Microstructural Characterization of Coatings Produced by Selective Laser Melting of Ni-Powder on Titanium Alloy Substrate

Danhe Chen and Sergey Konovalov*
Department of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing, China
Email: juliachen@njust.edu.cn, ksv@ssau.ru

Anastasia Golubeva, Vitalii Smelov, and Kirill Osintsev
Department of Metals Technology and Aviation Materials, Samara National Research University, Samara, Russia
Email: gol.nastya2018@yandex.ru, pdla_smelov@mail.ru, kirilloss@yandex.ru

Yurii Ivanov
Institute of High Current Electronics of Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia
Email: yufi55@mail.ru

Irina Komissarova
Department of Natural Sciences, Siberian State Industrial University, Novokuznetsk, Russia
Email: i.r.i.ss@yandex.ru

***Abstract*—The authors used selective laser melting of heat-resistant nickel alloy powder to assess applicability of additive technologies to deposition of nickel coatings on titanium substrate. Structure, element and phase composition of the coating was analyzed, revealing a multi-phase nature of the coating. Titanium atoms were detected in main phases of the coating, indicating diffusion saturation of sintered layer with elements of the substrate. Using methods of scanning electron microscopy sub-microcrystalline grains were found in the formed structure, owing to high-speed laser melting of the metal. Nano-dimensional particles of the second phase, which improve strength of the coating, are detected in the material and on edges of grains and sub-grains.**

***Index Terms*—selective laser melting, Ti alloy, Ni alloy, structure, phase composition.**

I. Introduction

All metals (except for gold and platinum) are corrodible due to oxidation. As a result of metal and environment reaction oxides, hydroxides and sulfides are formed on its surface. Corrosive degradation of a metal is possible, since the energy of a metal oxide is lower than that of a pure metal. Any measures to resist corrosion require understanding of fundamentals of corrosive reactions, their factors and kinetics. The simplest way ever is to isolate a metal from the environment; that is possible with the help of different coatings [1].

Metal-based protective coatings are used to form a shielding, design, special or combined layer on the surface of machine parts. Protection of the base metal from corrosion and fracture is a key function of a metal-based coating. Furthermore, depending on the composition, coatings can improve hardness, wear resistance, electrical conductivity and other properties of the surface.

Tin-plating and galvanization are thought to be the first technologies. A study [2] gives an insight into issues of hot galvanization, and research [3] summarizes data on tin-plating and new studies in this field. Coatings deposited in different laser-based processes are believed to be the most up to date ones.

Among the most frequently used techniques of coating deposition there are electro-spark alloying [4-8], surfacing [8-11], gas-dynamic spraying [12], magnetron spraying [13-15], boriding [16], nitriding [17], chrome-plating [18]. In recent years, however, they want to abandon the use of Chromium VI. Despite being an effective anti-corrosion agent, Cr (VI) is a health hazard [19]. Zirconium-plating is a promising technique for chromium replacement. For instance, deposition of a three layered nano-coating of zirconium oxide on aluminum alloy and its further heat treatment at 250°C has the same anti-corrosion effect as chromium-plating [20].

Over the last 10 years additive technologies have made a breakthrough from manufacturing elements of simple plastic and polymer compounds to aircraft engine parts. They are being developed in all industries, and can probably replace many classical subtractive manufacturing technologies [21, 22].

Manuscript received July 25, 2019; revised May 11, 2020.

doi: 10.18178/ijmerr.9.7.954-959

Selective laser melting (SLM) is believed to be one of the most prospective additive technologies, applied widely in different branches of a present-day industry. A majority of studies has used selective laser melting for synthetizing a pure or a composite material. However, this technique can be applied to deposition of coatings on traditionally manufactured materials, i.e. rolling or stamping. Deposition of wear resistant coatings using this technique might become a new stage in the development of this technology [23]. For instance, studies [24-25] report on SLM of composite materials. These works highlighted a possibility to combine heatproof ceramic materials with different metal-based alloys via layer-by-layer melting of powders by a powerful laser. Synthesized materials demonstrated high adhesion properties and under condition of sufficient laser irradiation power high density of samples, comparable with traditional techniques [26].

So far, however, there has been little discussion on SLM-deposition of coatings on different traditionally manufactured elements, so this study aims at SLM-deposition of nickel-based coating on titanium alloy substrate. This work provides an opportunity to access a potential of SLM-deposition of heatproof coatings on titanium plates. Further studies can be focused on deposition of coatings on samples with a complex physical configuration, making it possible to apply this method to manufacturing heatproof machine elements in airspace industry.

II. Materials and Methods of Research

Carrying out experiments we used samples (200×25×4 mm3) of VT20 titanium alloy (4.77 Al, 2.3 Zr, 0.97 V, 0.90 Mo, 0.1 other impurities; remainder Ti, mass. %) as a substrate. This material is important for manufacturing parts exposed to high temperatures for a long time. Chemical composition of VT20 alloy was determined with the help of a portable X-ray fluorescent analyzer X-Met 5100 applied to assess chemical composition of metals and alloys.

The powder of heat-resistant VV751P nickel alloy (alternative Inconel 718) was processed using SLM; its chemical composition is given in Table I. The powder is manufactured by All-Russian Institute of Light Alloys (Russia). Particles are 50 μm; the percentage of particles bigger 50 μm is around 20 % [27].

TABLE I. Chemical Composition of VV751P Alloy Powder (wt. %).

Al	Co	Cr	Fe	Mo	Nb
3.91	15.6	11.1	0.06	4.48	3.38
Ti	V	W	C	Fe	Ni
2.73	0.52	3.19	0.049	0.06	Balanced

Coatings were deposited by the industrial laser printer SLM 280 HL (SLM Solutions Group AG, Lubeck, Germany) of CAM common use technology Samara National Research University. Processing conditions are as follows: laser irradiation power – 325 W, laser speed – 760 mm/s, layer thickness – 50 μm, laser step – 120 μm, shielding medium – argon. Laser was moved in a cross-hatching manner, the lines passed at an angle of 45˚ with each other. Cross hatching was carried out twice.

To assess element and phase composition, defect sub-structure of the obtained coating we applied methods of scanning electron microscopy (SEM) (device Philips SEM-515 equipped with a micro-analyzer EDAX ECON IV), electron diffraction of thin foils via transmission electron microscopy (TEM) (device JEOL JEM-2100 F) and X-Ray structural analysis (X-Ray diffractometer Shimadzu XRD 6000). For preparation of foils plates were cut of samples parallel and close to the surface. Using this procedure for preparation of samples to be examined, the structure of material was analyzed in relation to the distance to the sample surface (0, 50 and 200 μm).

III. Results and Discussion

SEM has revealed a striped pattern typical for this melting technique of powder materials (Fig. 1, a) [23]. On the sintered surface there are longitudinal and transversal micro-cracks (relative to melting paths) (Fig. 1, b, micro-cracks are shown by arrows).

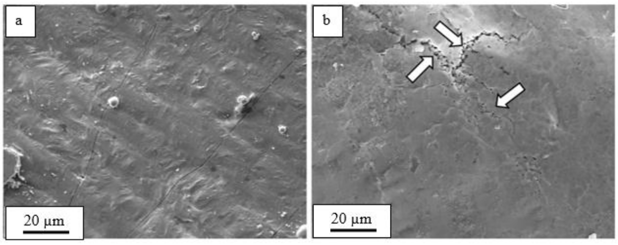


Figure 1. The surface of coating deposited in SLM

Analyzing the structure of cross-cut sections it was found out that in the process of SLM a solid layer is formed, its thickness varies 70 to 130 μm (Fig. 2, a). In the sintered layer there are micro-cracks, which are identified at an angle of 45-90˚ with the surface of modification (Fig. 2, a). Apparently, cracking appears due to non-corresponding thermal expansion coefficients of coating and substrate. The researchers [12] have reported on this problem after detecting cracks in the cross-section of ceramic coatings deposited on tungsten substrate. They think that micro-cracks are possible because of the significantly different thermal expansion coefficients of coating and substrate. The specified thermal expansion coefficient of the coating ($5.4 \cdot 10^{-6}$ K^{-1}) exceeded that of the substrate ($4.59 \cdot 10^{-6}$ K^{-1}). Nickel alloy powder used in this study also has a thermal expansion coefficient ($13 \cdot 10^{-6}$ K^{-1}) higher than that of titanium alloy substrate ($9 \cdot 10^{-6}$ K^{-1}) [24]. Micro-cracks on the interface of the sintered layer and substrate were not found. Analyzing the structure of a section, an etching pattern was revealed, its elements range 1.2 to 1.9 μm (Fig. 2, b).

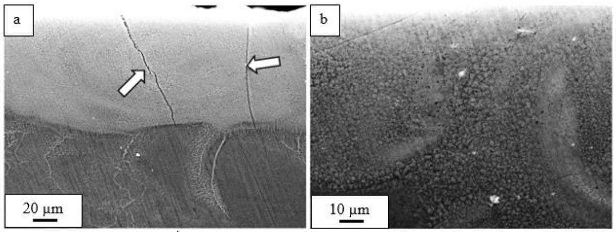


Figure 2. The cross-cut section of material synthesized in SLM

Using methods of X-Ray phase analysis, a multiphase nature of the surface formed in SLM was revealed (Fig. 3). Its main phases contain titanium atoms in different percentages, for instance, TiNi (47 wt. %), $TiCo_{0.5}Ni_{0.}5$ (29 wt. %), TiCrAl (20 wt. %), and $Ti_{0.25}Al_{0.75}$ (4 wt. %), indicating, this way, a high concentration of substrate atoms (titanium-based alloy VT20) in the sintered layer.

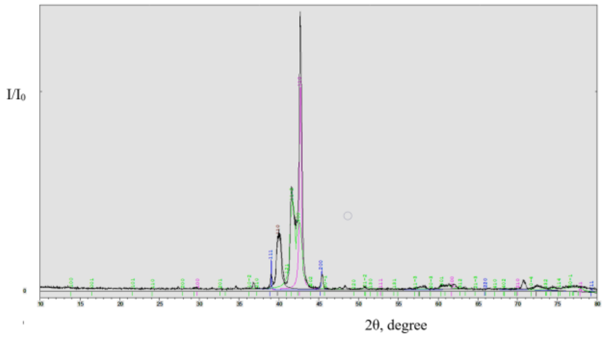


Figure 3. X-Ray picture of the surface layer in SLM-synthesized material

Electron diffraction via TEM was used to assess element and phase composition, morphology of phases in the surface layer. Sections to be examined were at different depths from the sample surface in a layer ≈200 µm.

Fig. 4 gives a SEM-image of a layer section structure adjacent to the treated surface. Focusing on findings of the dark-field analysis (Fig. 4, b), a conclusion about the polycrystalline structure in the surface layer is made; dimensions of crystallites are 0.8 to 1.2 µm. The crystallites are formed with NiTi phase. Particles (80 – 200 nm) of the second phase containing $CoTi_2$ (Fig. 4, c) are found mainly on edges of crystallites.

According to element composition determined by X-Ray micro-spectral analysis of thin foils (Fig. 5), main elements of the surface layer are components of alloy VV751P powder, as well as titanium (substrate element) with a quite high relative concentration (Fig. 6). This fact being of high importance for the phase composition of material layer to be analyzed indicates deep melting of powder and surface layer of the substrate.

Fig. 6 provides results of X-Ray micro-spectral study on element composition of this layer. Significantly, the relative concentration of titanium atoms in the sintered layer increases with the distance from the treated surface. This fact undoubtedly indicates diffusion saturation of the sintered layer with elements of the substrate, principally, atoms of titanium.

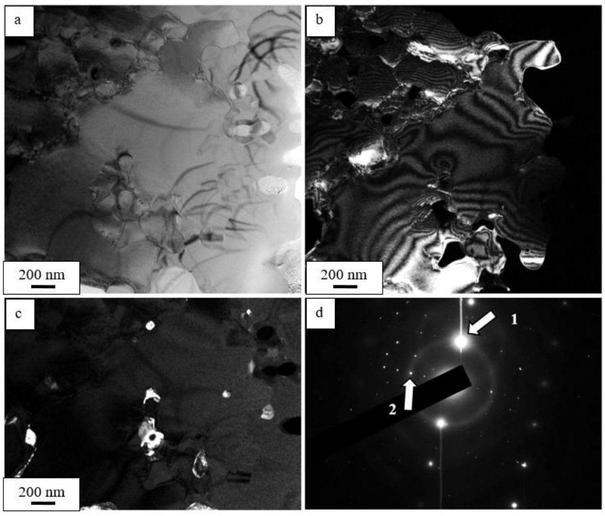


Figure 4. SEM-image of the coating structure: a – bright field; b, c – dark fields, obtained in reflexes [110]NiTi and [333]$CoTi_2$; d – electron-diffraction micro-pattern, arrows show 1 – reflex for the dark field (b), 2 – (c)

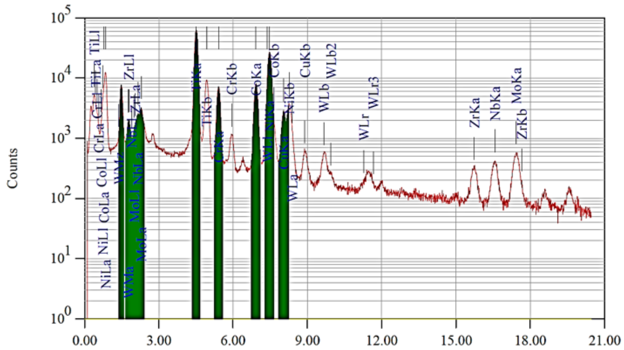


Figure 5. Power distribution on the coating surface

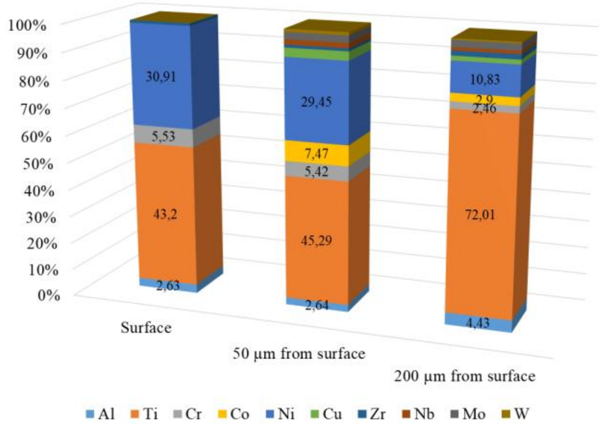


Figure 6. Element composition of the coating vs. distance

Fig. 7 gives a SEM-image of structure in the layer at a depth 50 µm. the layer has a sub-microcrystalline structure, crystallites vary 350 to 400 nm (Fig. 7, a, b). Inclusions of the second phase (50 nm to 130 nm) are found primarily on the edges of crystallites (Fig. 7, c). Indexing electron-diffraction micro-pattern obtained on this section of foil, it has been revealed that the sub-microcrystalline structure is formed mainly with α-titanium; second phase inclusions shown in Fig. 7, c, are titanium nickelide (Ni_3Ti). Element composition in the layer at a depth of 50 µm is quite similar to that of the surface layer.

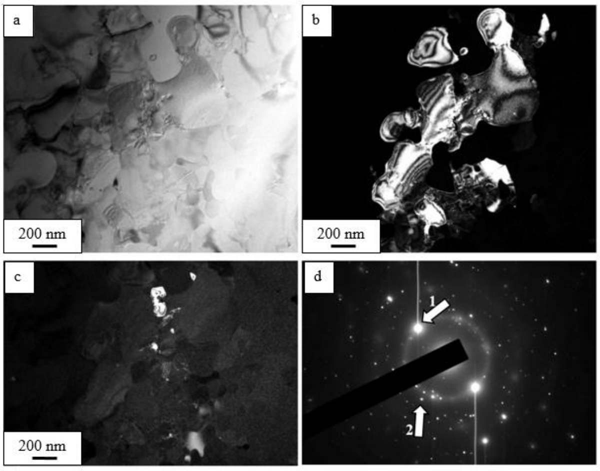


Figure 7. SEM-image of the coating structure (depth ≈50 µm): a – bright field; b, c – dark fields obtained in reflexes [101]Ti and [004]Ni_3Ti; d – electron-diffraction micro-pattern, arrows show 1 – reflex for a dark field (b), 2 – (c).

The layer of SLM-processed alloy VV751P powder adjacent to the substrate (titanium-based alloy VT20) is a polycrystalline aggregate; its main phase - α-titanium forms grains of 10-15 µm. Particles of the second phase (dimensions ranging from ones to tens nm) are detected among the grains (Fig. 8, a). In the process of micro-diffraction analysis reflexes of phases were found: $NiTi_2$ (Fig. 8, c) and $TiCo_2$ (Fig. 8, d), as well as phase Ni_7Zr_2.

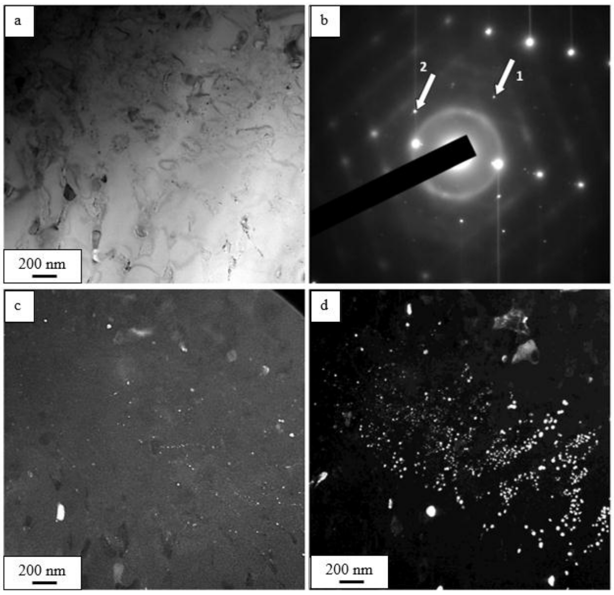


Figure 8. SEM-image of the coating structure (depth ≈200 µm); a – bright field; b, c – dark fields obtained in reflexes [733]$NiTi_2$ and [311]$TiCo_2$; d – electron-diffraction micro-pattern, arrows show 1 – reflex for a dark field (c), 2 – (d).

Therefore, carrying out studies by electron diffraction of thin foils via TEM, a multiphase multi-element sub-micro and nanocrystalline material was detected in the layer formed in SLM of alloy VV751P powder.

IV. Conclusion

Structure, element and phase composition of the coating deposited in SLM of alloy VV751P powder were assessed. The studies conducted with the help of SEM and electron diffraction via TEM, as well as X-Ray phase analysis, have determined, first, a significant difference of element composition in the formed layer and in the original powder. The formed layer contains mainly titanium (element of the substrate); its relative concentration increases with the distance from the treated surface. Second, the structure formed is a multiphase one; its main components are titanium-containing phases. Third, a polycrystalline structure is made of sub-microcrystalline grains, being caused, probably, by a high-speed mode of laser sintering. Forth, nano-dimensional particles of the second phase are found among grains and on edges of grains and sub-grains, as a result, strength and wear resistance of the sintered surface layer are improved.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Danhe Chen analyzed results and wrote paper; Sergey Konovalov conducted the research and wrote the paper; Anastasia Golubeva analyzed the data of SEM and XRD research; Vitalii Smelov made SLM tests; Kirill Osinsev and Irina Komissarova made XRD research; Yurii Ivanov made SEM and TEM analysis; all authors had approved the final version.

Acknowledgment

Standard samples for mechanical testing were manufactured on the equipment of the center of CAM common use technology of Samara National Research University (RFMEFI59314X0003). The authors wish to thank Ekaterina Nosova for technical assistance.

References

[1] S. Virtanen, “Corrosion and passivity of metals and coatings,” in *Proc. Tribocorrosion of Passive Metals and Coatings*, Elsevier, 2011, pp. 3–28.

[2] M. Sun and J. A. Packer, “Hot-dip galvanizing of cold-formed steel hollow sections: a state-of-the-art review,” *Front. Struct. Civ. Eng.*, vol. 13, no. 1, pp. 49–65, Feb. 2019.

[3] M. Munoz, H. Chen, and J. Hernandez, “Tin plating investigation as a potential alternate to silver plating in plug in connection for low voltage low amp miniature circuit breakers,” in *Proc. 2016 IEEE 62nd Holm Conference on Electrical Contacts (Holm)*, 2016, pp. 187–191.

[4] A. E. Kudryashov, Z. V. Eremeeva, E. A. Levashov, V. Y. Lopatin, A. V. Sevost’yanova, and E. I. Zamulaeva, “On application of carbon-containing electrode materials in technology of electrospark alloying: part 1. Peculiarities of coating formation using electrospark treatment of titanium alloy OT4-1,” *Surf. Eng. Appl. Electrochem.*, vol. 54, no. 5, pp. 437–445, Sep. 2018.

[5] A. D. Verhoturov, V. D. Vlasenko, and L. A. Konevtsov, “Investigation of the adhesive strength of antifriction coatings depending on the energy parameters of electro-spark alloying,” *J. Frict. Wear*, vol. 39, no. 3, pp. 232–240, May 2018.

[6] A. V. Kozyr, L. A. Konevtsov, S. V. Konovalov, S. V. Kovalenko, and V. I. Ivashenko, "Research of heat resistance of the multilayer coating after electro-spark alloying of C45 steel Cr-Ni alloys," *Lett. Mater.*, vol. 8, no. 2, pp. 140–145, May 2018.

[7] J. Tang, "Mechanical and tribological properties of the TiC–TiB2 composite coating deposited on 40Cr-steel by electro spark deposition," *Appl. Surf. Sci.*, vol. 365, pp. 202–208, Mar. 2016.

[8] L. Zhang, C. Wang, L. Han, and C. Dong, "Influence of laser power on microstructure and properties of laser clad Co-based amorphous composite coatings," *Surfaces and Interfaces*, vol. 6, pp. 18–23, Mar. 2017.

[9] L. L. Zhai, C. Y. Ban, and J. W. Zhang, "Investigation on laser cladding Ni-base coating assisted by electromagnetic field," *Opt. Laser Technol.*, vol. 114, pp. 81–88, Jun. 2019.

[10] J. Zhao, Q. Gao, H. Wang, F. Shu, H. Zhao, W. He, et al., "Microstructure and mechanical properties of Co-based alloy coatings fabricated by laser cladding and plasma arc spray welding," *J. Alloys Compd.*, vol. 785, pp. 846–854, May 2019.

[11] S. V. Konovalov, V. E. Kormyshev, V. E. Gromov, Y. F. Ivanov, E. V. Kapralov, and A. P. Semin, "Formation features of structure-phase states of Cr–Nb–C–V containing coatings on martensitic steel," *J. Surf. Investig. X-ray, Synchrotron Neutron Tech.*, vol. 10, no. 5, pp. 1119–1124, Sep. 2016.

[12] R. N. Raoelison *et al.*, "Cold gas dynamic spray technology: A comprehensive review of processing conditions for various technological developments till to date," *Addit. Manuf.*, vol. 19, pp. 134–159, Jan. 2018.

[13] B. Ren, Z. Shen, and Z. Liu, "Structure and mechanical properties of multi-element (AlCrMnMoNiZr)Nx coatings by reactive magnetron sputtering," *J. Alloys Compd.*, vol. 560, pp. 171–176, May 2013.

[14] J. Musil, "Flexible hard nanocomposite coatings," *RSC Adv.*, vol. 5, no. 74, pp. 60482–60495, 2015.

[15] M. Braic, M. Balaceanu, A. Vladescu, C. N. Zoita, and V. Braic, "Deposition and characterization of multi-principal-element (CuSiTiYZr)C coatings," *Appl. Surf. Sci.*, vol. 284, pp. 671–678, Nov. 2013.

[16] S. G. Ivanov, M. A. Guriev, M. V. Loginova, V. B. Deev, and A. M. Guriev, "Boriding of titanium OT4 from powder saturating media," *Russ. J. Non-Ferrous Met.*, vol. 58, no. 3, pp. 244–249, May 2017.

[17] Y. G. Khusainov, K. N. Ramazanov, R. D. Agzamov, I. V. Zolotov, and R. S. Esipov, "Ion nitriding of martensitic and austenitic steels after SPD at different temperatures," *J. Phys. Conf. Ser.*, vol. 1115, p. 032033, Nov. 2018.

[18] C. L. Ko, Y. L. Kuo, W. J. Lee, H. J. Sheng, and J. Y. Guo, "The enhanced abrasion resistance of an anti-fingerprint coating on chrome-plated brass substrate by integrating sputtering and atmospheric pressure plasma jet technologies," *Appl. Surf. Sci.*, vol. 448, pp. 88–94, Aug. 2018.

[19] D. B. Mitton, A. Carangelo, A. Acquesta, T. Monetta, M. Curioni, and F. Bellucci, "Selected Cr(VI) replacement options for aluminum alloys: a literature survey," *Corros. Rev.*, vol. 35, no. 6, pp. 365-381, Dec. 2017.

[20] F. Andreatta, P. Aldighieri, L. Paussa, R. Di Maggio, S. Rossi, and L. Fedrizzi, "Electrochemical behaviour of ZrO2 sol–gel pre-treatments on AA6060 aluminium alloy," *Electrochim. Acta*, vol. 52, no. 27, pp. 7545–7555, Oct. 2007.

[21] ASTM F2792-12, "Standard terminology for additive manufacturing technologies," *ASTM International*. 2012.

[22] Y. Wang, X. Chen, and S. V. Konovalov, "Additive manufacturing based on welding arc: A low-cost method," *J. Surf. Investig. X-ray, Synchrotron Neutron Tech.*, vol. 11, no. 6, pp. 1317–1328, Nov. 2017.

[23] W. E. Frazier, "Metal additive manufacturing: A review," *J. Mater. Eng. Perform.*, vol. 23, no. 6, pp. 1917–1928, Jun. 2014.

[24] J. Koopmann, J. Voigt, and T. Niendorf, "Additive manufacturing of a steel–ceramic multi-material by selective laser melting," *Metall. Mater. Trans. B*, vol. 50, no. 2, pp. 1042–1051, Apr. 2019.

[25] D. King, J. Middendorf, K. Cissel, T. Key, and C. Carney, "Selective laser melting for the preparation of an ultra-high temperature ceramic coating," *Ceram. Int.*, vol. 45, no. 2, pp. 2466–2473, Feb. 2019.

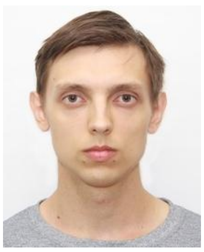
[26] E. Liverani, S. Toschi, L. Ceschini, and A. Fortunato, "Effect of Selective Laser Melting (SLM) process parameters on microstructure and mechanical properties of 316L austenitic stainless steel," *J. Mater. Process. Technol.*, vol. 249, pp. 255–263, Nov. 2017.

[27] A. V. Sotov, A. V. Agapovichev, V. G. Smelov, V. V. Kokareva, and M. V. Zenina, "Investigation of the Ni-Co-Cr alloy microstructure for the manufacturing of combustion chamber GTE by selective laser melting," *Int. J. Adv. Manuf. Technol.*, vol. 101, no. 9–12, pp. 3047–3053, Apr. 2019.

Danhe Chen got her PhD and master degree in Moscow Bauman State Technical University at Department of Ballistics, Dynamics and Flight Control of Spacecraft in 2016. She received the bachelor in power engineering in Nanjing University of Science and Technology. Currently, she is working as a lecturer of Nanjing University of Science and Technology and Department of Mechanical Engineering, and a specialist of Research Center of Micro/Nano satellite. Dr. Chen's research interests focus in the surface engineering, ballistic and dynamic problems of spacecraft, including formation flying and deep space exploration.

Sergey Konovalov graduated from the National Research Tomsk State University (Tomsk, Russia) with a BA and MA in solid state physics in 1998 and he received his Ph.D. in 2002 and his Doctoral Degree (Solid State Physics) in 2013 from the Siberian State Industrial University (Novokuznetsk, Russia). Currently, he is working as a head of Department of Metals Technology and Aviation Materials Samara National Research University (Samara, Russia) and expert of Nanjing University of Science and Technology. Professor Konovalov's research interests are in the areas of materials science, mechanical and surface engineering.

Anastasia Golubeva got her bachelor's degree in engine manufacturing, a master's degree in innovative production at the Samara National Research University. Currently, she is a PhD student at the Department of Metals Technology and Aviation Materials at Samara University. Ms. Golubeva's research area - properties of protective nanocoatings and technologies for their application.



Kirill A. Osintsev got his bachelor's degree in Materials Science and Materials Technology at Siberian State Industrial University, Novokuznetsk, Russia in 2018. Now he is Engineer of Department of Metals Technology and Aviation Materials and a master's student of the 2nd course in Metallurgy at Samara National Research University, Samara, Russia. Mr. Osintsev K.A. has got the scholarship of the President of the Russian Federation for studying abroad and has been studied in Wenzhou University, Wenzhou city, People's Republic of China for 6 months. Mr. Osintsev's research interests are in the areas of materials design and engineering.

Irina Komissarova got her PhD degree in Siberian State Industrial University at Department of Naturals Science, Solid State Physics in 2019. She received the masters in standardization and certification in Siberian State Industrial University. Currently, she is working as a junior research fellow of Siberian State Industrial University. Research interests Dr. Komissarova focus in the technically pure titanium and its alloys, transmission electron microscopy, scanning electron microscopy and external energy influences, including pulsed current processing and electron beam processing.