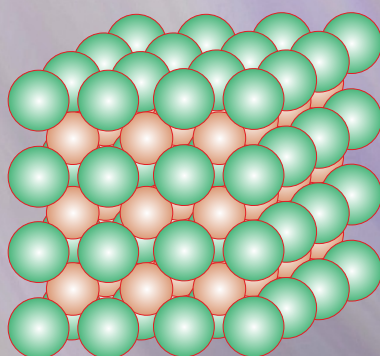


XI INTERNATIONAL SCIENTIFIC CONFERENCE

MATERIAL SCIENCE.

NONEQUILIBRIUM PHASE TRANSFORMATIONS

01-04.09.2025, VARNA, BULGARIA



PROCEEDINGS

ISSN 2535-0218 (Print)

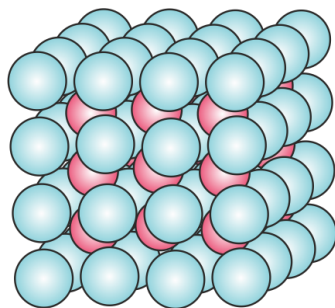
ISSN 2535-0226 (Online)

**SCIENTIFIC-TECHNICAL UNION OF MECHANICAL ENGINEERING
BULGARIA**

1000 Sofia, 108 Rakovski str., office 411,
www.material-science.eu, office@material-science.eu
www.mech-ing.com, phone: +359 2 9877290

XI INTERNATIONAL SCIENTIFIC CONFERENCE
MATERIAL SCIENCE
„NONEQUILIBRIUM PHASE TRANSFORMATIONS”

01-04 SEPTEMBER 2025, VARNA, BULGARIA



MATERIAL SCIENCE
NONEQUILIBRIUM PHASE TRANSFORMATIONS

YEAR IX

ISSUE 1 (8)

SEPTEMBER 2025

ISSN: (Print) 2535-0218

ISSN: (Online) 2535-0226

All articles are published after peer review by two independent reviewers.

PROCEEDINGS

ORGANIZERS:



SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING
“INDUSTRY 4.0”

INTERNATINOAL EDITORIAL BOARD

CHAIR:

Prof. Tsanka Dikova Medical University - Varna

MEMBERS:

Prof. Adel Mahmud	Iraq
Prof. Angel Anchev	Bulgaria
Prof. Anna Dobrzańska-Danikiewicz	Poland
Prof. Gennagiy Bagluk	Ukraine
Dr. Darius Mazeika	Lithuania
Prof. Dipten Misra	India
Assoc. Prof. Eugeniy Grigoriev	Russia
Assoc. Prof. Ibrahim E. Saklakoglu	Turkey
Prof. Irina Charnyak	Belarus
Dr. Lech B. Dobrzanski	Poland
Prof. Leszek Dobrzanski	Poland
Prof. Maria Nikolova	Bulgaria
Prof. Masaki Hashida	Japan
Prof. Neli Mintcheva	Bulgaria
Prof. Nikolay Dolgov	Ukraine
Prof. Rasa Kandrotaitė Janutiene	Lithuania
Prof. Ruslan Kusin	Belarus
Prof. Satoru Iwamori	Japan
Prof. Sergei Kulinich	Japan
Prof. Sergey Dobatkin	Russia
Prof. Sergey Nikulin	Russia
Prof. Svetlana Gubenko	Ukraine
Prof. Sveto Cvetkovski	North Macedonia
Prof. Souren Mitra	India
PhD Tomasz Matula	Poland
Prof. Vladimir Dunchev	Bulgaria
Prof. Vladimir Todorov	Bulgaria

NATIONAL ORGANIZING COMMITTEE

CHAIRPERMAN:

Dr. Raicho Georgiev Scientific-Technical Union Of Mechanical Engineering

MEMBERS:

Assoc. Prof. Sonya Vachinska	Technical University - Varna
Assoc. Prof. Daniela Spasova	Technical University - Varna
Assoc. Prof. Dzhendo Dzhendov	Medical University – Varna
Dr. Ivan Ivanov	„Prof. Asen Zlatarov” University – Burgas

CONTENTS

Physical properties study of ferromagnetic Permalloy thin films Ahmed Kharmouche	5
AI-optimized angled multimode interference splitter with buried sin waveguide for high-performance O-band photonic networks Dror Malka	9
Wave nature of the processes of high-speed mass transfer and local microalloying of laser-hardened steels Svetlana Gubenko	14
Radiation shields and their potential applications in space Leszek Tomasz Pawlicki	18
Features of structure formation and properties of cast titanium bronzes obtained using thermally synthesized powder ligatures Bagliuk G.A., Voropaiev V.S., Fedoran Yu.O., Molyar O.H., Demydyk O.M., Sydorchuk O.M., Radchenko O.K.	20
Investigation of wear resistance of welded duplex steels after surface chemical-thermal treatment инж. Чолаков Л., гл. ас. д-р Янкова Р., ас. инж. Стоянов П.	23
Investigation of the Effect of Heat Treatment on S355J2 Steel: Quenching and Subsequent Tempering at Different Temperatures Eng. Lyudmil Cholakov, MSc, Eng. Stratsimir Dimov	26
Regeneration of filter elements for cleaning hydrocarbon compounds from powdered polyethylene particles Aliaksandr Ilyushchanka, Iryna Charniak, Aliaksei Kusin, Anastasia Astapenka, Ruslan Kusin, Margaryta Kuntsevich, Ilya Buhtoyarov	30
Densification and formation of structure and properties of inconel 625 alloy during direct powder forging Tolochyn O. I., Bagliuk G. A., Kyryliuk S. F., Tolochyna O. V., Kyryliuk Y. S., Danylenko V. I.	32
Anatase or Rutile TiO₂ Nanolayer Formation on Ti Substrates by Laser Radiation: Mechanical and Photocatalytic Properties Arturs Medvids, Aleksandrs Michko, Aleksejs Jakimovichs, Iuriy Naseka	36
Quantum Cone - Nano Source of Light with Dispersive Spectrum Distributed Along Height Artūrs Medvids	40
The Interplay of Laser Metal Processing and Non-Equilibrium Phase Transformations Nikolaos Papageorgiou	44
Extraction of Antimony as a Critical Element from Secondary Waste Sources Neli Mintcheva, Marinela Panayotova, Gospodinka Gicheva	47

Physical properties study of ferromagnetic Permalloy thin films

Ahmed Kharmouche

Laboratory of Surfaces and Interfaces Studies of Solid Materials (LESIMS), Faculty of Technology, Ferhat ABBAS Sétif1 University, Sétif, 19000, Algeria
kharmouche_ahmed@univ-setif.dz, kharmouche_ahmed@yahoo.fr

Abstract. We fabricated Permalloy thin films of different thicknesses, using thermal evaporation under vacuum, onto Si (100) substrates. We examined the influence of Py thickness on their physical properties. The surface morphology, structure, microstructure, chemical compositions and electrical properties, are performed by atomic force microscopy (AFM), X-ray diffraction (XRD), scanning electron microscopy equipped with an energy dispersive X-ray analyzer (SEM-EDS), and the Hall Effect measurement system (HMS-5300). The analyses of X-ray diffraction spectra confirmed the formation of the Ni_3Fe phase and inferred that all the films crystallize in a CFC structure with a preferential $\langle 111 \rangle$ orientation. The crystallites size and the lattice parameter, computed from the dominant (111) X-ray diffraction peak, decreased with increasing Py/Si film thickness. Also, the lattice parameter values, obtained for all samples, were fairly close to the bulk value. SEM micrographs of the samples clearly exhibited a non-uniform distribution of quasi-spherical aggregates on the granular surface of the Py/Si films, as well as the presence of micro-cracks for the thickest film. Furthermore, AFM images indicated the formation of crystallites according to Stranski-Krastanov mode for the Py/Si films, with roughness values ranging from 0.2 to 2.5 nm. Electrical measurements revealed that the electrical resistivity decreased with increasing film thickness whereas the mobility increased. The spontaneous magnetization increases with thickness from 600 to 760 emu/cm³, and the coercivity decreases following a t^{-n} Néel law.

KEYWORDS: PERMALLOY FILMS; XRD; RESISTIVITY; MAGNETIZATION; COERCIVITY

1. Introduction

Co, Fe, and Ni transition metals are considerably used in spintronics as anisotropic devices in numerous magnetic tools [1-6]. Iron-Nickel alloys, and particularly the so-called Permalloy (Py) $\text{Fe}_{20}\text{Ni}_{80}$, present excellent ferromagnetic properties, chiefly null coercivity and magnetostriction and very low magnetic anisotropy added to a giant permeability [7-11]. Py is mostly used in functional materials, as spin-valve and magnetoresistive devices. As thin films, Py has been produced by electrodeposition, thermal evaporation as well as DC, and RF magnetosputtering [12-15]. This work aims to explore the impact of the thickness on the electrical and magnetic properties of Py thin films, produced using thermal heating under vacuum. We present, in section 2, the home-made evaporation chamber, as well as the various characterizations tools used in this study. In section 3, we present the main experimental results and discussions. The quantifications measurements of the films are presented in section 3.1. The structural properties carried out using X-ray diffraction (XRD) method are summarized in section 3.2, and section 3.3 is devoted to the electrical properties carried using Hall Effect measurement system (HMS-5300) based on the Van der Pauw method under an excitation magnetic field ($B=0.56\text{T}$) and an intensity current ($I=1\text{mA}$). In section 3.4, we present the magnetization curves recorded using Vibrating Sample Magnetometer (VSM) tools, and discuss the impact of the layer thickness on the spontaneous magnetization and the coercivity. A conclusion is presented in section 4.

2. Experimental procedures

Thin films deposition process

The experimental setup of the working evaporation chamber is exhibited in figure 1. In this chamber, we elaborated series of Py thin films, under vacuum and at room temperature. These materials are evaporated onto Si (111) substrates. The working chamber is made of a glass bell, where we put the desired quantities of the mixed powders to be evaporated. Nickel and Iron powders are placed inside a boat made of tungsten enrobed with alumina, above which we set a metallic shelter, manually dirigible from the outside. The substrate holder is fixed just above this cover. This metal shelter protects the substrates before the beginning of evaporation until the end of the degassing process. This operation contributes not only to improve the quality of the deposited films, but also to control and regulate the required duration of the evaporation. Two pumps constitute the vacuum pumping group, a primary vane pump, and a secondary oil diffusion pump, cooled by a system of water circulation coil. To deposit our thin Py films, we

set the base pressure as 10^{-7} mbar, and the working pressure better than 10^{-6} mbar. The electric current intensity was fixed at 280 A, which ensures an evaporation rate of the materials estimated at 2 Å/s. More details regarding the thin film deposition process may be found in previous works [16-20].

3. Results and discussion

3.1. Quantifications of the thin films

The surface morphology, thickness and chemical compositions were carried out by means of a scanning electron microscope (SEM, JSM-7001F from JEOL, Japan) coupled to energy dispersive X-ray analyzer facility (EDS, E2V Scientific Instruments, model 8700-2014A). The operating voltage was fixed at 15 kV. The estimated compositional analysis confirm that the weight percentage (wt%) ratio of Ni and Fe is near the initial powder with a deviation not exceeding 2% to that of Permalloy ($\text{Ni}_{81}\text{Fe}_{19}\%$) material, the thickness of the Py films being 15, 20, 25, 30, 40 and 50 nm.

3.2 Structural properties

In figure 2, we display X-ray diffraction (XRD) spectra, performed for all Py/Si(111) samples. We analyzed the diffraction diagrams with X'Pert High Score Plus software which allows an estimation of the intensity and the position of the peaks. After stripping analytically, the contribution of $\text{K}\alpha_2$ line and the instrumental contribution ($\beta_{\text{instrumental}}$) from all profiles in order to identify the present phases and the preferential orientation, we present the X-ray diffractogram patterns for these thin films in the reduced diffraction angle range $30-55^\circ$. The prepared samples display high intensity peaks at $2\theta \approx 44.05^\circ$, corresponding to (111) diffraction plane with an fcc FeNi_3 crystal structure and associated to space group $\text{Pm}\bar{3}\text{m}$. The increase in thickness is accompanied by an increase in the height of the Bragg (111) diffraction peak an improvement in crystallinity. These results indicate that the films are polycrystalline and grow according to a normal deposition geometry in which the dominant peak is (111) and the preferred orientation in all cases is along $\langle 111 \rangle$ direction.

3.3 Electrical properties

Measurements of electrical resistivity and mobility of the Py thin films were performed with an Ecopia HMS 5300 Hall Effect Measurement System and Van der Pauw geometry, at room temperature beneath the experimental conditions defined in section 2. The average values of the electrical resistivity and mobility, for the Py films, are presented in Table 1. The electrical resistivity ρ is obtained by the product of the sheet resistance R and the film

thickness t . The variation of the computed resistivity ρ of the deposited Py material as a function of film thickness with an accuracy equal to 3%, is depicted in figure 3. The bold spheres are the experimental data while the continuous line is a fitted curve.

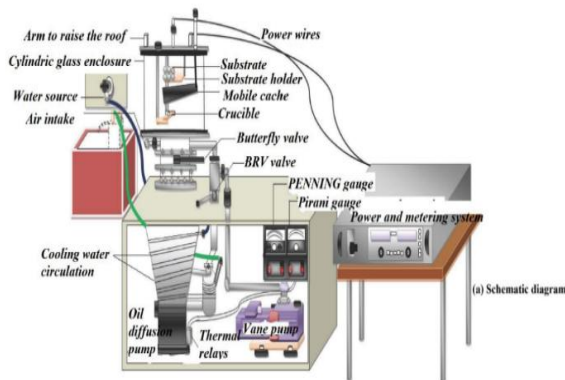


Fig.1 Working evaporation chamber

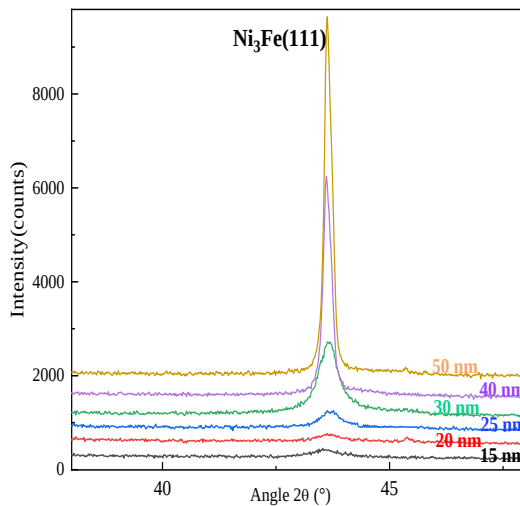


Fig.2 X-ray diffractions spectra for all the Permalloy films.

Table1 Electrical resistivity, ρ , mobility, μ , saturation magnetization, M_s , and coercivity, H_c , as functions of thickness t

$t(\text{nm})$	ρ ($\mu\Omega\cdot\text{cm}$)	μ ($\text{cm}^2/\text{V}\cdot\text{s}$)	M_s ($\text{emu}\cdot\text{cm}^{-3}$)	H_c (Oe)
15	42.2	5	600	7.5
20	37.5	8	650	5
25	33.2	11.5	708	3.5
30	25.9	13.5	735	2.7
40	15	19.5	752	2.2
50	7.5	26	760	2

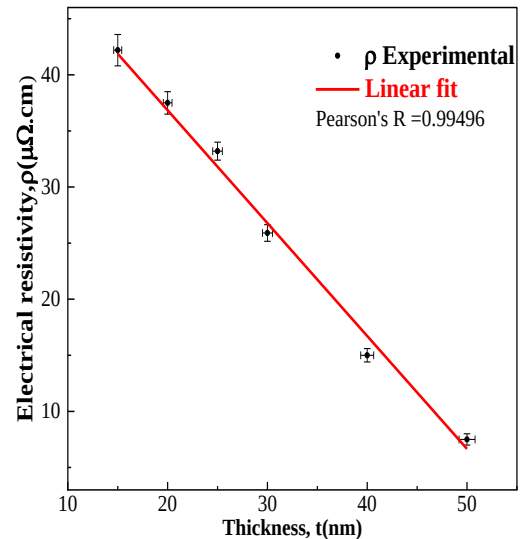


Fig.3 Electrical resistivity as a function of Py thickness

As clearly seen in figure 3, the resistivity decreases linearly increasing film thickness, following the well-known Fuchs/Sondheimer Model [21]. This might be probably due to the reduction of continuity of electron percolation consequently to the decrease of metallic nanogranular dimensions. More, this linear decrease of ρ may be attributed to the actions of the scattering of the conduction electrons relating to the grain boundaries due to the increase of the crystallite size with thickness, and consequently, the decrease of the number of the grain boundaries.

Figure 4 exhibits the evolutions of electron mobility versus the thickness of the Py film. A linear increase of μ is clearly observed as the thickness of the film increases. Since electrical resistivity and conductivity are inversely proportional, their individual variations are thus also inversely proportional. The electrical conductivity and the electron mobility are closely linked. This behavior is in agreement with the curves exhibited in figures 3 and 4. This behavior of the mobility may possibly be due to the improvement of crystallinity of the evaporated Py thin films with thickness. Comparable results have been reported by other authors [10,22].

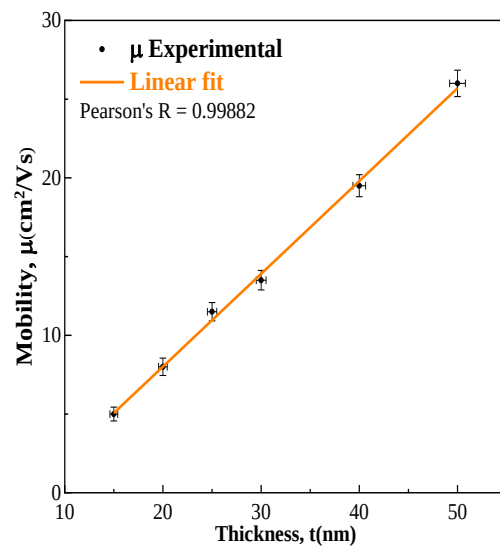


Fig.4 Mobility as a function of Py thickness

3.4 Magnetic properties

Under the experimental conditions described in section 2, we recorded magnetizations curves for thin Py films, at room temperature. The external magnetic field was applied in the film plane (longitudinal configuration), and perpendicularly to the surface of the film (polar configuration). In figure 5, we exhibit a specimen of hysteresis loops for the 30 nm Py film, in the longitudinal configuration, and in the inset we present the hysteresis loop in the polar configuration. For the longitudinal configuration, it was very easy to reach the saturation after applying an external field of ≈ 50 Oe. As for the polar configuration, the saturation is not reached after applying a field of intensity as high as 18 kOe. Further, the quasi-rectangular shape of the longitudinal configuration-and the oblong shape of the polar configuration- infer that the easy magnetization axis lies in the film plane. From the recorded hysteresis loops and the volume of the samples (surface of the film x thickness), we computed the spontaneous magnetization and present its evolution as a function of Py film thickness in figure 6. M_s increases from 600 emu/cm^3 , for the 15 nm Py film, and reaches 760 emu/cm^3 , for the thickest 50 nm Py film, close to the spontaneous magnetization of the bulk material. Similar results have been reported by other authors [23,24].

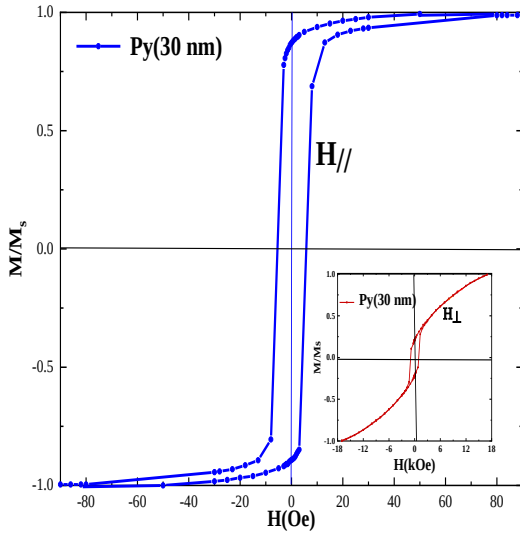


Fig.5 Hysteresis curve for Py(30 nm) in the longitudinal configuration($H_{//}$). In the inset, the polar configuration ($H_{\perp}$).

From the recorded hysteresis loops in the longitudinal configuration, we extracted the coercive field values for all the samples and present these values in table 1. In figure 7, we display the evolution of the coercive field as a function of the film thickness. As can be observed in figure 7, H_c decreases from 7.5 to 2 Oe as the magnetic layer thickness increases from 15 to 50 nm, suggesting an inverse proportionality, following a t^{-n} Néel law [25]. On another hand, if these values of H_c are somewhat higher than the standards values of Py, it is because the surface of the film is not smooth, the rough mean square roughness being equal to a few nm.

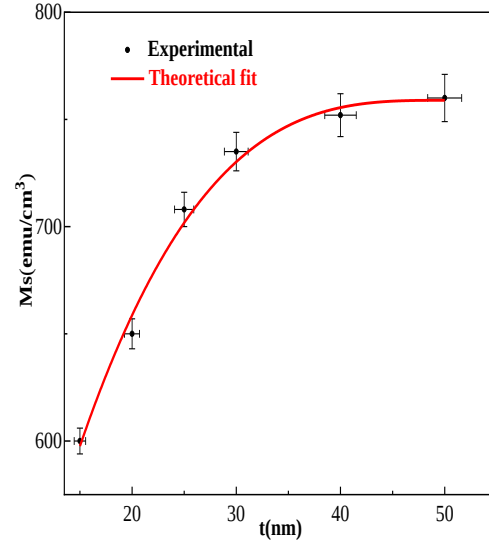


Fig.6 Spontaneous saturation magnetization as a function of Py thickness

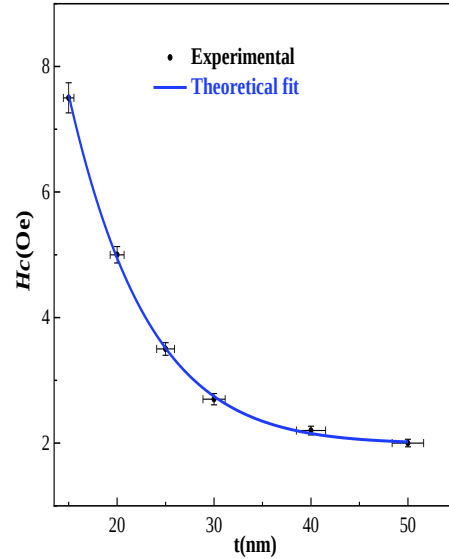


Fig.7 Coercive field as a function of Py thickness

4. Conclusion

Permalloy thin films have been produced by means of the thermal evaporation technique under vacuum. We explored the impact of the layer thickness on the electrical and magnetic properties of these materials. The electrical resistivity has been found to decrease with thickness, while the electron mobility increases. Spontaneous magnetization increases with increasing thickness from 600 to 760 emu/cm^3 , where it reaches the bulk value for the thickest 50 nm Py film. Coercivity decays with increasing thickness following t^{-n} Néel law. These results add to the database of physical properties of Py and thus contribute to a better understanding of the behavior of this material.

References

1. L. Sun, Y. Hao, C.-L. Chien, P. C. Searson, Tuning the properties of magnetic nanowires, IBM J. RES. & DEV. 49(2005)79. <https://doi.org/10.1147/rd.491.0079>
2. A. Melloul, A. Kharmouche, Synthesis, structure and magnetic properties of $\text{Co}_x\text{Fe}_{100-x}$ thin films thermally evaporated onto Si (111) substrate, J Mater Sci: Mater Electron 30(2019)13144-13150.
3. F. Pfeifer, C. Radeloff, Soft magnetic Ni-Fe and Co-Fe alloys some physical and metallurgical aspects. J. Magn. Magn. Mater. 19(1980) 190. [https://doi.org/10.1016/0304-8853\(80\)90592-2](https://doi.org/10.1016/0304-8853(80)90592-2)
4. A. Kharmouche, Magnetic anisotropy factors of vapor deposited CoCr thin films on Si and glass substrates, J. Magn. Magn. Mater. 327 (2013) 91–94. <https://dx.doi.org/10.1016/j.jmmm.2012.09.015>
5. A. Benhamoud, A. Kharmouche, Synthesis, Structural, and Magnetic Properties of $\text{Fe}_{100-x}\text{Pd}_x$ Thin Films, J. Supercond. Nov. Magn. 33(2020) 1521-1526. <https://doi.org/10.1007/s10948-019-05412-1>
6. K.Song, Z.Li, M.Fang, Z.Xiao and Q.Lei, Structural and magnetic properties of micropolycrystalline cobalt thin films fabricated by direct current magnetron sputtering. Int J Miner Metall Mater 31(2024)384–394. <https://doi.org/10.1007/s12613-023-2715-5>
7. Sara Niaz, and Ali Saidi, Magnetic and chemical properties investigation of Fe–Ni electrodeposited alloy on titanium substrate at the presence of alumina, J Mater Sci: Mater Electron 32(2021)22013. <https://doi.org/10.1007/s10854-021-06655-2>
8. Mikio Kishimoto, Eiji Kita, Hideto Yanagihara, Structure and magnetic properties of nitrides in FeNi and FeNiCo alloy particles synthesized via co-precipitation, reduction, and nitriding, J. Magn. Magn. Mater. 548 (2022) 168970. <https://doi.org/10.1016/j.jmmm.2021.168970>.
9. Ounissa Cherrad and Ahmed Kharmouche, Thickness dependent physical properties of evaporated Permalloy/GaAs (100) thin films, Eur. Phys. J. Appl. Phys. 98(2023) 14. <https://doi.org/10.1051/epjap/2023220262>
10. L. Taberkani and A. Kharmouche, Structural, electrical and magnetic properties of evaporated $\text{Fe}_x\text{Ni}_{1-x}$ thin films, Physica B: Condensed Matter 656(2023) 414782. <https://doi.org/10.1016/j.physb.2023.414782>
11. A.V. Trukhanov, S.S. Grabchikov, A.A. Solobai, D.I. Tishkevich, S.V.Trukhanov, E.L. Trukhanova, AC and DC-shielding properties for the $\text{Ni}_{80}\text{Fe}_{20}/\text{Cu}$ film structures, J.Magn.Magn.Mater 443(2017)142. <https://doi.org/10.1016/j.jmmm.2017.07.053>
12. Movaffaq Kateb, Hamidreza Hajihoseini, Jon Tomas Gudmundsson and Snorri Ingvarsson, Comparison of magnetic and structural properties of permalloy $\text{Ni}_{80}\text{Fe}_{20}$ grown by dc and high-power impulse magnetron sputtering, J. Phys. D: Appl. Phys. 51(2018) 285005. <https://doi.org/10.1088/1361-6463/aaca11>.
13. A. Kharmouche, and O. Cherrad, Electrical properties of permalloy/Si (100) thin films. J Mater Sci: Mater Electron 35(2024) 759. <https://doi.org/10.1007/s10854-024-12482-y>
14. A. Kharmouche, O. Cherrad, Structural, microstructural and morphological properties of Permalloy/Si(100) thin films, Physica B680(2024) 415803. <https://doi.org/10.1016/j.physb.2024.415803>
15. N. Guechi, A. Bourzami, A. Guittoum, A. Kharmouche, S. Colis, N. Meni, Physica B 441 (2014) 47-53. <http://dx.doi.org/10.1016/j.physb.2014.01.023>
16. A. Bourezg, A. Kharmouche, Synthesis, structural and magnetic properties of $\text{Co}_{100}\text{Pd}_x/\text{GaAs}$ thin films, Vacuum 155(2018)612–618. <https://doi.org/10.1016/j.vacuum.2018.06.062>
17. A. Kharmouche and A. Melloul, Structural and Magnetic Studies of $\text{Co}_x\text{Fe}_{100-x}$ Thin Films Thermally Evaporated on Glass, J Mater Sci: Mater Electron 31(2020)19680. <https://doi.org/10.1007/s10854-020-04494-1>
18. M. Tinouche, A. Kharmouche, B. Aktas, F. Yildiz, A. N. Koçbay, Magnetic and Structural Properties of Co Thin Films Evaporated on GaAs Substrate, J Supercond NovMagn 28(2015)921. <https://doi.org/10.1007/s10948-014-2863-y>
19. A.Kharmouche, An experimental study of the static magnetic properties of Co thin films, Eur. Phys.J.B97(2024)87. <https://doi.org/10.1140/epjb/s10051>
20. A. Kharmouche, Cobalt Thin Films Synthesis and Structural and Morphological Properties, IJMSE 22(1) (2025)27-36. <https://doi.org/10.22068/ijmse.3902>
- 21.E.H. Sondheimer, The mean free path of electrons in metals, Adv.Phys.1(1952)1-42. <http://dx.doi.org/10.1080/00018735200101151>
22. I.M. Pazukha, O.V. Pylypenko, L.V. Odnodvoret, A comprehensive investigation of electrophysical and magnetoresistive properties of thin films based on permalloy and silver, Mater.Res.Express 5(2018)106409. <https://doi.org/10.1088/2053-1591/aadb54>
23. K. Ounadjela, H. Lefakis, V. S. Speriosu, C. Hwang and P. S. Alexopoulos, Thickness dependence of magnetization and magnetostriction of NiFe and NiFeR films, J. Phys. Colloques 49, C8-1709-C8-1710 (1988). <http://dx.doi.org/10.1051/jphyscol:19888776>
- 24.C. H. Bajorek, C.H. Wilts, A comparison of ferromagnetic resonance with magnetic moment and x-ray film thickness measurements for thin Permalloy films, J. Appl. Phys. 43, 3538 (1972). <https://doi.org/10.1063/1.1661751>
- 25.L. Néel, Remarks on the theory of magnetic properties of thin films and fine grains, J. Phys. Radium17, 250 (1956). <http://dx.doi.org/10.1051/jphysrad:01956001703025000>

AI-optimized angled multimode interference splitter with buried sin waveguide for high-performance O-band photonic networks

Dror Malka

Faculty of Engineering, Holon Institute of Technology (HIT), Holon 5810201, Israel
dorm@hit.ac.il

Abstract: Traditional 1×2 multimode interference (MMI) splitters often encounter challenges such as high back reflections and limited output flexibility, which typically require additional structures like tapers or S-bends. These constraints limit their performance in advanced photonic networks. To overcome these issues, we propose an AI-optimized angled multimode interference (AMMI) splitter featuring a buried silicon nitride (SiN) core with silica cladding. By employing an angled propagation path, the device minimizes reflections to the source and allows greater adaptability for waveguide interconnections in dense photonic circuits. The design optimization was performed using a combination of artificial intelligence (AI) algorithms integrated with full-vectorial beam propagation method (FV-BPM) and finite-difference time-domain (FDTD) simulations. AI-driven parameter scanning enabled efficient exploration of the design space, improving device performance and robustness compared to manual optimization. The proposed AMMI splitter achieves an excess loss of 0.22 dB and an output imbalance of 0.001 dB at $1.31 \mu\text{m}$, with total device length of $101 \mu\text{m}$ and thickness of $0.4 \mu\text{m}$. Over the full O-band (1260–1360 nm), performance remains stable, with excess loss below 1.57 dB and imbalance below 0.05 dB, while maintaining back reflections as low as -40 dB. The compact CMOS-compatible design demonstrates high tolerance to fabrication deviations, making it highly suitable for large-scale integration. With its AI-enhanced optimization process, the proposed splitter supports high-speed, low-loss transmission for O-band photonic networks and data-center interconnects, offering scalability and reliability for next-generation optical systems.

KEYWORDS: ANGLED MULTIMODE INTERFERENCE; AI ; SILICON NITRIDE; BACK REFLECTION

1. Introduction

Microscale integrated photonics enables task-specific optical systems by interconnecting devices with complementary guiding physics and materials [1]–[4]. Common waveguide cross-sections include strip, slot, and buried profiles for tight field confinement and routing [5]–[7]. These building blocks support lasers, sensors, amplifiers, fiber transmitters, and reflectors across near-infrared windows, notably the C- and O-bands [8]–[14], with O-band links widely deployed in modern data centers [15], [16]. Multimode-interference (MMI) couplers leverage Talbot self-imaging to replicate field profiles along the propagation axis, and serve as the kernel for WDM de/multiplexers, power and polarization splitters, and photonic logic [17]–[21]. Silicon photonics offers CMOS-process compatibility that yields compact footprints, low cost, and robustness to fabrication spreads while maintaining low loss at telecom wavelengths [22], [23]. Within this family, angled-MMI (AMMI) geometries tilt the access waveguides with respect to the multimode section, suppressing detrimental back reflections compared with conventional MMIs and AWGs, which is advantageous for reflection-sensitive O-band sources and links [14], [24], [25], [28]. Splitters remain fundamental primitives for distributing power to multiple channels, and their early placement and stability strongly influence system-level performance [26], [27]. Device behavior is further shaped by geometry-driven beat length, propagation loss, index contrast management, and reflection control, as well as doping and process complexity [29]–[32]. Silica provides low optical absorption, while SiN offers favorable thermo-optic and tolerance properties with intrinsically low back reflections; both are mature and CMOS-compatible through thermal oxidation and LPCVD or PECVD flows. We introduce an AI-optimized angled MMI 1×2 splitter with a buried SiN core in silica for O-band operation. An AI controller couples full-vectorial BPM and FDTD solvers to drive multiobjective search over the AMMI geometry, including body length and width, input/output tilt and offsets, slab thickness, and transition regions. The pipeline blends Bayesian optimization with evolutionary refinement to minimize excess loss and output imbalance while constraining back reflection and footprint. Surrogate models are retrained on-the-fly from BPM sweeps, then validated by high-accuracy FDTD to enforce physical consistency and accelerate convergence beyond manual or grid-based scans. The outcome is a compact, manufacturable splitter that sustains low loss, near-equalized ports, and strongly suppressed return power across the O-band, consistent with CMOS-foundry tolerances. Beyond data-center photonics, the same low-reflection fan-out benefits wearable neurotechnology. When co-packaged with EEG front-ends, the splitter can distribute O-band light to fiber-coupled photonic sensors and interferometric probes that capture

physiological correlates of attention and arousal. Fusing these optical channels with EEG spectral features [33–34] enables AI-based estimation of cognitive states, including mind-wandering detection [35–36], in real time. This positions the device as a bridge between high-performance optical interconnects and AI-enhanced cognitive monitoring systems, while preserving the scalability, stability, and integration advantages of SiN-on-silica photonics.

2. AI-AMMI splitter Structure

A single-mode tapered input waveguide was implemented to facilitate coupling between the Gaussian, monochromatic, quasi-TE polarized laser beam and the MMI region, ensuring efficient optical power transfer. A multilayer cross-sectional stack was designed, consisting of a silicon nitride (SiN) guiding core shown in blue, and silica cladding layers above and below displayed in white. Figure 1a presents the schematic in the x-y plane, illustrating the material layout by their chemical formulas. The vertical thickness of the device, maintained uniformly along its propagation length, is denoted as H . The tilt angle, θ , specifies the intentional misalignment of the tapered access and therefore the propagation trajectory of the guided mode.

Figure 1b illustrates the x-z plane schematic of the complete 1×2 AMMI power splitter, including the tapered input waveguides with gradual width transitions. The total width of the multimode region is represented by W_{MMI} , while the separation between the two output channels is indicated as W_g . The longitudinal extent of the input access waveguides along the z-axis is marked as L . The effective length of the multimode section itself is defined as L_{MMI} , with the two output ports designated as Port 1 (right side) and Port 2 (left side).

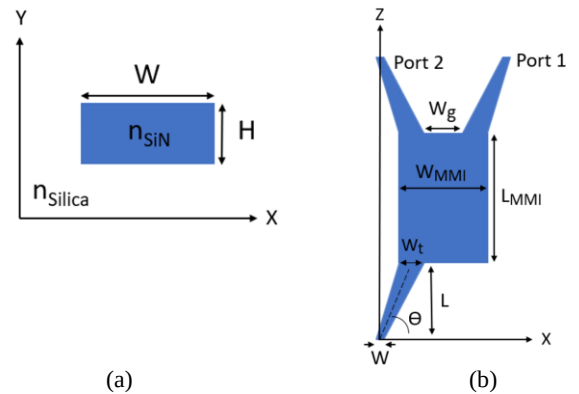


Figure 1. Schematic sketch of the AMMI splitter: (a) x-y plane, (b) x-z plane.

For the chosen simulation, the wavelength of $1.31\ \mu\text{m}$ was analyzed. For this NIR wavelength in the O-Band communication spectral range, the refractive indices of SiN and silica were set by RSoft-CAD to the values of 1.994 and 1.447, respectively. Although the width of the MMI core does not undergo changes in the direction of propagation, for the single mode access waveguide a tapered structure is introduced in which width changes from narrow width (W) to broad width (W_t) for the input and by a similar manner is inverted for the output.

The input and output tapered access waveguides serve as a source-MMI and MMI-forward couplers, respectively, in which a mode spot size conversion is achieved. To exploit the advantages of the stated low back reflections and to gain adequate optical field progression, the input access waveguide is tilted in an angle to the direction of propagation, which also causes the output ports, which are equal but inverted to the input access waveguides, to be tilted at the same angle due to the now tilted optical path.

3. Simulation Results

For the simulation of the proposed 1×2 AMMI splitter, the RSoft Photonics CAD suite was employed together with the BEAMProp solver. This solver applies the full-vectorial beam propagation method (FV-BPM) to numerically approximate solutions of the wave equation, tracking energy evolution along the propagation axis while accounting for both primary and secondary field components. Using this platform, we designed and modeled the device, simulated light transmission for the input monochromatic wavelength, and obtained results for modal solutions, propagation dynamics, and power distribution. Material definitions and geometric parameters were integrated into the simulations, allowing accurate evaluation of device behavior. To enhance this process, AI algorithms were incorporated into the workflow, linking RSoft solvers with optimization routines. AI was applied to guide parameter selection, accelerate convergence, and predict high-performance regions of the design space beyond conventional parameter sweeps. Device optimization was further refined with the MOST module, and post-processing of simulation data was carried out with MATLAB scripts.

A single-mode SiN waveguide core was analyzed to determine the optimal vertical dimension (H) for stable mode confinement. The thickness was set to $0.4\ \mu\text{m}$, as shown in Fig. 2, normalized to an input power of 1. At this thickness, the fundamental mode is well supported, enabling efficient propagation. Large deviations from this value may result in increased propagation loss, modal distortion, coupling mismatches, or the need for longer devices.

A wide range of thicknesses was tested to assess tolerance. Simulation results revealed nearly lossless power transmission at the chosen value, with only $\sim 0.035\ \text{dB}$ excess loss at the limits of $\pm 0.04\ \mu\text{m}$ ($\pm 40\ \text{nm}$). Minor deviations showed even lower losses, confirming robustness. AI-assisted optimization verified these outcomes, providing additional confidence in manufacturability. Modern CVD-based deposition technologies possess the precision necessary to achieve the suggested thickness range, ensuring stable fabrication of the proposed splitter.

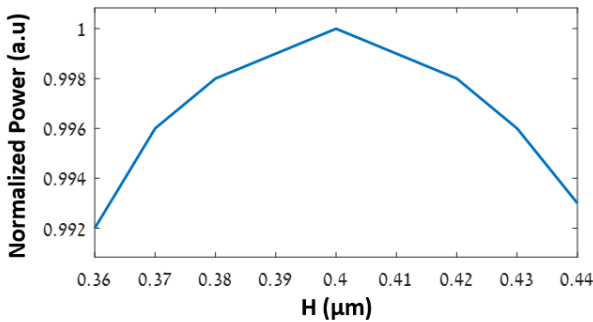


Figure 2. SiN waveguide core transmittance as a function of core thickness H (normalized).

We also simulated a straight, non-tilted and non-tapered single-mode access waveguide in order to resolve the supported quasi-TE mode. The optical field distribution was characterized in terms of lateral size, core confinement, evanescent decay, and the corresponding transverse refractive index profile. The excitation source was defined as a Gaussian-shaped monochromatic beam at $1.31\ \mu\text{m}$, which was consistently used for all simulations unless otherwise specified. The horizontal dimension of the waveguide, denoted as W , was selected to ensure strong confinement of optical power in the SiN core and was set to $0.7\ \mu\text{m}$, as shown in Fig. 3a. The results confirmed stable single-mode operation in the proposed geometry. The simulation further yielded an effective refractive index of $n_{\text{eff}} \approx 1.64$. Figure 3b presents the normalized power distribution of the guided mode along the y -axis.

During propagation through the tapered access region, the guided mode undergoes a gradual spot-size transformation as the waveguide width changes. At the junction between the taper and the multimode region, the waveguide width was set to $1.1\ \mu\text{m}$, while the taper length along the z -axis, L , was designed to be $21.45\ \mu\text{m}$. As illustrated in Fig. 3b, the mode power is concentrated around a vertical position of $0.2\ \mu\text{m}$, coinciding with the physical center of the SiN core in the y -direction.

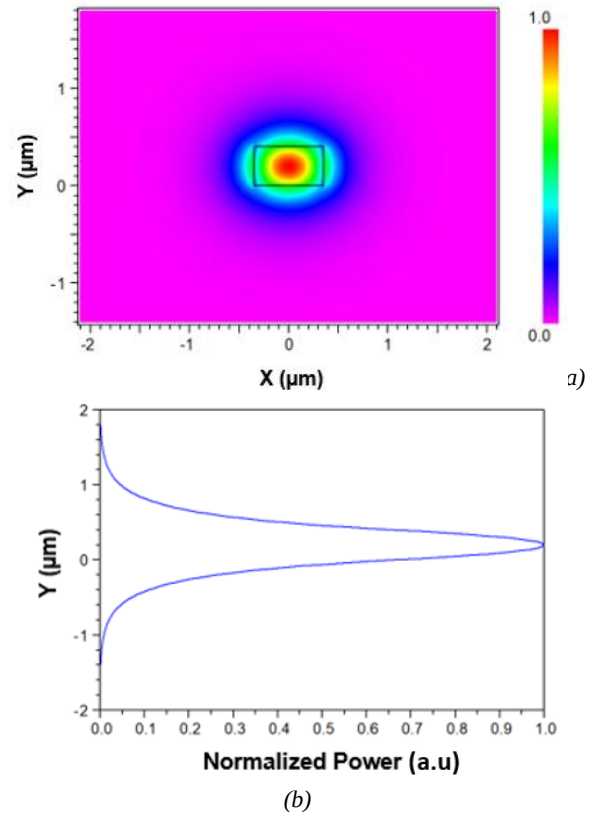


Figure 3. (a) The fundamental quasi-TE mode solution in the x - y plane with normalized power color coded scale. (b) Mode power distribution in y -axis.

The theoretical optical path length along the z -axis and, consequently, the bulk length of the MMI section were derived from Eqs. (1)–(3), assuming an intended multimode width (W_{MMI}) of $4.5\ \mu\text{m}$. From Eq. (3), the effective width was calculated as $5.04\ \mu\text{m}$. Using Eq. (2) with $p = 1$ to represent the first repetition cycle (corresponding to the shortest possible imaging length) and a beat length of $42.3\ \mu\text{m}$ obtained from Eq. (1), the estimated multimode length was $63.45\ \mu\text{m}$ for $N = 2$. These theoretical values served as starting points for defining the final device dimensions.

In general, splitters with geometric asymmetry introduce a degree of preference toward one port, leading to small variations in power balance between the outputs. Figure 4a presents the

simulated dependence of device performance on the multimode length L_{MMI} , where excess loss (orange, open squares) and imbalance (blue, open circles) are plotted on the right and left y-axes, respectively.

To evaluate robustness against fabrication tolerances, a variation of $\pm 2 \mu\text{m}$ was applied to the MMI length. Within this range, the maximum observed excess loss and imbalance were 1.4 dB and 0.1 dB, respectively. An optimized multimode length of $58.5 \mu\text{m}$ was selected, offering the lowest combined losses and aligning closely with theoretical predictions.

Similarly, the impact of varying the SiN bulk width was studied, as shown in Fig. 4b. The chosen W_{MMI} value of $4.5 \mu\text{m}$ provided minimal losses, with excess loss of 0.21 dB and imbalance of 0.001 dB. However, across a tested width range of $\pm 0.2 \mu\text{m}$, the splitter exhibited higher excess loss exceeding 4 dB and imbalance increasing to nearly 3 dB, highlighting sensitivity to lateral dimension deviations.

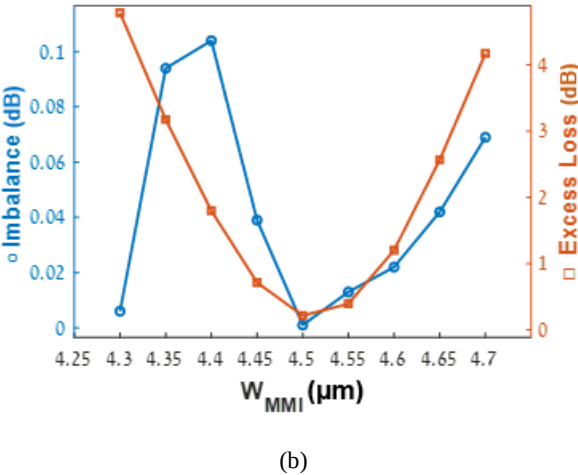
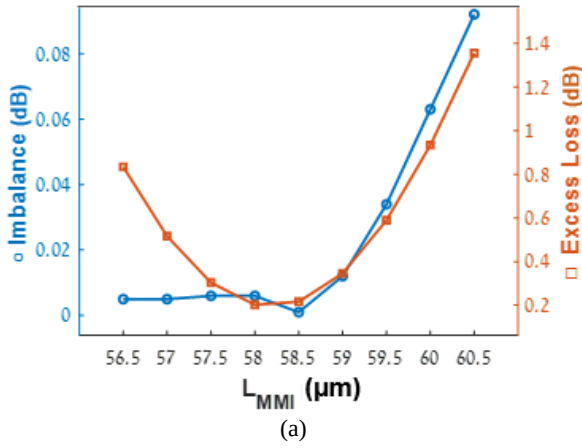


Figure 4. Output ports imbalance and excess loss for (a) MMI length L_{MMI} , (b) MMI width W_{MMI} .

To identify the most suitable tilt angle for the input and output access waveguides, a series of simulations was performed across a range of angles in order to balance two main objectives: minimizing back reflection and reducing insertion loss. Introducing this angular offset effectively transforms the structure into a functional AMMI device. Since the tilt angle directly modifies the optical path length of the guided mode, it also influences the overall device size, particularly along the z-axis. Figure 5 illustrates the variation of excess loss and output imbalance as functions of the tilt angle θ .

Device performance was assessed over a tolerance window of $\pm 2^\circ$ to evaluate the impact of angular deviations on transmission. The chosen operating value of $\theta = 5^\circ$ yielded an excess loss of 0.21 dB and an output imbalance of 0.001 dB. Although this configuration does not provide the absolute minimum excess loss, it represents a balanced solution once secondary dependencies such as

MMI length and width adjustments are taken into account. At the extreme ends of the tested range, the losses and imbalance were measured at 0.53 dB and 0.021 dB, respectively.

As expected, the device sensitivity to optical loss increases proportionally with the tilt angle, but the overall variation remains moderate within the examined range. While selecting a smaller tilt may slightly improve transmission efficiency, it would also compromise the goal of achieving ultra-low back reflection and could enlarge the device footprint, particularly in scenarios where multiple splitters or cascaded couplers are integrated. Thus, adjusting θ provides useful design flexibility for tuning z-axis dimensions while maintaining stable operation.

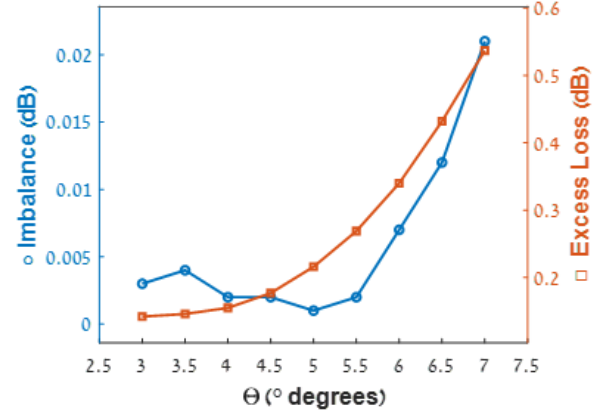
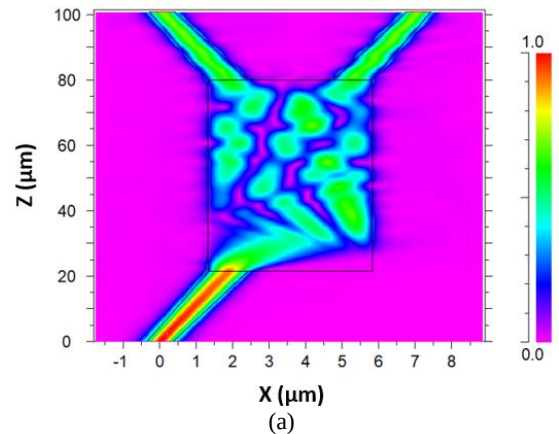


Figure 5. Output port imbalance and excess loss as a function of the tilt angle, θ .

Figure 6a illustrates the final interference distribution of the transmitted optical field across the device, together with the corresponding color-coded power scale, where the input power is normalized to 1. The optimized quasi-TE mode was launched into the final geometry, which incorporates adiabatically tapered access waveguides at both input and output. These tapered sections act as spot-size converters, are angled relative to the MMI body, and couple into the multimode region to form the AMMI 1×2 splitter.

The simulations confirmed effective power division at the target wavelength, yielding an excess loss of only 0.22 dB and an extremely small imbalance of 0.001 dB. The overall footprint of the device is $101 \mu\text{m} \times 7.8 \mu\text{m}$, with an inter-port separation (W_g) of $3.57 \mu\text{m}$.

Figure 6b presents the calculated excess loss and imbalance as functions of wavelength across the O-band spectrum, providing insight into device performance under wavelength shifts of the input signal while keeping the physical design unchanged. At the operating wavelength of $1.31 \mu\text{m}$, the splitter achieves optimal transmission characteristics, consistent with its optimized parameters. Even at the spectral edges of the O-band, the coupler remains functional, with maximum excess loss limited to 1.57 dB and imbalance not exceeding 0.05 dB.



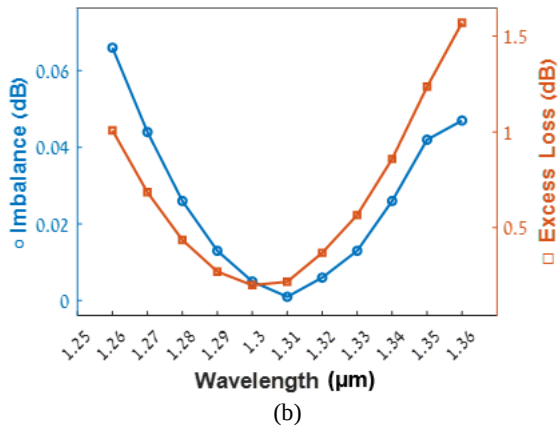


Figure 6. (a) Overall device interference pattern and light path (left) with normalized colored power scale (right) at the x-z plane. (b) Spectral response for O-band in terms of imbalance and excess loss.

The altered optical path results from tilting the access waveguide at the junction between the input source and the main device. This adjustment was introduced to suppress back reflection to extremely low levels, thereby minimizing the amount of optical power returning into the source. In doing so, the passive coupler exerts less influence on the transmitter, ensuring stable and reliable operation of the source within a telecommunication system.

Figure 7a shows the FDTD simulation contour obtained using the FullWAVE solver. To further evaluate reflections, an additional input waveguide segment (orange) with the same dimensions was inserted ahead of the elongated access region, and an anti-forward monitor (green) was placed to detect any backward-propagating light that might otherwise couple back into the source. The simulation results confirm that the designed AMMI splitter achieves very low back reflection, with a measured value of -40.96 dB at the central operating wavelength and up to -39.67 dB across the O-band, as presented in Fig. 7b. These values are consistent with theoretical expectations for angled MMI structures employing SiN cores. Such performance underscores the device's suitability for data-center environments, where stable and predictable optical distribution is critical for high-capacity and low-loss operation.

4. Conclusions

This work presented further exploration of the geometric innovation within the AMMI coupler family, focusing on tilting the single-mode access waveguide and redirecting the input signal at an angle relative to the multimode interference region. The investigated structure employed a silicon nitride (SiN) core with a thickness of $0.4 \mu\text{m}$ and silica cladding, where the access waveguide was inclined by 5° with respect to the propagation axis. The multimode section dimensions were defined as $58.5 \mu\text{m}$ in length and $4.5 \mu\text{m}$ in width, resulting in a compact overall footprint of $101 \mu\text{m} \times 7.8 \mu\text{m}$. The device was designed for operation at the O-band central wavelength of $1.31 \mu\text{m}$, with an output port spacing (Wg) of $3.57 \mu\text{m}$. Simulation results demonstrated efficient power transfer, yielding an excess loss of only 0.22 dB and an almost negligible imbalance of 0.001 dB. Across the full O-band, the splitter maintained strong performance, with maximum excess loss of 1.57 dB and imbalance of 0.05 dB. Back reflection was exceptionally low, measured at -40.96 dB. Among all tested tolerances, variations in the multimode section width were found to have the greatest influence on excess loss, confirming its sensitivity compared to other parameters. The chosen dimensions, effective mode conversion, compact footprint, robust interference properties, and suppressed reflections aligned well with theoretical predictions and compared favorably with other devices of its class. Beyond classical optical communication systems, the device is especially attractive for data-center integration, where its reduced segmentation, compact design, and stable multi-channel transmission capabilities enable high-speed, low-loss operation in dense computing

environments. A key contribution of this work was the integration of AI into the design and optimization cycle. AI-assisted routines, coupled with BPM and FDTD solvers, accelerated parameter exploration, predicted performance trends, and identified optimal configurations more efficiently than traditional iterative sweeps. This approach ensured minimal excess loss and ultra-low reflection while maintaining manufacturability within CMOS-compatible tolerances.

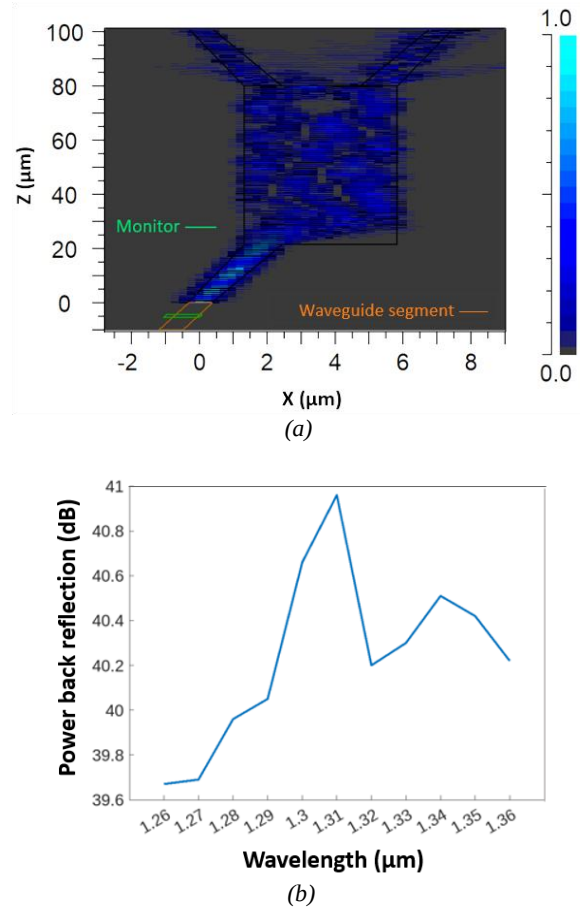


Figure 7. (a) FDTD analysis power distribution of the device (left) with normalized colored power scale (right) at the x-z plane with added waveguide segment (orange) and a monitor section (green). (b) Power back reflection spectral response.

References

1. Malka, D.; Zalevsky, Z.; Sintov, Y. Design of a 1×4 Silicon Wavelength Demultiplexer Based on Multimode Interference in Slot Waveguide Structures. In *2014 IEEE 28th Convention of Electrical & Electronics Engineers in Israel*; IEEE: Eilat, Israel, 2014; pp. 1–4. <https://doi.org/10.1109/EEEI.2014.7005746>.
2. Frishman, A.; Malka, D. An Optical 1×4 Power Splitter Based on Silicon–Nitride MMI Using Strip Waveguide Structures. *Nanomaterials* **2023**, *13*, 2077. <https://doi.org/10.3390/nano13232077>.
3. Malka, D. 1×4 Visible Light MMI Wavelength Demultiplexer in GaN Slot-Waveguide Structure. In *2018 IEEE International Conference on the Science of Electrical Engineering in Israel*; IEEE: Eilat, Israel, 2018; pp. 1–5. <https://doi.org/10.1109/ICSEE.2018.8646159>.
4. Ben Zaken, B.; Zanzury, T.; Malka, D. Slot Silicon–Gallium Nitride Waveguide in MMI Structures Based 1×8 Wavelength Demultiplexer. In *Digital Optical Technologies 2017*; SPIE: Munich, Germany, 2017; Volume 10335, p. 103350P. <https://doi.org/10.1117/12.2271686>.
5. Malka, D. WDM C-Band Four Channel Demultiplexer Using Cascaded Multimode Interference on SiN Strip Waveguide

- Structure. *EPJ Web Conf.* **2024**, *305*, 00010. <https://doi.org/10.1051/epjconf/202430500010>.
6. Malka, D. A Silicon Nitride MMI O-Band Power Combiner Based on Slot Waveguide Structures. In *Integrated Optics: Design, Devices, Systems and Applications VII*; SPIE: Prague, Czech Republic, 2023; Volume 12575, p. 125750B. <https://doi.org/10.1117/12.2669881>.
7. Menahem, J.; Malka, D. 1×4 Wavelength Demultiplexer C-Band Using Cascaded Multimode Interference on SiN Buried Waveguide Structure. *Materials* **2022**, *15*, 5067. <https://doi.org/10.3390/ma15145067>.
8. Moatlhodi, O.; Ditshego, N.M.J.; Samikannu, R. Vertical Cavity Surface Emitting Lasers as Sources for Optical Communication Systems: A Review. *J. Nano Res.* **2020**, *65*, 51–96. <https://doi.org/10.4028/www.scientific.net/JNanoR.65.51>.
9. Lal, S.; Link, S.; Halas, N.J. Nano-Optics from Sensing to Waveguiding. In *Nanoscience and Technology*; Co-Published with Science Press: Beijing, China, 2009; pp. 213–220.
10. Wang, X.; Zhuang, X.; et al. High Gain Submicrometer Optical Amplifier at Near-Infrared Communication Band. *Phys. Rev. Lett.* **2015**, *115*, 027403. <https://doi.org/10.1103/PhysRevLett.115.027403>.
11. Zhao, Q.; Yuan, W.; et al. Optical Fiber-Integrated Metasurfaces: An Emerging Platform for Multiple Optical Applications. *Nanomaterials* **2022**, *12*, 793. <https://doi.org/10.3390/nano12050793>.
12. Hainberger, R.; Mueller, P.; et al. PECVD Silicon Nitride Optical Waveguide Devices for Sensing Applications in the Visible and <1 μm Near Infrared Wavelength Region. In *Optical Sensing and Detection VI*; SPIE: Brussels, Belgium, 2019; Volume 11031, p. 110310A. <https://doi.org/10.1117/12.2527439>.
13. Rouified, M.S.; Littlejohns, C.G.; et al. Ultra-Compact MMI-Based Beam Splitter Demultiplexer for the NIR/MIR Wavelengths of 1.55 μm and 2 μm . *Opt. Express* **2017**, *25*, 10893–10900. <https://doi.org/10.1364/OE.25.010893>.
14. Bucio, T.D.; Khokhar, A.Z.; et al. N-Rich Silicon Nitride Angled-MMI for Coarse Wavelength Division (De)Multiplexing in the O-Band. *Opt. Lett.* **2018**, *43*, 1403–1406. <https://doi.org/10.1364/OL.43.001403>.
15. Seiler, P.M.; Georgieva, G.; Winzer, G.; et al. Toward Coherent O-Band Data Center Interconnects. *Front. Optoelectron.* **2021**, *14*, 414–425. <https://doi.org/10.1007/s12200-021-1151-6>.
16. Wang, K.; Zhang, J.; et al. High-Speed PS-PAM8 Transmission in a Four-Lane IM/DD System Using SOA at O-Band for 800G DCI. *IEEE Photonics Technol. Lett.* **2020**, *32*, 293–296. <https://doi.org/10.1109/LPT.2020.2971648>.
17. Chuan, N.B.; Premadi, A.; et al. Optical Power Budget and Cost Estimation for Intelligent Fiber-to-the-Home (i-FTTH). In *2010 International Conference on Photonics*; IEEE: Langkawi, Malaysia, 2010; pp. 1–5. <https://doi.org/10.1109/ICP.2010.5604473>.
18. Isakov, O.; Frishman, A.; Malka, D. Data Center Four-Channel Multimode Interference Multiplexer Using Silicon Nitride Technology. *Nanomaterials* **2024**, *14*, 486. <https://doi.org/10.3390/nano14030486>.
19. Katash, N.; Khateeb, S.; Malka, D. Combining Four Gaussian Lasers Using Silicon Nitride MMI Slot Waveguide Structure. *Micromachines* **2022**, *13*, 1680. <https://doi.org/10.3390/mi13101680>.
20. Brand, O.; Wolfstson, B.; Malka, D. A Compact Polarization MMI Combiner Using Silicon Slot-Waveguide Structures. *Micromachines* **2023**, *14*, 1203. <https://doi.org/10.3390/mi14061203>.
21. Cahill, L.W.; Le, T.T. Optical Signal Processing Using MMI Elements. In *2008 10th Anniversary International Conference on Transparent Optical Networks*; IEEE: Athens, Greece, 2008; pp. 114–117. <https://doi.org/10.1109/ICTON.2008.4598621>.
22. Mao, S.C.; Tao, S.H.; et al. Low Propagation Loss SiN Optical Waveguide Prepared by Optimal Low-Hydrogen Module. *Opt. Express* **2008**, *16*, 20809–20816. <https://doi.org/10.1364/OE.16.020809>.
23. Ioudashkin, E.; Malka, D. High-Performance O-Band Angled Multimode Interference Splitter with Buried Silicon Nitride Waveguide for Advanced Data Center Optical Networks. *Photonics* **2025**, *12*, 322. <https://doi.org/10.3390/photonics12040322>.
24. Ioudashkin, E.; Malka, D. A Three Demultiplexer C-Band Using Angled Multimode Interference in GaN–SiO₂ Slot Waveguide Structures. *Nanomaterials* **2020**, *10*, 2338. <https://doi.org/10.3390/nano10112338>.
25. Hu, Y.; Thomson, D.J.; Khokhar, A.Z.; Stanković, S.; Mitchell, C.J.; Gardes, F.Y.; Penades, J.S.; Mashanovich, G.Z.; Reed, G.T. Angled Multimode Interferometer for Bidirectional Wavelength Division (De)Multiplexing. *R. Soc. Open Sci.* **2015**, *2*, 150429. <https://doi.org/10.1098/rsos.150429>.
26. Serecunova, S.; Seyringer, D.; Uherek, F.; et al. Design and Optimization of Optical Power Splitters for Optical Access Networks. *Opt. Quantum Electron.* **2022**, *54*, 365. <https://doi.org/10.1007/s11082-022-03775-2>.
27. Wang, R.; Vasiliev, A.; et al. III–V-on-Silicon Photonic Integrated Circuits for Spectroscopic Sensing in the 2–4 μm Wavelength Range. *Sensors* **2017**, *17*, 1788. <https://doi.org/10.3390/s17081788>.
28. Song, J.H.; Snyder, B.; et al. Grating Coupler Design for Reduced Back-Reflections. *IEEE Photonics Technol. Lett.* **2018**, *30*, 217–220. <https://doi.org/10.1109/LPT.2017.2779830>.
29. Wu, S.; Mu, X.; Cheng, L.; et al. State-of-the-Art and Perspectives on Silicon Waveguide Crossings: A Review. *Micromachines* **2020**, *11*, 326. <https://doi.org/10.3390/mi11030326>.
30. Urbonas, D.; Mahrt, R.F.; Stoferle, T. Low-Loss Optical Waveguides Made with a High-Loss Material. *Light Sci. Appl.* **2021**, *10*, 15. <https://doi.org/10.1038/s41377-020-00451-1>.
31. Bar Gelkop; Malka, D. Design of a Four Channel Green-Wavelength Multiplexer Based on Multicore Polymer Optical Fiber. *Opt. Laser Technol.* **2025**, *192* (Part B), 113635. <https://doi.org/10.1016/j.optlastec.2025.113635>.
32. Pugachov, Y.; Gulitski, M.; Mizrahi, O.; Malka, D. Design of All-Optical Logic Half-Adder Based on Photonic Crystal Multi-Ring Resonator. *Symmetry* **2023**, *15*, 1063. <https://doi.org/10.3390/sym15051063>.
33. Avital, N.; Nahum, E.; Levi, G.C.; Malka, D. Cognitive State Classification Using Convolutional Neural Networks on Gamma-Band EEG Signals. *Appl. Sci.* **2024**, *14*, 8380. <https://doi.org/10.3390/app14188380>.
34. Avital, N.; Shulkin, N.; Malka, D. Automatic Calculation of Average Power in Electroencephalography Signals for Enhanced Detection of Brain Activity and Behavioral Patterns. *Biosensors* **2025**, *15*, 314. <https://doi.org/10.3390/bios15050314>.
35. Rabinovitch, A.; Baruch, E.B.; Siton, M.; Avital, N.; Yeiri, M.; Malka, D. Efficient Detection of Mind Wandering During Reading Aloud Using Blinks, Pitch Frequency, and Reading Rate. *AI* **2025**, *6*, 83. <https://doi.org/10.3390/ai6040083>.
36. Avital, N.; Egel, I.; Weinstock, I.; Malka, D. Enhancing Real-Time Emotion Recognition in Classroom Environments Using Convolutional Neural Networks: A Step Towards Optical Neural Networks for Advanced Data Processing. *Inventions* **2024**, *9*, 113. <https://doi.org/10.3390/inventions9060113>.

Wave nature of the processes of high-speed mass transfer and local microalloying of laser-hardened steels

Svetlana Gubenko

Iron and Steel Institute of National Academy of Science of Ukraine,

²Ukrainian State University of Science and Technologies: Prydniprovsk State Academy of Civil Engineering and Architecture
Dnepr, Ukraine

sigubenko@gmail.com

Abstract. The goal of this investigation was to research the nature of the formation of gradient and composite zones near non-metallic inclusions during laser treatment of the steels. The materials for investigation were commercial steels containing different non-metallic inclusions. The specimens of different steels were exposed to laser beaming on the installations GOS-30M. The research methods were applied: petrography, X-ray microscopy (MS-46 Cameca, "Nanolab - 7") and optical microscopy (Neophot-31) to study steel matrix near non-metallic inclusions and to identify of the inclusions. Nanohardness of the steel matrix near inclusions ("Nano Indenter II") was analyzed. Peculiarities of saturation of the steel matrix by elements of non-metallic inclusions during different regimes of laser action were investigated. It was shown the role of that process in the formation of local structure of steel matrix near non-metallic inclusions. The features of the formation of gradient and micro composite saturation zones of a steel matrix under conditions of abnormal mass transfer from nonmetallic inclusions during laser processing are discussed. The difference in the rates of abnormal mass transfer of chemical elements of non-metallic inclusions into a steel matrix at the moment of laser melting is shown.

KEYWORDS: NON-METALLIC INCLUSIONS, STEEL, MICRO COMPOSITE ZONES, ABNORMAL MASS TRANSFER, LASER TREATMENT, STRENGTHENING, NANO HARDNESS

1. Introduction

Laser processing is widely used for surface strengthening of steels and steel products [1]. It is known that the mechanism of laser strengthening of steels is associated with a number of factors that create a total strengthening effect [1, 2]. First of all, these are high-speed phase transformations, thermoplastic stresses, microchemical heterogeneity, partial or complete dissolution of carbides and non-metallic inclusions, etc. High-speed shear phase transformations in the steel matrix generate stresses from high-temperature and phase hardening during rapid heating and cooling, including the local influence of inclusions on these transformations.

Non-metallic inclusions that are present in any steel affect the local processes occurring during laser treatment. In process of laser treatment non-metallic inclusions are fully or partly melted down or are remained hard [2 - 7]. In spite of short-term treatment energy of laser ray turns out sufficient for melting of the high-melting and low-melting inclusions, and also for the development of mass transfer processes which lead to enrichment of steel matrix by the elements of inclusions and also transfer of matrix elements to the surface zone of the inclusions. In the vicinity of non-metallic inclusions due to microalloying, areas appear that are supersaturated by inclusion elements solid solutions [4 - 6]. The level of the strengthening of steels near non-metallic inclusions depends on some factors: chemical composition of steel and non-metallic inclusion and also character of speed structural and phase transformations which flow in steel matrix, phase, deformation and high temperature hardening. It was found that the strengthening zones of the steel matrix near non-metallic inclusions have different structures and phase compositions [3 - 7]. At the same time, the nature of the formation of these zones is not always clear. The goal of this investigation was to research the nature of the formation of gradient and composite zones near non-metallic inclusions during laser treatment of the steels.

2. Materials and Procedures.

Samples of different steels (R7, 08Yu, 08T, 08Kp, 08Ch18N10T, ShCh15, NB-57, 12GS, E3) were laser treated by GOS-30M installation with parameters: an excitation voltage of 2,5 kV, pulse energy of 10...30 J, heating rate of 10^5 °C / s, cooling rate of 10^6 °C / s, action time of $(1,0...6,0) \cdot 10^{-3}$ s. Identification of non-metallic inclusions was carried out by metallographic (Neophot-31), X-ray microspectral and petrographic methods [3]. Distribution of the elements by X-ray microanalysis (MS-46 "Cameca", "Nanolab -

7") and nanohardness of the steel matrix near non-metallic inclusions ("Nano Indenter II") were analyzed.

3. Results and discussion.

Some transformations in non-metallic inclusions and steel matrix under laser action took place. The type of inclusion determines of their behavior at the time of laser beam action. High-melting non-metallic inclusions (oxides Al_2O_3 , Cr_2O_3 , SiO_2 , TiO , $MnO \cdot Al_2O_3$, $MgO \cdot Al_2O_3$, $MnO \cdot Cr_2O_3$, $TiCN$) are melted or remained hard during laser treatment. Some low-melting inclusions (iron-manganese silicates and sulfides) are melted under laser action and spread over a surface under shock wave [8]. The components of inclusions penetrate into steel matrix and saturate it [2 - 7]. In the process of laser action between a non-metallic inclusion and a steel matrix, a high-speed exchange of atoms occurs through the interface under conditions of an abnormal high mobility of the atoms that does not meet the conditions of classical diffusion (abnormal mass transfer) [9 - 12]. The processes of mass transfer during laser exposure are facilitated by the following factors: heating to high temperatures and high-speed movement of the defects in the crystal structure that occur during thermal shock; the possibility of formation of a thermally nonequilibrium plasma; the appearance of convective and wave flows in the melt [13]; relaxation of thermoplastic stresses arising during irradiation; melting; electronic and electromagnetic interaction of inclusions and matrix [3]; formation in the surface areas of the inclusions of zones with an increased density of dislocations [3, 8].

Analysis of the oversaturated areas of steel matrix near non-metallic inclusions was shown that their structure is heterogeneous. There are a few versions of their structure revealing by heat etching under laser action. It may be one zone, or two zones, or three zones (Fig. 1). The number of saturation zones near the inclusions did not depend on the type and state of the inclusion at the time of laser exposure, however, it depended on the laser processing mode: the higher the pulse energy and the longer the exposure time, the greater the tendency for the appearance of multilayer formations. This is due to the activation of the process of mass transfer of elements from the inclusions to steel matrix with an increase in the energy of the laser pulse and an increase in the possibility of its implementation with an increase in the duration of exposure. By that in non-metallic inclusions the surface zone saturated by the element of steel matrix may or may not be available.

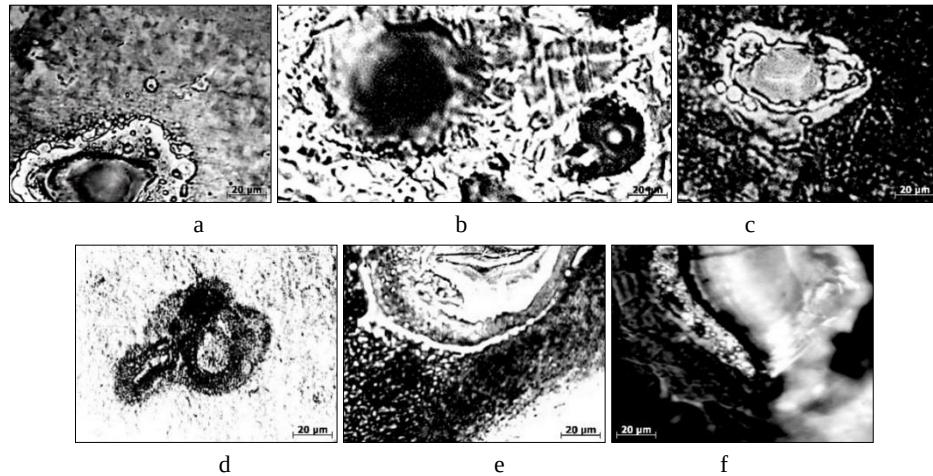


Figure .1. Zones of interaction between non-metallic inclusions and steel matrix under laser treatment: a - SiO_2 steel E3; b - Al_2O_3 , $\text{MnO}\cdot\text{Al}_2\text{O}_3$, R7, c - TiCN , R7, d - $(\text{Fe},\text{Mn})\text{O}$, R7, e - $\text{FeS}\cdot(\text{Fe},\text{Mn})\text{S}$, steel NB-57, f - Al_2O_3 , 08Yu.

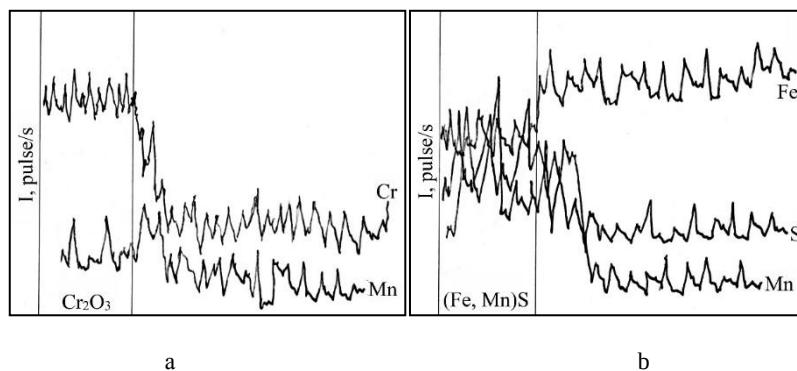
The number of saturation zones near the inclusions did not depend on the type and state of the inclusion at the time of laser exposure, however, it depended on the laser processing mode: the higher the pulse energy and the longer the exposure time, the greater the tendency for the appearance of multilayer formations. This is due to the activation of the process of mass transfer of elements from inclusions to the steel matrix with an increase in the energy of the laser pulse and an increase in the possibility of its implementation with an increase in the duration of exposure.

Oversaturated areas of steel matrix near non-metallic inclusions are differed by distribution of chemical elements. At presence of one oversaturated zone near inclusion the gradual decrease of quantity of elements of non-metallic inclusion by removing from inclusion was observed (Fig. 2, a, b). At presence of two or three oversaturated zones in each of them gradual decrease of quantity of elements of non-metallic inclusion by removing from inclusion was observed but quantity of elements in second zone was less than in first zone and also quantity of elements in third zone was less than in the first and second zones. Thus at the presence of a few oversaturated zones in steel matrix the cascade of elements concentration near non-metallic inclusion with gradual decrease of quantity of the chemical elements in each zone were observed (Fig. 2, c).

It is known that under shock compression pressure, the normal stresses in steel exceed the yield point, while shear stresses become higher than the critical value and the material flows [14]. As a result, dislocations multiply, dislocation reactions occur, which contributes to the appearance of vacancies and an increase in the dislocation density in the laser impact zone up to $10^9 \dots 10^{12} \text{ cm}^{-2}$ [20]. New mobile dislocations appear, their movement is associated with the relaxation of thermoplastic stresses arising during

irradiation, which contributes to the implementation of anomalous mass transfer [15 - 17].

Stress relaxation in the zone of laser action is carried out by plastic shears and rotations, as well as by twinning [20]. Microplastic processes of stress relaxation are localized near non-metallic inclusions, where zones of shear-rotational deformation are observed. Laser exposure is essentially thermal shock. During abrupt heating to high temperatures, the high pressures develop in shock waves, which create a concentration of thermal and deformation stresses near the inclusions. For the relaxation of these stresses there is an extremely short time of shock compression. The described conditions provoke an avalanche relaxation of stresses near the inclusions (Fig. 3, a, b), where complexly deformed zones appear (Fig. 3, c), indicating high-speed shear-turn plastic deformation processes with elements of a wave nature. In some areas of these zones, there are signs of recovery and recrystallization high-speed processes (Fig. 3, d, e). And yet, despite the rather significant heating temperature, the main mechanism of stress relaxation is high-speed plastic deformation [18]. During thermal shock near non-metallic inclusions, the wave relaxation of stresses occurs [18, 19]. It can be assumed that stress relaxation waves accompany abnormal mass transfer of inclusion components into the steel matrix (Fig. 3, f): the first wave is the farthest; the second one is shorter in the distance of action from the inclusion and is superimposed on the zone of action of the first wave; the third one is correspondingly even shorter and is superimposed on the zones of action of the first and two waves. It should be noted that plastic relaxation near non-metallic inclusions occurs against the background of their dissolution and melting, leading to local saturation of the steel matrix with inclusion elements, which undoubtedly affects the mechanism and rate of the processes under study.



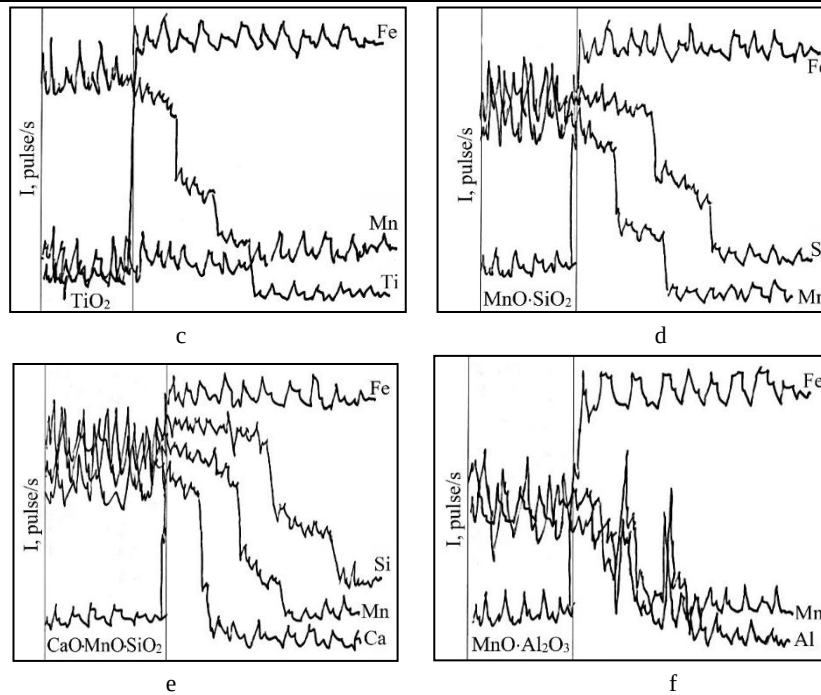


Figure 2.. Wave distribution of chemical elements in inclusions and steel matrix after laser treatment.

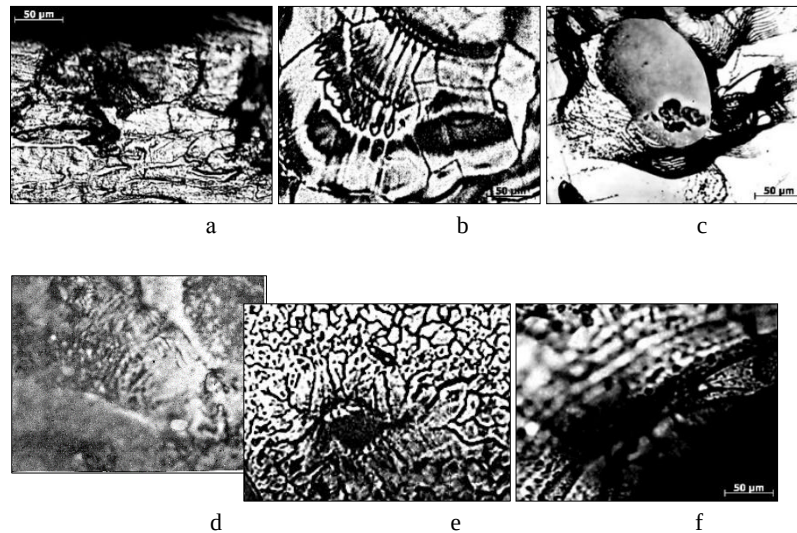


Figure 3. Plastic stress relaxation near inclusions under laser action

A detailed analysis of the curves of the gradient cascade distribution of elements near the inclusions (on the example of R7 wheel steel) made it possible to reveal some of their features. They are related to the fact that, along with clear drops in the radiation intensity of elements in the presence of two or three saturation zones, there are cases of mismatch of these drops for different elements near one inclusion (Fig. 2, d, e). The boundaries of the first, second and third saturation zones were determined by the most active chemical element that penetrated to the maximum distance from the initial inclusion

Within the indicated saturation zones, Mn atoms penetrate to the greatest distance from the initial inclusion, then Si atoms, and finally S atoms. At the same time, Ca atoms, as a rule, penetrate a short distance from the initial inclusion, and in the presence of two or three saturated zones, only in the one that is adjacent to it. These data indicate the different rates of migration of atoms of various elements in molten steel in the laser melting zone.

Obviously, there is some relationship between these results and the difference in the diffusion coefficients of various alloying elements in liquid iron [20]. Undoubtedly, the conditions under which the indicated diffusion coefficients were determined are far from those that are realized at the moment of pulsed laser action,

when abnormal mass transfer occurs, rather than diffusion processes. The authors of [20] showed that alloying elements diffuse in liquid iron at rates that differ significantly from each other, which is associated with their different solubility in clusters and the disordered zone of the melt. In this work, alloying elements are divided into three groups according to the degree of solubility in liquid iron. Elements of the first group (Mn, Ni, Co, Pd, Pt) easily dissolve in clusters, their diffusion coefficient D is close to the self-diffusion coefficient of the iron atoms, they dissolve indefinitely in liquid and solid iron. Elements of the second group (Cr, N, C, Zn, Cu, Mo, V, Nb, Al, Cd, W, Ti, Zr, O, S) have an increased solubility in the disordered zone. They are infinitely soluble in liquid iron and sparingly soluble in solid iron. Their diffusion coefficients fluctuate over a wide range relative to D of the iron atoms. Elements of the third group (Na, Mg, Ca, H) are sparingly soluble in both liquid and solid iron, their diffusion coefficients depend on the atomic radius.

As for the conditions of pulsed laser exposure, the sharp heating of the melt in a thin surface layer obviously violates its equilibrium structure and also causes cluster polymorphism [20], which should significantly and differently affect the nature of the abnormal mass transfer of the atoms of various chemical elements.

At the same time, there is a relationship between the rates of diffusion of impurities in liquid iron with the rates of their abnormal mass transfer in the melt under laser exposure. Relationships of elements concentration in oversaturated zones were different and were oscillated in interval 1,2 ... 1,8 that connects with heterogeneous field of temperatures and stresses and also with wave character of speed mass transfer in the conditions of laser pulse.

There is another type of distribution of elements of non-metallic inclusions in areas of steel matrix. By collective mass transfer connecting with dissolution of nano-grains of non-metallic inclusion [5, 6] “spot” distribution of elements of inclusion in areas of steel matrix was observed (Fig. 2, f).

The results of distribution of nanohardness of steel matrix were shown that its value (H_n^i) near non-metallic inclusions (one oversaturated zone or first zone) is bigger than far from non-metallic inclusions [3, 21]. Its value depends from chemical composition and structure of steel defining degree of strengthening by laser action. In the first (or sole) oversaturated zone values of H_n^i in 1,45 ... 1,8 times bigger then in steel matrix far from inclusion. Coefficient K_i is determined by the ratio of the nanohardness of the steel matrix in the saturation zone to the nanohardness of the steel matrix away from the non-metallic inclusion [4, 5]. These results are closed to the results of determining the microhardness near inclusions after laser exposure obtaining in [5, 6]. In the second and third oversaturated zones values of nanohardness lower than in the first zone but exceeds values of H_n far from non-metallic inclusions accordingly in 1,25 ... 1,64 and 1,1 – 1,3 times. Thus the cascade of nanohardness values by removal from non-metallic inclusions was observed. Value of nanohardness of steel matrix in all oversaturated zones near non-metallic inclusions and value of coefficient K_i depends from the condition of non-metallic inclusion and steel matrix in the moment of laser action. Values of H_n^i and K_i are maximum by fusion of non-metallic inclusions and steel matrix, they are decreased by fusion of steel matrix near hard non-metallic inclusion and they are minimum in the cases of hard condition of non-metallic inclusion and steel matrix. This connects with phenomenon of maximum saturation of liquid steel matrix by fusion or full melting of non-metallic inclusions. In cases of fusion of oxides, sulfides, silicates in the moment of laser action nanohardness of steel matrix near non-metallic inclusions bigger then near hard non-metallic inclusions and values of coefficient K_i in all oversaturated zones increase. Saturation of steel matrix by the elements of non-metallic inclusions and their fix in solid solution promotes increase of H_n^i and K_i values. Degree of steel matrix saturation in the second and third zones less then directly near non-metallic inclusions (in the first zone) that is confirmed by difference of H_n^i and K_i values. Dependence of nanohardness of the first (or sole) oversaturated zone of steel matrix near non-metallic inclusions has non-monotonic view for all laser action time [3, 21]. This evidence about existence of certain ranges of laser beam energy values that correspond to maximum strengthening of local layers of steel matrix.

Main factor of laser strengthening of local areas of steel matrix is its microalloying from inner sources - non-metallic inclusions. The appearance of cascade saturation zones during the formation of liquation strengthened areas contributes to formation of micro composite layers near non-metallic inclusions. Structure of these zones maybe single-phase (oversaturated solid solutions) but often dispersal microphases and nanophases – “satellite” particles are observed (Fig. 1, a, f). The initial inclusion and composition of steel matrix determine the chemical composition of “satellite” particles [3 - 6].

4. Conclusions.

The possibilities of transformation of non-metallic inclusions how sources of inside alloying of steel matrix are shown. Features of the formation of gradient and micro composite saturation zones of the steel matrix under conditions of abnormal mass transfer from non-metallic inclusions during laser processing are associated with the

formation of segregation-strengthened zones. Gradient saturation zones with a cascade and “spot” distribution of elements and nanohardness, dispersed zones, and zones with a combined structure were formed. The formation of a cascade distribution of chemical elements in the saturation zones is due to the wave nature of the relaxation of thermo-deformation stresses near non-metallic inclusions at the time of laser exposure. Signs of different rates of abnormal mass transfer of chemical elements of non-metallic inclusions into the steel matrix at the time of laser melting are revealed

5. Literature.

1. Dowden J, Schulz W. The Theory of Laser Materials Processing: Heat and Mass Transfer in Modern Technology. 2nd ed. Berlin/Heidelberg: Springer. 2017, 432 p.
2. Gubenko SI. Analysis of the effect of nonmetallic inclusions on steel strengthening upon laser treatment. Steel in Translation, 2021, v.51, No 3, pp. 217–228.
3. Gubenko S. Transformation of inclusions during laser processing of steels. v.1. Local strengthening. Локальное упрочнение. London - UK, Republic of Moldova - EU, Dodo Books abd OmniScriptum S.R.I. publishing group – Indian, LAP LAMBERT academic publishing/ 2023, 317 p.
4. Gubenko SI. Possibilities of transformation of non-metallic inclusions and interphase inclusion-matrix boundaries under high-energy treatments. Metal Physics. New Technologies, 2014, v. 36, No 3, pp. 287-315.
5. Gubenko S. Structural Effects near Nonmetallic Inclusions in Laser Treatment of Steels. Materials Science, 2000, v. 35, No 6, pp. 818-827.
6. Gubenko S.I. Zones of contact interaction in steel matrix near inclusions under the laser action. Materials Science, 2011, v. 46, No 4, pp. 448-452.
7. Gubenko S. Formation of Gradiental and Composite Zones Near Non-Metallic Inclusions Under Laser Treatment of Steels. Proceedings of the 9th International Congress «Mechanics, Technologies, Materials». 2012, Varna, Bulgaria, 2012, pp. 19-22.
8. Gubenko S. Melting and Crystallization of Nonmetallic Inclusions and Steel Matrix in the Course of Laser Treatment. Material Science. 2010, v. 46, No 3, pp. 365 – 371.
9. Bekrenev AN. Mass transport in metals under intensive impulse reactions. J. Phys. Chem. Solids. 2002, No 63, pp. 1627–1631.
10. Mazanko VF, Kozlov AV, Riasniy AV, Prokopenko GI, Piskun NA. The mass transfer in metals at ultrasonic treatment. Metallofiz. Noveishie Tekhnol. 2001, No 23, pp. 232–234.
11. Filatov A, Pogorelov A, Kropachev D, Dmitrichenko O. Dislocation mass-transfer and electrical phenomena in metals under pulsed laser influence. Defect Diffus 2015, No 363, pp. 173–177.
12. Mazanko VF, Mironov DV, Hertziiken DS, Bezv, VP. Influence of simultaneous action of an electric current and plastic deformation by compression on migration of atoms in copper and nickel. Metallofiz. Noveishie Tekhnol. 2007, v. 29, pp. 483–494.
13. Kuznetsov LI. Screening properties of the erosion torch and pressure oscillations at a laser—irradiated target. SPIE 1990, v. 1440, pp. 222-228.
14. Sano Y, Akita K, Sano T. A mechanism for inducing compressive residual stresses on a surface by laser peening without coating. Metals, 2020, No 10, pp. 816-822.
15. Gertsriken DS, Ignatenko AI, Mazanko VF, Mironova OA, Fal’chenko YV, Kharchenko GK. Determining the duration of mass transfer and the temperature of metal subjected to pulsed deformation. Phys. Met. Metallogr. 2005, v. 99, pp. 187–193.
16. Mazanko VF, Gertzriken DS, Bezv VP, Mironov VM, Mironova OA. Mass transfer under the shock compression in metal-defects systems with interlayer. Metallofiz. Noveishie Tekhnol. 2010, v. 32, pp. 1267–1275.
17. Vasil’ev LS. To the theory of the anomalously high diffusion rate in metals under shock action: I. Basic equations of diffusion mass transfer upon plastic deformation of materials. Phys. Met. Metallogr. 2009, v. 107, pp. 330–340.
18. Gubenko S. Specific features of stresses relaxation and recrystallization of steel under laser heating. Materials Science. 2023, v. 59, No 3, pp. 267-74.
19. Smirnov LI. Transport of interstitial atoms with an elastic wave in metals. Phys. Met. Metallogr. 2000, v. 89, pp. 327–31.
20. Ershov GS, Chernyakov VA. Structure and properties of liquid and solid metals. Moscow: Metallurgy, 1978, 165 p..
21. Gubenko S. Influence of non-metallic inclusions on the strengthening of steels under laser action. Material science. Non-equilibrium phase transformations. Varna, Bulgaria, 2015, No 3, pp. 18-24.

Radiation shields and their potential applications in space

Leszek Tomasz Pawlicki

Warsaw University of Technology, Faculty of Physics, Koszykowa 75, 00-662 Warsaw, Poland

ABSTRACT: *There is a mixture of different types of radiation in space. It includes both electrically charged particle radiation, electrically neutral particle radiation, and electromagnetic radiation. For this reason, building radiation shields for space equipment or vehicles is a challenge. This work presents old and new solutions for radiation shields that have potential for use in space, along with their advantages and disadvantages.*

KEY WORDS: RADIATION SHIELDS, MAGNETIC FIELD, NEUTRONS, ELECTRONS, POSITONS, NUCLEUS, IONS, GAMMA, ELECTROMAGNETIC SPECTRUM.

INTRODUCTION

Radiation shields are a crucial structural element in areas exposed to radiation. This applies to areas on the Earth's surface, beneath its surface, in the atmosphere, and in outer space. They are important not only for protecting living creatures (including humans) but also for protecting various types of equipment susceptible to radiation (including research equipment).

There are four categories of radiation important for safety: nucleus and ionic, beta, neutron and electromagnetic radiation.

Nucleus and ionic radiation is radiation composed of various types of atomic nucleus stripped completely or partially of their electrons. If they are completely stripped of their electrons, we refer to them as nucleus radiation. The most common type of such radiation is alpha radiation. This radiation is helium nucleus stream. In space, radiation composed of hydrogen nucleus is also important. When dealing with atomic nucleus containing a certain number of electrons, we refer to them as ionic radiation. Both types of radiation have similar properties. They are characterized by a relatively large mass of the radiation particles and a electric charge. Beta radiation is divided into two types. Beta minus radiation is radiation composed of electrons. This radiation has a negative electric charge. Beta plus radiation is radiation composed of electron antiparticles, i.e., positrons. This radiation has a positive charge. Both types of beta radiation contain particles much lighter than ions and atomic nuclei. This makes beta radiation much more penetrating than radiation from atomic nucleus and ions.

Neutron radiation, as its name suggests, consists of neutrons. Although neutrons have a mass similar to the hydrogen nucleus (proton), they lack an electric charge. This explains their weak interaction with matter and their high penetrating power. At the same time, their large mass allows neutrons to carry significant energy. This makes such radiation highly harmful.

Electromagnetic radiation is the alternating generation of electric and magnetic fields. We observe it as electromagnetic waves or particles called photons. These particles have no electric charge. The penetrating power and harmfulness of electromagnetic radiation strongly depend on its wavelength. For this reason, electromagnetic radiation is divided into several types: radio (above 30 cm), microwaves (from 1 mm to 30 cm), terahertz (from 100 μ m to 1 mm), infrared (from 780 nm to 100 μ m), visible (from 380 nm to 780 nm), ultraviolet (10 nm to 380 nm), X-rays (10 pm to 10 nm), and gamma rays (below 10 pm). Electromagnetic radiation interacts significantly with charged particles [1-4].

RADIATION SHIELDS

Shields against radiation from atomic nucleus, ions and beta

Atomic nucleus (including the helium nucleus – the alpha particle), ions, and beta particles are created during the radioactive decay of heavy elements, which constitute the components of many planets and other celestial bodies. They are also created during nuclear fusion in stars. Additionally, free ions and electrons can be created during lightning discharges (occurring both towards the surface of a celestial body and towards space) and in the outer atmospheres of many planets and moons under the influence of bombardment by cosmic rays of various types and origins.

Because radiation from atomic nuclei, ions, and beta-rays contains charged particles, the magnetic field around many planets provides a natural shield against this type of radiation. On the other hand,

perturbations in the magnetic field on the surface of stars can cause ejections of charged particles, increasing the intensity of this type of radiation in space.

To stop radiation from atomic nuclei, including alpha ions, and radiation from ions, a thin solid object, such as a sheet of paper, is usually sufficient. In space, shields based on aluminum or titanium are typically used. In this case, these shields prove fully effective, and no additional radiation shielding is required.

When it comes to beta radiation, a thin layer of metal is usually sufficient to absorb it. Here again, titanium and aluminum shields for space objects prove effective. However, the shield's effectiveness against beta radiation depends on the energy of the radiation. At low radiation energy, a metal shield fully fulfills its role. However, if we are dealing with high-energy beta radiation, X-rays may appear on the metal shield structure during its deceleration. Additionally, beta plus radiation consists of positrons. Positrons, reacting with electrons during annihilation, will convert into gamma photons. For this reason, in this case, additional X-ray and gamma radiation shielding must be installed beneath the metal shield [1-6].

Neutron radiation shields

Neutron radiation consists of neutrons produced during the radioactive decay of heavy elements and the nuclear fusion occurring in stars. Light elements, which contain negligible amounts of neutrons, have the greatest cross-section for neutron absorption. For this reason, hydrogen-rich compounds, such as various organic compounds, are used to protect against this type of radiation. Because neutrons are electrically neutral, and substances containing large amounts of hydrogen tend to be low-density, a thick layer of material is usually required to shield this radiation. This poses a problem in space. For equipment launched into space, it is important that the equipment be as light as possible and that as much of it as possible be useful, not only as radiation shielding. For this reason, it's worthwhile to use substances that are also useful for other purposes as radiation shielding against neutron radiation. If the equipment we're sending contains fuel (currently most often oxygen and hydrogen), it can be placed just beneath the metal outer shield. This will protect the interior of the object from neutrons and simultaneously provide propulsion. Similarly, if a spacecraft carries humans, it must carry the water they need for life. Placing this water in tanks in the vehicle's outer layer will provide radiation shielding without compromising its usefulness for sustaining life on board. High-energy neutron radiation can result in secondary gamma radiation, which also requires protection [1-6].

Shields against radio, microwave and terahertz radiation

Radio and terahertz radiation are usually harmless to living creatures, including humans. However, microwave radiation causes significant heat production in water due to the vibrations it induces (we utilize this phenomenon in microwave ovens). Because living creatures contain large amounts of water, exposure to microwave radiation can cause serious injury.

All three types of radiation described in this section can also cause uncontrolled electric currents to flow through the electronics of a spacecraft via Faraday induction, causing damage. Such radiation caused a global power outage in Canada in 1989. This radiation was secondarily generated by a coronal mass ejection from the Sun.

On Earth's surface, electric lines are distributed throughout the entire surface, so special fuses are required to protect them. Small electronics can be shielded using a Faraday cage, which is also used in space. This involves a Faraday cage. To be effective against various types of electromagnetic radiation, the Faraday cage is made as a solid metal box. A similar shielding solution for space vehicles is a conductive outer shield made of titanium or aluminum. It should be noted, however, that windows may not provide such protection. Therefore, a thin conductive coating can be applied to such windows, which can block the types of radiation mentioned here without significantly impairing visibility [1-5, 7-8].

Shields against infrared, visible and ultraviolet radiation.

In small amounts, infrared, visible, and ultraviolet radiation are usually harmless to both humans and equipment. However, infrared radiation heats the substance it hits. Excessive intensity can cause burns in humans, and overheating or melting in equipment. Visible and ultraviolet radiation can degrade certain substances, such as yellowing and embrittlement of some plastics, and can trigger the uncontrolled photoelectric effect (causing static electricity and possibly electrical current). Metal layers provide effective protection against these three types of radiation. They reflect most of this radiation (this phenomenon is exploited in the production of mirrors). However, it should be remembered that the ability to reflect electromagnetic radiation depends on the metal's characteristic plasma frequency, which is the characteristic frequency of an electromagnetic wave. If the wave has a frequency lower than the plasma frequency, it will reflect from the metal surface. If its frequency is higher than the plasma frequency, the wave will pass through the metal. At sufficiently high radiation frequencies, above the plasma frequency, the metal becomes transparent. For example, if a shield is made of brass, gold, or copper, such a shield may be ineffective against ultraviolet, blue, or green light. This is because their plasma frequency is in the visible light spectrum. This is where the color of non-ferrous metals comes from. To provide the broadest possible radiation protection, shields for space equipment and spacecraft should be made of silver metals (their plasma frequency is in the ultraviolet) with the highest possible plasma frequency, e.g., aluminum [1-5, 7-8].

X-ray and gamma radiation shields

Metals with the highest plasma frequencies have them in the ultraviolet range. Therefore, there are no substances that reflect X-rays or gamma rays. The attenuation of X-rays and gamma rays in materials occurs differently and is based on three physical phenomena: the Compton effect, the photoelectric effect, and the creation and annihilation of electron-positron pairs.

The Compton effect is the scattering of X-rays or gamma rays by free or weakly bound electrons in valence shells. This phenomenon changes the photon's momentum and the resulting electromagnetic wavelength. This phenomenon plays a dominant role in the attenuation of electromagnetic radiation with photon energies ranging from tens of keV to several MeV.

The photoelectric effect occurs when gamma radiation quanta incident on the atoms of a substance are absorbed by their electrons. As a result, the atoms undergo ionization. The energy required for this reduces the photon's energy, which usually also reduces its harmfulness. When such an electron recombines, the photon is emitted in a random direction, resulting in scattering of the radiation.

The creation of electron-positron pairs involves the creation of particles: an electron and a positron from a high-energy gamma photon, assisted by an atomic nucleus. Upon gamma radiation entering matter, creation occurs. The resulting electrons are decelerated, and the positrons annihilate back into a gamma photon with the electrons of the substance. This process results in the scattering of the gamma radiation.

X-ray and gamma radiation attenuation in a radiation shield is more effective the more electrons the atoms of the substance comprising it have, are more concentrated, and are more numerous. For this reason, passive X-ray and gamma radiation shields must be thick

and high-density. This causes such shields to be very massive. This poses a serious problem for space vehicles. Therefore, work is underway on active shields against this type of radiation that combine smaller mass with greater efficiency [1-5, 7, 9-10].

SUMMARY AND CONCLUSIONS

All the types of radiation mentioned in this paper are present in space. Aluminum-based metal shields are sufficient for protection against most types. However, X-rays and gamma rays, either present in space or generated by the braking of high-energy charged particles on our radiation shield, pose a problem. Therefore, an X-ray and gamma radiation shield must be placed beneath the metal shield. Due to the large mass of such shields and the difficulty of transporting them into space, work is currently underway to develop active (lighter) shields of this type. Placing a layer of water or fuel within or just beneath the shield structure will provide a radiation shield against neutron radiation [1-10].

REFERENCES

- [1] D. Holliday, R. Resnick, J. Walker, Podstawy Fizyki, Wydawnictwo naukowe PWN, Warszawa 2021
- [2] D. Griffiths, Podstawy elektrodynamiki, Wydawnictwo naukowe PWN, Warszawa 2020
- [3] E. Hecht, Optyka, Wydawnictwo naukowe PWN, Warszawa 2018
- [4] H. Karttunen, P. Kroger, H. Oja, M. Poutanen, K. J. Donner, Astronomia ogólna, Wydawnictwo Naukowe PWN, Warszawa 2020
- [5] Z. Ablewicz, Osłony przed promieniowaniem jonizującym, Wydawnictwo Arkady, Warszawa 1986
- [6] W. Heinrich, Cosmic rays and their interactions with the geomagnetic field and shielding material, Radiation Physicist and Chemistry v. 43, i. 1-2, pp. 19-34, 1994
- [7] F. Forstmann, R. R. Gerhardt, Metal optics near the plasma frequency, Advances in Solid State Physics v. 22, pp. 291-323, 2007
- [8] A. D. Chave, J. R. Booker, Electromagnetic induction studies, Reviews of Geophysicist v. 25, i. 5, pp. 989-1003, 1987
- [9] E. A. Amirabadi, M. Salimi, N. Ghal-Eh, G. R. Etaati, H. Asadi, Study of Neutron and Gamma Radiation Protective Shield, International Journal of Innovation and Applied Studies, v. 3, i. 4 pp. 1079-1085, 2013
- [10] K. W. Fornalski, Aktywna osłona przeciwradiacyjna, PL Patent P.234385, Warszawa, 2017

Features of structure formation and properties of cast titanium bronzes obtained using thermally synthesized powder ligatures

Bagliuk G.A., Voropaiev V.S., Fedoran Yu.O., Molyar O.H. *, Demydyk O.M.,
Sydorchuk O.M., Radchenko O.K.

I.M. Franchevich Institute for Problems of Material Science, NAS of Ukraine, Kyiv *
G. V. Kurdyumov Institute for Metal Physics of the NAS of Ukraine, Kyiv

Abstract: The study of the effect of heat treatment regimes on the structure and physical and mechanical properties of smelted titanium bronzes showed that after quenching castings from 800 °C, their structure of cast alloys has a significantly dendritic character and significantly lower hardness compared to the as-cast state. A significant increase in the level of hardness and strength of the alloys is achieved by aging at a temperature of 400 °C. The highest level of hardness and strength is characterized by the Cu – 2,7 % Ti alloy without aluminum. The dependence of the electrical conductivity of bronze additionally alloyed with 0,5 % Al and 3,0 % (wt.) Ni on the titanium content is extreme: the maximum conductivity (~33 % IACS) is observed for the alloy with 1,5 % (wt.) Ti. The alloying of titanium bronze (3 % Ti, 0,7 % Ni, 0,03 % B) and heat treatment of quenching at 900 °C, aging at 450 °C with isothermal holding for 0,5 h, contributed to an increase in the complex of physical and mechanical properties (tensile strength 870 MPa, yield strength 830 MPa, and hardness 106 HRB).

Copper-based alloys are widely used in the electrical and electronic industries, as well as in mechanical engineering, to manufacture various electrical wires and cables, transformer coils, breakaway and sliding electrical contacts, heat sink substrates for electrical appliances and computer equipment, electrodes for spot welding, etc. The wide range of their industrial use is due to the harmonious combination of high thermal and electrical conductivity, strength, ductility, and hardness [1-3]. A special place among copper-based alloys is occupied by high-strength copper alloys, among which the most commonly used are Cu-Be alloys, which are characterized by high mechanical and electrical characteristics [4-6]. However, the high cost of beryllium, as well as the high toxicity and harmfulness to the human body of beryllium vapors formed during the melting of Cu-Be alloy, limits its processing and wider industrial use [7]. As a result, research areas devoted to the development of copper alloys that can replace Cu-Be alloys and efficient technologies for their production have become extremely relevant. In recent years, alloys of the Cu-Ti system have been attracting more and more attention due to their increased mechanical strength, satisfactory electrical conductivity, relatively low cost, and environmental friendliness compared to Cu-Be alloys [7-10]. The problems that arise in the manufacture of titanium bronzes include the high affinity of titanium for oxygen, nitrogen, and hydrogen. This necessitates the protection of titanium metal when it is introduced into the copper melt during alloy smelting. In addition, there are certain difficulties in obtaining a homogeneous melt due to a significant difference in the density of copper and titanium (almost twofold) and the difference in melting points: 1089 °C for copper and 1668 °C for titanium. To overcome these problems, titanium bronzes are smelted using a number of complex technological operations that significantly complicate the process. In particular, the stirred casting method or the technology of triple melting of the alloy is used to increase the homogeneity of titanium distribution over the casting volume. At the same time, there are examples of successful application of powder metallurgy methods to produce titanium bronzes [11], which provide high homogeneity and dispersed structure of the alloy by sintering at relatively low temperatures compared to melting technologies.

Given the above, the aim of the study was to evaluate the possibilities of using powder metallurgy methods in the manufacture of cast titanium bronzes by using the scheme of alloying copper melt with powdered titanium-containing ligature.

Powders of titanium hydride TiH_2 ($\leq 63 \mu m$), obtained by hydrogenation of a titanium sponge, and electrolytic copper with a particle size of $63 \mu m$ were used as starting components for the synthesis of the titanium-containing ligature. The use of titanium hydride as a titanium component instead of commercial titanium powder is due to the fact that during sintering it provides a significant activation of diffusion processes due to the increased density of the hydride crystal lattice, as well as the possibility of additional cleaning of interfacial boundaries due to atomic hydrogen released during the decomposition of hydride. The cost-effectiveness of using TiH_2 is also due to its lower cost compared to standard titanium powders. The initial powder mixture required for the

synthesis of TiCu intermetallic in the required proportions was mixed in a ball mill. From the charge obtained by co-grinding, pressings were formed on a hydraulic press in the form of cylindrical briquettes with a diameter of 40 mm, the relative density of which was about 70% (to ensure the removal of hydrogen and water vapor formed during the decomposition of titanium hydride and the reduction of oxides on the surface of powders by hydrogen during sintering). The actual thermal synthesis of the titanium-containing ligature was carried out by sintering in a vacuum furnace at a temperature of 750-850 °C. The titanium-containing ligature briquettes obtained by thermal synthesis were introduced into the copper melt during the melting of the alloy in an induction furnace using argon as a protective atmosphere. The first stage involved heating the furnace to a temperature of 1200 °C and melting copper, followed by introducing the ligature and holding the melt at 1300 °C for 10 minutes. The resulting melt was poured into a cast iron ladle. Experimental melts for the smelting of titanium bronze ingots were carried out for three calculated compositions of bronzes: Cu – 2,7 % Ti; Cu – 2,7 % Ti – 0,5 % Al; Cu – 2,7 % Ti – 1,0 % Al.

The structure and microanalysis of the phase components of the obtained ligatures showed that as a result of thermal synthesis, Cu-Ti intermetallic grains of 20-60 μm in size are formed in the alloy, with the titanium content varying mainly from 20 to 60 %. No grains of pure titanium were found in the alloy structure. At the same time, the results of microanalysis in the formed intermetallic grains indicate that heterodiffusion of titanium and copper in the process of thermal synthesis is incomplete. According to the results of local microanalysis of the structure, the distribution of elements across the cross-section of most intermetallic grains is markedly gradient: the outer layers of the grains are enriched in copper, the concentration of which decreases along the depth of the grain cross-section, while their central zones are predominantly enriched in titanium. Similar results were reported in [11], where the effect of forming the layered nature of Ti-Cu intermetallic grains in the structure of sintered titanium bronze obtained by the SPS method from a mixture of copper and titanium powders was noted.

In further experiments, we used a ligature with a titanium content of 70 % (wt. %) and ligatures of the copper-titanium-aluminum system obtained by a similar thermal synthesis technology. As shown by the results of experimental melts, the structure of the obtained alloys is expected to consist of a copper matrix phase with evenly distributed inclusions of copper-titanium intermetallic grains with a size of 2-8 μm .

After quenching from 800 °C, the microstructure of the cast alloys is essentially dendritic. As shown by the results of the studies (Table 1), due to the fact that during quenching the excessive α' phase of Cu_4Ti does not have time to be released in sufficient quantities, the alloy consists mainly of a supersaturated solid solution and is marked by a significantly lower hardness compared to the as-cast state (without heat treatment) for all three studied alloys. At the same time, the highest level of hardness, both for the cast state and after quenching, is observed in the Cu – 2,7% Ti alloy without aluminum in its composition.

Table 1: Effect of heat treatment modes of cast materials on hardness

Content of alloying elements, % (wt.)	Hardness, HRB			
	Lithuania (without heat treatment)	Hardening 800 °C	Aging 400 °C*	Aging 400 °C**
2,7 Ti	86	42	72	86
2,7 Ti + 0,5 Al	75	32	72	84
2,7 Ti + 1,0 Al	80	33	70	84

* - isothermal exposure for 3 hours, ** - isothermal exposure for 5 hours

An aging operation is used to increase the hardness and strength of copper-titanium alloys after quenching. The influence of the aging regimes of cast alloys after quenching on their mechanical properties was studied by evaluating their hardness values after appropriate heat treatment. Aging at 400 °C of alloys previously quenched and increasing its duration from 3 to 5 hours leads to a significant (up to 2 times or more) increase in the level of hardness.

The mechanical properties of titanium bronzes after quenching and subsequent aging at 400 °C for 5 hours are shown in

Table 2. As can be seen from the table, similar to the hardness characteristics, the highest strength level is observed for the Cu – 2,7 % Ti alloy without aluminum with a sufficiently high level of ductility ($d = 26 \%$, $\Psi = 41 \%$). The introduction of 0,5 % aluminum into the alloy leads to a decrease in strength characteristics and a slight increase in ductility, while an increase in Al content to 1,0 % causes a more noticeable decrease in strength and a significant deterioration in ductility compared to the alloy without aluminum.

Table 2: Basic mechanical properties (at room temperature) of titanium bronze after quenching at 800 °C and aging at 400 °C for 5 hours

Content of alloying elements, % (wt.)	Tensile strength, MPa	Yield strength, MPa	Relative elongation, %	Relative narrowing, %
2,7 Ti	581	360	26	41
2,7 Ti + 0,5 Al	537	342	32	43
2,7 Ti + 1,0 Al	493	329	17	16

The work was continued with the smelting of titanium bronze ingots with the following chemical composition (% , wt.): 3 % Ti; 0,7 % Ni; 0,03 % B; the rest Cu. After extrusion (bar diameter 33 mm) and cold drawing (bar diameter 29 mm), samples of the studied alloy were quenched at a temperature of 900 °C with

an isothermal holding time of 1 hour and cooling in water. The results of microhardness (HV) are presented in Table 3. Subsequently, the aging of the studied alloy was carried out at different temperature conditions and isothermal aging (Table 4).

Table 3. Microhardness of bronze (3 % Ti, 0,7 % Ni, 0,03 % B)

Technological process	Bar diameter, mm	Microhardness, (center of the sample), HV	Microhardness, (at the edge of the sample), HV
Extrusion	33		250
Drawing	29		270
Hardening*	29		140

* - at 900 °C, isothermal exposure for 1 hour

Table 4. Mechanical properties (at room temperature) of bronze (3 % Ti, 0,7 % Ni, 0,03 % B)

Aging at temperature, °C	Isothermal exposure, hours	Hardness, (sample center), HRB	Hardness, (at the edge of the sample), HRB
425	0,25	103-104,5	101-103
	0,50	105-106	105-107
	0,75	105,5-106	104,5-107
	1,00	106-107	106,5-107
	1,25	105-106,5	106,5-107
	1,50	105,5-106	105,5-106
450	0,25	106-107	105-107
	0,50	105-106,5	106-107
	0,75	101-106	105-106,5
	1,00	105-106	105-106
	1,25	106-107	106,5-107
	1,50	105,5-106	104,5-106,5
475	0,25	103,5-107,5	105-106
	0,50	105,5-106	104-105,5
	0,75	104,5-105	104,5-105
	1,00	105	105
	1,25	104	103,5
	1,50	103-104	103-103,5

As a result of the experimental work, it was found that it is optimal to age bronze (3 % Ti, 0,7 % Ni, 0,03 % B) at a temperature of 450 °C with an isothermal holding time of 0,5 hour (Table 4), which increases the set of mechanical properties: tensile strength of 870 MPa, yield strength of 830 MPa, and hardness of 106 HRB.

Conclusions

1. According to the results of local microanalysis of the structure of the ligature thermally synthesized from a mixture of titanium hydride and copper powders, it was found that heterodiffusion of titanium and copper was incomplete during the thermal synthesis process. The distribution of elements across the cross-section of intermetallic grains is markedly gradient: the outer layers of the grains are enriched in copper, the concentration of which decreases with the depth of the grain cross-section, while their central zones are predominantly enriched in titanium.

2. The structure of the cast alloys obtained using powder ligatures consists of a copper matrix phase with evenly distributed inclusions of copper-titanium intermetallic grains of 2-8 μm in size. After quenching from 800 $^{\circ}\text{C}$, the microstructure of the cast alloys is essentially dendritic.

3. The highest level of hardness and strength is characterized by the Cu - 2.7 % Ti alloy without aluminum in its composition.

4. The dependence of the electrical conductivity of titanium bronze additionally alloyed with 0,5 % Al and 3,0 % (wt. %) Ni on the titanium content is extreme: the maximum conductivity (~ 33 % (IACS)) is observed for an alloy with 1,5 % (wt. %) Ti. A further increase in the Ti content in the alloy leads to a significant deterioration in electrical conductivity.

5. Alloying additives of 0,7 % nickel and 0,03 % boron in the chemical composition of titanium bronze (at 3 % Ti by weight), taking into account the optimization of heat treatment (quenching temperature 900 $^{\circ}\text{C}$, aging 450 $^{\circ}\text{C}$ with isothermal holding for 0,5 hours), contributed to an increase in the complex of physical and mechanical properties.

References

1. Mao Q., Liu Y., Zhao Y. A review on copper alloys with high strength and high electrical conductivity. *Journal of Alloys and Compounds*. 990, 174456 (2024).
<https://doi.org/10.1016/j.jallcom.2024.174456>
2. Kuo Ya., Wang Y., Guo M. et al. Recent development of advanced precipitation-strengthened Cu alloys with high strength and conductivity: A review. *Progress in Materials Science*, 138, 101141 (2023).
<https://doi.org/10.1016/j.pmatsci.2023.101141>
3. Morshed-Behbahani Kh., Aliyu A., Bishop D. P., Nasiri A. Additive manufacturing of copper-based alloys for high-temperature aerospace applications: A review. *Materials Today Communications*. 38, 108395 (2024).
<https://doi.org/10.1016/j.mtcomm.2024.108395>
4. Zhang W., Zhao Z., Fang J. et al. Evolution and strengthening mechanism of metastable precipitates in Cu-2.0 wt% Be alloy. *Journal of Alloys and Compounds*. 857, 157601 (2021).
<https://doi.org/10.1016/j.jallcom.2020.157601>
5. Huang X., Xie G., Liu X., Fu H. et al. The influence of precipitation transformation on Young's modulus and strengthening mechanism of a Cu-Be binary alloy. *Materials Science and Engineering: A*. 772, 138592 (2020).
<https://doi.org/10.1016/j.msea.2019.138592>
6. Zhang H., Jiang Y., Xie J. et al. Precipitation behavior, microstructure and properties of aged Cu-1.7 wt% Be alloy. *Journal of Alloys and Compounds*. 773: 1121-1130 (2019).
<https://doi.org/10.1016/j.jallcom.2018.09.296>
7. Okechukwu C. C., Edoziuno F. O., Adediran A. A. et al. Experimental and process modelling of chemical composition and thermal ageing of Ti-doped cast Cu-Ni alloy for microstructural, conductivity, and mechanical properties. *Journal of Alloys and Metallurgical Systems*. 9: 100141 (2025).
<https://doi.org/10.1016/j.jalmes.2024.100141>
8. Nagarjuna S, Srinivas M, Balasubramanian K, Sarma DS. Influence of polycrystalline grain size on yield and flow stress in Cu-1.5 wt% Ti alloy. *Scripta Metallurgica et Materialia*. 30 (12): 1593-1597 (1994).
[https://doi.org/10.1016/0956-716X\(94\)90314-X](https://doi.org/10.1016/0956-716X(94)90314-X)

9. Nagarjuna S, Srinivas M, Balasubramanian K, Sarma DS. On the variation of mechanical properties with solute content in Cu-Ti alloys. *Mater Sci Eng. A259*: 34-42 (1999).

[https://doi.org/10.1016/S0921-5093\(98\)00882-X](https://doi.org/10.1016/S0921-5093(98)00882-X)

10. Soffa W.A., Laughlin D.E. High-strength age hardening copper-titanium alloys: redivivus. *Progress in Materials Science*, 49 (3-4): 347-366 (2004).

[https://doi.org/10.1016/S0079-6425\(03\)00029-X](https://doi.org/10.1016/S0079-6425(03)00029-X)

11. Wang F., Li Y., Wakoh K. et al. Cu-Ti-C alloy with high strength and high electrical conductivity prepared by two-step ball-milling processes. *Materials and Design*. 61: 70-74 (2014).

<https://doi.org/10.1016/j.matdes.2014.04.034>

Изследване на изнosoустойчивост на наварени дуплексни стомани след повърхностна химико-термична обработка

Investigation of wear resistance of welded duplex steels after surface chemical-thermal treatment

инж. Чолаков Л.¹, гл. ас. д-р Янкова Р.¹, ас. инж. Стоянов П.¹

Технически Университет Варна, България¹,

lcholakov0782@gmail.com; radyankova@abv.bg; plamen_2002@abv.bg.

Abstract: Austenitic-ferritic stainless steels, better known as duplex steels, are increasingly important in modern engineering practice due to their unique complex resistance, providing high strength, good ductility, excellent corrosion resistance, as well as remarkable characteristics in aggressive environments. When duplex steels are operated in areas with increased friction, abrasion or mechanical wear, it is necessary to improve the wear resistance of the surface without compromising corrosion stability. This article presents the results of wear tests on duplex stainless steel 1.4410 (X2CrNiMoN25-7-4) in the untreated state and after surface improvement by hardfacing and subsequent nitriding. The nitriding process was carried out in both gas and ionic environments. The wear was carried out using the “pin-on-flat” method. It was found that under the applied wear conditions, the best wear resistance was recorded in the friction pair with the sample subjected to ion nitriding. This confirms the effectiveness of the chemical-thermal treatment in improving the wear resistance of the steel.

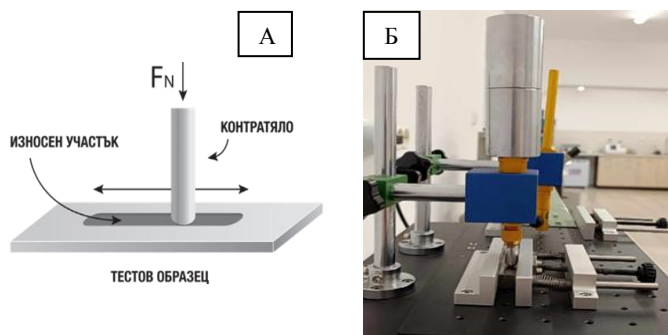
Keywords: DUPLEX STAINLESS STEEL, THERMOCHEMICAL TREATMENT, WEAR RESISTANCE, MICROSTRUCTURE, HARDNESS

1. Увод

В настоящата работа фокусът е поставен върху дуплексна стомана 1.4410 (X2CrNiMoN25-7-4), която е представител на високолегирани дуплексни стомани - Super Duplex Stainless Steel, UNS S32750/S32760) с типичен химичен състав: 25.8% Cr, 7.0% Ni, 3.8% Mo и 0.30% N, PREN индекс над 40, гарантиращ изключителна устойчивост на питингова и междукристална корозия дори в агресивни хлоридни среди. Механичните свойства включват граница на провлачване ≥ 550 МПа, якост на опън ~ 750 – 800 МПа и твърдост около 300 HV в отгрято състояние. Стомана 1.4410 се отличава с оптимално съотношение между аустенит и ферит, което води до балансиран механични характеристики и подобро поведение при заваряване. [1, 2]. Прилага се при агресивни условия и се характеризира повишени изисквания към контрол на топлинния вход и последваща обработка, за да се избегне образуване на нежелани фази. В зони с повишено триене, абразия или механично износване, възниква необходимост от подобряване на повърхностната изнosoустойчивост, без компромис в корозионната стабилност. Два основни подхода за подобрене на повърхностните свойства са механизираното наваряване с устойчиви на износване сплави и нискотемпературната химико-термична обработка, поспециално азотиране. При азотиране под 500°C в дуплексните стомани се формира специална метастабилна S-фаза – свръхнасищен аустенит с азот, която проявява твърдост, многократно по-висока от базовата структура. Твърдостта на S-фазата е съизмерима или дори надвишава тази на типичния нитриден слой, образуван при температури над 500°C , като същевременно се запазва устойчивостта на корозия – основно предимство при дуплексните материали. Тази повишена твърдост се дължи на азотна кластеризация и микропластични деформации в аустенитната фаза. Атомите на азота се внедряват в решетката на γ -фазата (аустенит) и предизвикват разширяване на FCC решетката. [3, 4, 5]. Въпреки това, малката дебелина на S-слоя създава предизвикателства при количествена оценка на ефекта върху износване при реални натоварвания.

Настоящата статия представя резултати от изпитване на износване на дуплексна неръждаема стомана 1.4410 (X2CrNiMoN25-7-4) в изходно (необработено) състояние и след подобрене в повърхностния слой, чрез наваряване и последващо азотиране. Наваряването е изпълнено чрез ръчно електродръгово напластяване (процес 111) с електроди подходящи за дуплексни стомани. Процесът на азотиране е проведен както в газова, така и в йонна среда при $T = 490^\circ\text{C}$ с продължителност 13ч. Износването е проведено по метод pin-on-flat, който позволява симулиране на сухо плъзгащо триене при постоянни параметри - нормална сила, скорост и

контактна геометрия. Използван е стенд за изпитване на износване Glomro BXT-MAR306, в режим на сухо триене – фиг.1. За да се оцени ефективността на допълнителните обработки на стомана 1.4410 в конкретни експлоатационни условия е използвана триеща двойка, в която контрпартялото е от идентичен материал в необработено състояние.

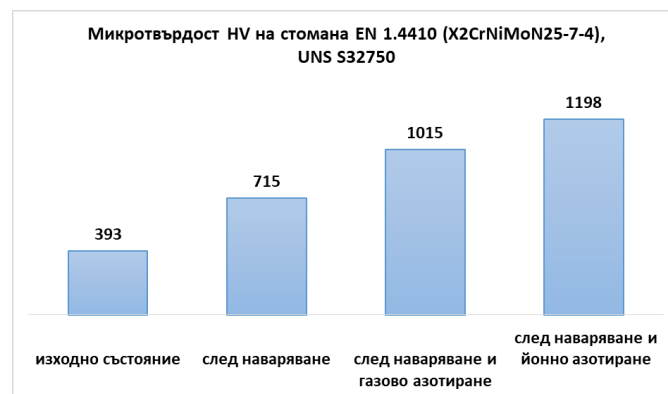


Фиг.1 Стенд за изпитване на износване

А) Принципова схема; Б) Стенд за износване Glomro BXT-MAR306

2. Резултати и дискусия

Отчетена е микротвърдост HV1 по повърхностния слой на пробните образци, при което е установено, че стойността се увеличава значително след допълнителните обработки-наваряване и азотиране – фиг.2.



Фиг.2 Микротвърдост HV на стомана EN 1.4410 (X2CrNiMoN25-7-4), UNS S32750 в изходно състояние и след наваряване и азотиране.

След процеса на електродъгово наваряване на изходния образец, микротвърдостта HV се повишава от 393HV до 715HV. При допълнителната химико-термична обработка, микротвърдостта достига до 1015HV при газовото азотиране и 1198HV при йонното азотиране. Това потвърждава модифицирането на аустенитната структура, чрез насищане с азот и формиране на S-фаза, която е ключов фактор за подобряване на твърдостта и износоустойчивостта на дуплексните стомани след азотиране.

В определени експлоатационни условия, триещата двойка се състои от материали с различна твърдост и коефициент на триене. При сухо плъзгане на метални повърхности коефициентът на триене и износването са свързани индиректно. По-висок коефициент на триене, обикновено означава по-голяма тангенциална сила и потенциал за по-голямо механично износване. [6, 7, 8]. След азотиране, стойността на коефициента на триене при super duplex stainless steel EN 1.4410 (UNS S32750) обикновено се намалява или стабилизира, благодарение на повишената твърдост и образуването на защитни слоеве. [9, 10]. При тестове на износване са използвани пробни образци с размери 80×20×12 mm, с идентична начална грапавост, потигната чрез шлифование. Образец 6 е подложен на допълнителна обработка електродъгово наваряване и последващо азотиране, в газова среда, а Образец 14 – на електродъгово наваряване и последващо йонно азотиране. Противотялото е изработено от еталонния материал стомана 1.4410 (X2CrNiMoN25-7-4) в изходно състояние. По време на теста за износване, полусферичното противотяло с диаметър 10 mm се натоварва с 1,0 kg и се плъзга по пробния образец с траектория от 60 mm и скорост 60mm/s. Извършени са три серия от 2 000 цикъла с общ път на износване S=360m. Изследвано е поведението на изходния образец в конкретните условия на трибологичното изпитване. Степента на износване се определя по тегловния метод, чрез използване на аналитична везна с точност до 0,0001 g., като противотялото се почиства, изсушава и претегля в началото и в края на всяка серия от изпитвания.

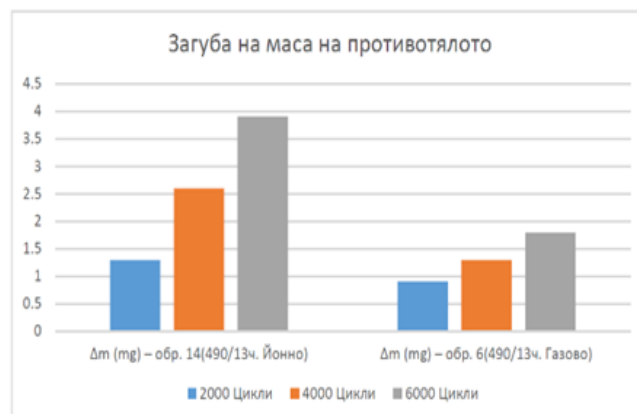
Таблица 1: Параметри на износване на противотяло от стомана 1.4410 (X2CrNiMoN25-7-4).

Брой Цикли	2000	4000	6000
Път на износване S, m	120	240	360
Противотяло с Образец 14			
Загуба на маса на противотяло Δm , mg	1.3	2.6	3.9
Загуба на обем на противотяло $\Delta V = \Delta m / \rho$, m ³	2E-10	3E-10	5E-10
Скорост на износване на противотяло $I = \Delta m / S$, mg/m	0.011	0.011	0.011
Противотяло с Образец 6			
Загуба на маса на противотяло Δm , mg	0.9	1.3	1.8
Загуба на обем на противотяло $\Delta V = \Delta m / \rho$, m ³	1E-10	2E-10	2.3E-10
Скорост на износване на противотяло $I = \Delta m / S$, mg/m	0.008	0.005	0.005

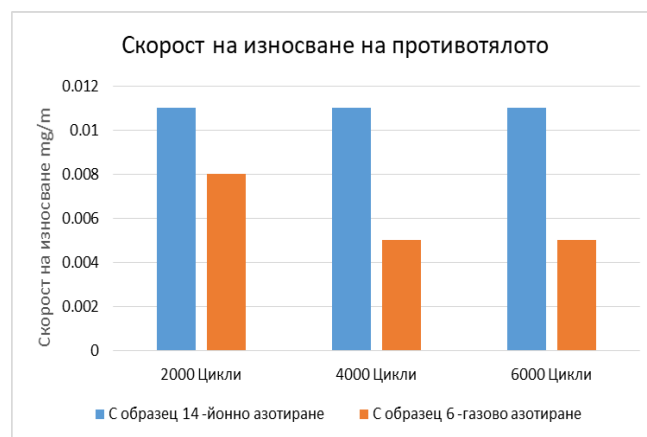
Промяната в масата на пробата след изпитване, позволява да се определи степента на износването. Определено е масовото износване Δm и обемното износване ΔV на противотялото. Получени са стойности за скорост на износване I , представляваща отношението между масовото износване и изминатия път на износване – Табл.1.

Установено е, че в приложените условия на износване най-голяма загуба на маса в противотялото, изработено от изходния материал се регистрира в триещата двойка с образца, подложен на йонно азотиране (Образец 14) и при трите режима на изпитване – фиг.3. Това потвърждава ефективността на химико-термичната обработка за подобряване на износоустойчивостта на стоманата. В триещата двойка с Образец 14 се наблюдава линейна зависимост между масовото износване и пътя на износване на противотялото, като при удвояване на пътя от 120 до 240 m, масовата загуба на противотялото също се удвоява от 1.3 mg до 2.6 mg. В триещата двойка с образец 6, загубата на маса на противотялото не расте пропорционално на пътя на износване. За първия режим с път на износване 120 m., се регистрира загуба на маса от 0.9 mg. При втория режим загубата нараства с 0.4 mg, а при третия режим – нараства с 0.5 mg. В противотялото се наблюдава типична трибологична крива с бързо начално износване и преход към равномерно износване с по-ниска скорост.

Скоростта на износване на противотялото се запазва в триещата двойка с Образец 14 и се понижава в триещата двойка с Образец 6 – фиг.4. За конкретните параметри на изпитване, износването е в стационарен етап, в който скоростта на износване става приблизително линейна, спрямо пътя на плъзгане.



Фиг.3 Загуба на маса Δm (mg) на противотялото в триеща двойка с азотирани образци.



Фиг.4 Скорост на износване I (mg/m) на противотялото в триеща двойка с азотирани образци.

Това е най-дългият и предсказуем етап, важен за експлоатационния живот на детайлите. За период от 6000 цикъла с път на износване 360m. не се наблюдава измерим износен отпечатък в образците с допълнителна обработка наваряване и азотиране, което показва значително по-високата им устойчивост на триене. Йонното азотиране ускорява дифузията на азот и формирането на плътен и устойчив слой (S фаза), който увеличава твърдостта по повърхността и повишава значително устойчивостта на адхезивно и абразивно износване. Високата твърдост на образеца с наваряване и йонно азотиране води до намаляване коефициента на триене. Това обуславя и значително по-високата степен на износване на противотялото в тази триеща двойка.

3. Заключение

- Проведените изпитвания потвърждават, че повърхностната обработка чрез азотиране, значително повишава твърдостта и износоустойчивостта на дуплексната неръждаема стомана 1.4410, особено при съчетаване с деформационно наваряване.
- Йонното азотиране осигурява по-висока твърдост на S-фазата и по-ниска интензивност на износване спрямо газовото, като същевременно запазва по-добре структурата в зоните, подложени на динамично триене. Режим на йонно азотиране при 490 °C за 13 часа на дуплексна стомана 1.4410 с дебелина 12 mm, осигурява добър баланс между твърдост и износоустойчивост.
- Високата твърдост на стомана 1.4410 след газово или йонно азотиране намалява коефициента на триене и води до значителна степен на износване в триеща двойка с изходния материал.
- Анализът предоставя насоки за приложението на дуплексни неръждаеми стомани в инженерни компоненти, критични за износването.

4. Литература

1. Yiqi Zhang, Shaojie Wu, Fangjie Cheng, A specially-designed super duplex stainless steel with balanced ferrite:austenite ratio fabricated via flux-cored wire arc additive manufacturing: Microstructure evolution, mechanical properties and corrosion resistance, Materials Science and Engineering: A, Volume 854, 2022,
2. Li, T.; Wang, K.; Lei, Y. A Review of Welding Process for UNS S32750 Super Duplex Stainless Steel. Materials 2024, 17, 5215.
3. Zhou, X., Dong, H., & Bell, T. "Study on the phase transformation in low temperature plasma nitrided 316 austenitic stainless steel". Materials Science and Engineering: A, Vol. 368, Issues 1–2, 2004, pp. 223–231.
4. Christiansen, T., & Somers, M. A. J. "Characterization of the low temperature surface hardened zone in stainless steel." Metallurgical and Materials Transactions A, 2006, 37(3), pp. 675–682.
5. Bell, T. "Surface engineering of austenitic stainless steel." Surface Engineering, 2002, Vol. 18, No. 6, pp. 415–422.
6. Liang XM, Xing YZ, Li LT, Yuan WK, Wang GF. An experimental study on the relation between friction force and real contact area. Sci Rep. 2021 Oct 13;11(1):20366.
7. S. Jahanmir, The relationship of tangential stress to wear particle formation mechanisms, Wear, Volume 103, Issue 3, 985, Pages 233-252, ISSN 0043-1648.
8. Lontin, K., Khan, M. Interdependence of friction, wear, and noise: A review. Friction 9, 1319–1345 (2021).
9. Rakhadilov, B.; Satbayeva, Z.; Maulit, A.; Kozhanova, R.; Kurmangaliyev, R.; Rustemov, A. Comprehensive Study of Electrolytic Plasma Nitriding of Austenitic Stainless Steels. Crystals 2025, 15, 456.
10. Carrera Espinoza, R.; Alvarez Vera, M.; Wettlaufer, M.; Kerl, M.; Barth, S.; Moreno Garibaldi, P.; Díaz Guillen, J.C.; Hernández García, H.M.; Muñoz Arroyo, R.; Ortega, J.A. Study on the Tribological Properties of DIN 16MnCr5 Steel after Duplex Gas-Nitriding and Pack Boriding. Materials 2024, 17, 3057.

Авторите изказват своята благодарност за подкрепата на научноизследователски проект ПД 15/2025, финансиран целево от държавния бюджет, в рамките на научноизследователската дейност на ТУ-Варна.

Изследване на влиянието на термична обработка върху стомана S355J2: Закаляване и последващ отпуск при различни температури Investigation of the Effect of Heat Treatment on S355J2 Steel: Quenching and Subsequent Tempering at Different Temperatures

инж. Людмил Чолаков, магистър, IWE/EWE, Римакем ЕООД, icholakov0782@gmail.com

Eng. Lyudmil Cholakov, MSc, IWE/EWE, Rimakem Ltd., icholakov0782@gmail.com

инж. Страцимир Димов, магистър, Римакем ЕООД, s.dimov1@mail.bg

Eng. Stratsimir Dimov, MSc, Rimakem Ltd., s.dimov1@mail.bg

Abstract

This study investigates the effect of tempering temperature on the microstructure and mechanical properties of low-carbon structural steel S355J2 after quenching. Commonly delivered in the normalized condition with a ferrite–pearlite microstructure, S355J2 was subjected to a heat treatment process consisting of full austenitization at approximately 880 °C, followed by water quenching and tempering at three different temperatures: 250 °C, 450 °C, and 600 °C. Four samples with dimensions of 22 × 22 × 85 mm were prepared—one in the as-received (untreated) condition and three heat-treated at the specified tempering temperatures.

The experimental methodology involved microstructural characterization via optical microscopy after standard metallographic preparation and Nital etching, Brinell hardness measurements, and Charpy-V notch impact testing. The tempering process is expected to result in a progressive transformation of the as-quenched martensitic structure into tempered martensite, troostite, or sorbite, depending on the applied temperature. Tempering at 250 °C is anticipated to reduce internal stresses while maintaining high hardness. At 450 °C, partial carbide precipitation is expected to improve the balance between strength and toughness. Tempering at 600 °C is likely to produce a sorbitic microstructure, offering enhanced impact toughness with a reduction in hardness.

The aim of this investigation is to evaluate the influence of tempering temperature on microstructural evolution, hardness, and impact resistance of quenched S355J2 steel. The results are intended to support the optimization of mechanical performance for dynamic or safety-critical applications by identifying the most suitable tempering conditions that balance strength and ductility.

Keywords

S355J2, heat treatment, tempering, quenching, hardness, microstructure, impact toughness, martensite, sorbite, structural steel.

I. Въведение

Стоманата S355J2 е нисковъглеродна конструкционна стомана с приблизително 0,20% C (макс. 0,22% по ladle анализ) и около 1,5% Mn, по стандарт EN 10025-2. Обикновено се доставя в нормализирано състояние (обозначение “+N”), при което има феритно-перлитна структура с твърдост около 150–190 HB. S355J2 притежава минимална граница на провлачване 355 МПа и добри свойства на ударна жилавост (27 J при -20°C). Ниското съдържание на въглерод и легиращи елементи (основно Mn) обуславя добра заваряемост, но сравнително ограничена прокаляемост. Това означава, че при обемно закаляване може да не се получи изцяло мартензитна структура в целия срез на детайли с по-голяма дебелина.

Аустенитизиране (температура на закаляване). За обемно закаляване S355J2 детайлът първо се нагрява до температура над критичната за образуване на аустенит (A_{c3}). Препоръчват се температури на аустенитизация в диапазона ~860 – 920°C. Обикновено оптималната температура е около 880–900°C, достатъчно над A_{c3} (~820°C за тази стомана) за да се получи еднороден дребнозърнест аустенит. Задържането на тази температура е ~30–60

мин (често ~0,5–1 час за детайл ~30 mm) – достатъчно време, за да се изравни температурата в целия обем и да се разтворят карбидните фази. Прегряването над 920°C не е желателно, тъй като води до излишно нарастване на аустенитното зърно и понижена ударна жилавост след закаляване. След темпериране на зададената температура, детайлът се изважда за последващо охлаждане (закаляване).[1,2,3,]

II. Теоретична част

Охлаждащи среди и скорост на охлаждане

- **Вода:** основна среда за закаляване на S355 при масивни детайли. Осигурява необходимата скорост за избягване на феритно/перлитно превръщане. При ~30 mm сечение гарантира дълбочинно прокаляване чрез бързо преминаване през критичния температурен интервал (~600–300°C). Въпреки риска от напрежения и деформации, ниското съдържание на C ($\leq 0,22\%$) намалява опасността от пукнатини.
- **Масло:** по-слабо охлаждащо от водата. Подходящо при нужда от равномерно охлаждане и по-нисък риск от деформации.

При ~30 mm сечение може да е гранично – сърцевината може да не се охлади достатъчно за формиране на мартензит.

- **Въздух** не позволява формиране на мартензит в S355J2. Прилага се само при нормализационно отгряване.
- **Скорост на охлаждане:** За формиране на мартензит, стоманата трябва бързо да премине под Ms (~400°C). S355J2 има умерена прокаляемост поради ~1,3–1,6% Mn, но изисква висока критична скорост. Водното охлаждане от ~880–950°C формира основно иглест мартензит с малко бейнит – особено в по-бавно охлаждащата се сърцевина. При маслен закал, делът на бейнит и ферит е по-голям поради по-бавното охлаждане.[4,5,6]

Прокаляемост и очаквана структура

S355J2 има ограничена прокаляемост – при дебелина ~30 mm се формира градиент на структурата:

- **Повърхност (~5–10 mm):** Бързо охлаждане води до почти изцяло мартензитна структура. Твърдостта достига ~360–400 HV (~35–40 HRC), спрямо ~160 HB в нормализирано състояние.
- **Преходна зона (~10–20 mm):** Смесена мартензитно-бейнитна структура. Mn (~1,5%) подпомага образуване на долен бейнит.

- **Сърцевина (~15 mm):** Най-бавно охлаждане. Вероятна структура – долен бейнит с включвания от ферит/перлит. Дори при водна закалка не се гарантира пълен мартензит в сърцевината.

След закаляване материалът е твърд, но крехък. Затова се препоръчва нискотемпературно отвярщане (200–300°C) за редуциране на напреженията с минимална загуба на твърдост. Ако е необходим баланс между твърдост и жилавост, по-добро е среднотемпературно отвярщане (450–600°C), което възстановява жилавостта.

Закалено и отвярнато състояние: ReH до 550–700 MPa и Rm до 800–1000 MPa (спрямо 355 MPa ReH в нормализирано състояние), т.е. якостта нараства с 50–60%, при умерена загуба на пластичност.[7,8,9]

Типични структури:

- **Преди термична обработка:** феритно-перлитна структура (~20–30% перлит, ~150–180 HB), често с лентовидност.
- **След закаляване:** аустенитът се трансформира в мартензит (твърда, иглеста структура).
- **След отвярщане (~450°C):** получава се отпуснат мартензит (троостит/сорбит) – феритна матрица с дисперсни карбиди. Структурата се стабилизира, твърдостта достига ~280 HB, а механичните свойства значително се подобряват. [1,2,3,4,5,6]

Таблица 1: Препоръчителни параметри на закаляване и отвярщане за S355J2 (дебелина 30 mm)

Етап на обработка	Температура (°C)	Време на задържане	Охлаждане	Очаквана твърдост / Микроструктура
Аустенитизация (за закаляване)	860–900	30–60 мин	Вода или масло (бързо)	360–400 HV (~35–40 HRC); мартензит + малко бейнит
Отвярщане – нискотемпературно	200–300	~1 час	Въздух	Запазена висока твърдост; частично намалени напрежения; ниска жилавост
Отвярщане – среднотемпературно	450–500	1–2 часа	Въздух	250–300 HV; temperиран мартензит/троостит; добър баланс твърдост–жилавост
Отвярщане – високотемпературно	550–600	1–2 часа	Въздух	200–240 HV; сорбитна структура; отлична жилавост, по-ниска твърдост

III. Методика на експеримента

- **Материал и проби**
За експеримента са използвани 5 пробни тела, изрязани от S355J2 по EN 10025-2, с размери 22×22×85 mm. Материалът е

доставен в нормализирано състояние (+N), с типична феритно-перлитна структура и твърдост ~160 HB.

C	Si	Mn	P	S	N	Cu	Cr	Ni	Mo
0.017	0.19	1.48	0.025	0.004	0.011	0.05	0.04	0.02	0.041

Таблица 2. Химичен състав и механични свойства на S355J2 в

нормализирано състояние.

Reh N/mm ²	Rm N/mm ²	A %	KV	KV1-40° J	KV2-40° J	KV3-40° J	Ceq
385	506	26	157	170	141	160	0.39



Фиг. 1. Заготовки от стомана S355J2 преди различни режими на термична обработка

• Термична обработка

Една от пробите е оставена в изходно състояние (контролна), а останалите четири са подложени на обемно закаляване. Процесът включва нагряване до ~900°C с изотермично задържане от 60 минути и последващо охлаждане във вода при стайна температура.

След закаляването, трите образеца са подложени на отвърщане при следните режими:

- Проба 1: 200°C / 1 час
- Проба 2: 400°C / 1 час
- Проба 3: 600°C / 1 час

Отвърщането е извършено с последващо охлаждане на въздух.

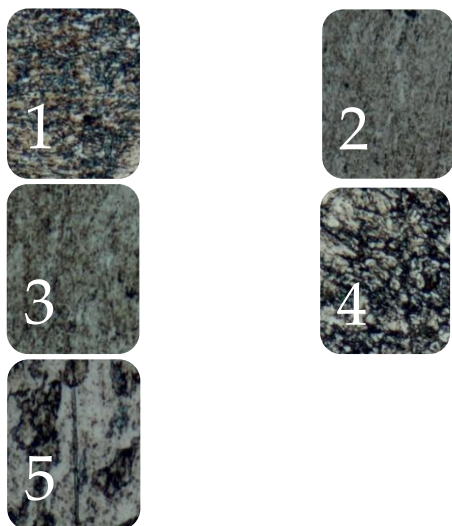
Методи на изпитване: След термичната обработка са извършени:

- **Металографски анализ:** Изготвени са микрошлифове от напречно сечение на всички образци (вкл. изходен). След шлифване и полиране, структурите са ецвани с 3% разтвор на HNO₃ и наблюдавани под оптичен микроскоп при увеличения 200x, 500x и 800x
- **Измерване на твърдост:** Извършени са измервания по метода Рокуел (HRC) на всяка от обработените повърхности.
- **Изпитване на ударна жилавост:** Всички обработени образци са подложени на изпитване по Charpy-V,
- **Цел на експеримента**
Целта е да се изследва влиянието на трите температурни режима на отвърщане върху микроструктурата и твърдостта на стомана S355J2 след обемно закаляване. Сравнява се ефектът на всеки

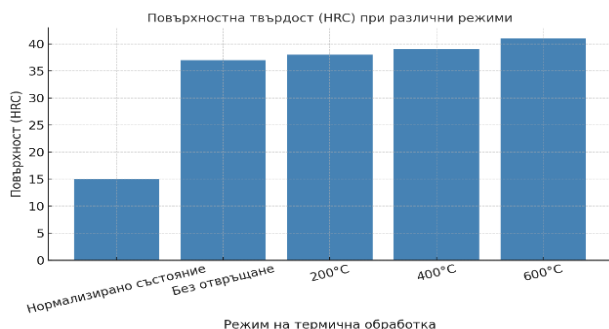
режим спрямо изходното състояние, с акцент върху стабилизацията на структурата и постигане на баланс между твърдост и пластичност.

IV: Резултати и анализ.

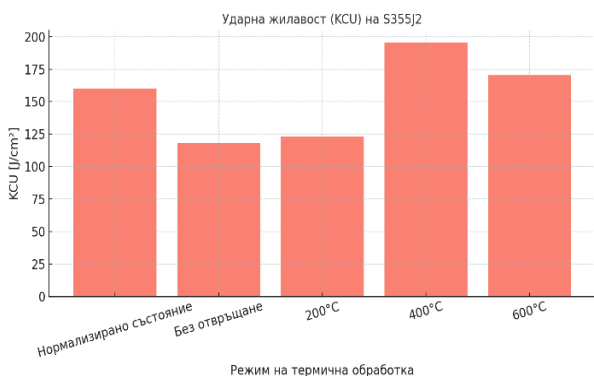
- Проведеният комплексен анализ на стомана S355J2 след обемно закаляване и отвърщане при различни температури разкрива ясно изразена корелация между приложените термични режими, формираната микроструктура и получените механични свойства.
- В изходно състояние материалът демонстрира типична феритно–перлитна структура с лентовидна морфология, характерна за нормализирани нисковъглеродни стомани. Началната твърдост е приблизително 160 HB, с висока пластичност, но ограничени якостни показатели.
- След аустенитизация при ~900°C и бързо охлаждане във вода, микроструктурата в повърхностните слоеве се трансформира в иглест мартензит, което води до значително повишаване на твърдостта (до 41 HRC). В преходната зона и сърцевината се регистрира наличие на бейнит и остатъчен ферит поради намалената скорост на охлаждане, съответстваща на типичните ограничения в прокаляемостта на S355J2.
- Отвърщането при 200°C води до формиране на отпуснат мартензит с частично разсеяни карбиди и частична релаксация на вътрешните напрежения. Твърдостта остава висока (~38 HRC), докато ударната жилавост достига 123,1 J/cm².
- При отвърщане на 400°C се наблюдава структура от темпериран мартензит (троостит), характеризираща се с хомогенна феритна матрица и фино диспергирани карбиди. Това състояние осигурява оптимален баланс между твърдост (~28 HRC) и жилавост (195,3 J/cm²), като показва най-добра комбинация от якост и пластичност.
- Отвърщането при 600°C индуцира сорбитна структура с изразена сфероидализация на карбидната фаза, водеща до значително подобрена пластичност и жилавост (170,4 J/cm²), но съпроводена с редуция на твърдостта (~150–165 HB).



Фиг.2 Микроструктури на стомана S355J2 при различни режими на термична обработка, (1)-закаляване + отвярщане при 200°C, (2) при 400°C и (3) при 600°C, (4) закаляване без отвярщане и (5) нормализирано състояние.



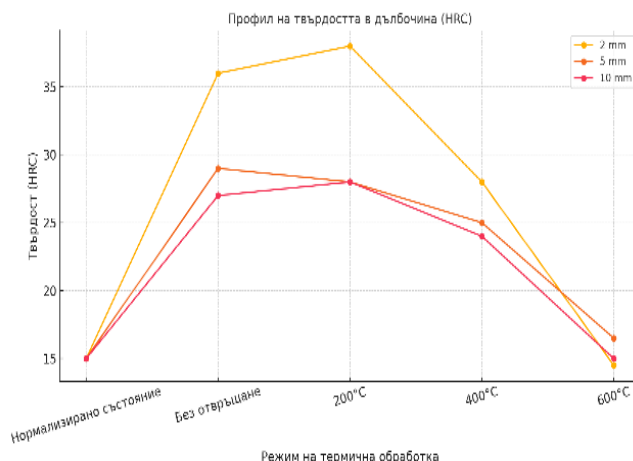
Фиг. 3. Повърхностна твърдост (HRC) на S355J2 при различни режим на термична обработка



Фиг. 4. Ударна жилавост (KCU) на стомана S355J2 при различни режим на термична обработка.

VII. ЛИТЕРАТУРА

1. EN 10025-2:2019. Hot rolled products of structural steels – Part 2: Technical delivery conditions for non-alloy structural steels.
2. ASM Handbook, Volume 4: Heat Treating. ASM International, 1991.



Фиг. 5. Профил на твърдостта в дълбочина на стомана S355J2 при различни режим на термична обработка

V Изводи:

- Термичната обработка на стомана S355J2 оказва съществено влияние върху микроструктурната морфология и съответните механични характеристики.
- Аустенитизацията при 900°C и последващото охлаждане във вода водят до формиране на повърхностен мартензит и структуриран градиент в дълбочина, включващ бейнит и ферит.
- Отвярщането при 200°C частично редуцира вътрешните напрежения, запазвайки висока твърдост, но с умерено възстановяване на жилавостта.
- Отвярщането при 400°C се отличава като най-ефективен термичен режим, осигуряващ оптимално съотношение якост–пластичност чрез формиране на стабилизирана трооститна микроструктура.
- Температури на отвярщане от 600°C благоприятстват сорбитизацията и пластичното поведение, но с цената на понижена твърдост, което ограничава приложението при високо натоварване.

VI. БЛАГОДАРНОСТИ:

Авторите изказват своята благодарност за подкрепата на научноизследователски проект НП 10/2025, финансиран целево от държавния бюджет, в рамките на научноизследователската дейност на ТУ-Варна.

3. Callister, W.D., Rethwisch, D.G. *Materials Science and Engineering: An Introduction*. 9th Ed., Wiley, 2014.
4. Totten, G.E. *Steel Heat Treatment: Metallurgy and Technologies*. CRC Press, 2006.
5. Kubaschewski, O., Hopkins, B.E. *Metallurgical Thermochemistry*. Pergamon Press, 1982.
6. Górka, J., *Effect of heat treatment on the structure and mechanical properties of S355 steel*, Journal of Achievements in Materials and Manufacturing Engineering, 2016.
7. Bains, A.S., Rajput, S., *Influence of tempering temperature on impact toughness and hardness of quenched low-carbon steel*, Materials Today: Proceedings, 2020.
8. Лекционен курс: *Металознание и термична обработка на металите*. Технически университет – Варна, катедра МТМ, 2022.

Regeneration of filter elements for cleaning hydrocarbon compounds from powdered polyethylene particles

Aliaksandr Ilyushchanka ^{1, 2}, Iryna Charniak ², Aliaksei Kusin ², Anastasia Astapenka ², Ruslan Kusin ², Margaryta Kuntsevich ², Ilya Buhtoyarov ³

State research and production powder metallurgy association – Minsk, Republic of Belarus ¹

State Scientific Institution “O.V. Roman Powder Metallurgy Institute” – Minsk, Republic of Belarus ²

A limited liability company «INNO» – Ramenskoye, Russia ³

E-mail: alexil@mail.belpak.by, irinacharniak@tut.by, 2312444@mail.ru, anasnasy2012@gmail.com, 19081877@mail.ru, kunczkvich@gmail.com, bic@innoo.ru

Abstract: The article presents information on the regeneration of filter elements (filter components) made of tin-phosphorus bronze powders that were tested during polyethylene production in the unloading unit of the ethylene polymerization reactor for cleaning hydrocarbon compounds from polyethylene powder particles. It was found that during the testing period, the filter elements met the requirements specified in the equipment regulatory documents. After completing the tests, two thermal regeneration cycles were carried out: at LLC “Stavrolen” and at O.V. Roman Powder Metallurgy Institute. It was found that in the first case, the filter element throughput was restored to 67.5% of the initial value, and in the second case, to 97.2%, which indicates the multiple regeneration possibility of spent powder filter elements when used to clean hydrocarbon compounds from polyethylene powder particles.

KEYWORDS: FILTER POWDER ELEMENTS, HYDROCARBON COMPOUNDS, SEPARATION OF POLYETHYLENE PARTICLES, THERMAL REGENERATION OF FILTER ELEMENTS.

1. Introduction

Polyethylene is the most mass plastic in packaging material production. It refers to the oldest polymers and remains today indispensable for the production of special films, bags, containers, cans etc. [1, 2]. Polyethylene production is inextricably linked to the negative impact on the environment. Generation of toxic waste, sewage pollution and gaseous emissions accompany the technological process of production at all stages. Polyethylene producers, like all petrochemical industry enterprises, carry out environmental management in three main areas: protection of water resources; protection of atmospheric air; waste management [3].

Among the enterprises producing polyethylene in Russia, one of the leading companies is LLC «Stavrolen», a member of «LUKOIL» group and the second largest producer of low-pressure polyethylene in Russia [4, 5]. One of the technological challenges related to the protection of ambient air is the purification of the hydrocarbon compounds flow from the powdered polyethylene particles in the discharge unit of the polyethylene polymerization reactor. The problem is currently being solved at the plant with PSS-type metal-ceramic filter elements manufactured by Pall Fuels and Chemicals from corrosion resistant steel. It is of interest to test the use of less costly tin-phosphorus bronze filter elements for this purpose, while exploring the possibility of regenerating contaminated filter elements for reuse.

In relation to the cleaning process under consideration, the most appropriate is the use of thermal regeneration of contaminated filter elements, which is associated with heating (calcination). It serves mainly to remove organic contaminants and is possible in the case where the filter element has sufficient thermal stability [6, 7]. Its effectiveness is evidenced by the results given in patents [8, 9], obtained during the regeneration of filter elements contaminated with synthetic resins. The quality of regeneration can be assessed by changes in a number of operational indicators of the product [6], in the case under consideration it is preferable to assess it by the throughput capacity restoration.

The purpose of the work is to study the possibility of regenerating powder filter elements after their use for cleaning hydrocarbon compounds from powdered polyethylene particles.

2. Materials and research methods

To carry out the research, the Engineering Center «INNO», Ramenskoye (Russia) has designed and manufactured 16 experimental long-dimensional tubular filter elements, which have been awarded the label F-M-CSZ-72-68-10 INNO by the developer. The filter elements were obtained by rolling sintered

porous plates of 3 mm thickness from tin-phosphorus bronze powder of the BrO10F1 brand, produced by O.V. Roman Powder Metallurgy Institute, Minsk (Belarus). The pilot filter elements were installed in the “Polymerization of Ethylene” workshop of LLC “Stavrolen” in the discharge unit of the ethylene polymerization reactor to replace the standard filter elements type PSS at the plant of LLC «Stavrolen». The tests were carried out for two months, during which the rate of gas pressure relief was monitored monthly (produced through the gas discharge unit: the pressure peak at injection was 1900-2100 kPa, the time of the pressure value rise from the initial (87-137 kPa) to the maximum value in all cases was 1 min), during which the time period of the drop from the maximum pressure to the initial value was monitored. According to the technology regulations, the time of pressure relief should not exceed 2 minutes, which corresponds to the good throughput capacity of the material of the filter elements. At the same time as diagnosing the throughput on the operability of filter elements, the pressure relief procedure actually ensures their regeneration without the equipment disassembling.

After the completion of production tests, two stages of thermal regeneration were carried out under different processing conditions: in the «Polymerization of Ethylene» workshop of the LLC «Stavrolen» and in the experimental production of O.V. Roman Powder Metallurgy Institute; After each regeneration, the product permeability factors were investigated to determine the regeneration degree.

3. The results of experiment and their discussion

The filter elements tests for cleaning hydrocarbon compounds from powdered polyethylene particles were carried out between 12.01.2023 and 07.03.2023. In accordance with the factory program tests once a month (13.01.2025, 10.02.2025, 06.03.2025) carried out above-described monitoring of gas pressure drop rate. During the monitoring process, the time of release never exceeded 2 minutes and was in an interval of 1.55-2.0 minutes, which indicates a good throughput of the filter elements material throughout the test cycle. This led to the conclusion that the developed filter elements of F-M-CSZ-72-68-10 INNO type are not inferior in performance to products of PSS type produced by Pall Fuels and Chemicals.

After the production tests completion, filter elements type F-M-CSZ-72-68-10 INNO were removed from the ethylene polymerization reactor discharge unit and subjected to thermal regeneration. Figure 1 shows the removal of the cap with filter elements mounted on it from the working capacity.



Fig. 1. Filter elements removal from reactor discharge unit

As noted above, thermal regeneration of filter elements was carried out in two stages: the first stage was carried out in the «Polymerization of Ethylene» workshop of the LLC «Stavrolen», the second - on a pilot production of O.V. Roman Powder Metallurgy Institute. After each step, the product permeability coefficients were determined in order to assess the degree of regeneration. Details of heat treatment regimes and research results are given in Table 1.

Table 1: Heat treatment regimes and results.

Place of heat treatment	Processing modes			Permeability coefficient, $\text{m}^2 \times 10^{13}$	Regeneration degree, %
	Temperature, °C	Time, min	Atmosphere		
LLC «Stavrolen»	450	60	Air	101,3	67,5
O. V. Roman Powder Metallurgy Institute	700	60	Dissociated ammonia	145,9	97,2

* - the regeneration rate was defined as the ratio of the filter element permeability after regeneration to the filter element permeability before testing

As can be seen from the data in Table 1, studies of the heat treatment process have established that after the first stage of regeneration the filter cell capacity was restored to 67.5% compared to the original, in the second - to 97.2%. The data obtained indicate the possibility of spent powder filter elements multiple regeneration when used to clean hydrocarbon compounds from polyethylene powders.

After the first heat treatment phase, there was a change in colour (darkening) of the filter elements due to the material contact with the air. After the second stage of heat treatment, the original color was restored by using a restorative atmosphere (dissociated ammonia). Deformations and integrity of filter elements as a result of heat treatment not detected at any stage.

At the same time, at the end of the tests, a crack was observed in the circumferential zone of three filter elements ($\approx 19\%$). The presence of these defects is due to high pressure surges during gas pressure relief operations and load cycles. In order to eliminate the occurrence of such defects, it is necessary to adjust the modes of welding and to tighten the method of strength tests when checking with 100% products coverage.

4. Conclusion

Information on the efficiency and regeneration of filter elements of powder tin-phosphorus bronze, tested during polyethylene production in the discharge unit of the ethylene polymerization reactor for the purification of hydrocarbon compounds from powdered particles of polyethylene. It was established that the filter elements had a good flow rate throughout the test period and met the requirements set out in the regulatory documents for equipment. After completion of the tests, two cycles of thermal regeneration were carried out: in the conditions of LLC «Stavrolen» and in the conditions of O. V. Roman Powder Metallurgy Institute. In the first case, the capacity of the filter elements was restored to 67.5% from the original, in the second - to 97.2%. This shows the possibility of multiple regeneration of spent powder filter elements when used to clean hydrocarbon compounds from polyethylene powders.

It was also established that after the first stage of heat treatment, a change in color (darkening) of the filter elements was observed as a result of product material contact with air. After the second stage of heat treatment, the original color was restored by using a reducing atmosphere (dissociated ammonia). Deformations and damage to the integrity of the filter elements as a result of heat treatment were not detected at any of the stages.

When using structures associated with the presence of welded seams on the working surfaces of filter materials, increased requirements should be imposed on the strength tests of the manufactured products, taking into account of their operation features.

5. Reference

- 1 A.Y. Melnikov. Optimization of the technological process of polyethylene production. Science journal. **5 (50)**. I. 5. (2022). pp. 273–279.
- 2 J.L. White, D.D. Choi. *Polyethylene, polypropylene and other polyolefins*. Transl. from eng. edited by E. S. Zobkallo. (Saint-Petersburg, Profession). (2006).
- 3 Melentjeva E. N., Rumyantseva A. V. Environmental aspects of polyethylene production. Text: electronic. System of management of ecological safety: collection of works of the XVIII international scientific-practical conference (Yekaterinburg, 23-24 May 2024). Yekaterinburg, UffU. (2024). pp. 123-128.
- 4 A.A. Akutov, Formation of a strategic management system for the development of the Russian polyethylene market. Journal of Monetary Economics and Management. **9**, (2024). pp. 135-141.
- 5 S.I. Samodelkin, A. Anisimov. Competitiveness of russian polyethylene manufacturers using benchmarking analysis. Journal of economics, law and sociology. **2**. (2025). pp. 111-119.
- 6 P.A. Vityaz, V.M. Kaptsevich, R.A. Kusin. *Filter materials: properties, application fields, manufacturing technology*. (Minsk, SSU PM with PP). (1999).
- 7 A. Ph. Ilyushchanka, R.A. Kusin, Zakreyski I.V., Yakimovich N.N., Charniak I. N., Kusin A.R., Zhehdryn D.I. *Powder filter materials: structure and property management and agricultural applications* (Minsk, BSATU). (2018).
- 8 A.S. 668695 USSR. Method of metallic regeneration porous filters from polymer contaminants. P.A. Vityaz [et al.]. Discoveries. Inventions. (1979). Bulletin. No 23.
- 9 A. a. 1163887, USSR. Method of titanium filter regeneration. L.M. Ekstas [et al.]. Discoveries. Inventions. (1985). Bull. No 24.

Densification and formation of structure and properties of Inconel 625 alloy during direct powder forging

Tolochyn O. I., Bagliuk G. A., Kyryliuk S. F., Tolochyna O. V., Kyryliuk Y. S., Danylenko V. I.
Frantsevich Institute for Problems of Materials Science National Academy of Science of Ukraine
E-mail: gbag@ukr.net

Abstract: This study investigates the compaction and deformation behavior of Inconel 625 powder using direct powder forging at temperatures of 950 °C and 1150 °C. Finite element modeling was conducted and validated with experimental data. The residual porosity after deformation was 6.5% at 950 °C and 2% at 1150 °C. Samples forged at 1150 °C demonstrated superior mechanical properties, including a bending strength of 1750 MPa and fracture toughness of 42 MPa·m^{1/2}. In contrast, lower temperature deformation resulted in poorer grain boundary quality and reduced mechanical performance. Post-deformation annealing at 950 °C enhanced microstructural integrity through recrystallization, improving strength to 1540 MPa and toughness to 30.9 MPa·m^{1/2}. Flow stress at 700 °C ranged from 450 to 650 MPa, confirming the material's suitability for high-temperature aerospace applications. The findings indicate that 1150 °C is the optimal forging temperature for producing dense, high-strength components from Inconel 625 powder.

Keywords : DIRECT POWDER FORGING, DENSIFICATION, MODELLING, INCONEL 625, STRUCTURE

1. Introduction

One of the most important components of aircraft is the power unit—turbine or engine—whose performance is determined by the elements of hot section structures: turbine blades, disks, nozzles, and other parts that withstand enormous thermal and mechanical loads. Based on the tasks assigned to UAVs, the turbine (engine) design aims to minimize its weight and dimensions [1–3]. The selection of optimal heat-resistant materials should ensure the maximum possible temperature in the combustion chamber to achieve the highest thermal efficiency (minimum fuel consumption per unit weight).

Ni-Cr based alloys are widely used in aircraft engines, offering a combination of relative affordability and efficiency. Examples include various modifications of Inconel alloys [4–6]. However, in the cast state, these alloys tend to develop dendritic structures and segregation zones. The production of heat-resistant structural elements typically involves casting-deformation technologies. Given the challenges of post-processing finished products (achieving the required shape and dimensions), manufacturing proves to be quite lengthy and costly. To overcome this drawback, recent studies have proposed using additive manufacturing (AM) to produce components in the required shape by 3D printing [7, 8]. Yet, even in this case, significant post-processing is required to achieve the necessary structure and properties [9]. Furthermore, additive technologies are characterized by low productivity. Among various powder metallurgy methods, those based on hot pressure processing are gaining traction, as, unlike free sintering, they avoid residual porosity [10 – 13]. Methods of dynamic hot deformation allow, under optimal technological conditions, the production of highly dense samples with a homogeneous fine-grained structure at relatively low temperatures [14, 15].

An alternative to AM technology is being developed at the Frantsevich Institute for Problems of Materials Science National Academy of Science of Ukraine—a powder technology known as DPF (Direct Powder Forging) [16–18], where the desired product shape is formed at the stage of cold and hot deformation of powders, and the required final structure is achieved by optimal thermomechanical treatment.

The aim of this work is to model the distribution of flow deformation characteristics and porosity changes during hot powder forging, with the development of thermomechanical processing regimes for Inconel 625 powder alloy to achieve an optimal set of mechanical properties over a wide temperature range.

2. Materials and experimental procedure

Spherical Inconel 625-type alloy powder was produced by plasma rotating electrode process (PREP). The sprayed powder, in the required amount, was poured into a cylindrical steel container, followed by hermetic pressing at 450 MPa (Fig. 1). Forging of prepared samples in containers with the heat-resistant powder alloy was carried out on an FB1732 a screw press with a force of 1.6 MN and a kinetic energy of moving parts at the end of the acceleration stroke of at least 6.18 kJ. The ram speed during densification was 0.35 m/min. A semi-closed die with an upper flash was used for forging. Forging of Inconel 625-type alloy powder was performed at temperatures of 950 and 1150 °C. Heating was carried out by immersing the sample in a furnace preheated to the required temperature with argon atmosphere and holding at this temperature for 20 minutes. After forging, cone-shaped samples with a flash of 42 mm diameter and 10 mm height were obtained (Fig. 1). Some samples underwent thermal treatment after deformation—annealing at 1030 °C with a holding time of 60 minutes, followed by rapid cooling.



Fig. 1. Steel container with Inconel 625 powder before and after processing by the DPF scheme.

Sample density was determined by the hydrostatic method, and electrical resistivity was measured by voltage drop on the experimental and reference samples. The material structure and fracture surface were examined using a JEOL Superprobe-733 scanning electron microscope. Bending strength and fracture toughness were measured at room temperature at a loading rate of 1 mm/min using a CERAMTEST SYSTEM testing machine on samples of 25×5×5 mm with a support span of 20 mm. To assess fracture toughness, notches were made on samples using an electric discharge wire with a diameter of 0.1 mm. Compressive strength was measured on samples of 5×3×3 mm at temperatures of 20 and 700 °C using a UTM-100 universal testing machine.

The continuum rheological approach to analyzing the flow process of a porous body allows significant simplification of the computational base and provides a reliable overview of the

deformation process, taking into account the influence of technological parameters. The development of a technological scheme for hot forging involves analyzing the evolution of stress, strain, and porosity distribution throughout the deformed billet. Calculations were carried out using modern computer software packages—DEFORM 2D/3D. The container used in the modeling was made of steel 15 (DIN-C15). The physical and mechanical properties of the container material and the heat-resistant Inconel 625 alloy were provided by the DEFORM 2D/3D database. To clarify the uneven distribution of porosity throughout the billet, computer simulation of the densification process for the initial billet was performed. The resulting porosity distribution was then used in the primary calculations.

3. Results and discussion

Figure 2 presents calculated dependencies of deformation force on the displacement of the moving part of the tooling for two forging temperatures. As shown in [18], regardless of the chosen scheme and deformation temperature, the densification process of the powder body can be divided into three stages (Fig. 2).

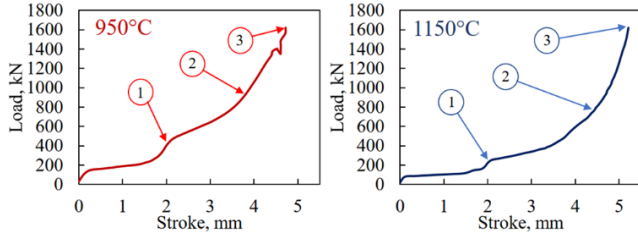


Fig. 2. Calculated loading force curves as a function of the displacement of the moving part of the tooling during die closure at temperatures of 950 and 1150 °C.

At the first (initial) stage of deformation, as the loading system moves, the main force is absorbed by the die case. The loading force required at this stage for compaction of the billet depends on the deformation temperature, primarily due to differences in the high-temperature properties of the die case material. Notably, the contribution of the porous billet to the overall deformation stress at this stage is insignificant: the change in porosity during the first stage at both forging temperatures does not exceed 5% (Figs. 2 and 3, position 1).

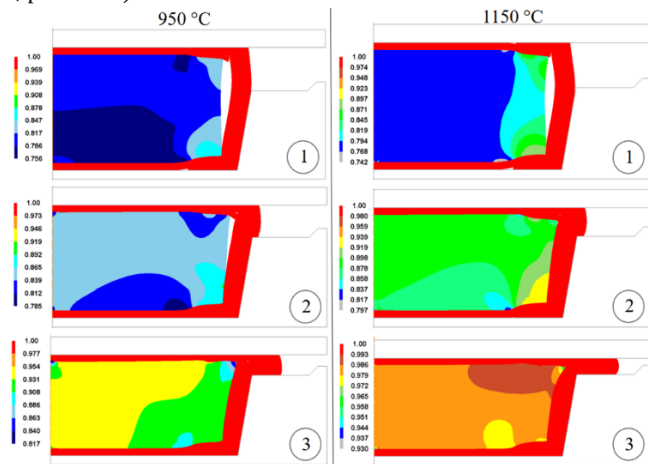


Fig. 3. Calculated distribution of relative density in the Inconel 625 powder sample during deformation at temperatures of 950 and 1150 °C.

The second stage is the densification of the porous billet. In Fig. 2, its onset is marked by a stress jump. The duration of this stage

can be calculated assuming that further reduction in the stamping volume occurs solely due to a decrease in the billet's porosity. Since the flow stress of the heat-resistant alloy significantly depends on temperature, accounting for the compaction rate of the powder body and depending on the applied stress, the porosity values at the end of the second stage, according to the densification curve, differ substantially—16% and 10% at deformation temperatures of 950 °C and 1150 °C, respectively (Figs. 2 and 3, position 2).

The third (final) stage essentially represents final densification, which occurs simultaneously with flash formation, sharply accelerating the increase in stress depending on the ram displacement. At the third stage, the stress sharply rises up to the moment when the maximum load of 1650 kN is reached. The calculated final porosity of the sample forged at 950 °C is 7%, while for the sample forged at 1150 °C it is 2%, which is in good agreement with the experimental values (Table 1). The porosity distribution across the section at the last stage (Fig. 3, position 3) indicates that by the end of the third stage, the sample deformed at 1150 °C is practically free of porosity. This is confirmed by the microstructures in Fig. 4. The sample deformed at 950 °C shows noticeable non-uniformity of porosity across the cross section. In the peripheral area of the sample (closer to the die case), porosity remains at about 10% (Fig. 3, position 3). The residual porosity is mainly concentrated in the regions of triple junctions of the primary spherical powder particles (Fig. 4). The spherical pores, as a rule, end with planar defects of considerable length (Fig. 4), which can significantly affect the ultimate low-temperature strength due to the increase in the size of the critical defect leading to fracture.

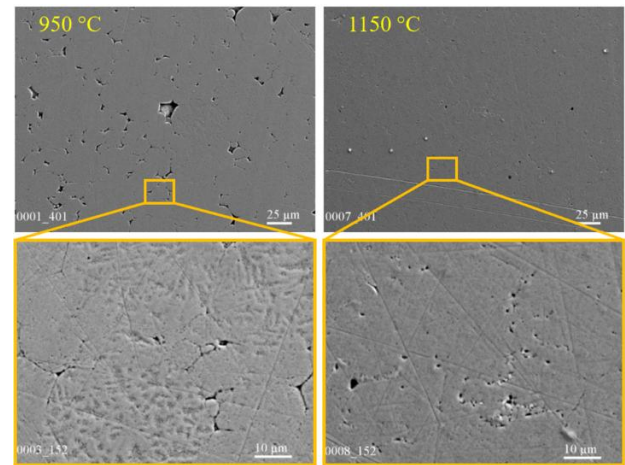


Fig. 4. Structure of Inconel 625 powder alloy after deformation processing at temperatures of 950 and 1150 °C.

The theoretical calculation performed enables evaluation of the total deformation of the sample, which mainly occurs due to the change in porosity and the formation of flash. A simplified version of this calculation was proposed in our work [18], where the Skorokhod formula [19] was used for deformation analysis:

$$\epsilon = \frac{4}{3} \left(\theta_{\text{int}}^{\frac{1}{2}} - \theta_{\text{fin}}^{\frac{1}{2}} \right); \quad (1)$$

where θ_{int} θ_{fin} is initial and final porosity, respectively.

However, this approach does not take into account the distribution of stresses and strains, which can be accounted for using the DEFORM 2D/3D software package.

At the end of the third deformation stage, the sample forged at 950 °C attains a maximum true strain (strain intensity) of 0.3, while after forging at 1150 °C it reaches 0.55 (Fig. 5).

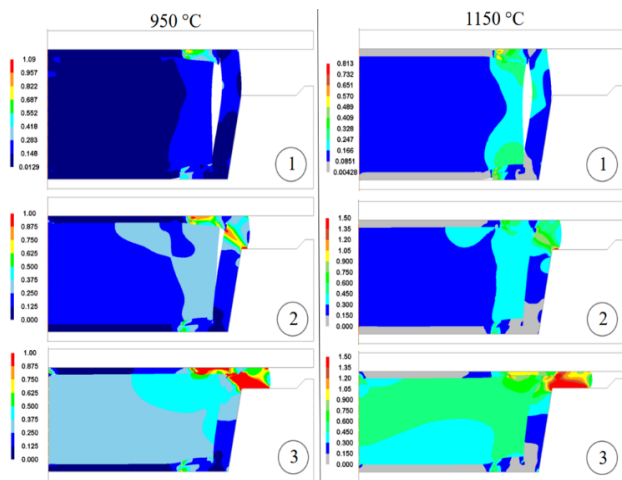


Fig. 5. Calculated distribution of relative density in the Inconel 625 powder sample during deformation at temperatures of 950 and 1150 °C.

The physical and mechanical properties of the forged samples of the heat-resistant Inconel 625 alloy, presented in Table 1, are determined by structural changes that occurred in the powder material during deformation. The electrical resistivity of the sample forged at 950 °C is somewhat higher due to greater residual porosity and the presence of slit-shaped pores. These structural defects have the most significant effect on the low-temperature strength under bending tests. The bending strength of the sample after forging at 950 °C is 310 MPa, and after densification at 1150 °C it reaches 1750 MPa, which is close to the strength of cast Inconel 625 alloy. The low strength of the sample deformed at 950 °C is associated with high residual porosity and the large size of critical defects. However, even with a large artificially introduced crack (fracture toughness tests), the sample forged at the lower temperature fails at lower loads ($K_{Ic} = 8$ and 42 MPa·m^{1/2}, respectively, for 950 and 1150 °C), since after low-temperature forging, the samples have lower strength of interparticle contacts, which illustrates the interparticle nature of the fracture, Fig. 6. The fracture toughness of the sample forged at 1150 °C approaches the properties of cast analogs; however, the fracture surface shows a mixed mode—intergranular with signs of dimple fracture, Fig. 6.

Table 1. Physical and mechanical properties of Inconel 625 powder alloy after DPF and heat treatment.

Temperature		Porosity, %	Electrical resistivity, $\mu\Omega \cdot \text{cm}$	Bending strength, MPa	Yield strength (0.2), MPa	Fracture toughness, MPa m ^{1/2}
DPF	Heat treatment					
950	—	6.5	149	310	—	8
	1030 °C	5.2	139	1540	1200	30.9
1150	—	1.9	135	1735	1070	42.4
	1030 °C	1.1	135	1750	1035	59.2

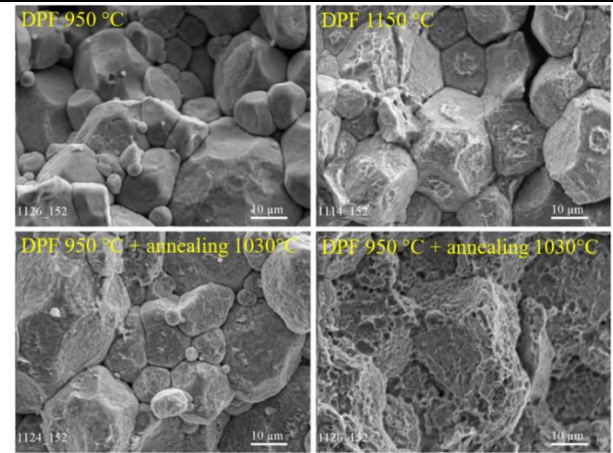


Fig. 6. Fracture surface of Inconel 625 powder alloy produced by DPF at 950 °C and 1150 °C, as well as after annealing at 1030 °C.

Annealing at 1030 °C with rapid cooling slightly increases the grain size in the samples, which results in a decrease in yield strength; however, fracture toughness noticeably improves due to enhanced contact quality between particles and recrystallization of the prior powder boundaries (PPB). Thus, the experiment demonstrated that the optimal hot deformation temperature for Inconel 625 is 1150 °C, where the samples have low porosity and high mechanical properties comparable to cast analogs.

As a result of additional annealing, the precipitation of dispersed particles occurs, which positively affects the heat resistance. As shown in Table 2, annealing led to an increase in compressive yield strength at both room temperature and the test temperature of 700 °C. The yield stress at this temperature, reaching 450 MPa, indicates the potential of this manufacturing method for producing Inconel 625 parts intended for high-temperature applications in the aerospace industry.

Table 2. Yield strength of Inconel 625 alloy after deformation processing and annealing.

Temperature, °C			Yield strength, MPa	
test	forging	annealing	$\sigma_{0.01}$	$\sigma_{0.2}$
20	950	—	748	967
	1150	—	432	525
	1150	1030	459	585
700	950	—	510	638
	1150	—	385	449
	1150	1030	467	516

4. Conclusions

The compaction behavior during deformation of Inconel 625 powder was modeled at temperatures of 950 °C and 1150 °C. The simulation results were confirmed by experimental data. The residual porosity after deformation was 6.5% at 950 °C and 2% at 1150 °C. The proposed deformation scheme for powder compacts based on direct powder forging proved to be effective: the material deformed at 1150 °C exhibited high strength (1750 MPa) and fracture toughness (42 MPa·m^{1/2}). Deformation at 950 °C did not provide sufficient grain boundary quality, resulting in lower mechanical properties. However, annealing reduced the porosity of samples deformed at the lower temperature and improved grain boundary quality through recrystallization of prior powder boundaries. As a result, the strength increased to 1540 MPa and

fracture toughness to $30.9 \text{ MPa} \cdot \text{m}^{1/2}$. The flow stress at the test temperature of 700°C ranged from 450 to 650 MPa, indicating the potential of this processing method for manufacturing Inconel 625 parts intended for high-temperature aerospace applications.

Thus, the conducted experiments demonstrated that the optimal hot deformation temperature for Inconel 625 is 1150°C , at which samples exhibit low porosity and high mechanical properties comparable to those of cast counterparts.

5. Acknowledgements

The present work was financially supported by the National Research Foundation of Ukraine under Grant No. 2025.06/0096, "Development of an innovative thermomechanical processing technology for powders for the production of hot-section components of turbojet engines."

6. References

1. Large, J., & Pesyridis, A. (2019). Investigation of micro gas turbine systems for high speed long loiter tactical unmanned air systems. *Aerospace*, 6(5), 55.
2. Dutczak, J. (2016, September). Micro turbine engines for drones propulsion. In *IOP Conference Series: Materials Science and Engineering* (Vol. 148, No. 1, p. 012063). IOP Publishing.
3. Çoban, S., & Oktay, T. (2018). Unmanned aerial vehicles (UAVs) according to engine type. *Journal of aviation*, 2(2), 177-184.
4. Wee, S., Do, J., Kim, K., Lee, C., Seok, C., Choi, B. G., Kim, W. (2020). Review on mechanical thermal properties of superalloys and thermal barrier coating used in gas turbines. *Applied Sciences*, 10(16), 5476.
5. Cunningham, C. S., Ransom, D., Wilkes, J., Bishop, J., White, B. (2015, June). Mechanical design features of a small gas turbine for power generation in unmanned aerial vehicles. In *Turbo Expo: Power for Land, Sea, and Air* (Vol. 56796, p. V008T23A021). American Society of Mechanical Engineers.
6. Kommel, L. (2017). Microstructure and properties characterization of polycrystalline Ni-Fe-Cr-based superalloy EP-718E after electric upsetting. *Key Engineering Materials*, 721, 467-472.
7. Radhika, C., Shanmugam, R., Ramoni, M., Gnanavel, B. K. (2024). A review on additive manufacturing for aerospace application. *Materials Research Express*, 11(2), 022001.
8. Waugh, I., Moore, E., Greig, A., Macfarlane, J., & Dick-Cleland, W. (2021, March). Additive manufacture of rocket engine combustion chambers using the Abd R-900Am nickel superalloy. In *SP2020 Virtual Conf* (pp. 17-19).
9. Ojo, O. O., & Taban, E. (2023). Post-processing treatments–microstructure–performance interrelationship of metal additive manufactured aerospace alloys: a review. *Materials science and technology*, 39(1), 1-41.
10. Brooks, J. W. (2000). Forging of superalloys. *Materials & design*, 21(4), 297-303.
11. Park, N. K., Kim, I. S., Na, Y. S., & Yeom, J. T. (2001). Hot forging of a nickel-base superalloy. *Journal of Materials Processing Technology*, 111(1-3), 98-102.
12. Laptev, A. V., Tolochin, A. I., Kovalchenko, M. S., Evich, Y. I., & Okun', I. Y. (2016). Structure and properties of Ni3Al intermetallic under vacuum impact sintering. *Powder Metallurgy and Metal Ceramics*, 54(9), 554-567.
13. Tolochyna, O., Tolochyn, O., Bagliuk, G., Podrezov, Y., Zgalat-Lozynskyy, O., & Okun, I. (2023). Effect of Heating Rate and Hot Forging Temperature on Phase Formation and Complex Physical and Mechanical Properties of Powdered Iron Aluminide: Tolochyna, Tolochyn, Bagliuk, Podrezov, Zgalat-Lozynskyy, and Okun. *JOM*, 75(3), 825-836.
14. Pérez, M., Dumont, C., Nodin, O., & Nouveau, S. (2018). Impact of forging direction on the recrystallization behaviour of nickel base superalloy AD730 billet material at subsolvus temperatures. *Materials Characterization*, 146, 169-181.
15. Alabort, E., Reed, R. C., & Barba, D. (2018). Combined modelling and miniaturised characterisation of high-temperature forging in a nickel-based superalloy. *Materials & Design*, 160, 683-697.
16. Tolochyn, O. I., Tolochyna, O. V., Podrezov, Y. M., Danylenko, V. I., & Bagliuk, G. A. (2025). The Role of Deformation Conditions and Mo-Doping on the Evolution of Structure and Mechanical Properties of Powdered Iron Aluminide. *JOM*, 1-14.
17. Tolochyn, O., Tolochyna, O., Bagliuk, G., Yevych, Y., Danylenko, V., & Podrezov, Y. (2024). Mechanical behavior of powdered iron aluminide Fe–28Al manufactured by direct powder forging. *Intermetallics*, 175, 108537.
18. Tolochyn, O., Kyrlyuk, S., Bagliuk, G., Podrezov, Y., & Tolochyna, O. (2025). Multilevel analysis of deformation and structure formation processes in powdered iron aluminide products obtained by different technological schemes of direct powder forging. *International Journal of Material Forming*, 18(1), 1-14.
19. Skorokhod, V. V. (1972). Rheological basis of the theory of sintering. *Naukova Dumka, Kiev*, 146 p. (in Russian)

Anatase or Rutile TiO₂ Nanolayer Formation on Ti Substrates by Laser Radiation: Mechanical and Photocatalytic Properties

Arturs Medvids¹, Aleksandrs Michko¹, Aleksejs Jakimovichs¹, Iuriy Naseka²
 Riga Technical University, Paula Valdena 3/7, Riga LV 1048, Latvia¹. E-mail: medvids@latnet.lv
 Institute of Semiconductor Physics, Academy of Science Ukrainian, Kiiv Pr.Nauky 158, Ukraine²

Abstract: A laser-induced oxidation method for the formation of a TiO₂ layer on a Ti substrate was used. The TiO₂ phase can be controlled by an Nd:YAG laser with fundamental frequency at an intensity $I = 52.8 \text{ MW/cm}^2$ and three different doses. Dose $D1 = 3.1 \times 10^{20} \text{ phot/cm}^2$ forms a TiO₂ layer in the anatase phase, which possesses the highest photocatalytic, antibacterial and adhesion properties. As the laser dose increases, the TiO₂ layer thickness increases from 40 nm to 100 nm, but the photocatalytic decomposition reaction constant decreases. The observed super-linear increase of the TiO₂ layer thickness with the laser dose is explained by the presence of positive feedback during the irradiation process. The temperature rises with increasing of the thickness due to the interference-caused decrease of the reflection coefficient. As the thickness increases, TiO₂ on Ti structure adhesion decreases from 800 mN to 400 mN due to the formation of a layer with a mixture of phases.

KEYWORDS: TiO₂ ON TI, RUTILE, ANATASE, LASER RADIATION, PHOTOCATALYSIS, HARDNESS

1. Introduction

Titanium (Ti) and its alloys boast excellent properties, including high corrosion resistance and an optimal balance of strength and ductility.

In particular, titanium dioxide in the form of powder or thin coatings has attracted attention in space applications due to its high chemical and radiation resistance, ability to protect surfaces from corrosion and ionizing radiation, as well as photocatalytic properties that can reduce contamination accumulation and improve the durability of materials in outer space conditions [1, 2]. Recently, their use has also been extended to biomedical applications, such as implants, due to their low allergenicity and high compatibility with bone tissue [3, 4]. Titanium (Ti) is coated with a layer of titanium dioxide (TiO₂), and its alloys are increased in corrosion resistance and biocompatibility. Photocatalytic activity is provided, and the material's radiation resistance is increased, which is especially important for use in space conditions [5 - 8]. TiO₂ has various polymorphic phases, including rutile, anatase, and brookite. On the macroscopic scale, rutile is thermodynamically more stable than the other two phases due to its smaller Gibbs free energy [9]. Moreover, an anatase layer on a Ti implant improves its compatibility with bone [5, 6, 10]. Furthermore, anatase and composites of anatase + rutile and anatase + brookite exhibit high levels of photocatalytic activity [11, 12]. Thermal oxidation in a gas atmosphere is a simple and economical method to synthesize a TiO₂ layer on Ti. TiO₂ layers synthesized by thermal oxidation adhere well to Ti substrates. In addition, thermal oxidation can be used for Ti substrates with complex geometries. Many reports have examined the formation of the rutile phase by thermal oxidation of Ti [13].

The anatase phase of TiO₂ is preferable for use in medicine owing to its antibacterial property [3-8]. Additionally, it is the preferred phase for photocatalytic processes such as hydrogen generation at water dissolution [14] and organic molecules disrupting in water or air [15]. On the other hand, TiO₂ in the rutile phase is preferable for use in optoelectronics devices such as UV photodetectors [16] and UV light sources [17]. Such strong application-dependent preferences are due to the different physical properties. First, the band structure is phase dependent. A TiO₂ crystal is an indirect semiconductor in the anatase phase, but it is a direct one in the rutile phase [18]. Therefore, the absorption coefficient of a TiO₂ crystal in the anatase phase is somewhat lower than that in the rutile phase in the range of 3 to 5 eV [19]. Second, the electron lifetime in the anatase phase of a TiO₂ crystal is 100-times higher than that in the rutile phase, which leads to different chemical and biological activities. For example, the anatase phase has better photocatalytic properties than the rutile one. Specifically, the anatase phase has a 100-times larger bipolar diffusion length [18], [20]. Due to the long

lifetime of electrons in the anatase phase (greater than 1 μs), the electron diffusion reaches lengths of more than 10 μm , which are much longer than those in the rutile phase (100 nm) [20].

Claus Hammerl et al. [21] and Elver Juan De Dios Mitma Pillaca et al. [22] used high-fluence oxygen ion implantation to demonstrate the formation of a TiO₂ layer consisting of α -, β -, δ -TiO, rutile TiO₂, and Ti₃O₅ on a Ti substrate. Unfortunately, these methods do not form the anatase phase. Moreover, they cannot control the anatase/rutile phase ratio, which is a very important parameter for photocatalysis, environment purification, etc. To date, laser technology is not often employed in such fine processes as the phase transformation from rutile to anatase [23] or color center formation [24]. One exception is a study where the fourth harmonic of Nd:YAG laser was used for formation of black TiO₂ after irradiating a TiO₂ suspended solution [25]. The XRD patterns suggest that the anatase phase of TiO₂ tends to transform into the rutile phase under a relatively high dose of laser radiation because the rutile phase is more stable at high temperatures and high pressures induced by pulsed laser irradiation. However, an opposite result, where the rutile phase transforms into the anatase one when irradiating a TiO₂ single crystal by a femtosecond Ti cor laser under ablation condition, was reported in [26]. Crystals smaller than 50 nm tend to be in the anatase phase, whereas those larger than 50 nm tend to be in the rutile phase. This phenomenon can be explained by the high pressure produced by a femtosecond laser pulse, although theoretical calculations [9] indicate that the anatase phase is more stable at low pressure. Very often CO₂ laser radiation is used for annealing after TiO₂ layer deposition by the sol-gel method [27] or electron beam evaporation at 200 °C on glass [28]. In these cases, laser radiation is similar to annealing in a furnace. In paper [29], spherical TiO₂ nanoparticles with diameters 4–35 nm were formed by pulsed laser ($\lambda = 1064 \text{ nm}$) ablation of Ti target in water. An advantage of this method is a narrow range of size distribution of nanoparticles, but a disadvantage is their conglomeration. In paper [30], the possibility to transform white TiO₂ to black TiO₂ nanoparticles using Nd:YAG laser radiation ($\lambda = 532 \text{ nm}$) in water was shown. At the same time, the phase transformation from anatase to rutile takes place. Therefore, such a TiO₂ powder can be used in optoelectronics, but, as a photocatalytic, it exhibits low activity [18, 19] due to the decrease of optical band gap and lifetime of electron-hole pairs. Advantages of this method are low cost and limited usage of toxic reagents. In paper [31], photocatalytic water splitting of TiO₂ colloids after an irradiation by nanosecond laser ($\lambda = 532 \text{ nm}$) was studied. It was shown that the efficiency of hydrogen production increases up to a factor of three due to some structural changes in these colloids. This is an unusual effect, since a phase change from anatase towards rutile was also observed, but the efficiency of rutile is known to be

lower than that of the anatase [32]. In paper [33], TiO_2 layer on glass was prepared by spin-coating technique using nanopowder P25. The structure was irradiated by Nd:YAG laser ($\lambda = 266 \text{ nm}$) at intensity $I = 7.1 \text{ MW/cm}^2$ followed by a thermal annealing in air for 1 h at $T = 450^\circ \text{ C}$. The irradiation of the structure has led to a transformation of TiO_2 layer from anatase to rutile phase, as in the case of annealing in furnace [34]. As a result of this treatment, the TiO_2 layer became dark. The authors have explained this effect by a decreasing of size of TiO_2 particles. This effect can be more plausibly explained by a surface oxygen depletion, because TiO_2 becomes dark when it is transformed into TiO_x , and the same effect of black TiO_x synthesis in water by a laser-based method was observed in papers [7], [35]. Irradiation of Ti foil by Nd:YAG laser in water [36] leads to formation of a nanoporous black TiO_x . Analysis of surface morphology has shown a certain dependence of surface structure on intensity and number of the pulses. Thus, cracks appeared on the irradiated surface of TiO_x at low intensities and small number of laser pulses, whereas pits were formed at intensities above 300 MW/cm^2 . The specific accumulated fluence for formation of nanopores is about 100 J/cm^2 . The enhancement of the quantum photocatalytic efficiency of $\text{TiO}_x/\text{Ti}/\text{PtNps}$ structure formed by Nd:YAG laser radiation in water is explained as an effect of electron scavenging by the Pt nanoparticles [37]. Advantages of such a technology are its economy, stability, abundance, non-toxicity and high quantum photocatalytic efficiency. In distinction from the reviewed here laser-based methods, we have examined a possibility to form TiO_2 layer on Ti substrate directly by a laser oxidation of Ti plate in air. Because this laser technology is relatively simple, quick, and environmentally friendly, the

formation of TiO_2 by laser oxidation has a great potential for practical applications. The aim of this study is to demonstrate that the phase of TiO_2 layer formed on a Ti substrate by laser oxidation method, can be controlled by irradiation intensity and dose.

2. Experimental

2.1. Laser-induced oxidation method

Prior to the experiments, a pure titanium plate was cut into samples with dimensions about $40.0 \times 15.0 \times 0.3 \text{ mm}^3$. These samples were washed in isopropyl alcohol via an ultrasonic bath and then dried under a dry air flow. TiO_2 thin films on Ti substrates were formed by a laser irradiation method using pulsed Nd:YAG laser radiation ($\lambda = 1064 \text{ nm}$, pulse duration $\tau = 6 \text{ ns}$, with $I = 52.8 \text{ MW/cm}^2$). Scanning of the laser beam was performed normally to the Ti surface with the different hatch spacing distances $700 \mu\text{m}$, $550 \mu\text{m}$ and $400 \mu\text{m}$ resulted in different doses applied on the Ti surfaces: $D1 = 3.1 \times 10^{20} \text{ phot/cm}^2$, $D2 = 3.9 \times 10^{20} \text{ phot/cm}^2$, or $D3 = 5.4 \times 10^{20} \text{ phot/cm}^2$, respectively at constant scanning speeds of the laser ($v = 1 \text{ mm/s}$). The laser beam diameter was 6 mm . Optical microscope images of TiO_2/Ti structure after irradiation by the laser are shown in Fig.1. Experiments were performed under an atmospheric pressure of 1 atm at 20° C and 60% humidity. Kinetics of methyl orange photo degradation by TiO_2 formed by laser radiation on Ti substrate with doses $D1$, $D2$, $D3$ are shown in Fig.2.

2.2. Sample characterization

A Raman back scattering spectra identified the phase structure of the TiO_2/Ti samples after laser irradiation with doses $D1$, $D2$, and $D3$ are shown in Fig. 3.



Fig. 1. Optical microscope image of TiO_2/Ti structure after irradiation by the laser doses $D1$, $D2$, and $D3$ at laser intensity 52.8 MW/cm^2 .

Irradiating with doses $D1$, $D2$, and $D3$ form a 40-nm , 70-nm , and 100-nm thick TiO_2 thin film, respectively.

The Raman spectra were measured by a Renishaw InVia90V727 micro-Raman spectrometer with a He-Ne red laser excitation at $\lambda = 633 \text{ nm}$. The Raman spectra of Ti in the spectral range of $100 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$ after laser irradiation with different doses (Fig. 4) were used for the phase determination.

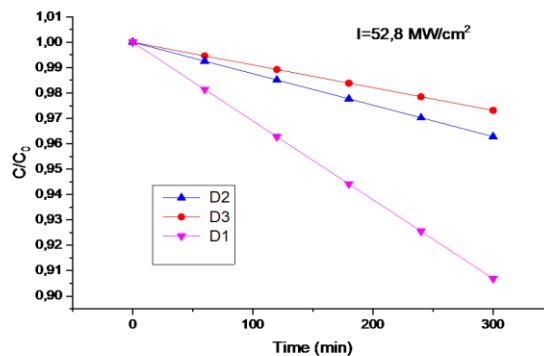


Fig. 2. Kinetics of methyl orange photo degradation by TiO_2 formed by laser radiation on Ti substrate with doses: $D1$ – pink curve, $D2$ – blue curve, and $D3$ – red curve, at laser intensity 52.8 MW/cm^2 .
 $\alpha_{\text{max}} = 3.4 \times 10^{-3} \text{ min}^{-1}$.

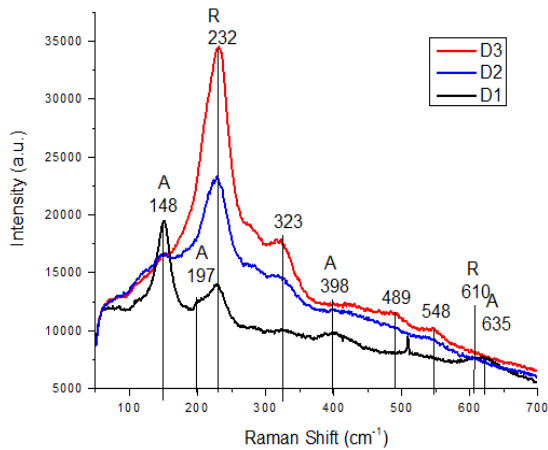


Fig. 3. Raman spectra of TiO₂ thin film on Ti plate formed by the laser radiation with doses D1, D2 and D3.

2.3. Testing of the photocatalytic properties

The photocatalytic TiO₂ layer properties were evaluated by the bleaching of a methylene orange (MO) solution with a concentration of 10 mg/L under UV-A irradiation. Each sample was placed in a beaker and 20 mL of the MO solution was poured over the top. To minimize evaporation, a PS plate was placed on top of the beaker. The samples were then irradiated with a 125-W mercury vapor lamp (365-nm peak wavelength) at a distance of 10 cm. To ensure that the lamp did not heat up the samples, a constant air flow was supplied and the temperature was monitored throughout the experiment. After each hour, 1 mL of the MO solution was extracted to determine the concentration via UV/V is spectroscopy (ThermoScientific, Genesys 10S). After the measurement, the aliquot was returned to the test beaker. Fig. 2 plots the kinetics of MO photodegradation by the samples.

2.4. Scratching method to study TiO₂ on Ti adhesion

The resistance to delamination was investigated by the scratching method (CSM Micro-Combi Tester) using a conical diamond indenter (Rockwell). The scratch force on the scanning indenter was gradually increased from 10 mN to 3.0 N. Fig. 4 shows the critical loads of delamination of TiO₂ thin film on Ti for samples D1, D2 and D3.

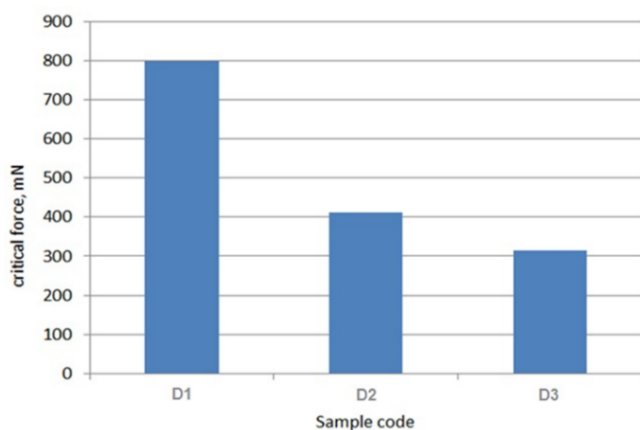


Fig. 4. Critical load of the sample's delamination.

Increasing of the thickness causes a decrease of TiO₂/Ti structure adhesion (critical delamination force) from 800 mN for D1 to 400 mN for D2 and 300 mN for D3 due to the formation of a nonhomogeneous TiO₂ layer.

3. Results and discussion

In this study, the impact of the laser radiation on the surface morphology was examined. Irradiating neither does affect the surface smoothness and uniformity nor does form defects or cracks. However, the Ti samples turn dark blue (Fig. 1) after the irradiation by Nd:YAG laser. This change of color is connected to the increased thickness of TiO₂ layer, modifying the picture of interference. Irradiating with doses D1, D2, and D3 form a 40-nm, 70-nm, and 100-nm thick TiO₂ thin film, respectively.

According to the MO bleaching experiment (Fig. 2), the first order reaction constants are $3.2 \times 10^{-4} \text{ min}^{-1}$, $1.1 \times 10^{-4} \text{ min}^{-1}$, and $8.0 \times 10^{-5} \text{ min}^{-1}$ for laser doses D1, D2, and D3, respectively. The D1 dose yields the highest decomposition ratio, while the sample treated using the D3 dose has the lowest decomposition ratio. This can be explained by the decrease in the TiO₂ anatase phase as the laser dose increases.

The analysis of XRD patterns revealed the formation of TiO, Ti₂O₃, anatase TiO₂ and very small amounts of rutile TiO₂ depending on irradiation dose. The most intensive peaks are attributed to Ti, which was observed due to substrate. The most intensive anatase peak is (1 0 1) at 25.3° which was observed after D1 irradiation only. The anatase peak disappeared after irradiation by D2 and D3 doses and peaks of Ti₂O₃ compound became weaker with higher irradiation dose as well. Meanwhile, the intensity of TiO peaks increased with irradiation dose. The simultaneous presence of two phases, as shown in Fig. 3, indicates a TiO₂ heterostructure, having better photocatalytic properties in comparison with the pure anatase or rutile phases, as shown in [11, 12].

The phases change dependence on irradiation dose were evaluated by applying Rietveld deconvolution. The results showed that TiO₂ anatase (which was fixed after D1 irradiation only) constitute about 1.6%. The tendencies showed that the amount of TiO increased from approximately 1.4% to 6.3%, while the amount of Ti₂O₃ compound decreased from approximately 7.3% to 2.8% after the irradiation doses D1 and D3 respectively. The rutile peaks were not included in these calculations due to very weak intensities. The amounts of Ti and O compounds detected are relatively small due to the effect of bulk Ti substrate.

Fig.3 shows the Raman spectra of the three samples after the D1, D2, and D3 doses. The Raman active modes at 148 cm⁻¹, 238 cm⁻¹, 445 cm⁻¹, 610 cm⁻¹, and 829 cm⁻¹ are associated with rutile single crystals, according to [38, 39]. An important property of the anatase and rutile phases in the Raman spectra is the ratio between the band at 148 cm⁻¹ and the band at 610 cm⁻¹. For the anatase phase, the ratio is greater than one, but is less than one for the rutile phase [40]. In our experiments, after the D1 dose, this ratio is ~6, suggesting the presence of the anatase phase. However, the Raman spectrum changes after the D2 and D3 doses. The ratio of bands decreases and a new band appears at 232 cm⁻¹, which may be associated with the rutile phase and the increased laser dose. The small regular peaks in regions of 150 cm⁻¹– 300 cm⁻¹ and 500 cm⁻¹– 700 cm⁻¹ are related to the disorder induced scattering or second order processes [41].

4. Conclusions

In this paper, the laser oxidation of Ti plate has been investigated. The thickness of TiO₂ layer increases from 40 nm to 100 nm with the laser dose. A positive feedback during the irradiation process is observed: the temperature rises with the increase in the thickness of the TiO₂ layer due to the interference-caused decrease of the reflection coefficient. The thickness of TiO₂/Ti layer rises by increasing the laser irradiation dose from D1 to D3, but adhesion (critical delamination force) of the TiO₂/Ti structure reduces from 800 mN for D1 to 400 mN for D2 and 300 mN for D3 due to the formation of a nonhomogeneous TiO₂ layer at doses D2 and D3. This behavior can be explained by mixing of the phases in TiO₂ layer. At D1, the TiO₂ layer is mostly in the anatase phase. However, at D2 and D3, the TiO₂ layer partially transforms into the rutile phase. This

transformation, at least partly, can be explained by the rise of the maximal temperature in the TiO₂ layer at larger doses, as suggested by our calculations, based on the modified Wagner oxidation model. It can be also explained by the deficit of O atoms deeper than 50 nm in Ti substrate at doses D2 and D3 due to the low diffusion of O atoms in Ti.

5. References

- [1] A. Kozlovskiy, M. Zdorovets, *Journal of Nanostructure in Chemistry* (2020) 10(4) pp.331-346.
- [2] E.Deionno, M. Looper, *IEEE Aerospace Conference Proceedings* (2013) pp.15-17.
- [3] P.-I. Branemark, *J. Prosthet. Dent.*, 50 (3) (1983), pp. 399-410,
- [4] P.I. Brånemark, B.O. Hansson, R. Adell, U. Breine, J. Lindström, O. Hallén, A. Ohman. *Scand. J. Plast. Reconstr. Surg., Suppl.* 16 (1977), pp. 1-132.
- [5] B. Liang, S. Fujibayashi, M. Neo, J. Tamura, H.M. Kim, M. Uchida, T. Kokubo, T. Nakamura, *Biomaterials.*, 24 (27) (2003), pp. 4959-4966.
- [6] C.M. Lin, K. Yen. *Mater. Sci. Eng. C.*, 26 (1) (2006), pp. 54-64.
- [7] X.-F. Yang, Y. Chen, F. Yang, F.-M. He, S.-F. Zhao. *Dent. Mater.*, 25 (4) (2009), pp. 473-480.
- [8] A. Fujishima, T.N. Rao, D.A. Tryk. *J. Photochem. Photobiol. C Photochem. Rev.*, 1 (1) (2000), pp. 1-21.
- [9] D.A.H. Hanaor, C.C. Sorrell. *J. Mater. Sci.*, 46 (4) (2011), pp. 855-874.
- [10] X. Cui, H. Kim, M. Kawashita, L. Wang, T. Xiong, T. Kokubo, T. Nakamura. *Dent. Mater.*, 25 (1) (2009), pp. 80-86.
- [11] T. Kawahara, T. Ozawa, M. Iwasaki, H. Tada, S. Ito. *J. Colloid Interface Sci.*, 267 (2) (2003), pp. 377-381.
- [12] T. Ozawa, M. Iwasaki, H. Tada, T. Akita, K. Tanaka, S. Ito. *J. Colloid Interface Sci.*, 281 (2) (2005), pp. 510-513.
- [13] H. Dong, X.Y. Li. *Mater. Sci. Eng. A* 280 (2000), pp.303–310.
- [14] T. Jafari, E. Moharreri, A. Amin, R. Miao, W. Song, S. Suib. *Molecules.*, 21 (2016), pp. 900-920.
- [15] S. Varnagiris, A. Medvids, M. Lelis, D. Milcius, A. Antuzevics. *J. Photochem. Photobiol. A Chem.*, 382 (2019), p. 111941.
- [16] Z.S. Hosseini, M. Shasti, S. Ramezani Sani, A. Mortezaali, J. Appl. Phys., 119 (1) (2016), p. 014503.
- [17] C. Zhu, C. Lv, C. Wang, Y. Sha, D. Li, X. Ma, D. Yang. *Opt. Express.*, 23 (3) (2015), p. 2819.
- [18] T. Luttrell, S. Halpegamage, J. Tao, A. Kramer, E. Sutter, M. Batzill. *Sci. Rep.*, 4 (1) (2015), pp.123-128.
- [19] M.H. Samat, A.M.M. Ali, M.F.M. Taib, O.H. Hassan, M.Z.A. Yahya. *Results Phys.*, 6 (2016), pp. 891-896.
- [20] Y. Yamada, Y. Kanemitsu. *Appl. Phys. Lett.*, 101 (13) (2012), p. 133907.
- [21] C. Hammerl, B. Renner, B. Rauschenbach, W. Assmann. *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms.*, 148 (1-4) (1999), pp. 851-857.
- [22] E.J.D.M. Pillaca, M. Ueda, K.G. Kostov, H. Reuther. *Appl. Surf. Sci.*, 258 (24) (2012), pp. 9564-9569.
- [23] E. Dauksta, A. Medvids, P. Onufrijevs, M. Shimomura, Y. Fukuda, K. Murakami. *Curr. Appl. Phys.*, 19 (3) (2019), pp. 351-355.
- [24] J. Chen, L.-B. Lin, F.-Q. Jing. *J. Phys. Chem. Solids.*, 62 (7) (2001), pp. 1257-1262.
- [25] X. Chen, D. Zhao, K. Liu, C. Wang, L. Liu, B. Li, Z. Zhang, D. Shen. *ACS Appl. Mater. Interfaces.*, 7 (29) (2015), pp. 16070-16077.
- [26] H.L. Ma, J.Y. Yang, Y. Dai, Y.B. Zhang, B. Lu, G.H. Ma. *Appl. Surf. Sci.*, 253 (18) (2007), pp. 7497-7500.
- [27] C.-K. Chung, S.L. Lin, K.P. Chuang, S.Y. Cheng, K.Y. Shei. *Micro Nano Lett.*, 7 (8) (2012), pp. 701-705.
- [28] M. Jing, R. Hong, W. Shao, H. Lin, D. Zhang, S. Zhuang, D. Zhang. *Opt. Express.*, 25 (2017), pp. 2377-2382.
- [29] A. Singh, J. Vihinen, E. Frankberg, L. Hyvärinen, M. Honkanen, E. Levänen. *Nanoscale Res. Lett.*, 11 (2016), pp. 1-9.
- [30] V.A. Zuñiga-Ibarra, S. Shaji, B. Krishnan, J. Johny, S. Sharma Kanakillam, D.A. Avellaneda, J.A.A. Martinez, T.K. DasRoy, N.A. Ramos-Delgado. *Appl. Surf. Sci.*, 483 (2019), pp. 156-164.
- [31] S. Filice, G. Compagnini, R. Fiorenza, S. Scirè, L. D'Urso, M.E. Fragalà, P. Russo, E. Fazio, S. Scalese. *J. Colloid Interface Sci.*, 489 (2017), pp. 131-137.
- [32] J. Zhang, P. Zhou, J. Liu, J. Yu. *Phys. Chem. Chem. Phys.*, 16 (38) (2014), pp. 20382-20386.
- [33] M. Sawczak, M. Górski, H. Rachubiński, A. Cenian, *Laser Technol. 2012 Appl. Lasers*. 8703 (2013) 87030M.
- [34] H. Rath, S. Anand, M. Mohapatra, P. Dash, T. Som, U.P. Singh, N.C. Mishra, D. Kanjilal, D.K. Avasthi, S.M. Bose, S.N. Behera, B.K. Roul. *AIP Conf. Proc.*, AIP (2008), pp. 250-255.
- [35] G. Cacciato, M. Zimbone, F. Ruffino, V. Privitera, M.G. Grimaldi. *Phys. Status Solidi Basic Res.*, 254 (7) (2017), p. 1600835.
- [36] G. Cacciato, M. Zimbone, F. Ruffino, V. Privitera, M.G. Grimaldi. *Phys. Status Solidi Basic Res.*, 254 (7) (2017), p. 1600835.
- [37] M. Zimbone, G. Cacciato, R. Sanz, R. Carles, A. Gulino, V. Privitera, M.G. Grimaldi. *Catal. Commun.*, 84 (2016), pp. 11-15.
- [38] S. Mändl, G. Thorwarth, M. Schreck. *Surf. Coatings Technol.*, 125 (2000), pp. 84-88.
- [39] M. Malekshahi, Byranvand, A. Nemat, Kharat, L. Fatholahi, Z. Malekshahi Beiranvand. *J. Nanostructures.*, 3 (2013), pp. 1-9.
- [40] W.F. Zhang, Y.L. He, M.S. Zhang, Z. Yin, Q. Chen. *J. Phys. D Appl. Phys.*, 33 (8) (2000), pp. 912-916.
- [41] H. Schmalzried, A.T. Fromhold, North Holland Publishing Co. 1976. 547 Seiten, *Berichte Der Bunsengesellschaft Für Phys. Chemie*. 81 (1977) 353–354.

Quantum Cone - Nano Source of Light with Dispersive Spectrum Distributed Along Height

Artūrs Medvids

Riga Technical University, Paula Valdena 3/7, Riga LV 1048, Latvia.

E-mail:medvids@latnet.lv

Abstract: A quantum cone is a structure consisting of a large number of quantum dots with a gradually decreasing diameter from the base to the top of the cone. This distribution of quantum dots leads to a dispersive radiated spectrum. The red edge of the spectrum is determined by the band gap of the bulk semiconductor, and the blue edge by the quantum confinement of excitons on top of the cones. We observe the kinetics of photoluminescence, obeying the stretched exponential law, from quantum cones formed on the surface of DLC. They are explained by an increase in the lifetime of excitons along the height of the cone from the top to the base of the cone and an increasing concentration of excitons at the base due to their drift in the quasi-built-in electric field of the quantum cone. Such time dependence of the photoluminescence spectrum gives the possibility of its discrimination spectrum on time. The possible visualization of the quantum cones of DLC using irradiation by a UV light source is shown. A quantum cone is a new type of nano light source, as it replaces two elements in a conventional spectrometer – a light source and a dispersive element: an ultra-fast monochromator. These features will make it possible to build a spectrometer to measure the absorption spectrum of individual nanoparticles or viruses.

KEYWORDS: QUANTUM CONE, LIGHT, DISPERSIVE SPECTRUM, Si, Ge, SiGe SOLID SOLUTION, DLC, PHOTOLUMINESCENCE

1. Introduction

Light plays a crucial role in the existence of humanity and nature. The primary light source on Earth is the Sun. Still, artificial light sources that improve our daily life, equipment, and technologies have also appeared with improving modes of life, such as heated bodies, plasma, lamps, lasers, LEDs, etc. The tendency to reduce the size of artificial light sources allowed the use of such sources in microelectronics, medicine, and biology to study micro-objects. At the same time, the requirements for improving the quality of such sources, increase in intensity, and expansion of the spectrum of radiation, its uniformity, and controllability of its parameters have increased. The importance of this trend is confirmed by the appearance of international conferences and monographs in this direction. Spectroscopy research of microscopic objects, for example, microbes, molecules, and blood cells, requires non-traditional research methods, for example, optical prob because the size of such objects is smaller than the wavelength of visible light; therefore, the micro-object neither absorbs nor scatters it effectively. The study of a micro-object requires a light source much smaller than the object itself, such as quantum dots - 0D.

The award of the 2023 Nobel Prize in Chemistry to Munga J. Bawendi, Louis E. Brus, and Alexei I. Ekimov “for the discovery and synthesis of quantum dots” confirms that the quantum confinement effect is a major focus in solid state physics today. Therefore, one of the main tasks of scientists is to develop new optical and electronic devices and technologies based on quantum dots. As you know [1], a quantum dot has one line in the luminescence spectrum, the so-called monochromatic radiation. A new quantum system called quantum cones [2, 3] on the surface of a Ge single crystal irradiated by a Nd:YAG laser was found. These cones possess unique optical properties: a huge “blue shift” of the photoluminescence (PL) spectrum by 1.1 eV, an increased intensity of more than a million times, and a “red shift” of the frequency of the LO-phonon line by 6 cm^{-1} in the Raman spectrum. The symmetry of the PL band and the sharp LO phonon line in the Raman scattering spectrum are proof of the presence of the cone-like quantum dot. This is a disadvantage, monochromatic radiation, of a single quantum dot for use in spectroscopy. To measure the absorption or reflection spectra of an object, it is necessary to have a light source with a broad and preferably continuous radiation spectrum. Such requirements can be met by a set of quantum dots

with a gradual change in diameter, for example, a Quantum cone [4], or by a quantum dot changing its diameter over time due to changing temperature or pressure. Decreasing semiconductor elements to nano size has led to a quantitative change in all electronic devices. At the same time, decreasing the semiconductor crystal size has led to a qualitative change in the properties of materials. So, the statement “every material has a nonchanging absorption and luminescence spectra” is not valid. For example, depending on the size of the Si crystal quantum dot, the PL spectrum can change in the region from $1\text{ }\mu\text{m}$ to $300\text{ }\mu\text{m}$, depending on its diameter. In comparison, bulk Si crystals have a maximum in the PL spectrum at $1\text{ }\mu\text{m}$. All physical properties of matter are changing. This provides the possibility to construct new electronic and optical elements and devices. Therefore, this study aims to elaborate principally on a new nano light source with a dispersive broad spectrum. It was shown that irradiation of the SiO_2/Si structure with a Nd:YAG laser led to the formation of nanocones on the Si surface that have a unique PL spectrum: a “blue shift” on 1.2 eV, asymmetric broadband from 1.1 eV to 2.3 eV with a gradual decrease PL intensity in the red part of the spectrum, a rainbow-like spectrum, and a maximum PL intensity increase of more than a million times, as shown in Fig.1a [5]. These properties of the PL spectrum are characteristic of a graded bandgap semiconductor. This means that a quantum cone with a solid angle of less than 60° at the top is a one-dimensional system ID with a gradual decrease in diameter from the base to the top of the cone, as shown in Fig.1b. Therefore, where the cone's diameter is equal to or less than the Bohr radius of an electron or an exciton, the quantum confinement effect takes place [1, 6, 7]. A colossal increase in the PL spectrum intensity and a shift of its maximum to the blue part of the spectrum occurs due to the transformation of the Si crystal from indirect to quasi-direct and the confinement of the electron-hole pairs (EHP) in the quantum cone.

On the other hand, the cone can be considered a set of dots with gradually decreasing diameter from the base to the top of the cone. Theoretically, the paper [8] shows that the lifetime of an exciton in a quantum dot decreases with the decreasing diameter of the quantum dot. Therefore, in the case of the quantum cone, the lifetime of EHPs must depend on the height of the cone due to a change in the overlap of the Ψ functions of electrons and holes. This means that radiation from the quantum cone is discriminated by the frequency too.

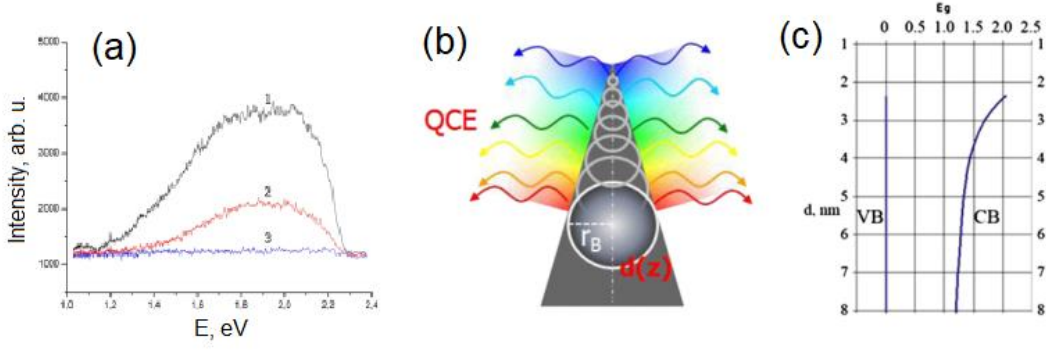


Fig. 1. (a) PL spectra of the irradiated SiO₂/Si structure at a laser radiation intensity of 2.0 MW/cm² (curve 1) and after removing of SiO₂ layer (curve 2) and PL of the nonirradiated surface (curve 3). (b) A schematic image of a nanocone with a gradually decreasing diameter from the Si substrate to the top of the cone; (c) The calculated bandgap structure of Si as a function of the nanocone diameter [9].

This property is significant for optical communication systems. A colossal increase of the PL intensity spectrum and a shift of the maximum in the blue part of the spectrum takes place due to the transformation of Si crystal from an indirect band to a quasi-direct one due to the confinement of the EHPs in the quantum cone. These facts speak to the possibility of a gradual decrease in the lifetime of EHPs or excitons from the base to the top of a cone. This means that a long quantum cone is a source of light with a dispersive spectrum - gradually increasing the energy of a photon from the base to the top of the cone. For example, for a Si crystal height of a cone up to 10 nm [10], estimation of the quasi-build-in electric field in a graded bandgap structure gives an intensity of approximately $E_z = e^{-1}dE_g/dz = 12$ MV/cm. So, a strong electric field can cause ionisation and exciton polarisation in the quantum cone [11, 12]. Such a colossal electric field can influence the radiative recombination process in the quantum cone, which means having an impact on the EHPs or excitons lifetime and, therefore, on the intensity and spectral range of luminescence, which is a very important task for new fundamental knowledge in the field of solid-state physics. Therefore, the use of the kinetics of the PL method for

studying time dependence radiation of cone along height is a very important task and will be shown experimentally below.

2. Experimental

The last of our experiments on diamond-like carbon (DLC) films [13] with cones on the surface have shown that the properties of the cone are the same as those formed by laser radiation on surfaces of Si, Ge, and CdTe [2-7], for example, the "blue shift" of the PL spectra. Studies of the PL kinetics of DLC films with nanocones with a diameter of 100 nm at the base, 2 nm at the top, and a height of 60 nm were formed by magnetron sputtering (more technological details are in [13]). PL spectra and decays of the studied samples were measured using a streak camera and 5-th harmonic of femtosecond Yb:KGW laser at 213 nm (10 kHz). The AFM measurements (Fig. 2a, b, c) show an increase in cone height and population enhancement in sample 3A vs. samples 1A and 2A. The fluorescent microscope images show that nanocones also emit blue light from tops more intensively at UV excitation obtained from filtered Xe lamp (Fig. 2d, e, f). This method can be used for visualization of nano-scale semiconductors, for example, Si cantilever in AFM.

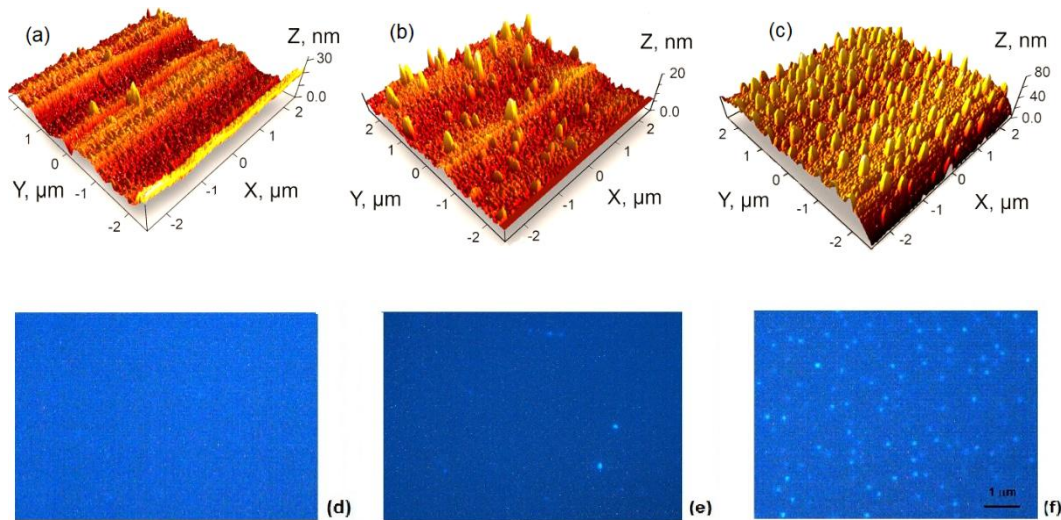


Fig. 2. AFM images of DLC samples: 1A (a), 2A (b), and 3A (c). Fluorescent microscope images of 1A (d), 2A (e), 3A (f) samples at UV excitation.

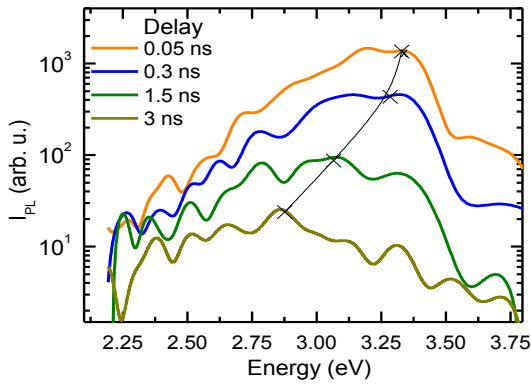


Fig. 3. PL spectra of DLC sample 3A with a time delay of 0.05 ns, 0.3 ns, 1.5 ns, and 3 ns. The spectral resolution is 24 meV. Excitation fluence is 1.2 mJ/cm² and wavelength 213 nm.

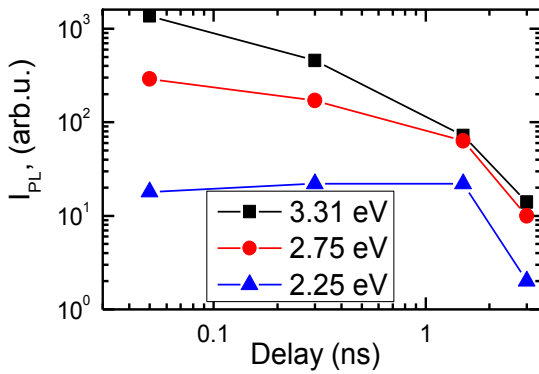


Fig. 4. PL intensity dependence on delay time at $E = 3.31$ eV, 2.75 eV, and 2.30 eV energies.

Figure 3. demonstrates that the intensity of the PL spectra of DLC sample 3A depends on the time delay of 0.05 ns, 0.3 ns, 1.5 ns, and 3 ns which is unusual behaviour. The maximum intensities of the PL spectra are shifted to the red part of the spectra with time, as shown by the thin black line. For example, the maximum of the PL spectrum for sample 1A is usually at $E = 2.5$ eV and does not change position with time [13]. This peculiarity is explained by the drift of EHPs in a quasi-build-in electric field from the top to the base of the cone in a graded band gap structure [14], as shown in Fig.1 c. Evidence of this phenomenon is demonstrated in Figure 4. The speed of EHPs recombination with a delay time is significant for photon energy, 3.31 eV, slow for 2.75 eV, and it becomes negative for 2.25 eV (at least in the region from 0.05 nm to 1.5 nm). This means that an additional concentration of EHP appears at the base of the cone after laser irradiation of the sample due to the drift of EHPs. A comparison of PL decay profiles and rates for the three samples at the highest energy of a photon quantum (blue edge) and the lowest energy “red edge” is shown in Figure 5. These curves coincide only for sample 1A, but for samples 2A and 3A, “red edges” are at higher IPL in comparison with “blue edges”. The fitting formula for PL kinetics $I_{PL} = I_0 \exp(-(t/\tau_0)^\beta)$ is the stretch exponent, and the corresponding parameters are listed in Table 1.

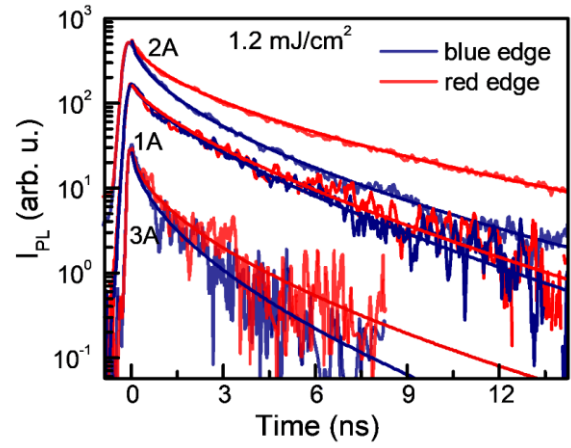


Fig. 5. PL Kinetics of samples 3A, 2A, and 1A on the edge PL luminescence spectrum at 1.2 mJ/cm² excitation.

Sample 3A features the sharpest cones and demonstrates the shortest decay time $\tau_0 = 0.35$ ns and lower $\beta = 0.55$ in comparison to sample 2A ($\tau_0 = 0.6$ ns and $\beta = 0.56$). Such differences in PL kinetics are explained by the difference in surface morphology of the samples. The presence of nanocones leads to the stretch exponent of PL kinetics and a sharper cone corresponds to lower β and τ_0 . The near coincidence of both curves for sample 1A means that, indeed, PL kinetics obeys the exponential law in the absence of cones. Very often in the literature for the kinetics of PL, the stretch exponent law is used to explain the properties of the disordered system [15]. Samples 2A and 3A are very ordered. Corresponding to theory [8], the smallest excitons are at the top of every cone, and the size of the excitons gradually increases to the base of the cone. Therefore, the stretch exponent law is applicable to PL kinetics due to τ_0 gradually increasing from the top to the base of the cone. Parameters of quantum cones as sources of light are in the spectral range of $\Delta\lambda = 350 - 550$ nm; the active part of the nano cone $h = 16$ nm; the linear dispersion of the quantum cone $dh/d\lambda = 0.1$ (a height 0.1 nm contains the spectral range of 1 nm); the relaxation time $\tau = 10$ ps. An expression nano source of light or nanolight source [16] is very often used in literature due to the study of nanostructures, and elaborating nanotechnology is the main strim in up-to-date science. Very often, the nano does nothing changes in fundamental physics compared with the micro, only decreasing the light source's volume [17]. Still, our quantum cone is a fundamentally new type of nano source of light because the quantum cone is a light source with a dispersion spectrum distributed along the coordinate and time due to the Quantum confinement effect [1-7]. Possible applications of the quantum cone as a nano source of light are as follows: it can be the main part of a spectrometer - a monochromator. Such a light source would replace two elements in a conventional spectrometer - a light source and a dispersive element. Another application of this research is in the visualization and estimation of the diameter of the invisible tip of the nanocone. This is an essential task for the user and manufacturer, for example, for measuring the diameter of a cantilever in an atomic force microscope.

Table 1. Exponential fitting parameters for three samples.

Sample	Red edge		Blue edge	
	τ_0 , ns	β	τ_0 , ns	β
1A	1.2	0.7	1.2	0.7
2A	1.1	0.56	0.6	0.56
3A	0.5	0.55	0.35	0.55

3. Conclusions

This study shows the possibility of constructing a nano source of light quantum cone with a dispersive spectrum distributed in time and along cone height. Different semiconductors (Ge, Si, and DLC crystals) and cone growth methods, such as laser processing and magnetron sputtering, can be used. The range of the dispersive spectrum depends on the material of the cone and its parameters. The red edge of the spectrum is determined by the band gap of the bulk semiconductor and the blue edge by the quantum confinement of electron-hole pairs on top of cones. The kinetics of photoluminescence from cones obeys the stretch exponential law and is explained by the increase in the lifetime of electron-hole pairs/excitons with the height in the cone from the top to the base of the cone and increasing the concentration of excitons at the base due to their drift in the quasi-build-in electric field of the quantum cone. The visualization and estimation of the diameter of a non-visible nano cone's top is a very important task for the user and producer, for example, the diameter of a cantilever in an AFM. A quantum cone as a nano source of light with a dispersive spectrum distributed in a coordinate is a basic part of a spectrometer - monochromator. It is principally a new type of nano source of light because a quantum cone substitutes for two elements in conventional spectrometer – the source of light and the dispersive element.

4. References

- [1] L.E. Brus, J. Chem. Phys. 80 (1984) 4403-4444, <https://doi.org/10.1063/1.447218>
- [2] A. Medvid, Y. Fukuda, A. Michko, P. Onufrijevs, Y. Anma, Appl. Surf. Sci. 244 (2005) 120-123.
- [3] A. Medvid, I. Dmytruk, P. Onufrijevs, I. Pundyk, Phys. Stat. Sol. C 4 (2007) 3066–3069.
- [4] A. Medvid, A. Mychko, V. Gnatyuk, S. Levytskyi, Y. Naseka, Opt. Mater. 32 (2010) 836-839.
- [5] A. Medvid, I. Dmytruk, P. Onufrijevs, I. Pundyk, Diffusion and Defect Data Pt. B: Solid State Phenomena 131 (2008) 559-562.
- [6] A. Medvid, P. Onufrijevs “Properties of nanocones formed on a surface of semiconductors by laser radiation: QC effect of electrons, phonons, and excitons.” Nanoscale Res. Lett., 6 (2011) 582-528.
- [7] A. Medvids, A. Mychko, P. Onufrijevs, E. Dauksta "Application of Nd:YAG laser in semiconductors nanotechnology", Ed. Dan Dumitras, INTECH (2012), <https://doi.org/10.5772/37093>
- [8] T. Takahahara and K. Takeda, Physical Review B 46 (1992) 15578-15581.
- [9] J. Li, Lin-Wang, Chem. Mater. 16 (2004) 4012-4015, <https://doi.org/10.1021/cm0494958>
- [10] A. Evtuh, A. Medvids, P. Onufrijevs, M. Okada, H. Mimura, J. Vac. Sci. Technol. 2 (2010) C2B11-C2B13.
- [11] J. Xu, X. Zhuang, P. Guo, W. Huang, W. Hu. Q. Zhang. Q. Wan, X. Zhu, Z. Yang, L. Tong, X. Duan and A. Pan, Sci. Rep. 2 (2012).
- [12] A. Asgari, S. Asadzadeh, J. Phys.: Conf. Ser. 248 (2010) 012020, <https://doi.org/10.1088/1742-6596/248/1/012020>
- [13] C. Carra, A. Medvids, D. Litvinas, P. Ščaje, T. Malinauskas, A. Selskis, E. Hector, K. Bazaka, I. Levchenko, C. Riccardi, ACS Applied Nano Materials 5 (2022) 4787 – 4800.
- [14] W. Deng, J. Zou, X. Peng, J. Zhang, W. Wang, Y. Zhang, and D. Zhang, Opt. Express, 24 (2016) 24347-24360
- [15] G. Zatoryb, A. Podhorodecki, J. Misiewicz, J. Cardin , F. Gourbilleau, Nanoscale Res. Lett. 6 (2011) 106- 110.
- [16] Misaki Tanaka, Yuka Sato, and Prabhat Verma “White nanolight source for optical nanoimaging”, SCIENCE ADVANCES, 3 (2020) 100-108.
- [17] You-Shin No, “Electrically Driven Micro- and Nano-Scale Semiconductor Light Source” Appl. Sci. 2019, 9(4), 802-808.

The Interplay of Laser Metal Processing and Non-Equilibrium Phase Transformations

Nikolaos Papageorgiou

Ship propulsion plants Department of the Faculty of Engineering Nikola Vaptsarov Naval Academy

Abstract: *This comprehensive report explores the intricate relationship between modern laser metal processing techniques and the non-equilibrium phase transformations they induce in a wide range of materials. The central thesis is that methods such as laser cutting, welding, and additive manufacturing are not merely thermal processes, but rather precise engineering tools that fundamentally alter a material's state by subjecting it to extreme conditions.*

Introduction

The focused, high-energy input of a laser creates an incredibly localized thermal event, which is defined by heating and cooling rates that can reach an astonishing 104 to 107 K/s, along with steep temperature gradients from 106 to 107 K/m [4, 5]. These extreme conditions are what prevent a material from ever reaching thermodynamic equilibrium, leading to the formation of unique microstructures and properties that are simply impossible to achieve with conventional, slower thermal methods. By manipulating these non-equilibrium phenomena, engineers can create materials with tailored properties for high-performance applications. The document outlines the fundamental principles governing this process, explores specific material responses through a series of case studies, and discusses the critical role of advanced computational modeling and characterization in predicting and controlling the outcomes. It concludes with an outlook on future research directions in this field, which the author refers to as "kinetic materials science."

1. The Unique Thermal Landscape and Fundamentals of Laser Processing

The unique thermal environment created by laser processing is a direct consequence of the laser beam's inherent properties, specifically its exceptional directivity and monochromaticity [1]. The high-power density of a focused laser beam can heat a small volume of metal to its melting point in a fraction of a second [2]. This highly localized energy input, often concentrating 1013 W or more in a spot as small as 0.01 mm in diameter [17, 18], generates steep spatial and temporal temperature gradients. As the laser moves and the molten spot cools rapidly due to the surrounding cooler bulk material acting as a heat sink, the material's response is governed by kinetics rather than equilibrium thermodynamics [8]. There is simply not enough time for atomic diffusion to occur at a rate sufficient to keep pace with the lightning-fast thermal changes, which is the very essence of non-equilibrium phenomena [6, 19].

The versatility of laser processing is evident in its wide array of applications, including laser cutting [37], welding [35], and additive manufacturing [32]. A particularly significant example is Laser Powder Bed Fusion (LPBF), a method where the thermal conditions are most extreme. During LPBF, cooling rates typically range from 105 to 107 K/s, and temperature gradients are as high as 106 to 107 K/m [3]. These extreme conditions prevent atoms from settling into their lowest energy, equilibrium states, instead of forcing them into metastable configurations [34]. This kinetic limitation is the direct causal link between the unique thermal conditions of laser processing and the prevalence of non-equilibrium phase transformations.

2. Non-Equilibrium Phase Transformations: A Materials Science Perspective

Non-equilibrium phase transformations are fundamentally distinct from the equilibrium transformations that are traditionally represented on standard phase diagrams. While equilibrium transformations occur in a system at a state of minimum free energy, non-equilibrium transformations take place when a system is kinetically constrained and has not reached its lowest energy state [6]. This results in the formation of metastable phases, which exist at a higher energy level than the true equilibrium but are not unstable. The ability to "freeze" a material in this metastable state is highly valuable for materials science, as it allows for the creation of

unique properties, such as the exceptional hardness and strength of martensite in steels [20, 31].

The formation of these non-equilibrium phases is a direct result of rapid cooling rates, typically in the range of 105 to 108 K/s [4]. These high rates lead to a significant degree of undercooling, which in turn increases the thermodynamic driving force for nucleation [7]. The most well-known example is the martensitic transformation, a diffusionless, crystallographic shear-based phase change that occurs upon very rapid cooling from a high-temperature parent phase like austenite. Because martensite is a non-equilibrium phase, it does not appear on conventional equilibrium phase diagrams [9, 10]. To effectively predict the outcome of such rapid thermal events, traditional phase diagrams are insufficient. The paper highlights the critical importance of Time-Temperature-Transformation (TTT) and Continuous Cooling Transformation (CCT) diagrams, which incorporate the dimensions of time and cooling rate. CCT diagrams are particularly relevant for laser processing because they accurately map the transformation products as a function of continuous cooling rates [9]. For instance, the complete conversion of austenite to martensite in low carbon steels requires a critical quenching rate exceeding 1200 °C/s, a rate that is practically unachievable with conventional thermal processing but is a routine outcome of laser processing [21].

A crucial aspect of this process is rapid solidification, which occurs at cooling rates ranging from 103 to 106 K/s [4]. This rapid cooling leads to a high degree of undercooling and promotes the formation of a much finer grain structure [11, 12]. A key phenomenon associated with this is "solute trapping," where alloying elements do not have enough time to diffuse away from the solidifying interface [13]. This effect results in a more uniform distribution of alloying elements, effectively mitigating microsegregation and significantly improving the material's overall homogeneity.

3. Case Studies and Impact on Material Properties

The paper uses several case studies to illustrate how laser processing induces these non-equilibrium phases and their subsequent impact on material properties. In steels, the rapid cooling rates trigger a martensitic transformation, forming a diffusionless, crystallographic shear-based phase change that is known for its exceptional hardness and strength [20]. The research highlights that low carbon steels, for instance, need a critical quenching rate of over 1200 °C/s to fully convert austenite to martensite, a rate easily reached with laser processing but not with conventional thermal treatments [21].

For titanium alloys, particularly Ti-6Al-4V, the high cooling rates experienced during Laser Powder Bed Fusion (LPBF) are responsible for the formation of acicular alpha-prime (α') martensite [3]. The study finds that the combination of this (α') martensitic phase with low porosity is a major contributor to the material's high fatigue strength [23, 27]. However, the directional nature of laser processing can also lead to non-homogeneous and anisotropic properties, a critical challenge that the paper explores [15].

The paper also examines aluminum alloys, such as AlSi10Mg. Here, rapid cooling during LPBF leads to a refinement of the primary α -Al grains and a stronger solute capture effect, which reduces microsegregation and enhances homogeneity [12]. In the case of nickel-based superalloys, the rapid solidification during laser cladding and Selective Laser Melting (SLM) can result in fine grains, but it also introduces significant challenges like solidification and liquation cracking. These defects are an

unfortunate consequence of the steep thermal gradients and rapid solidification conditions [24, 25].

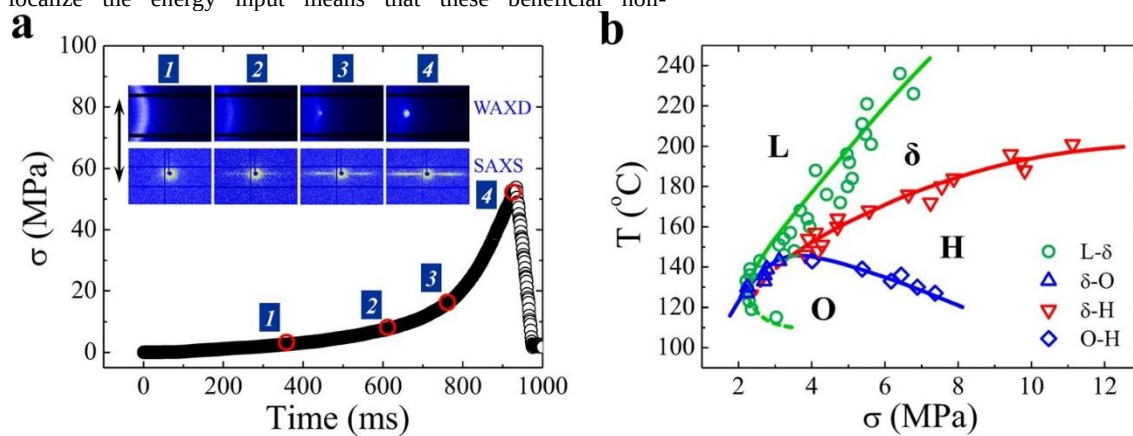
The non-equilibrium microstructures created by laser processing have a profound impact on a material's performance. The formation of martensite in steels, for example, dramatically increases hardness and strength, making it ideal for applications requiring high wear resistance. However, this enhanced strength often comes with a trade-off: a notable reduction in ductility and toughness [26]. The presence of non-tempered martensite is a key factor that is identified as limiting ductility [27, 26].

A significant challenge posed by laser processing is the introduction of substantial residual stress. These stresses arise from the large temperature gradients and rapid cooling, and they can cause deformation or even failure [28, 29]. The paper notes that these stresses typically need to be managed with post-processing heat treatments [22, 28]. Conversely, techniques like Laser Shock Processing (LSP) can be used to intentionally create beneficial compressive residual stresses that improve a material's durability against fatigue or stress corrosion cracking [29]. Another area where non-equilibrium processing excels is in surface engineering. Laser cladding can be used to apply protective coatings that improve wear, corrosion, and thermal resistance [30]. The ability to localize the energy input means that these beneficial non-

equilibrium transformations can be confined to the surface, allowing the bulk properties of the material to be preserved while the surface is enhanced [30].

4. Advanced Characterization, Computational Modeling, and Future Outlook

The dynamic and complex nature of laser-induced non-equilibrium transformations makes advanced characterization and computational modeling essential for this field of research. Techniques such as Electron Backscatter Diffraction (EBSD) are used for detailed microstructural analyses at multiple length scales, and X-ray diffraction (XRD) is employed to accurately measure residual stresses [28, 29]. Because direct experimental observation of these transient processes is extremely difficult, computational models are indispensable [11]. The paper highlights the use of Computational Fluid Dynamics (CFD), Phase Field (PF) models, and Cellular Automata (CA) to simulate complex solidification processes and predict microstructure evolution [11, 28]. This integrated approach is vital for establishing a predictive link between processing parameters and final material properties, thereby reducing the need for extensive physical testing and accelerating the development of new materials.



The non-equilibrium phase diagrams of flow-induced crystallization and melting of polyethylene

A deeper understanding of this interplay has significant implications for advanced manufacturing.

By precisely controlling laser parameters, engineers can effectively design the microstructure itself, creating materials with localized and custom-tailored properties, such as a hard surface combined with a ductile core [32]. Post-processing heat treatments are also a crucial part of this process. Since non-equilibrium phases are metastable, heat treatments can be used as a "second stage" of engineering to carefully modify properties, such as improving ductility or relieving residual stress [22]. The paper also addresses defect mitigation and outlines future research directions. The same extreme thermal conditions that create beneficial non-equilibrium phases can also cause defects like cracking and residual stress [25, 28]. The research explores strategies such as beam oscillation or the use of grain refiners to minimize these issues [25]. Looking ahead, the paper suggests that future research will likely focus on multi-material processing, AI-driven process optimization, and the design of novel non-equilibrium materials [33]. This represents a significant shift towards what the author calls "kinetic materials science," where the processing path becomes a primary design variable, opening new possibilities for high-performance materials.

References

- [1] trytaiga.com. "What is laser processing? Introduction of principles, typical processing machines, advantages and disadvantages"
- [2] shenchong.com. "Laser Cutting Machine Temperature Problems: Causes, Effects, Solutions"
- [3] tandfonline.com. "Full article: Recent advance in laser powder bed fusion of Ti-6Al-4V alloys: microstructure, mechanical properties and machinability - Taylor & Francis Online"
- [4] e3s-conferences.org. "RETRACTED: Rapid Solidification Techniques for Metal Processing: Microstructure and Properties - E3S Web of Conferences"
- [5] researchgate.net. "Effect of scanning speed on temperature gradient and cooling rate of molten pool."
- [6] en.wikipedia.org. "Non-equilibrium thermodynamics - Wikipedia"
- [7] cambridge.org. "Non-equilibrium phase transitions (Chapter 8) - Cambridge University Press"
- [8] youtube.com. "Lecture 16: Equilibrium and non-equilibrium cooling - YouTube"
- [9] slideshare.net. "Ttt cct diagrams | PPTX | Chemistry | Science"
- [10] elearn.psgcas.ac.in. "Lecture 21 - TTT and CCT curves - Materials Science and Engineering Dr. Vivek Pancholi Department of Metallurgical & Materials Engineering Indian Institute of"
- [11] researchgate.net. "Modeling of rapid solidification in Laser Powder Bed Fusion processes - ResearchGate"
- [12] scilit.com. "Study on the evolution mechanism of non-equilibrium solidification microstructure of AlSi10Mg alloy additive manufactured by LPBF | Scilit"
- [13] youtube.com. "Coring microstructure resulting from non-equilibrium cooling - YouTube"
- [14] adhmt.com. "Laser Cutting Machine Temperature: A Complete Guide"

- [15] researchgate.net. "The effect of laser welding parameters on the grain structure distribution in the resultant weld | Request PDF - ResearchGate"
- [16] scispace.com. "The Effect of Laser Power and Scan Speed on Melt Pool Characteristics of Pure Titanium and Ti-6Al-4V Alloy for Selective Laser M - SciSpace"
- [17] researchgate.net. "The effects of the laser spot size, R_0 ($t = 1.5 \text{ s}$, $v = 0.008 \text{ m/s}$, $\tau = 0.05 \text{ s}$)"
- [18] volkov.eng.ua.edu. "Effect of the spot size on ionization and degree of plasma shielding in plumes induced by irradiation of a copper target by multiple short laser pulses"
- [19] en.wikipedia.org. "Phase transition - Wikipedia"
- [20] wpfiles.mines.edu. "Martensite in steel: strength and structure - Mines Files"
- [21] researchgate.net. "(PDF) Effect of cooling rate on the microstructure and mechanical properties of microalloyed forging steel - ResearchGate"
- [22] mdpi.com. "The Influence of Heat Treatment and Laser Alternative Surface Treatment Methods of Non-Alloy Steels: Review - MDPI"
- [23] mdpi.com. "Microstructure and Mechanical Properties of Titanium Alloys Produced by Additive Technologies: New Approaches and Promising Areas of Research - MDPI"
- [24] researchgate.net. "Laser Cladding of Ni-Based Superalloys | Request PDF - ResearchGate"
- [25] mdpi.com. "Effect of the Laser Cladding Parameters on the Crack Formation and Microstructure during Nickel Superalloy Gas Turbine Engines Repair - MDPI"
- [26] mdpi.com. "Effect of Tempering Time on the Microstructure and Properties of Martensitic Stainless Steel"
- [27] pmc.ncbi.nlm.nih.gov. "The Influence of Thermomechanical Conditions on the Hot Ductility of Continuously Cast Microalloyed Steels - PMC"
- [28] pmc.ncbi.nlm.nih.gov. "A Review of the Evolution of Residual Stresses in Additive Manufacturing During Selective Laser Melting Technology - PMC - PubMed Central"
- [29] researchgate.net. "Residual stress measurements in laser shock processed materials - ResearchGate"
- [30] xometry.com. "Laser Cladding: Definition, Process, Types, Applications, and Features | Xometry"
- [31] dierk-raabe.com. "Metallurgical Materials Science and Alloy Design - Martensite alloys and transformations"
- [32] laserline.com. "Laser Additive Manufacturing: Metal Production | LASERLINE"
- [33] megmeet-welding.com. "Laser Welding Technology: Evolution History & Future Trend"
- [34] mdpi.com. "Special Issue: Non-equilibrium Phase Transitions - Entropy - MDPI"
- [35] oxygenservicecompany.com. "Explaining Laser Welding | Oxygen Service Company"
- [36] numberanalytics.com. "www.numberanalytics.com"
- [37] virmer.com. "Metal laser cutting: operating principles and advantages"

Extraction of Antimony as a Critical Element from Secondary Waste Sources

Neli Mintcheva^{1,*}, Marinela Panayotova², Gospodinka Gicheva²

Department of Engineering Geoecology, University of Mining and Geology, 1700 Sofia, Bulgaria ¹

Department of Mineral Processing and Recycling, University of Mining and Geology, 1700 Sofia, Bulgaria ²

Abstract: Recovering antimony from secondary sources is increasingly important to ensure a sustainable and secure supply of this critical metal. Industrial residues, waste materials, and by-products offer opportunities for recycling and reprocessing, reducing economic dependence on primary ores. This paper reviews potential waste streams and processing methods for achieving high-yield antimony recovery.

Keywords: ANTIMONY, SECONDARY SOURCES, RECOVERY, PRODUCTION WASTE, END-OF-LIFE PRODUCTS

1. Introduction

The strategic industrial use of antimony (Sb) in products such as flame retardants for electronics, plastics and textiles, lead-acid batteries, alloys, catalysts for polymers determine it as a key chemical element, which is considered as a critical raw material by the European Commission and the U.S. Geological Survey. The antimony supply faces significant risk because of geographical concentration of the natural ore deposits and global production (mainly in China), environmental requirements for the toxic waste, and little amounts of Sb that are mainly produced from lead, copper, silver and gold minerals (Figure 1). That's why recovering Sb from secondary sources is becoming increasingly important for ensuring sustainable production of this critical metal. Secondary waste sources of antimony include end-of-life products and waste materials, industrial residues, and by-products from which Sb can be recycled or reprocessed, rather than extracted Sb from primary sources such as natural ore stibnite.

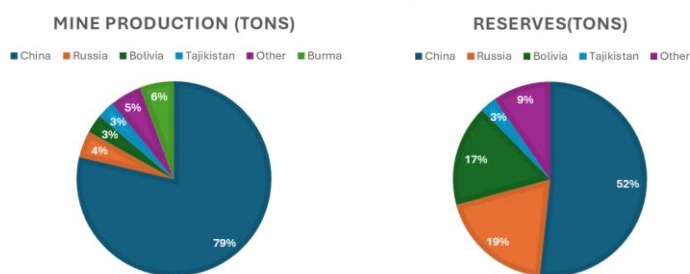


Fig. 1 Antimony production and ores reserves. Data for 2014 are adapted from [1].

In 2014, the European Commission classified antimony as a critical raw material. This classification was based on several factors, including the expected high supply–demand gap expected for 2015–2030, the metal's high economic importance, and the heavy geographical concentration of production, with about 79% of global output coming from China, which causes geopolitical dependence for European industry (Fig. 1). Moreover, reserves of primary natural resources are limited [1]. Antimony is mainly produced from stibnite ore (Sb_2S_3), other sources including oxide ore (Sb_2O_3) and ores containing mainly lead, copper, zinc, silver, and gold, that are known as primary sources. Secondary sources are end-up products and manufacturing residues.

In industry antimony is used in the form of metal and as an antimony oxide, Sb_2O_3 . Metallic Sb with high purity is used in new materials with unique properties. Around 90% of Sb_2O_3 produced is used for incorporation in fire-resistant coatings, plastics and electronics as a flame retardant. It shows synergistic effects with brominated organic compounds, which reduces the necessity of their amounts and increases the reliability of the electronic and plastic items. Antimony is used as hardener in lead alloys that are implemented as electrodes in lead-acid batteries for cars. Production

of widely used polymer polyethylene terephthalate (PET) is catalyzed by antimony compounds such as antimony oxide, antimony acetate, antimony ethylene glycolate. Antimony-containing catalysts are also applied to fluorination of chlorinated hydrocarbons and catalytic cracking of hydrocarbons. Other uses include additive for decolorizing optical glasses for cameras, binoculars, photocopiers; dopant in phosphors in fluorescent lamps; paint pigments; agents for vulcanizing red rubber; etc., that are shown in Figure 2.

Sb_2O_3	Flame retardant
- antimony oxide is used as a Flame retardant in plastics, electronics, coatings - this application takes up the majority of the world's production	
Sb_2O_3 $\text{Sb}(\text{CH}_3\text{COO})_3$	Catalysts
- compounds of Sb(III) are used as a catalysts in production of polyethylene terephthalate (PET) - as a catalyst in fluorination of chlorinated hydrocarbons	
Sb metal	Pb-Sb alloys
Sb is used as a hardener in lead alloys for electrodes in lead-acid batteries	
NaSbO_3	Additive in glass
antimony acts as decolourizing agent for optical glass in cameras, binoculars, photocopiers	
Sb^{3+} ion	Dopant in luminophours
Sb is used in phosphors for fluoriscent lamps	
Sb	Other uses
- Sb is used as paint pigments (Sb_2O_3, Sb_2S_3, Sb_2S_5) - in semiconductors (AsSb, GaSb, InSb) - vulcanizing agents in red rubber production	

Fig. 2. Industrial products contain different antimony species.

Herein, we review the importance of antimony for industry, the types of secondary antimony sources, the possibilities for extraction of antimony from various wastes and the applied methods of their processing to achieve the Sb recovery in high yield.

2. Secondary waste sources

Secondary antimony sources include manufacturing waste (mine process residues, scrap, slag, flue dust, anode slime, electrolyte solutions) from production of lead, copper, gold and antimony, and end-of-life products such as lead-acid batteries, plastics and electronics, spent catalysts from production of PET polymers and catalytic cracking, phosphor powders from spent fluorescent lamps, landfills and incineration ashes.

Manufacturing waste

These residues are formed during ores processing and different steps of production line. Most manufacturing wastes are currently discarded, causing environmental issues rather than being utilized as valuable resources for antimony recovery by using different methods, which strongly depend on the Sb content and its ratio with other metals.

Production residues are accumulated in different steps of antimony production from stibnite, gold production from gold-containing ores, copper production from copper ores such as chalcopyrite, which often contain antimony, arsenic and bismuth as impurities, lead production from mineral galena, PbS and lead recycling of lead alloys. Different residues containing antimony and potential source of Sb extraction are shown in Figure 3.

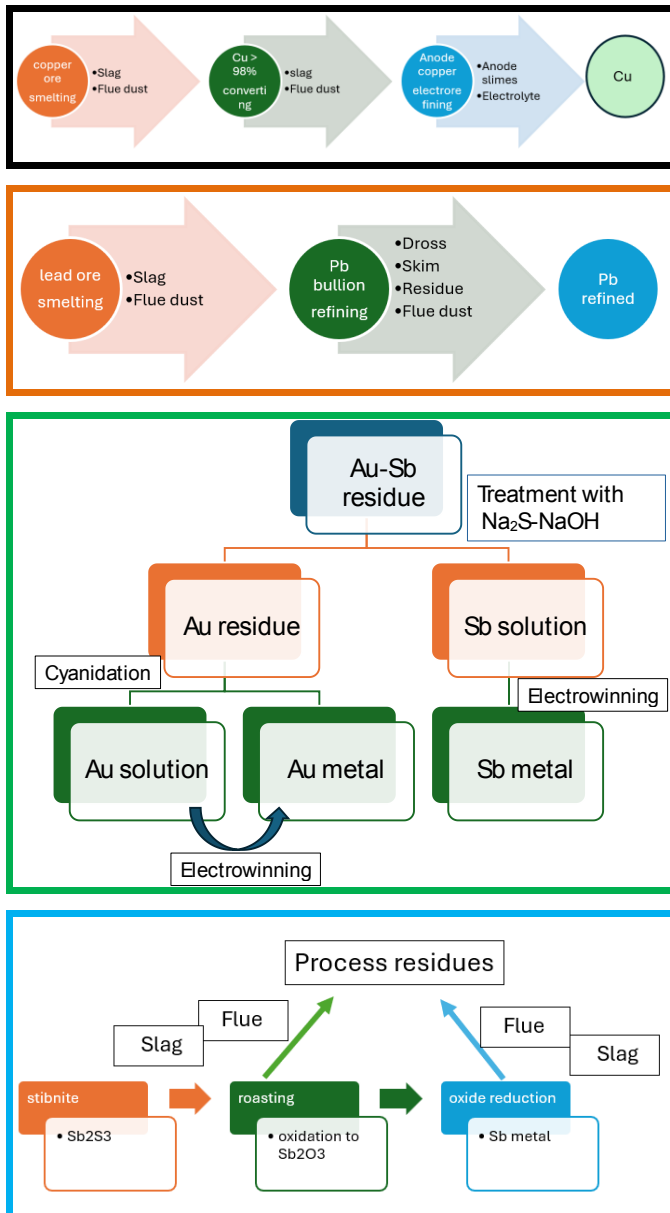


Fig. 3. Manufacturing Sb-containing wastes from production of copper, lead, gold and antimony.

Electronic and plastic waste

Antimony trioxide, Sb_2O_3 is incorporated into plastics, electronics, textiles to reduce the flammability of materials (fire retardant). Around 43% from the world production of Sb is consumed for flame retardants, but recycling methods are still

limited. Sb_2O_3 is combined with brominated organic compounds for synergistic effect. During recycling of waste, separation of plastics, brominated compounds and antimony oxide are the target products.

Lead-containing waste

Lead-acid batteries used in cars contain Pb-Sb alloy. Due to similar physical and chemical properties of both metals, efficient methods for their separation and purification are required. Lead alloy and lead oxide, used as electrodes in the batteries, are separated by mechanical processes. Lead oxide is reduced, and lead is melted to produce secondary lead and by-products containing antimony. It is extracted by formation of soluble compounds, when the residue is treated with a mixture of aqueous Na_2S and NaOH . After that antimony is selectively oxidized to Sb_2O_3 . Electrochemical recovery of antimony from a solution is often applied.

Spent catalysts

Sb(III)-containing catalysts are widely used in polymer production of textile fibers and food PET containers. Antimony can be recovered from spent catalysts by combustion of the waste and extraction of antimony from the ash. Other methods use hydrochloric acid for leaching antimony followed by its recovery from leach solution by precipitation, ion exchange or extraction.

Lamp phosphor waste

Phosphors are powders coated the glass surface of fluorescent lamps, that contain antimony as a dopant in halophosphates. The latter compounds are dissolved in acidic solutions and then antimony is extracted by ionic liquid with high selectivity.

Municipal incinerator waste

Heating of various Sb-containing end-up products at a temperature of 800-1000 °C forms several products like boiler ash, fly ash and residue. All of them contain antimony, but the highest amount was found in fly ash due to volatility of antimony and its compounds. Leaching of Sb can be carried out with acidic solutions such as hydrochloric acid, nitric acid, citric acid and/or chelating reagents (EDTA, etc.).

3. Methods for antimony recovery

Many methods are reported in the literature for recovery of antimony. Hydrometallurgy and solvometallurgy are often applied not only in industry for production of antimony from the ore stibnite, but also in laboratory tested ways for antimony recycling [2,3]. Additionally, pyrometallurgical methods for processing secondary sources are rarely used due to high energy consumption and environmental challenges for treatment of antimony and arsenic compounds, that may be released in the exhaust gases. Methods for extraction of antimony might be classified as follows: a) hydrometallurgy (leaching with alkaline sulfide solution, dissolution with HCl, extraction with quaternary ammonium chloride); b) Solvent extraction; c) separation by adsorption; d) solvometallurgy (using of non-aqueous solvents (organic, ionic liquids, supercritical liquids); e) bioleaching; f) microwave assistant methods; h) vacuum distillation. A summary of these methods is shown in Figure 4.

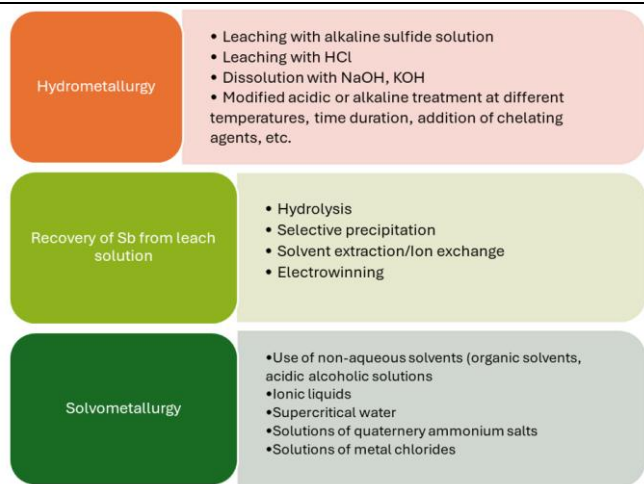


Fig. 4. Methods for antimony recovery from secondary sources.

4. Conclusions

The global ore resources of antimony are limited and gradually being depleted, making it essential to develop technologies for acquiring Sb supplies from alternative sources. This study provides an overview of secondary antimony sources, including manufacturing residues and end-of-life products, that could be processed to extract additional quantities of this critical element. Antimony-containing wastes—such as slurries, slags, flue dust, and slimes—generated during the processing of copper, lead, and gold ores remain generally unutilized at the industrial scale, although various recovery methods have been explored in laboratory scale. Among end-of-life products, only lead-acid batteries are currently recycled on a large scale to recover lead and antimony from Pb-Sb alloys. However, broader research to valorize waste and achieve a more sustainable life cycle of antimony is still under development. More efforts are needed to proceed towards a circular economy, where waste is considered as a valuable resource and zero-waste strategies are applied to the production and recovery of critical elements such as antimony.

5. References

1. D. Dupont, S. Arnout, P.T. Jones, K. Binnemans, Antimony Recovery from End-of-Life Products and Industrial Process Residues: A Critical Review. *J. Sustain. Metall.* 2, 79–103 (2016).
2. M. Panayotova, S. Pysmennyi, V. Panayotov, Antimony Recovery from Industrial Residues—Emphasis on Leaching: A Review. *Separations*, 12, 156 (2025).
3. A. Busurmanova, M. Tabylganov, A. Serikbayeva, S. Baimukasheva, M. Kizdarbekova, K. Agaidarova, Methods for processing of antimony-containing materials. *Journal of Chemical Technology and Metallurgy*, 58(5), 988-998 (2023).