

IN-SITU SYNTHESIS OF MULTICOMPONENT ALLOYS FROM Ni BASED ELEMENTAL POWDERS BY DIRECT LASER DEPOSITION

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Abstract

The paper investigates an approach to the synthesis of classical heat-resistant alloys by laser cladding (LC) or direct laser deposition (DLD). This approach corresponds to the concept of developing the production of small parties of metal products with the economically feasible use of additive technologies. The results of already obtained materials from pure elemental powders and the prospects for the development of such formation of alloys from the liquid phase, as well as metal-matrix composites by 3D printing, are discussed. The paper presents the result of a specimen formation from a mechanical mixture of Ni / Cr / Fe powder, in the mass ratio of the main components, close in composition to the alloy Inconel 600. The produced multilayer specimen was studied by optical and electron microscopy. Measurement of fluctuations in the chemical composition in the specimen to determine the degree of diffusion of elements in the alloy was carried out. The formation of chromium oxide clusters along the boundaries of the tracks, which, presumably, diffuse in the direction of heat removal during crystallization from the melt, was found. The structure of the specimen is represented by large, elongated grains up to 1-2 mm in size, significantly exceeding the height of one pass. The direction of grain growth corresponds to the growth direction of the specimen in the direction of the Z axis.

Keywords: Direct laser deposition, laser cladding, powder metallurgy, alloy synthesis, nickel and iron alloys

1. INTRODUCTION

The introduction of metal additive technologies in the real economic sector may now be a priority for maintaining the growth rate of this area of industrial production. The advantage of the introduction of additive technologies is the ability to reduce the number of operations when obtaining the final product from the raw material. Many people know about the technology of metal printing, using the method of powder bed fusions, which is called selective laser melting (SLM). The units that use this technology are supplied as a complete self-sufficient system that allows you to make parts from a variety of materials according to the modes already worked out by the manufacturer. The cost of such machines is quite high, and the maximum dimensions of the working chamber usually do not exceed 500 mm for each of the coordinates. There are alternative solutions – these are installations that work on the principle of direct feeding of the material into the melting zone, for example – laser cladding (LC) or direct laser deposition (DLD). This is more affordable equipment, usually based on a 6-axis industrial robot manipulator, which allows you to produce large parts with a size of 1500 mm or more.

The principle of operation of direct laser deposition consists in feeding the building material (powder or wire) into the melting zone with the formation of a melt bath by a laser beam and subsequent crystallization of the metal in the form of hemispherical tracks. As a starting material, powders from traditional alloys, from mechano-alloyed powders, as well as from mixtures of elemental powders can be used. The construction of parts made of pre-alloyed alloys has already been fully studied in scientific works [1-5]. The influences of the surfacing

parameters, the technological parameters of the powders themselves, as well as the physics of the main processes were studied. The method of obtaining alloys from mechano-alloyed powders is designed to reduce the cost of processing secondary raw materials, as well as to obtain materials from pseudo-alloys [6-8]. Alloys from powder element mixtures do not require special technological operations before DLD, so they may be the cheapest raw material to produce alloys. The main issue is the degree of uniformity of the final alloy and the stability of the chemical composition relative to the initial mixture. Known work on DLD from elemental powders of the Fe-Cr-Ni system [9]. The authors synthesized an alloy with different contents of the components of the elemental mixture. Thin walls were made as samples. The point-by-point EDS results have shown that optimizing the particle size of the finished blend is necessary to maintain the original blend and reduce the separation of the premixed powder. The produced heterogeneous and multifunctional Fe-Cr-Ni alloy has both corrosion resistance and sufficient toughness and ductility. In [10], critical technical problems of the synthesis of alloys from elemental powders for future development are discussed. It is noted that today there are many unresolved issues, such as overcoming the entropy of mixing, flow behavior for various metal powders, and how the interaction of laser and material affects the final composition of the finished part. In addition, it is necessary to deduce a predictable relationship between the initial atomic or mass composition and the final composition of the finished alloy. The field of research on the production of high-entropy alloys from a mixture of powders is developing, since it is almost impossible to obtain traditional alloys from this type of material. Various high-entropy alloys of the FeCoNiCrCu [11], 6FeNiCoSiCrAlTi [12], TiVCrAlSi [13] and others systems were synthesized using laser technologies.

The ability to synthesize the alloy in the growing process allows you to obtain alloys with different functional properties depending on the proportion of the components and allows you not to purchase many different powder alloys. Therefore, it can be assumed that the production of alloys from elementary powders may not only be of scientific interest, but also be a cost-effective method of production.

The purpose of this work was to evaluate the quality of the alloy obtained by the method of synthesis of elementary powders by DLD and to investigate the problems that arise in the formation of the material structure and the formation of the alloy in the process of constructing multilayer samples.

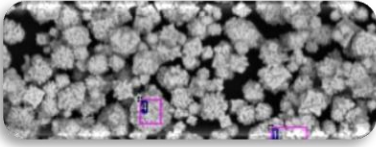
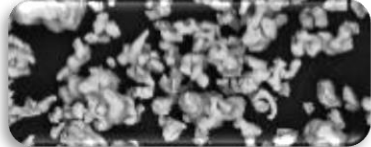
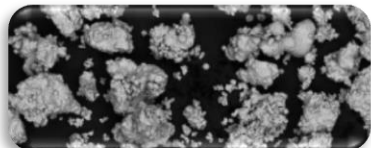
2. METHODOLOGY AND EXPERIMENT

Ni, Fe, and Cr elemental powders were used in the delivery state. The characteristics of these powders are presented in **Table 1**. Then, the elemental powders were mechanically mixed by gravity for 4 hours in a mass ratio of 73% Ni, 17% Cr, 10% Fe until a homogeneous mixture was formed. This mixture was loaded into the powder feeder of the laser surfacing unit. The surfacing was carried out on a sheet of structural low-alloy steel of the St.3 grade with a thickness of 5 mm. The chemical composition of the substrate (in wt%) is iron 97, carbon 0.22; nickel, copper, chromium – each no more than 0.3; manganese 0.65; silicon 0.17.

Synthesis and production of samples using laser cladding technology was carried out at the plant developed in SPBPU. The main components of the unit continuous ytterbium fiber laser iPG LS-3, powder feeder PF 2/2, optical system (cladding head) KUKA MWO-1 and Fanuc M20i robot. Method of melting zone protection: local protection by argon supply, without filling the working chamber with argon.

The experiment consisted in growing *c* samples from elemental powders by the DLD method to obtain a homogeneous alloy and simultaneously form the sample. The modes for which the process was carried out are shown in **Table 2**. First, a series of single tracks was made with a change in the amount of energy supplied due to a change in the laser power (900, 1200, 1500 and 2000 W). Then thin-walled and thick-walled samples were grown at a laser power of 1200 and 1500 W.

Table 1 Elemental powders for synthesis Ni-Cr-Fe alloy

Powder	Particle size (μm)	Particle shape	Chemical composition (wt%)
Ni	5 - 55		Ni – 99.25 The rest including O – 0.75
Cr	5 - 55		Cr – 98.76 Si – 0.22 The rest including O – 1
Fe	20-125		Fe – 98.19 Mn – 0.45 The rest including O – 1.36

All samples were cut and metallographic sections were made from them. Chemical etching of metallographic sections was carried out in a solution of 10 ml HNO_3 and 30 ml HCl. Photos of the microstructure were obtained using a Leica optical microscope. Chemical analysis was carried out on SEM Tescan Mira 3 electron microscope with EDS attachment. X-ray phase analysis was carried out on Bruker D8 Advance diffractometer in the range of 200 to 1000 angles with 0.02 step and 2 s exposure time at each step. Quantitative phase analysis was performed using TOPAS5 software.

Table 2 DLD parameters for growing samples from elementary powders

DLD parameter	Parameter value
Speed of movement	10 mm/s
Powder feed	15 g/min
Protective argon	12 l/min
Transport argon	6 l/min
Laser power	900–2000 W
Lifting height	0.6 mm
Offset	50 %
Laser spot size	3 mm

3. RESULT AND DISCUSSION

The structure of single tracks on a steel substrate is investigated. The etched samples in **Figure 1** show a clear boundary between the substrate and the synthesized alloy, as well as the heat affected zone (HAZ). According to the state of the structure for laser powers of 900–1500 W (**Figures 1 a-c**), one can note the presence of vortex flows and turbulent flow of liquid in a bath of dissimilar liquid melt prior to crystallization. At a laser power of 2000 W, there are no vortex flows on the structure, and there is directional crystallization characteristic of tracks of homogeneous alloys.

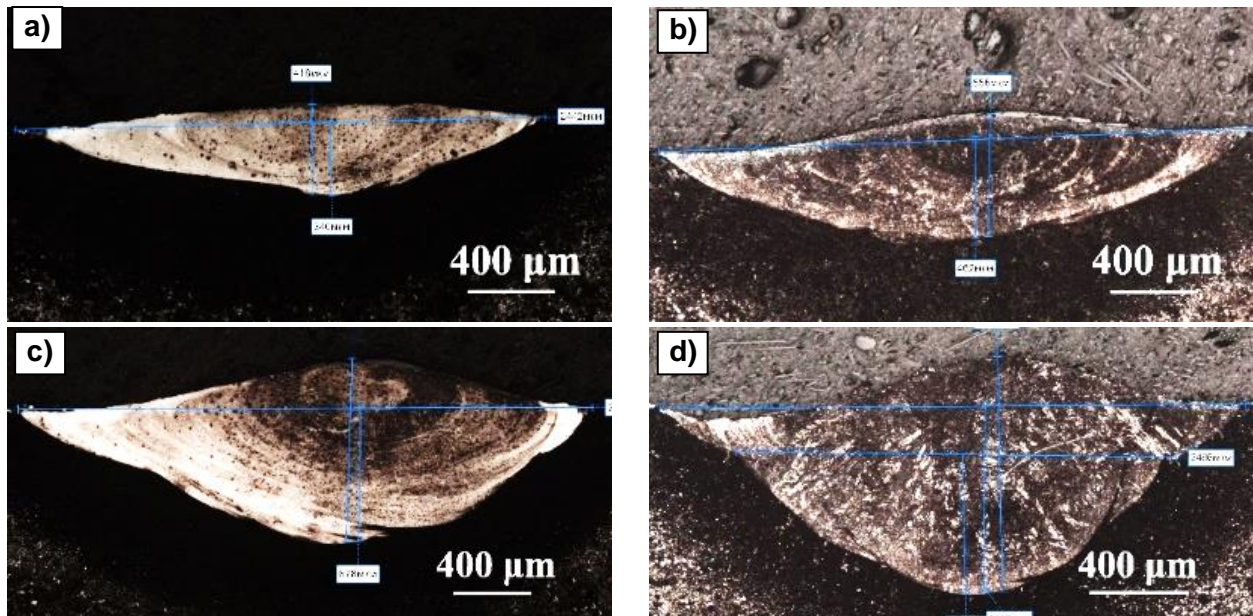


Figure 1 Single tracks from an iron-based Ni/Cr/Fe mixture: a) 900 W, b) 1200 W, c) 1500 W, d) 2000 W

The EDS method was used to determine the chemical composition of the tracks by area, which showed the presence of iron diffusion from the substrate (**Table 3**). Since the DLD process is characterized by the formation of a melt bath, it can be assumed that the volume of the molten substrate material significantly exceeds the volume of the introduced metal. For this reason, when surfacing a single track of elemental powders, the chemical composition is dominated by the elements of the substrate.

Table 3 The content of chemical elements (wt%) in the track depending on the laser power

Laser power (W)	Ni	Cr	Fe
900	3.5	4.9	91.6
1200	2.8	2.5	94.7
1500	6.1	4.6	89.3
2000	2.7	2.7	94.6

Also, the dependence of the size of the track bath (formed melt bath) depending on the laser power was revealed. This dependence, expressed in the final geometric size of the track, is shown in **Figure 2**.

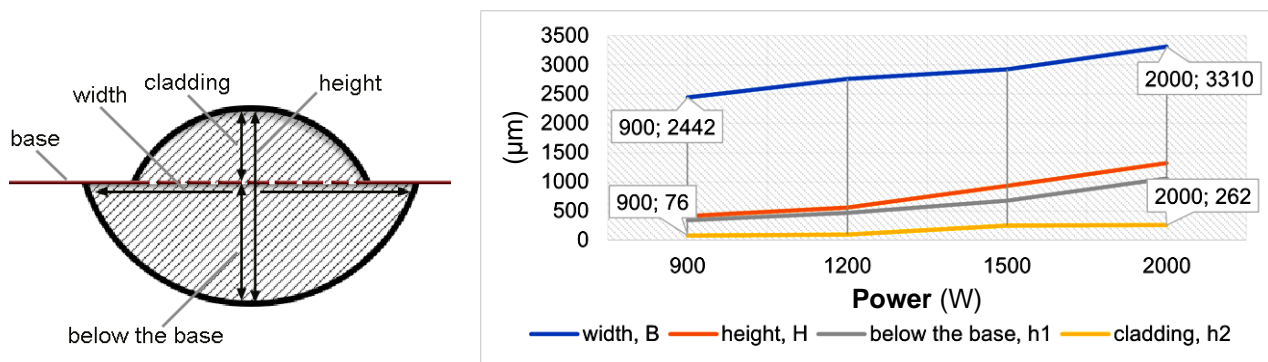


Figure 2 Parameters of the track geometry depending on the laser power

An SEM image with combined EDS analysis of a thin-walled sample grown at a power of 1500 W is shown in **Figure 3**.

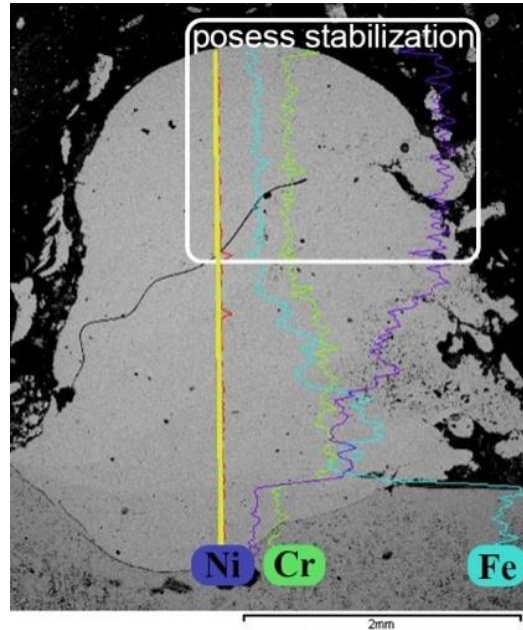


Figure 3 Cladding of a thin wall from an elemental Ni / Cr / Fe mixture at a power of 1500W

The thin wall has an irregular shape and many protrusions due to the too small size of the powder, which led to the penetration of the powder particles along the boundaries of the walls and the formation of satellites. About the chemical composition of the thin wall, there is a gradient of the chemical composition in height, but the stabilization of the chemical composition occurs at a wall height of 2 mm, which corresponds to approximately 3 layers. This result suggests that when synthesizing low samples or coatings, the chemical composition of the alloy will be significantly affected by the substrate material, which must be borne in mind when selecting a powder mixture.

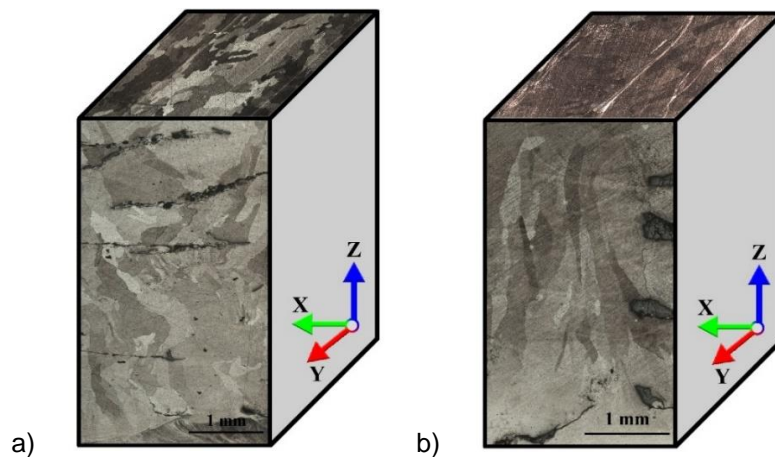


Figure 4 Structure of synthesized thick-walled samples of the Ni / Cr / Fe system. a) the laser power 1200 W, b) the laser power 1500 W. New layers were added in the Z direction

Further, the structure and chemical composition of the synthesized thick-walled samples were studied. Depending on the laser power, the sample structure changed significantly. At a laser power of 1200 W, the orientation of the grains was found mainly in the direction of the growth of the thick wall. At a laser power of

1500 W, the grain orientation becomes even more pronounced with a cell size in one direction of about 2 mm. This structure indicates the heating of the sample during thermal cycling above the recrystallization temperature and directed cooling.

To control the change in the chemical composition by volume, thin-walled samples were examined on EDS in three zones (**Figure 5**). The measurement results are shown in **Table 4**.

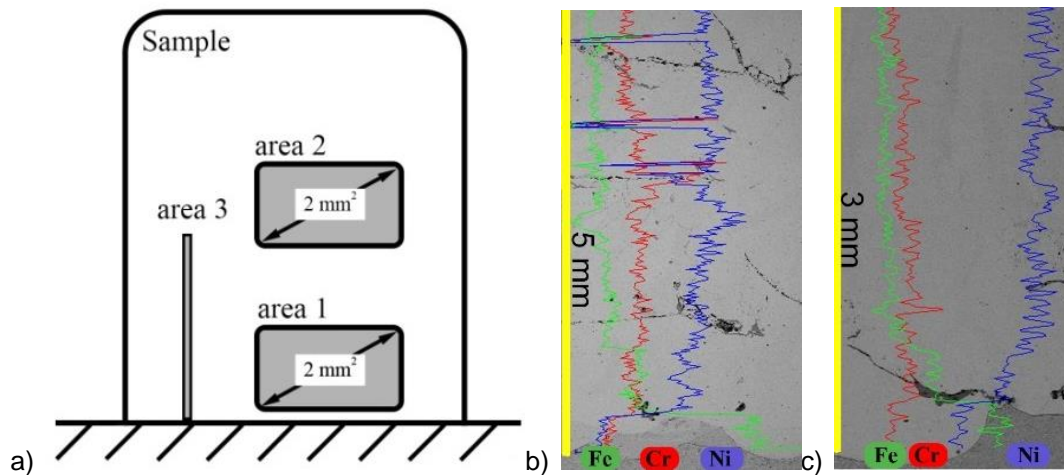


Figure 5 EDS analysis in thick-walled samples. a) diagram of the areas for measuring the chemical composition, measuring the change in the chemical composition in zone 3 for laser power: b) 1200 W and c) 1500 W

Table 4 Chemical composition (wt%) of samples from a Ni / Cr / Fe mixture for two laser powers in zones 1 and 2.

element	1200 W				1500 W			
	O	Cr	Fe	Ni	O	Cr	Fe	Ni
value for area 1	<0.5	18.3	12.0	69.7	1.6	13.4	13.1	72.0
value for area 2	2.8	16.9	8.9	71.4	<0.5	11.0	12.4	76.6

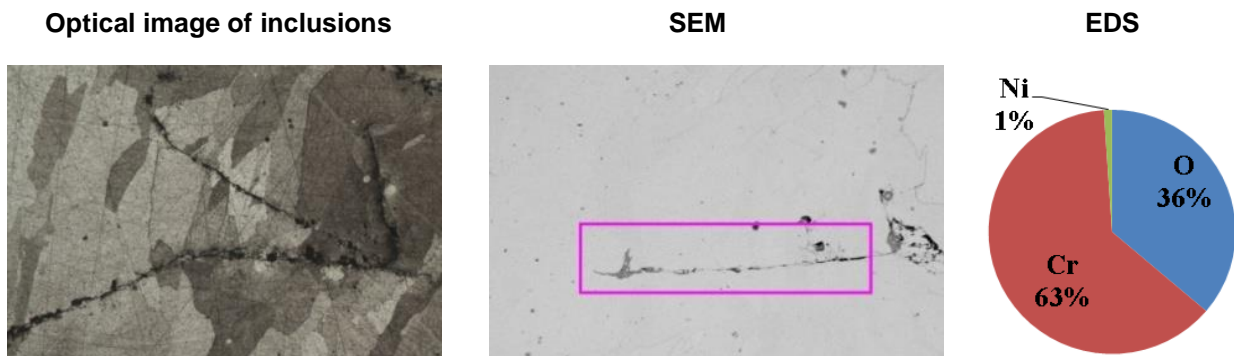


Figure 6 Study of defects in the Ni-Cr-Fe alloy

No unalloyed powder particles were found, but as can be seen from the structural images in **Figure 4**, there are a significant number of defects in the samples – inter-track oxide inclusions (**Figure 6**). With an increase in the laser power, the chromium content in the alloy decreased by 5% due to an increase in the number of oxide phases. A comprehensive study of the chemical composition by the EDS method of a thin-walled sample showed the instability of the distribution of elements within the volume of the material. The reason for this

instability is based on the formation of oxide inclusions, which were identified as chromium oxide. With an increase in the laser power from 1200 W to 1500 W, the distribution of oxide inclusions changed. Thin inclusions distributed mainly along the track boundaries agglomerated between tracks into ellipsoidal inclusions with a diameter of 0.3 - 0.5 mm.

4. CONCLUSION

The following results were obtained in the work:

- Synthesis of the alloy by the DLD method from elemental powders showed a high diffusion of the elements of the substrate material in the first 1–2 layers of surfacing, which can significantly change the chemical composition of the alloy;
- At a laser power of 1200 W, all the powder melted down and participated in the formation of an alloy;
- An increase in the laser power from 1200 W to 1500 W during DLD from elemental powders, the length of the grains increases to elongated crystals 12 mm long along the heat removal axis.
- The elimination of the conditions for the formation of oxide inclusions, namely the protective oxygen-free chamber, as well as the minimum oxygen content in the powders, should improve the quality of synthesis from elemental powders;
- It is planned to determine the functional properties of the material heat resistance and heat resistance, it is necessary to conduct additional studies and compare with the properties of pre-alloyed alloys of similar composition

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