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

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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 corroding 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], surfaceing [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]...
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 synthesizing 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 (200x25x4 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 substructure 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).

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 (5.4·10^{-6} K^{-1}) exceeded that of the substrate (4.59·10^{-6} K^{-1}). Nickel alloy powder used in this study also has a thermal expansion coefficient (13·10^{-6} K^{-1}) higher than that of titanium alloy substrate (9·10^{-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).
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.

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 $\approx$ 200 $\mu$m.

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 $\mu$m. 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.
titanium nickelide (Ni₃Ti). Element composition in the layer at a depth of 50 µm is quite similar to that of the surface layer.

![SEM-image of the coating structure (depth ≈50 µm): a – bright field; b, c – dark fields obtained in reflexes [101]Ti and [004]Ni₃Ti; d – electron-diffraction micro-pattern, arrows show 1 – reflex for a dark field (b), 2 – (c).](image)

![SEM-image of the coating structure (depth ≈200 µm); a – bright field; b, c – dark fields obtained in reflexes [733]NiTi₂ and [311]TiCo₂; d – electron-diffraction micro-pattern, arrows show 1 – reflex for a dark field (c), 2 – (d).](image)

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 microdiffraction analysis reflexes of phases were found: NiTi₂ (Fig. 8, c) and TiCo₂ (Fig. 8, d), as well as phase Ni₇Zr₂.

![SEM-image of the coating structure (depth ≈50 µm): a – bright field; b, c – dark fields obtained in reflexes [101]Ti and [004]Ni₃Ti; d – electron-diffraction micro-pattern, arrows show 1 – reflex for a dark field (b), 2 – (c).](image)

Therefore, carrying out studies by electron diffraction of thin foils via TEM, a multiphase multi-element submicro 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 submicrocrystalline grains, being caused, probably, by a high-speed mode of laser sintering. Forth, nanodimensional 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; Yuriy Ivanov made SEM and TEM analysis; all authors had approved the final version.

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