The development of heterogeneous materials based on Ni and B\textsubscript{4}C powders using a cold spray and stratified selective laser melting technologies

A A Filippov\textsuperscript{1}, V M Fomin\textsuperscript{1,2,3}, A E Buzyurkin\textsuperscript{1}, V F Kosarev\textsuperscript{1}, A G Malikov\textsuperscript{1}, A M Orishich\textsuperscript{1,3} and N S Ryashin\textsuperscript{1}

\textsuperscript{1} Khristianovich Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences, Institutskaya 4/1, Novosibirsk 630090, Russia
\textsuperscript{2} Novosibirsk State Technical University, Karl Marx Avenue 20, Novosibirsk 630092, Russia
\textsuperscript{3} Novosibirsk State University, Pirogova Street 2, Novosibirsk 630090, Russia

E-mail: filippov@itam.nsc.ru

Abstract. The work is dedicated to the creation of new ceramic-composite materials based on boron carbide, nickel and using a laser welding in order to obtain three dimensional objects henceforth. The perspective way of obtaining which has been suggested by the authors combined two methods: cold spray technology and subsequent laser post-treatment. At this stage, the authors focused on the interaction of the laser with the substance, regardless of the multi-layer object development. The investigated material of this work was the metal–ceramic mixture based on boron carbide, which has high physical and mechanical characteristics, such as hardness, elastic modulus, and chemical resistance. The nickel powder as a binder and different types of boron carbide were used. The ceramic content varied from 30 to 70\% by mass. Thin ceramic layers were obtained by the combined method and cross-sections of different seams were studied. It was shown that the most perspective layers for additive manufacturing could be obtained from cold spray coatings with ceramic concentrations more than 50\% by weight treated when laser beam was defocused (thermal-conductive laser mode).

1. Introduction

The cold spray technology with the laser post-treatment of surface is a modern method of production of materials. It refers to additive technology, opening up opportunities for creating 3D objects. This technology has significant advantages in geometric form produced products, allows you to restore worn parts, has same advantages for scaling the resulting articles. For example, in [1] shows that the use of laser treatment cold spray stainless steel coatings can reduce porosity in the surface layers and to increase the corrosion resistance of the coatings. The authors [2] have shown that laser post-treatment coating of aluminum and Ni–20Cr allows to obtain coatings with improved adhesion. In [3], the laser post-treatment helps significantly reduce the porosity and improve the mechanical properties of the aluminum coating. In the survey [4] on the effect of the laser post-treatment on the properties of cold spray coatings it noted that the method of combining cold spray and selective laser melting has significant potential for the rapid transfer of laboratory development in technology in various industries such as automotive, marine, biomedical, aviation, aerospace, energy, petrochemical.
Combining the methods of cold spray and laser post-treatment gives a wide range of issues related to the limitations of both methods, and requires detailed investigation. It needs a selection of powder fraction and composition, sputtering and scanning strategy that significantly affect the coating properties, including coefficient of absorption of laser radiation. It is necessary to investigate the effect of laser processing parameters such as power, beam diameter, scanning speed, the frequency of the radiation on the structure and properties of coatings.

2. Methods and materials

VT20 titanium alloy was used as substrate material. The size of substrate were 50 \times 50 \times 3 \text{ mm}^3. Air was chosen as working and bearing gas at cold spray technology. Boron carbide (B$_4$C) powders were used from OKB-BOR with median particle sizes $d_{50}$ equal to 2.9 and 64 \text{ µm}. Ni powder PNK-UT-1 was used from Kola MMC, Monchegorsk-7 with $d_{50} = 10.4$ \text{ µm}. The bulk particle size distribution for these powders was analyzed using a laser diffraction particle analyzer LS 13 320 (Beckman Coulter, USA). Mechanical mixtures of Ni and B$_4$C powders with a content of boron carbide in the initial mixture of 30, 50 and 70% by weight, respectively (30/70, 50/50 70/30 respectively, where the first figure means the content of boron carbide, and the second—nickel). Mixing of the powders was performed using a V-shaped mixer Venus FTLMV-02 (FILTRA VIBRACION, Spain) for 30 min for each mixture. In mixtures 30/70 and 50/50, fine boron carbide powder ($d_{50} = 2.9$ \text{ µm}) was used, the 70/30 mixture was made from a large B$_4$C ($d_{50} = 64$ \text{ µm}).

Sputtering of mixtures with fine powder was carried out using an axisymmetric ejection nozzle and atmospheric feed due to the low flowability of these mixtures, which eliminates sputtering in a typical scheme. Formation of a coating from a mixture with a coarse powder was carried out according to a typical cold spray scheme with a doser and a flat Laval nozzle at the experimental cold spray stand at ITAM SB RAS.

Laser radiation with a lens from ZnSe with a focal length of 304 mm was focused deep into the material, on the surface and above the material. The focus retraction $\Delta f$ was located at $-20$ mm, 0, +20 mm from the upper surface of the substrate, the spot diameter on the surface for keyhole laser mode $-20$ mm and thermal-conductive laser mode $+20$ mm [5] was approximately.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Two types of laser focus: (a) keyhole laser mode ($\Delta f = -20$ mm); (b) thermal-conductive laser mode ($\Delta f = +20$ mm).}
\end{figure}
Figure 2. SEM-images of cross-section of cold spray coating with weight content of B₄C to Ni (a) 30/70; (b) 50/50; (c) 70/30.

2 mm. Surfacing was carried out in the protective atmosphere of helium, fed through the nozzle, the gas flow was 5 cl/s.

Laser post-treatment of the samples was carried out at ALTC, created in ITAM SB RAS, including a continuous CO₂ laser with a power of up to 5 kW with a beam quality parameter $K = 0.7$, a computer control system for a laser and a technological table. The scheme of the process feed to the sample is shown in figure 1. Laser treatment of coatings 10/90 and 90/10 were not produced because of low ceramic content and low efficiency of coating respectively.

Cross sections of tracks were produced. The microstructure investigation by electron microscopy was carried out using a Zeiss EVO MA 15 scanning electron microscope (SEM). The microscope is equipped with detector of backscattered electrons (BSD), allowing to judge the phase composition and the secondary electron detector (SE) for the analysis of surface morphology. In addition, an energy dispersive x-ray spectrometer Oxford Instruments INCA Energy 350X-Max was used to estimate the quantitative elemental composition. For each object of the study, at least two photographs were obtained in each of the detectors with magnifications of 100X and 500X, and an analysis of the elements along the surface of the investigated region was carried out. In the case of identifying features, more detailed photos with a larger magnification were made, and elemental analysis was performed at the point.

3. Results

The SEM-pictures are shown in figure 2. The thickness of cold spray coating is about 200 µm. It can be shown that nickel has a much higher adhesion to the substrate and is capable of forming a continuous layer of deformed particles. Nickel reliably adheres to the surface, forming characteristic “splatls”. Boron carbide particles penetrate in a titanium substrate, to a depth of no more than its size. The ceramic particles do not stick to each other due to the high hardness and uniformly distributed throughout the coating thickness. Ceramic particles may bounce when interacting with coating or make denser the metal layer and adhere to nickel. With increasing concentration of boron carbide in the mixture and increases its volume content in the coating, but the proportion of solids in the coating is substantially less than in the initial mixtures, as evidenced by energy dispersive analysis data (figure 3).

After interaction laser with substrate a complex picture of the interaction of the substrate, coating and components of the mixture appears. It caused by significant temperature gradients, the difference in the physical and mechanical properties of the components, the coating structure. Laser tracks differ from coating both in color and in the surface and look like form of the straight lines with smooth edges and a sufficiently smooth undulating surface. This indicates on multiple
Figure 3. The dependence of the actual content of the components in the cold spray coating on the initial content of boron carbide.

phase melting and mixing the active cavity in the weld. A significant amount of titanium on the surface and the almost complete absence of it in the seam. EDX-analysis shows mixing zone the presence of titanium and nickel, presumably forming alloy. The significant factor affecting the depth of the cavity is, the method of focusing laser radiation. When focusing in the depth of the material, nickel and boron carbide penetrate deeper than in the case of a laser under defocusing, but melted mixture moves from the center to edges of cavity formed pores and cracks. It could be used in one layer laser welding for wear-resistant coatings. For thermal-conductive laser mode at the same power pores and cracks are less and it could be perspective for further cold spray layer-by-layer coating.

At the same time, the concentration of such a refractory component as boron carbide significantly changes the melt pattern. First of all, it is worth noting that the mass content is less than in the cold spray coating. Homogeneous particle distribution could evidence about high melt mixing speed. The change in the coefficient of surface tension with increasing concentration leading to a change in the shape of the seam, the direction of movement of the ceramic particles in the melt. It could be connected with change of viscosity of melt components. It is also noted that, under the influence of laser post-treatment, the particles split into smaller (figure 4), are mixed in the nickel melt, removed to the outside, or form a layer of particles near the coating-substrate boundary. It could be explained by chemical reactions between melted titanium and boron carbide at high temperatures. Liquid titanium–nickel mixture wets ceramic particles, forming metal borides and carbides. It could be seen in case of high boron carbide concentrations with particles size 64 µm. There are all defects on edges of cavity and high concentrations of hardening ceramic particles, good adhesion with substrate. These modes are prospective to further investigations for used combined method.
Figure 4. Changes of the shape of the track profile after laser treatment, depending on the content of ceramic particles in the original mixture. Left—focus $\Delta f = -20$ mm, right—focus $\Delta f = +20$ mm. (a) weight content, % $\text{B}_4\text{C}$ to Ni—30/70, $d_{50} = 2.9$ $\mu$m; (b) weight content, % $\text{B}_4\text{C}$ to Ni—50/50, $d_{50} = 2.9$ $\mu$m; (c) weight content, % $\text{B}_4\text{C}$ to Ni—70/30, $d_{50} = 64$ $\mu$m.
4. Conclusions
The experiments performed in this study proved feasibility of creation of wear-resistant coatings by combined method cold spray with further laser-treatment from metal–ceramic mixture. For the initial nickel–boron carbide mixtures with different weight ratio under chosen parameters of cold spray and laser beam modes showed metal–ceramics seams. Besides, the interaction of boron carbide with molten metal yielded new ceramic particles. The content of ceramic particles in cold spray coating decreases in comparison with initial mixture, especially in mixtures with high ceramic weight ratio. For cold spray method acceptable mixtures are 50/50 and 70/30. Besides, particle size limited by features of method: small particles stick to nozzle. For the two types of considered powders, the preferred is boron carbide with median particle sizes $d_{50} = 64 \mu m$. The form of cavity mainly depends on laser modes and ceramic content. Keyhole laser mode prevents to deep seam cavity but high temperature gradients on the edges of seam lead to cracks and pores. Thermal-conductive laser mode treatment has low pores and cracks. The significant factor of cavity form is a size of particles. The samples with big $B_4C$ particles showed smooth surface with form close to a biconvex lens with uniformly dispersed ceramic particles. The structure of such seams is most suitable for creating multilayer metal–ceramic coatings and three-dimensional products of simple shape.

Acknowledgments
This work is supported by basic research program of the Russian Academy of Science (No. 0323-2015-0002).

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