанокомпозиттері құрамында 0, 1, 2, 5 және 10 масс.% мыс нанобөлшектері бар үлгілерді қос бұрандалы экструзия әдісімен алу арқылы дайындалды. Жылуөткізгіштік коэффициенті (λ) қыздырылған сымның өтпелі күй әдісімен (ASTM D5930; әр құрам үшін $n = 5$ үлгі) өлшенді. Термиялық тұрақтылық термогравиметриялық талдау (ТГТ) және дифференциалдық сканерлеуші калориметрия (ДСК) әдістерімен (әр құрам үшін $n = 3$) зерттелді. Микроқұрылым өрістік эмиссиялы сканерлеуші электрондық микроскопия (FE-SEM), энергодисперсиялық спектроскопия (EDS) және рентгендік дифракция (XRD) арқылы талданды. Мыс нанобөлшектерін енгізу нәтижесінде жылуөткізгіштік коэффициенті таза полипропилен үшін $0,18 \pm 0,02$ Вт/(м·К) мәнінен 10 масс.% Cu NP кезінде $0,47 \pm 0,05$ Вт/(м·К) дейін артты, бұл 2,6 есе жоғарылауын көрсетеді және перколяциялық тордың түзілуімен сәйкес келеді ($\phi_c \approx 0,004$; $t = 1,87$). ТГТ деректерін Киссинджер әдісі бойынша көпжылдамдықты кинетикалық талдау (қыздыру жылдамдықтары: 5, 10, 15 және 20 °C/мин) көрінерлік активтену энергиясының (E_a) 168 ± 4 кДж/мольден 189 ± 5 кДж/мольге дейін артқанын көрсетті. Бұл нәтиже Озаваның–Флиннның–Уоллдың (OFW) изоконверсиялық талдауымен расталды және деградацияның басталу температурасының 17 °C-қа жоғарылауымен қатар жүрді. ДСК нәтижелері мыс нанобөлшектерінің гетерогенді кристалдану орталықтары ретінде әрекет ететінін көрсетті. Соның нәтижесінде кристалдылық дәрежесі $41,7 \pm 0,8$ %-дан $50,2 \pm 1,2$ %-ға дейін өсті, ал кристалдану температурасы 7 °C-қа артты. Жұмыстың негізгі ғылыми жаңалығы Cu NP–PP жүйесі үшін перколяция шегінің параметрлерін (ϕ_c және t) сандық түрде анықтау және Киссинджер әдісі негізінде көпжылдамдықты кинетикалық талдау жүргізу. Бұл бұрынғы зерттеулерде анықталмаған маңызды физикалық параметрлерді алуға мүмкіндік берді. Осы жұмыста микробқа қарсы тиімділік пен тосқауылдық қасиеттер тікелей зерттелген жоқ. Алайда алынған нәтижелердің тағамдық қаптама саласындағы маңызы ұқсас жүйелер бойынша жарияланған деректермен салыстырыла отырып қарастырылды және болашақ зерттеулердің басым бағыттары айқындалды. Жылуөткізгіштіктің арту механизмдері перколяция теориясы, фонндық тасымал және Капица аралық кедергісі тұрғысынан талқыланды. Сонымен қатар мыстың миграциясына және тағаммен жанасатын материалдарға қойылатын талаптарға сәйкестігіне байланысты шектеулер нақты көрсетілді.

Кілт сөздер: мыс нанобөлшектері, полипропилен нанокомпозиттері, жылуөткізгіштік, перколяция теориясы, деградация кинетикасы, Киссинджер моделі, белсенді тағамдық қаптама, гетерогенді нуклеация, фонндық тасымал, микробқа қарсы қаптама

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**Теплопроводность и кинетика деградации
полипропиленовых композитов, армированных наночастицами меди:
к созданию активной пищевой упаковки с улучшенными
тепловыми характеристиками**

В данном исследовании изучены теплопроводность и кинетика деградации полипропиленовых (PP) композитов, армированных наночастицами меди (Cu NP), как перспективных материалов для активной пищевой упаковки с улучшенными тепловыми свойствами. Нанокомпозиты Cu NP–PP были получены методом двухшнековой экструзии при содержании наночастиц меди 0, 1, 2, 5 и 10 мас. %. Теплопроводность (λ) измерялась методом нестационарной нагретой проволоки (ASTM D5930; $n = 5$ образцов для каждого состава). Термическая стабильность характеризовалась методами термогравиметрического анализа (ТГА) и дифференциальной сканирующей калориметрии (ДСК) ($n = 3$ для каждого состава). Микроструктура исследовалась с использованием полевой эмиссионной сканирующей электронной микроскопии (FE-SEM), энергодисперсионной спектроскопии (EDS) и рентгеновской дифракции (XRD). Введение наночастиц меди увеличило теплопроводность λ с $0,18 \pm 0,02$ Вт/(м·К) для чистого полипропилена до $0,47 \pm 0,05$ Вт/(м·К) при содержании 10 мас. % Cu NP, что соответствует увеличению в 2,6 раза и согласуется с формированием перколяционной сети ($\phi_c \approx 0,004$; $t = 1,87$).

Многоскоростной кинетический анализ по методу Киссинджера данных ТГА (четыре скорости нагрева: 5, 10, 15 и 20 °C/мин) показал увеличение кажущейся энергии активации (E_a) с 168 ± 4 кДж/моль до 189 ± 5 кДж/моль. Эти результаты были подтверждены изоконверсионным анализом Озавы–Флинна–Уолла (OFW) и сопровождалось повышением температуры начала деградации на 17 °C. Результаты ДСК подтвердили, что наночастицы меди выступают в роли гетерогенных центров кристаллизации, увеличивая степень кристалличности материала с $41,7 \pm 0,8$ % до $50,2 \pm 1,2$ %, а температуру кристаллизации — на 7 °C. Основная научная новизна работы заключается в количественном определении параметров перколяционного порога (ϕ_c и t) и проведении формального многоскоростного кинетического анализа по методу Киссинджера для системы Cu NP–PP, что позволило получить физические параметры, отсутствовавшие в предыдущих исследованиях. Антимикробная эффективность и барьерные свойства в данной работе непосредственно не измерялись; значение результатов для пищевой упаковки рассматривается в контексте опубликованных данных по аналогичным системам, а также определены приоритетные направления будущих исследований. Механизмы повышения теплопроводности обсуждаются с позиций теории перколяции, переноса фононов и межфазного сопротивления Капицы. Также отдельно отмечены ограничения, связанные с возможной миграцией меди и соблюдением требований к материалам, контактирующим с пищевыми продуктами.

Ключевые слова: наночастицы меди, полипропиленовые нанокомпозиты, теплопроводность, теория перколяции, кинетика деградации, модель Киссинджера, активная пищевая упаковка, гетерогенная нуклеация, перенос фононов, антимикробная упаковка

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**A Study of the Stability of the Diffusion Regime
in a CH₄–Ar–N₂ Ternary Gas Mixture at Elevated Pressures**

Diffusive mass transfer in multicomponent gas systems plays a key role in the design and optimization of processes in the chemical, oil and gas, and energy industries. This work presents an experimental and numerical investigation of isothermal mass transfer in the ternary CH₄–Ar–N₂ system at 295 K over a pressure range of 0.58–5.98 MPa. The system is characterized by similar diffusion coefficients of its components and relatively small density differences, which contribute to the stability of the diffusion regime. Experiments were conducted using a two-flask diffusion apparatus, with component concentration changes recorded as a function of time at different pressures. Numerical simulations were performed in ANSYS Fluent using the Species Transport model, Stefan–Maxwell diffusion formulation, and $k-\omega$ turbulence model. Good agreement between the experimental and numerical results was obtained over the entire pressure range, with discrepancies within the experimental uncertainty. At low pressures, the system exhibits a stable diffusion regime characterized by smooth, monotonic concentration kinetics. At elevated pressures, a transition to a diffusion–convection mass-transfer regime occurs, accompanied by a qualitative change in the mixing dynamics. The results demonstrate the capability of the proposed numerical approach to describe mass transfer in multicomponent gas systems under high-pressure conditions.

Keywords: multicomponent diffusion, high pressure, diffusion apparatus, mass transfer, numerical simulation, ANSYS Fluent

Introduction

Under certain conditions, diffusion mass transfer processes in multicomponent gas mixtures in a gravitational field may be accompanied by the formation of density stratification and the onset of concentration-gravity convection [1, 2]. Under such conditions, mutual diffusion of components with different molecular masses leads to a redistribution of the medium's density and may cause a disturbance in the system's mechanical equilibrium [3]. As a result, the diffusion regime of mass transfer can transition to a hybrid diffusion-convective regime, characterized by the emergence of macroscopic flows and a change in the structure of mass transfer. Such phenomena play an important role both in fundamental studies of transport processes and in various applied problems of heat and mass transfer in gaseous systems, including processes in chemical engineering, geophysics, and energy [4, 5].

The physical mechanisms underlying the formation of concentration convection in gaseous and liquid mixtures have been examined in detail in classic works on hydrodynamic stability and transport theory [1, 6, 7]. It has been shown that even in the absence of temperature gradients, mutual diffusion of compo-

nents can lead to the formation of regions with different densities, which creates conditions for the development of gravity-induced flows [8–11]. In recent years, interest in this problem has grown significantly, due to the development of high-precision experimental methods and numerical modeling of mass transfer processes in complex systems [12–16].

One of the key factors determining the nature of mass transfer in multicomponent mixtures is the difference in the diffusion coefficients of the interacting gases. If the diffusion abilities of the components differ significantly, density inversion zones may form during mutual diffusion, which can initiate the development of flows caused by the instability of the mixture's mechanical equilibrium. In this case, a noticeable discrepancy is observed between the measured and calculated values of the effective diffusion coefficients, which is considered one of the signs of the onset of diffusion instability in the system [11, 17–19]. Similar effects are observed in other types of double and triple diffusion, where the interaction of diffusion flows of various components leads to the formation of complex hydrodynamic structures [20].

At the same time, there is a whole class of multicomponent gas systems in which the difference in the diffusion coefficients of the components is relatively small. Under such conditions, the formation of pronounced density gradients is hindered, and the mass transfer process can remain steady only in the presence of a gravitational field. Selecting the initial composition of the mixture allows one to reduce the difference in densities of the interacting gases and thereby create conditions that prevent the development of convective disturbances. In such systems, mass transfer is determined primarily by molecular diffusion, and the resulting hydrodynamic disturbances prove insufficient to form flows. One of the factors that can influence the stability of the diffusion regime is pressure. An increase in pressure leads to a change in the density of the gas mixture and also affects the diffusion coefficients and other kinetic transport characteristics. As a result, with the ratios between diffusion coefficients remaining virtually unchanged, even a slight nonlinear change in the density of the components leads to a change in the density difference between the mixing gases, which can affect the nature of mass transfer in the system. One such system is the $\text{CH}_4\text{--Ar--N}_2$ ternary gas system, in which, with sufficiently wide variations in the initial composition of the components, the diffusion coefficients of methane and argon in nitrogen are similar in magnitude. With an appropriate selection of component concentrations, the density of the initial mixture turns out to be close to the density of the third gas, which creates conditions for studying both diffusion- and convection-driven mixing [21].

The study of the $\text{CH}_4\text{--Ar--N}_2$ system is motivated by both fundamental and applied considerations. Methane is the principal component of natural gas and mine gas, and its accumulation in nitrogen-rich mine atmospheres presents a well-documented safety hazard; understanding CH_4 transport in N_2 under elevated pressures is therefore relevant to ventilation and hazard assessment in underground environments. Argon, comprising approximately 0.93 % of the Earth's atmosphere, is also encountered as an inert component in various industrial gas streams. From a fundamental standpoint, the system is of particular interest because the diffusion coefficients of methane and argon in nitrogen are similar in magnitude, placing the mixture close to the stability boundary of the diffusion regime and making it sensitive to pressure-induced changes in mixture density.

Two additional aspects of the present study warrant mention. At pressures above approximately 5 MPa, methane exhibits pronounced real gas behaviour: its compressibility factor decreases to roughly 0.87–0.88 at 295 K, meaning the mixture density increases superlinearly with pressure and the effective threshold for convective onset may fall below the value predicted by ideal gas theory. This non-linearity introduces complexity into both experimental interpretation and numerical modelling, as transport coefficients and equation-of-state parameters require real gas corrections at elevated pressures [22]. At the same time, while experimental measurements of mole fractions provide reliable integral characterisation of the mass transfer process, they offer no direct insight into the spatiotemporal dynamics occurring within the diffusion channel and the flasks during the experiment—the transient formation of convective structures, the evolution of concentration fronts, and the development of density-driven instabilities remain inaccessible to end-state measurements alone. Numerical simulation addresses this limitation directly, providing full spatiotemporal resolution of the concentration and velocity fields and thereby enabling a mechanistic interpretation of phenomena that experiments cannot resolve in isolation.

This study experimentally and numerically investigates the isothermal diffusion and convective mixing of a ternary gas mixture of methane, argon, and nitrogen at various pressures (0.58–5.98 MPa) and initial compositions. The obtained values will be compared with experimental data, which will allow us to identify the effect of pressure on the nature of partial mass transfer.

Experimental

The subject of this study is the process of isothermal mass transfer in the ternary gas system $0.5504 \text{ CH}_4 + 0.4496 \text{ Ar} - \text{N}_2$, carried out in a two-flask diffusion apparatus [21]. This setup is widely used for the experimental study of the kinetics of diffusion processes in gas mixtures, as it allows for the analysis of component transport under closed-system conditions with controlled thermobarometric parameters [11, 21]. The apparatus design includes two flasks of equal volume $V_u = V_l = 55.6 \text{ cm}^3$, connected by a narrow cylindrical channel with a length $L = 64 \text{ mm}$ and a diameter $d = 4 \text{ mm}$, in which the main zone of diffusion interaction between the components is formed.

Experimental studies for this system were conducted at a temperature of 295 K over a pressure range from 0.58 to 4.02 MPa. Each experiment lasted 30 minutes, which allowed for the recording of changes in component concentrations sufficient for the subsequent determination of effective diffusion coefficients. The initial composition $0.5504 \text{ CH}_4 + 0.4496 \text{ Ar}$ was selected on the basis of prior experimental studies [23, 24]. The molar density of this mixture is lower than that of pure N_2 , placing the system in a mechanically stable configuration at low pressures. At the same time, the diffusion coefficients of methane and argon in nitrogen are similar in magnitude, which makes the system particularly sensitive to small pressure-induced changes in mixture density—conditions under which local density inversions can develop during diffusion and eventually trigger convective instability. Such a composition allows for the investigation of conditions under which the diffusion regime of mass transfer can remain stable even with significant changes in pressure.

To analyze the process under consideration, numerical simulations were performed using the ANSYS Fluent software package [23–26], which enables investigation of the spatiotemporal evolution of concentration fields in gas systems with complex geometries. The calculations utilized a three-dimensional model of the diffusion apparatus shown in Figure 1, whose geometry corresponded to the parameters of the experimental setup. This approach makes it possible to reproduce real mass transfer conditions and track changes in the distribution of components throughout the entire volume of the system.

The initial and boundary conditions of the numerical model were set in accordance with the conditions of the experiments. At the initial time, the upper flask of the diffusion apparatus contained a mixture of $0.5504 \text{ CH}_4 + 0.4496 \text{ Ar}$, while the lower flask and the diffusion channel were filled with nitrogen. This configuration fully reproduces the initial state of the system in real experiments and allows for a correct description of the mutual diffusion process of the components. The physicochemical properties of the gases were assumed to be constant and were specified based on data contained in the built-in substance library of the ANSYS Fluent 2025 R2 software package.

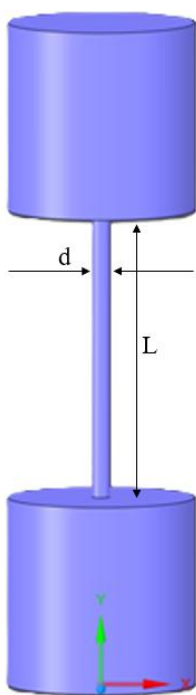


Figure 1. Three-dimensional model of a diffusion cell and the calculated simulation area

Since the diffusion apparatus is a closed system, impermeability conditions were applied to all its boundaries to prevent mass transfer across the external surfaces. To maintain isothermal conditions, the apparatus walls were modeled as a solid surface with material properties corresponding to stainless steel, which were also taken from the standard ANSYS Fluent library [26].

The computational domain was discretised, accounting for the geometric features of the apparatus. The flask volumes were approximated using an unstructured mesh, while the diffusion channel was discretised with a regular structured mesh to ensure accurate representation of concentration and velocity gradients in the primary zone of species interaction. The characteristic cell size was approximately 1 mm, with the total number of mesh elements of approximately 4.2×10^5 . This spatial resolution is consistent with mesh parameters employed in validated numerical studies of diffusion and concentration-driven convection in geometrically similar two-flask configurations [23, 25], and is considered sufficient for the accurate resolution of the transport phenomena governing mass transfer in the system under study.

Turbulence closure was provided by the standard $k-\omega$ model. Although the flow velocities in the two-flask diffusion apparatus are small and the overall Reynolds number remains low, the $k-\omega$ formulation is selected for several reasons. Unlike the $k-\varepsilon$ model, $k-\omega$ does not require wall functions and integrates directly to the wall, making it well-suited for near-wall regions where concentration and velocity gradients are steepest. In the limit of negligible turbulent kinetic energy—which prevails throughout most of the diffusion-dominated regime—the model effectively reduces to a laminar description, introducing no artificial diffusive contribution. As the pressure increases and weak convective disturbances develop, the $k-\omega$ model is capable of capturing the onset of low-intensity turbulent fluctuations without requiring a priori knowledge of the flow regime. The appropriateness of this choice is confirmed a posteriori by the close agreement between the simulated and experimental concentration profiles across all validated pressure levels.

The standard $k-\omega$ model is a semi-empirical model based on the model transport equations of turbulence kinetic energy (k) and specific dissipation rate (ω), which can also be viewed as the ratio of ε to k . The turbulence kinetic energy k and the specific dissipation rate ω are obtained from the following transport equations [25]:

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_i}(\rho k u_i) = \frac{\partial}{\partial x_j} \left(\Gamma_k \frac{\partial k}{\partial x_j} \right) + G_k - Y_k + S_k + G_b \quad (1)$$

$$\frac{\partial}{\partial t}(\rho \omega) + \frac{\partial}{\partial x_i}(\rho \omega u_i) = \frac{\partial}{\partial x_j} \left(\Gamma_\omega \frac{\partial \omega}{\partial x_j} \right) + G_\omega - Y_\omega + S_\omega + G_{\omega b}. \quad (2)$$

In these equations, G_k represents the generation of turbulence kinetic energy due to mean velocity gradients, ρ is the density, and u_i is the velocity component along x_i . G_k represents the generation of k . Γ_k and Γ_ω represent the effective diffusivity of k and ω , respectively. Y_k and Y_ω define the dissipation of k and ω , respectively. S_k and S_ω are initial parameters defined by the user.

The effective diffusion coefficients for $k-\omega$ model are given by the formulas

$$\Gamma_k = \mu + \frac{\mu_t}{\sigma_k} \quad (3)$$

$$\Gamma_\omega = \mu + \frac{\mu_t}{\sigma_\omega} \quad (4)$$

where Γ_k and Γ_ω are turbulent Prandtl numbers for k and ω , respectively, characterizes the effective diffusion behavior of turbulent kinetic energy (k) and its dissipation rate (ω). In this model they were given fixed values: $\sigma_k = 2$ and $\sigma_\omega = 2$. μ is the molecular viscosity, and the turbulent viscosity μ_t is calculated by combining k and ω as follows:

$$\mu_t = \frac{\rho k}{\omega} \frac{1}{\max \left[\frac{1}{\alpha^*}, \frac{SF_2}{a_1 \omega} \right]}, \quad (5)$$

where S is the strain rate magnitude and

$$\sigma_k = \frac{1}{\frac{F_1}{\sigma_{k,1}} + \frac{1-F_1}{\sigma_{k,2}}} \quad (6)$$

$$\sigma_\omega = \frac{1}{\frac{F_1}{\sigma_{\omega,1}} + \frac{1-F_1}{\sigma_{\omega,2}}} \quad (7)$$

A transport equation is solved to determine the species concentrations in the diffusion channel. The conservation equation represents the relations for convective diffusion by which the local mass fraction Y_i of each substance i can be predicted and is defined as follows:

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla(\rho \vec{v} Y_i) = -\nabla \vec{J}_i + R_i + S_i, \quad (8)$$

where ρ is the density of the mixture, $\vec{v}$ is the rate of diffusing substances, R_i is the net rate of production of species i by chemical reaction, and S_i represents any sources defined by the user. The last two terms in the right-hand side were not considered in this work because chemical reactions and additional sources were not present in the studies. $\vec{J}_i$ is the diffusion flux of a certain substance i , which for the density and temperature gradient can be calculated by the formula

$$\vec{J}_i = -\left(\rho D_{i,m} + \frac{\mu_t}{Sc_t}\right) \nabla Y_i - D_{T,i} \frac{\nabla T}{T}, \quad (9)$$

where μ_t is the turbulent viscosity and Sc_t is the turbulent Schmidt number calculated as $Sc_t = \mu_t/(\rho D_t)$, where D_t is the turbulent diffusion coefficient. The default value of Sc_t is 0.7. $D_{i,m}$ is the mass diffusion coefficient for substance i in the mixture, $D_{T,i}$ is the thermal diffusion coefficient for substance i in the mixture, T is the temperature. The last term in the equation was not considered, since in this work the isothermal type of mixing was considered. Also note that turbulent diffusion, as a rule, exceeds molecular diffusion, and a detailed description of the properties of molecular diffusion in turbulent flows, as a rule, is not required.

For multicomponent systems, the Stefan-Maxwell equations in the form of

$$\sum_{j=1, j \neq i}^N \frac{X_i X_j}{D_{ij}} (\vec{V}_j - \vec{V}_i) = \vec{d}_i - \frac{\nabla T}{T} \sum_{j=1, j \neq i}^N \frac{X_i X_j}{D_{ij}} \left(\frac{D_{T,j}}{\rho_j} - \frac{D_{T,i}}{\rho_i} \right), \quad (10)$$

where X is the mole fraction, $\vec{V}$ is the diffusion rate, D_{ij} is the binary mass diffusion coefficient of substance i into substance j . Since isothermal conditions are assumed, the thermal diffusion term in Eq. (10) vanishes [27, 28].

Table 1

Solution methods

Qntity	Discretization
Gradient	Least Square Cell-Based
Pressure	PRESTO!
Momentum	Second Order Upwind
Turbulent Kinetic Energy	Second Order Upwind
Specific Dissipation Rate	Second Order Upwind
Pseudo Time Method	Off
Transient Formulation	Second Order Implicit

All simulations were performed in a transient formulation using a pressure-based coupled solver with full pressure–velocity coupling within each iteration [29]. Convective terms were discretised using the Second Order Upwind scheme, and pressure interpolation was handled by the PRESTO! scheme, which provides improved accuracy in the presence of body forces arising from density gradients. Time integration was performed with a second-order implicit scheme at a fixed time step of $\Delta t = 1$ s over a total of 1800 steps, corresponding to 30 minutes of physical process time. Convergence at each time step was assessed using residu-

al criteria of 10^{-6} for the velocity and pressure fields and 10^{-8} for species concentrations, ensuring that the solution was fully converged before advancing to the next step.

Results and Discussion

Numerical simulations of the mutual diffusion process in the $\text{CH}_4\text{--Ar--N}_2$ system were performed for a pressure range of 0.58 to 5.98 MPa under isothermal conditions. The main objective of the calculations was to reproduce the mass transfer kinetics between the flasks of the diffusion apparatus and to compare the obtained results with experimental data.

Table 2 serves as the primary validation of the numerical model. The concentration differences Δc obtained from ANSYS Fluent are compared against both the Stefan–Maxwell analytical solution and independent experimental data [21] across the full pressure range of 0.58–4.02 MPa. Agreement between simulation and experiment is consistently within experimental error at all pressures studied, confirming that the model correctly reproduces the mass transfer kinetics of the system and that the selected boundary conditions, transport coefficients, and solver settings are appropriate for this class of problems.

Table 2

Dependence of gas concentration changes in flasks on pressure

0.5504 CH_4 + 0.4496 Ar — N_2 (T = 295 K, t=30 min)									
P, MPa	Δc , mole fraction								
	Calculated according to Stefan–Maxwell theory			Experiment [21]			Ansys Fluent		
	CH_4	Ar	N_2	CH_4	Ar	N_2	CH_4	Ar	N_2
0.58	0.4172	0.3495	0.7618	0.413	0.351	0.773	0.425	0.354	0.774
1.07	0.4172	0.3495	0.7618	0.413	0.349	0.762	0.418	0.347	0.758
2.05	0.4172	0.3495	0.7618	0.416	0.353	0.768	0.421	0.351	0.764
3.04	0.4172	0.3495	0.7618	0.412	0.349	0.774	0.414	0.346	0.770
4.02	0.4172	0.3495	0.7618	0.411	0.350	0.762	0.410	0.348	0.760
5.00	0.4172	0.3495	0.7618	-	-	-	0.405	0.340	0.745
5.98	0.4172	0.3495	0.7618	-	-	-	0.328	0.276	0.604

Under these pressures, the agreement between experiment and Stefan–Maxwell theory indicates that mass transport is governed primarily by molecular diffusion. This behaviour is consistent with the physical characteristics of the $\text{CH}_4\text{--Ar--N}_2$ system: the diffusion rates of methane and argon in nitrogen are similar in magnitude, so no pronounced density inversion zones develop during mutual diffusion, and the resulting concentration gradients remain insufficient to sustain gravity-induced convective flows. Under these conditions, molecular diffusion fully accounts for the observed mass transfer kinetics.

At pressures of 5.00 and 5.98 MPa, experimental data are unavailable; however, the ANSYS Fluent results show a progressive deviation from the Stefan–Maxwell theoretical values—a deviation that grows with increasing pressure. Given that the numerical model has demonstrated reliable agreement with both experiment and theory across all lower pressures, there is reason to treat these computed values with confidence. The observed divergence between simulation and Stefan–Maxwell theory at elevated pressures suggests a qualitative change in the mass transfer mechanism: the increased mixture density appears to create conditions under which concentration-driven gravitational convection begins to contribute to the overall transport, supplementing and eventually dominating over molecular diffusion. This interpretation is consistent with the concentration dynamics discussed in relation to Figure 2.

The time dependence of the argon concentration in the lower flask (Fig. 2) reveals a clear and systematic transformation of the mass transfer mechanism as pressure increases. At $p = 0.584$ MPa, the concentration profile rises smoothly and nearly linearly over the entire 1800 s observation window, reaching approximately 0.045 at the end of the experiment with no detectable inflection points or regions of accelerated growth. This behaviour is fully consistent with a diffusion-controlled regime in which transport is governed by the concentration gradient between the flasks and the system geometry. At $p = 2.05$ MPa, the overall monotonic

trend is preserved, and the final concentration remains comparable, but starting from approximately $t \approx 600\text{--}800$ s, low-amplitude oscillations become superimposed on the mean growth curve. These perturbations do not yet alter the dominant transport mechanism, but their emergence signals that the increased mixture density is sensitising the system to local composition inhomogeneities and that the threshold of mechanical equilibrium instability is being approached.

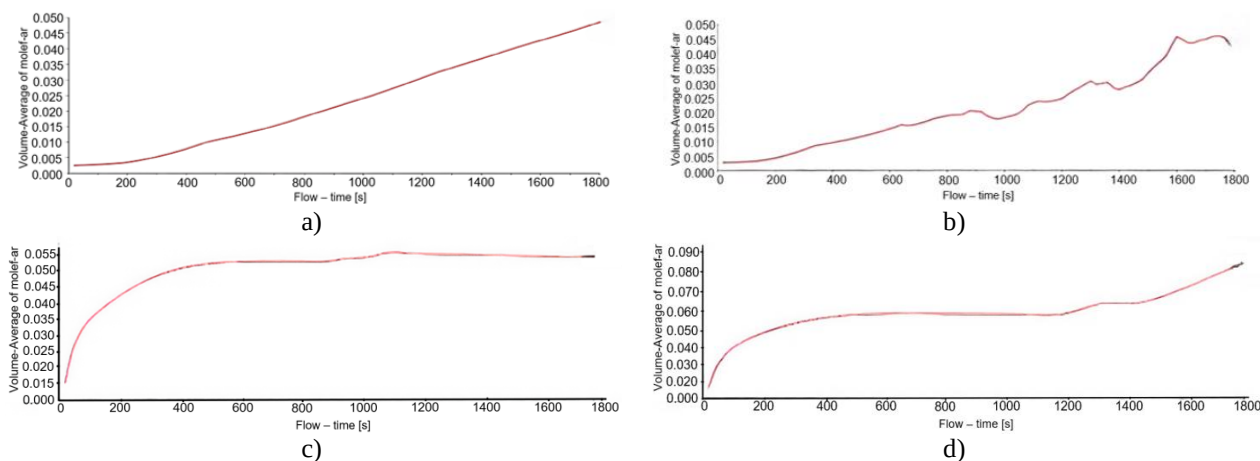


Figure 2. Time-dependent changes in Ar concentration in the lower flask as a function of pressure: a) $p=0.584$ MPa; b) $p=2.05$ MPa; c) $p=5.00$ MPa; d) $p=5.98$ MPa

At elevated pressures, the character of the concentration kinetics changes fundamentally. At $p = 5.00$ MPa, the curve exhibits a rapid initial rise reaching approximately 0.050 within the first 300–400 s, after which growth decelerates markedly, and the concentration enters an extended quasi-stationary plateau persisting through the remainder of the observation window. This two-stage profile reflects convective onset: the initial acceleration is driven by a high mixture density that lowers the threshold for gravitational instability, while the subsequent plateau indicates partial redistribution of the density field and a temporary restoration of mechanical stability. The most complex behaviour is observed at $p = 5.98$ MPa, where three distinct temporal stages can be identified. In the initial period up to approximately $t \approx 300$ s, a rapid rise occurs, after which the curve enters a deceleration phase lasting through $t \approx 1200$ s with the concentration increasing gradually from roughly 0.030 to 0.060. Beyond $t \approx 1200$ s, a pronounced secondary acceleration drives the concentration to approximately 0.085–0.090 by $t = 1800$ s—nearly twice the value observed at 0.584 MPa. This late-stage intensification reflects the accumulation of density inhomogeneities to a critical level at which mechanical equilibrium breaks down and gravity-induced macroscopic flows sustain transport well beyond diffusive rates.

The progression across the four pressure levels traces a coherent physical sequence from stable molecular diffusion through transitional perturbations to a fully developed diffusion–convective regime. Pressure acts as the governing parameter: it raises mixture density, reduces the critical gradient required for convective onset, and determines both the timing and intensity with which macroscopic flows contribute to overall mass transfer. The close agreement between computed and experimental profiles across this entire pressure range confirms that the numerical model captures not only the qualitative character of each regime but also the pressure-dependent dynamics of the transition between them.

The observed transition from diffusion-dominated to convection-influenced transport at pressures above 5 MPa is consistent with an increase in the solutal Rayleigh number $Ra = g\Delta\rho L^3/(\rho\nu D)$, where the rising mixture density at elevated pressures amplifies the buoyancy-driving term while the diffusion coefficient decreases, collectively pushing the system across the stability threshold.

The present study is subject to several limitations inherent to the adopted numerical framework. The ANSYS Fluent Species Transport model assumes ideal gas behaviour throughout; as discussed above, this assumption becomes progressively less accurate above 5 MPa, where real gas corrections to transport coefficients and mixture density are non-negligible. The simulations are performed under strictly isothermal conditions, neglecting the small temperature gradients associated with the Dufour effect; while this contribution is expected to be minor for the present system, its role at elevated pressures has not been assessed. Finally, the results reported here correspond to a single initial mixture composition (0.5504 CH_4 + 0.4496 Ar); extrapolation

tion to substantially different compositions requires independent verification, as the proximity of the diffusion–convective stability boundary is sensitive to the relative densities and diffusivities of the components.

Conclusion

This study presents an experimental and numerical investigation of mass transfer processes in a ternary gas system consisting of $\text{CH}_4\text{--Ar--N}_2$ under isothermal mixing conditions at elevated pressures. By comparing the results of calculations performed in ANSYS Fluent with experimental data, it is shown that the numerical model used adequately describes the kinetics of diffusion mass transfer in the considered parameter range, and that the discrepancies between the calculated and experimental values do not exceed the experimental error margin.

An analysis of the effect of pressure on mass transfer behavior showed that at relatively low pressures, the system remains in a steady-state diffusion regime in which mass transfer is determined primarily by molecular diffusion. As pressure increases, the mixing kinetics become more complex as evidenced by changes in the shape of the time-dependent concentration curves of the components. At high pressures, signs of multistage behavior are observed, including induction phases and subsequent acceleration of mass transfer, which indicates a possible disruption of mechanical equilibrium and an increased role of gravity-induced flows.

It has been established that in a $\text{CH}_4\text{--Ar--N}_2$ system, characterized by similar diffusion coefficients for the components and a small difference in their densities, pressure is the key parameter determining the stability of the diffusion regime. Under the conditions considered, an increase in pressure does not lead to an instantaneous transition to the convective regime but contributes to the formation of conditions under which diffusion transport may be accompanied by disturbances affecting its structure and intensity.

The results advance the understanding of mass transfer mechanisms in multicomponent gas systems at elevated pressures and can be used in the development and optimization of processes involving gas separation and mixing, as well as in the construction and validation of numerical models of diffusion-convective transport.

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Жоғары қысымдағы $\text{CH}_4\text{--Ar--N}_2$ үшкомпонентті газ қоспасында диффузия режимінің тұрақтылығын зерттеу

Көпкомпонентті газ қоспаларындағы диффузиялық масса тасымалы химиялық технология, мұнай-газ өңдеу және энергетика салаларындағы инженерлік процестерді модельдеу мен жетілдірудің іргелі негізі. Осыған байланысты, жоғары қысымды ортадағы газ жүйелерінің өзара диффузиялық заңдылықтарын айқындау заманауи ғылым мен өндіріс үшін маңызды басымдыққа ие. Бұл зерттеу аясында $\text{CH}_4\text{--Ar--N}_2$ үшкомпонентті жүйесіндегі изотермиялық массаалмасу құбылысы 295 К температурада және 0,58–5,98 МПа қысым аралығында кешенді түрде зерделенді. Қарастырылып отырған жүйенің ерекшелігі компоненттердің диффузиялық коэффициенттерінің жақындығымен және тығыздық градиентінің төмендігімен айқындалады, бұл өз кезегінде диффузиялық режимнің тұрақтылық деңгейін айқындайтын шешуші фактор саналады. Тәжірибелік зерттеулер екі колбалы диффузиялық қондырғыда жүргізіліп, компоненттер концентрациясының уақыт пен қысым параметрлеріне тәуелді өзгеру динамикасы нақты тіркелді. Теориялық негіздеу мақсатында ANSYS Fluent ортасында Стефан–Максвелл теңдеулері, $k-\omega$ турбуленттілік моделі және Species Transport әдістемесі қолданылып, сандық модельдеу жүзеге асырылды. Алынған эксперименттік деректер мен

есептеу нәтижелері арасындағы сәйкестік жоғары деңгейді көрсетіп, ауытқулардың рұқсат етілген қателік шегінен аспайтыны дәлелденді. Төмен қысым жағдайында жүйеде концентрациялық кинетиканың бірқалыпты өзгеруімен сипатталатын тұрақты режим байқалды. Алайда қысым мәні жоғарылаған сайын массаалмасу механизмінің сапалық трансформациясы орын алып, диффузиялық-конвективті режимге өту процесі тіркелді. Зерттеу қорытындысы ұсынылған сандық тәсілдің жоғары қысымды көпкомпонентті жүйелердегі күрделі физикалық процестерді сипаттаудағы тиімділігін толықтай растайды.

Кілт сөздер: көпкомпонентті диффузия, жоғары қысым, диффузия аппараты, массаалмасу, сандық модельдеу, ANSYS Fluent

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Исследование устойчивости диффузионного режима в тройной газовой смеси $\text{CH}_4\text{--Ar--N}_2$ при повышенных давлениях

Диффузионный массоперенос в многокомпонентных газовых средах является фундаментальным аспектом при проектировании и модернизации технологических циклов в химической, нефтегазовой и энергетической отраслях. В данной работе представлены результаты комплексного исследования изотермического массообмена в трехкомпонентной системе $\text{CH}_4\text{--Ar--N}_2$ при температуре 295 К и давлении от 0,58 до 6,02 МПа. Специфика изучаемой системы заключается в близости коэффициентов диффузии компонентов и незначительных различиях в плотности, что выступает решающим фактором устойчивости диффузионного режима. Экспериментальная часть выполнена на двухколбовой установке, фиксирующей динамику концентрационных изменений в зависимости от времени и барических условий. Параллельно в программном комплексе ANSYS Fluent проведено численное моделирование на основе уравнений Стефана–Максвелла, модели переноса веществ (Species Transport) и $k\text{--}\omega$ модели турбулентности. Сравнительный анализ показал высокую степень корреляции между эмпирическими данными и результатами вычислений: зафиксированные отклонения не выходят за рамки допустимой погрешности. Установлено, что при низком давлении процесс характеризуется стабильным режимом с монотонной кинетикой концентраций. Однако с ростом давления наблюдается качественная трансформация механизма смешения и переход к интенсивному диффузионно-конвективному массообмену. Итоговые результаты подтверждают высокую достоверность и применимость предложенного численного алгоритма для описания сложных процессов переноса в многокомпонентных газовых системах при условиях высокого давления.

Ключевые слова: многокомпонентная диффузия, высокое давление, диффузионная установка, массоперенос, численное моделирование, ANSYS Fluent

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